Modeling for Wastewater Treatment by Adsorption using Analytical-, Regression-, and Neural Network-Approaches

THESIS

Submitted in partial fulfilment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

RAMAKRISHNA VELLAMPALLI

Under the Supervision of

Prof. (Dr.) B.V. BABU

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

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CERTIFICATE

This is to certify that the Thesis entitled, **"Modeling for Wastewater Treatment by Adsorption using Analytical-, Regression-, and Neural Network-Approaches"** and submitted by **Mr. Ramakrishna Vellampalli,** ID No. **1997PHXF405** for award of Ph.D. Degree of the Institute, embodies the original work done by him under my supervision.

Signature of the Supervisor
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Date: 07/06/2004

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V. RAMAKRISHNA

ABSTRACT

The wastewater treatment system is comprised of many treatment techniques including Adsorption. A number of investigators have studied different novel adsorbents for their applications in wastewater treatment in an attempt to find an alternative to commercial activated carbon, taking the economic aspects into account, as the activated carbon is costlier. The selection of adsorbents is based on their characteristic properties. Isotherm studies are used to judge the suitability of adsorbents for a specific application. Due to the wide variety of novel adsorbents used by several investigators, a study probing into their characteristics, preparation methodologies, adsorbate (or pollutant) removal efficiencies (PRE) under different operating conditions etc. is useful. Modeling of the adsorption system will help in assessing the performance of the adsorbent under a wide range of operating conditions.

Adsorption as a phenomenon has not been completely understood and hence adsorption modeling becomes a big challenge. Various investigators have used both analytical and empirical approaches. But unfortunately, the resultant predictions of these models for the operating conditions other than those considered for development of these models is not very satisfactory. The present study focuses on understanding the physical phenomenon occurring in adsorption by modeling using dimensional analysis, regression analysis, Artificial Neural Networks (ANN) and analytical approaches. The analysis taken up in the present study covers wide range of operating conditions and huge amount of data collected from various literature sources for removal of various pollutants from wastewater.

A close look at the literature available on adsorption studies revealed that (i) the investigators are examining for more characteristics than prescribed by the Bureau of Indian Standards (BIS) code (ii) a wide spread in the values for isotherm constants and

(iii) an unanimity with reference to spontaneity of adsorption under a wide range of operating conditions for various materials with respect to free energy change (i.e., ΔG^0 negative). The results reported by an investigator may be accurate and adequate for his study (i.e., micro level) but when they are compared on a common basis with respect to the adsorbate (pollutant) /adsorbent/specific characteristic property etc. (i.e., macro level), inconsistent trends in the results are observed. It is extremely difficult to compare any indigenous data with that already published in literature, especially after observing the inconsistent and contrasting trends that are available in literature. This led to development of a model to predict the PRE from database from literature pertaining to batch studies of adsorption assuming that the database reported in the literature is accurate at micro level. The batch studies of adsorption are considered in this study since they are simple in operation and less complicated than continuous column studies for modeling purposes. The first step in any model development starts with identification of affecting parameters and making use of dimensional analysis and regression approaches. A model is developed using these two approaches. It is initially tested for its applicability and subsequently used for PRE prediction. Due to the inconsistent trends obtained from the results, ANN is used to improve the prediction from this model by mapping the network with the available data. The results obtained are relatively better than those obtained using dimensional analysis and regression approaches.

It is proved in literature that, existing analytical models such as Homogeneous Surface Diffusion Model (HSDM) can predict the PRE with better accuracy. To understand the efficiency of analytical model relative to empirical models, the HSDM is taken up for batch studies and analyzed using literature data. The model is simulated, validated and tested using input data available in literature. An exhaustive parametric study is conducted for eighty-one combinations of six different parameters that affect the adsorbate removal. Six parameters viz., external mass transfer coefficient, diffusion coefficient, adsorbent particle density, adsorbent diameter, adsorbent dose and initial concentration of adsorbate are considered for the parametric study. Results revealed that (i) the external mass transfer coefficient is dominant compared to that of diffusion coefficient in adsorption (ii) the adsorbate removal is increasing with increase in the value of external mass transfer coefficient and is independent for the variations in diffusion coefficient (iii) adsorbate accumulation is increased by higher concentration of adsorbate, lower values for size of particle, adsorbent particle density, and adsorbent doses. A relationship between the Biot number and distribution parameter is established and is verified both analytically and graphically. The inter-dependence of three functional groups in the Biot number is studied for a set of selected values. The results obtained from the above mentioned studies are encouraging.

Simultaneously, few comparative studies are carried out to assess the performance of novel adsorbents. Since, the performance of an adsorbent depends upon its characteristics, method of preparation, precursor material etc., a database is compiled from literature pertaining to different novel adsorbents. The database is analyzed with respect to the characteristic properties of adsorbents, their preparation methodologies, and the precursor material. The data analysis revealed the need for (i) no separate BIS code for defining the suitability of activated carbon for wastewater treatment (ii) a separate BIS code for selecting the suitability of an adsorbent for wastewater treatment (iii) a possible revision of the characteristics that are prescribed in the available BIS codes (iv) a separate set of characteristics to be prescribed for adsorbent based on the precursor material and (v) adsorbents prepared from agricultural wastes are showing better performance compared to those prepared from industrial wastes and mineral wastes. Methodologies have also been proposed to rank the adsorbents based on the precursor material, adsorbent preparation methodology, and on available characteristics.

During the preparation of adsorbent from a precursor material, a raw material (eg. sawdust) is being converted into a product (adsorbent) along with some other byproducts (waste releases). Hence, Life Cycle Inventory Analysis (LCIA) based on mass balance approach is carried out on adsorbent preparation from sawdust using available experimental data. The waste streams are identified and suggestions are floated to minimize the waste emissions during the material conversion.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOTATION

a	Langmuir isotherm constant, [-]
b	Langmuir isotherm constant, m^3/kg
d	Adsorbent particle diameter, m
e^r	Error in the output of Back Propagation Network, [-]
h	Output from hidden node of Back Propagation Network, [-]
k_f	External mass transfer coefficient, m/s
m	Constant
n	Freundlich isotherm constant, [-]
q	Amount adsorbed, [-]
q_0	amount adsorbed for $C = C_0$ (from isotherm equation)
q_e	Amount adsorbed at equilibrium, [-]
r, r_p	Adsorbent particle radius, m
t_c	Contact time, s
t_{eq}	Equilibrium time, s
w	Weights of the neurons in the BPN
x	Dimensionless space for discretization
y^a	Actual output of Back Propagation Network
y^d	Desired output of Back Propagation Network

Bi	Biot number, [-]
C	Concentration of adsorbate, kg/m^3
C_0	Initial concentration of adsorbate, kg/m^3
C_d	Adsorbent dose, kg/m^3
C_e	Equilibrium concentration of adsorbate, kg/m^3
C_f	Final concentration of adsorbate, kg/m^3
D	Diffusion Coefficient, m^2/s
H	Hidden node vector of Back Propagation Network, [-]
K	Linear isotherm constant, [-]
K_f	Freundlich isotherm constant, [-]
R	Universal gas constant = 8.32 J/mol.K
R_L	Separation factor, [-]
S	Hidden node vector of Back-Propagation Network, [-]
T	Temperature, ^0C
V	Volume of adsorbate, m^3
W	Mass of adsorbent used, kg
X	Input vector of Back-Propagation Network, [-]
Y	Output vector of Back-Propagation Network, [-]

GREEK SYMBOLS

α	Exponential constant (Eq. 3.3)
β	Exponential constant (Eq. 3.3)
γ	Exponential constant (Eq. 3.4)
Δ	Error constant used in BPN
η	Pollutant Removal Efficiency, [-]
θ	Dimensionless time for discretization
ω	Agitation speed, rpm
ρ	Adsorbent particle density, kg/m^3
λ	Distribution parameter used in analytical model, [-]
ΔG^0	Free Energy change, J/mol.
ΔH^0	Enthalpy change, J/mol.
ΔS^0	Entropy change, J/mol./K

ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ANN	Artificial Neural Network
APMD	Adsorbent Preparation Methodology Database
AT	Asymptotic Trend
AW	Agricultural Wastes
BDST	Bed-Depth Service Time
BIS	Bureau of Indian Standards
BPN	Back-Propagation Network
C	Chemical Treatment
CAC	Commercial Activated Carbon
CT	Chemical Thermal Treatment
DB	Data Base
ET	Error Tolerance
ETP	Effluent Treatment Plant
HSDM	Homogeneous Surface Diffusion Model
ISI	Indian Standards Institution
IW	Industrial Wastes
LAC	Laboratory Activated Carbon
LCA	Life Cycle Assessment
LCIA	Life Cycle Inventory Analysis
LDF	Linear Driving Force
LR	Learning Rate
LRM	Linear Regression Model
LRMA	Linear Ranking Model of Adsorbents
LRT	Linear Rising Trend
LSM	Least Squares Method
LSMM	Least Squares Method Model
MLD	Million Liters per Day
MNSS	Model based on Normalized Sum of Squares

MOAM	Method of Averages Model
MW	Mineral Wastes
N	Nominal Treatment
NE	Number of Epochs
NNHL	Number of Neurons in Hidden Layer
NNM	Neural Networks Model
P	Physical Treatment
PC	Physical Chemical Treatment
PCP	Penta-Chloro Phenol
PMMR	Physical Model based on Multiple Regression
PRE	Pollutant Removal Efficiency
PT	Physical Thermal Treatment
RDAM	Regression and Dimensional Analysis Model
RMCD	Raw Material Category Database
SD	Standard Deviation
SDW	Single Distilled Water
T	Thermal Treatment
TDW	Triple Distilled Water
TPL	Total Production Load
UNICEF	United Nations International Children Education Fund
WWF	World Wide Fund

CHAPTER
1

INTRODUCTION

The use of water by man, animals and plants is universal. The water consumption is rapidly increasing due to the growing population. Contamination of water sources such as streams, lakes, reservoirs, and wells due to improper disposal of wastewater has greatly impaired the quality of available water. The nation is witnessing struggle for saving each drop of available water. Effective treatment and reuse of treated wastewater become the priority issues in this scenario. Modeling approaches will help in monitoring and improving the quality of water/wastewater for discharge after treatment. The issues pertaining to water quality problems, available treatment techniques and modeling aspects are discussed in the following sections.

1.1 Water quality problems and need for Resource Utilization

The drinking water crisis in many Indian cities is reaching alarming proportions. Urban population is suffering from irregular water supply, sometimes leading to clashes among them. The population growth in India is rapid and recorded an increase of 330.80% from

1901 to 2001 for a population change of 23,83,96,327 in 1901 to 102,70,15,247 in 2001 respectively [MIB-GOI (2001)]. The continuous increase in population growth is increasing the demand and putting pressure on natural resources to cater to the needs of various requirements of the population in their day-to-day life. The urban population is also increasing at a very rapid rate (Babu and Ramakrishna, 2002a). In fact, it increased from 13.9% in 1941 to 28.77% in 2001 [MIB-GOI (2001)]. In India, the surface water resources carry 17,68,000 million cubic meters out of which only 50% can be put to beneficial uses. In addition, out of the 4,22,900 million cubic meters of ground water potential available for utilization, approximately 1,00,000 million cubic meters is being exploited. The statistics pertaining to water supply and sanitation status in India are alarming. The available statistics are compared (Biswas, 2003) for Class-I cities and Class-II towns for three decades, viz., 1978-79, 1988-89, and 1994-95 and are given in Table-1.1.

Table-1.1: Decadal trend of water supply and sanitation status in Class-I cities and Class-II towns in India

S.No.	Parameter	Class-I cities			Class-II towns		
		1978-79	1988-89	1994-95	1978-79	1988-89	1994-95
1	Number	142	212	299	190	241	345
2	Population (Millions)	60	102	128	12.8	20.7	23.6
3	Per capita water supply (lpcd)	143	147	183	125	78	103
4	Water supply (MLD)	8,638	15,191	20,607	1,533	1,622	1,936
5	Wastewater generated (MLD)	7,007	12,145	16,662	1,226	1,280	1,650
6	Wastewater untreated and disposed (MLD)	4,251	9,660	12,625	1,160	1,252	1,588
7	Percentage of wastewater untreated and disposed	61	79.5	76	94.56	97.88	96.27

Table-1.1 shows that the decadal change in water supply is very high for Class-I cities (75.8% & 35.65% from 1978-79 to 1988-89 and from 1988-89 to 1994-95 respectively) compared to Class-II towns (5.8% & 19.36% from 1978-79 to 1988-89 and from 1988-89 to 1994-95 respectively). The decadal change in the quantity of wastewater untreated and disposed is decreasing for Class-I cities (127.24% & 30.69% from 1978-79 to 1988-89 and from 1988-89 to 1994-95 respectively) and increasing for Class-II towns (7.93% & 26.84% from 1978-79 to 1988-89 and from 1988-89 to 1994-95 respectively). This information indicates improvement in the sanitation facilities in Class-I cities than in Class-II towns but still huge quantity of wastewater is being untreated and disposed. Further, the surface and groundwater quality is deteriorating rapidly all over the country (Garg et al., 2003; Ramakrishna and Babu, 1999a; Babu and Ramakrishna, 1998b; Garode et al., 1998; Garg et al., 1998; Mogal and Desai, 1998). The situation is hence alarming due to-

- increasing pressure on natural water resources
- deteriorating quality of available natural water resources and
- disposal of huge quantities of untreated wastewater.

A joint study conducted by United Nations International Children Education Fund (UNICEF) and the World Wide Fund (WWF) for nature also confirmed the alarming situation of fresh water depletion in the country (TOI, 1998).

1.1.1 Effects of wastewater quality parameters on receptors

Water is in a constant state of motion, which is known as Hydrologic cycle (Punmia et al., 1999; Duggal, 1988; Peavy et al., 1985). Precipitation is the main source of water on earth's surface. After falling on earth, water undergoes the following transformations:

- flows on the surface of the earth as run-off
- flows into aquifers through infiltration

- evaporates from surface water, such as river, lake, reservoir etc.
- undergoes Evapo-transpiration
- condensates as precipitation from atmosphere and falls on earth's surface thus completing the Hydrologic cycle.

Rainwater (Precipitation) is one of the purer forms of water on earth. But, during its movement through atmosphere, it absorbs various gases present in atmosphere and becomes polluted resulting in acid rain at places of high SO_2, NO_x concentration (Peavy et al., 1985). The surface run-off and ground waters get polluted with domestic and industrial pollution. They will finally reach the surface water bodies. Hence, it should be noted that, water pollution starts at the source of water i.e., precipitation itself. This will be subsequently increased due to the other forms of pollution on the surface of earth. The impurities in water are classified under three categories (Punmia et al., 1999, Duggal, 1988) viz.,

- physical impurities
- chemical impurities
- bacteriological impurities

The physical impurities give taste, odor, color and turbidity. The chemical impurities are either inorganic or organic in nature. The bacteriological impurities are caused by the presence of pathogenic type of bacteria in water thus making it unfit for direct human consumption. It can be inferred from the above discussion, that any change in the natural water quality implies pollution. Some natural events such as hurricanes, torrential rainfall, mudflows etc. also lead to local deterioration in water quality. The large-scale pollution problems are however attributed by anthropogenic pollution. As a result, the fresh water bodies, such as surface water and ground water are becoming polluted globally (Table-1.2). It is evident from Table-1.2 (Kiely, 1998) that, the extent of pollution is severe for surface water as compared to ground water.

Table 1.2: Major freshwater quality issues on a global scale

Issue	Water body			
	River	Lake	Reservoir	Groundwater
Pathogens	3	1[a]	1[a]	1
Suspended solids	2	NA	1	NA
Decomposable organic matter[b]	3	1	2	1
Eutrophication[c]	1	2	3	NA
Nitrate as a pollutant	1	0	0	3
Salinization	1	0	1	3
Trace elements	2	2	2	2[d]
Organic micropollutants	3	2	2	3[d]
Acidification	1	2	2	0
Modification of hydrological regimes[c]	2	2		1

0: Rare deterioration
1: Occasional or regional deterioration
2: Important deterioration
3: Severe or global deterioration found
NA: Not Applicable

a: Mostly in small and shallow water bodies
b: Other than resulting aquatic primary production
c: Algae and macrophytes
d: From landfill, mine tailings
c: Water diversion, damming, overpumping etc.

The surface water in India, for example, is classified into five categories based on the degree of treatment imparted to these sources for drinking purposes. The details are listed in Appendix-A. If water fulfils these requirements, it is said to be of good quality. Similarly, the permissible limits for the discharge of industrial wastewater into three disposal points viz., inland surface water, public sewer, and on land for irrigation are available in India, the details of which are listed in Appendix-B. It should be noted that, water quality standards vary depending on the use (Appendices-A and B). Hence, a lot of restrictions on the usage of water at consumer end are observed globally (Kiely, 1998) due to the water pollution (Table-1.3).

Table-1.3: Restrictions of water usage at consumer end on global scale

Pollutant	Consumer process						
	Drinking water	Aquatic wild life, fisheries	Recreation	Irrigation	Industrial uses	Power and Cooling	Transport
Pathogens	2	0	2	1	2^a	NA	NA
Suspended solids	2	2	2	1	1	1^b	2^c
Organic matter	2	1	2	+	2^d	1^e	NA
Algae	$1^{c,f}$	1^g	2	+	2^d	1^e	1^g
Nitrate	2	1	NA	+	2^h	NA	NA
Salts^j	2	2	NA	2	2^i	NA	NA
Trace elements	2	2	1	1	1	NA	NA
Organic micropollutants	2	2	1	1	?	NA	NA
Acidification	2	2	1	?	1	1	NA

0: No impairment
1: minor impairment
2: marked improvement causing major treatment or excluding the desired use
NA: Not Applicable
+: Degraded water quality may be beneficial for this specific use
?; Effects not yet fully realized
a: Food industries
b: Abrasion
c: Sediment settling in channels
d: Electronic industries
e: Filter clogging
f: Odor, taste
g: In fish ponds higher algae biomass can be accepted
h: Development of water hyacinth
i: also includes boron, fluoride etc.
j: Ca, Fe, Mn in textile industries etc.

1.1.2 Need for Resource Utilization

The above information reveals that, there is a need for effective utilization of natural resources. Since any developmental activity utilize natural resources in one form or the other, the efficiency of converting the resources into useful products becomes the key parameter for estimating the waste and pollution generated. The information given earlier about the accessibility, availability, and quality of some of the natural resources in India in general, and water resources in particular, reveals that, there is a need to bridge the gap between the availability and efficiency of utilization of natural resources. At the same time, it is also imperative on everyone to ensure that the natural resources are not exhausted and alternate sources are identified. Efficient usage of resources depends upon many parameters and the intricate relationship among them. A simplified schematic diagram representing the inter-relationship among the major parameters is given in Fig.1.1. (Babu and Ramakrishna, 2002a; Maudgal, 1995).

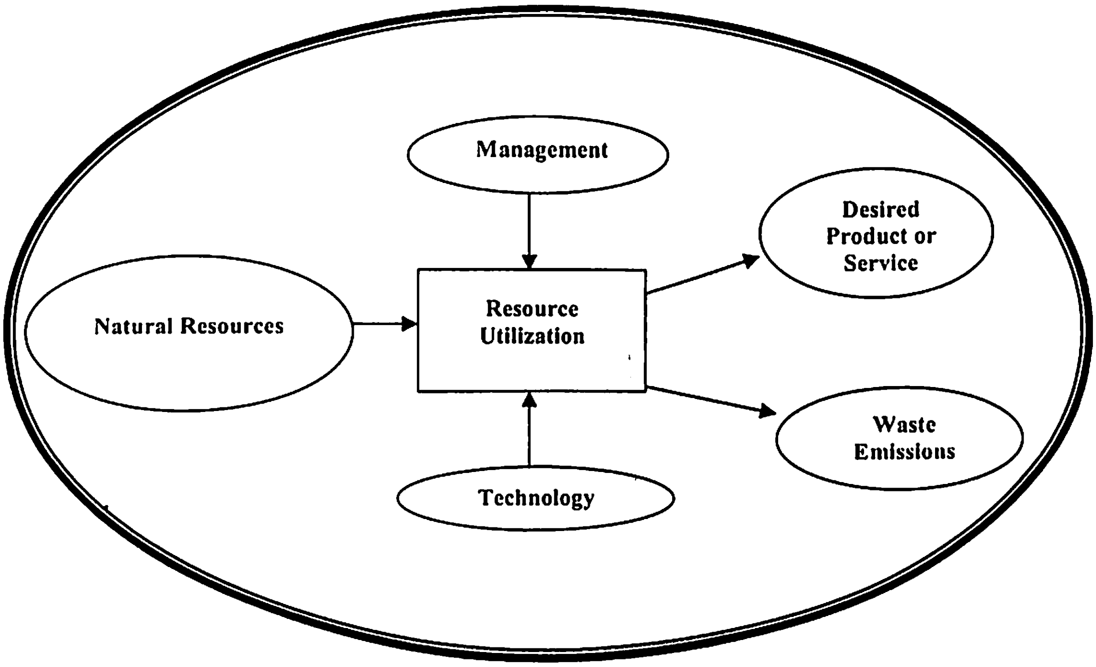


Fig.1.1: Factors affecting the Resource Utilization
(Source: Babu and Ramakrishna, 2002a; Maudgal, 1995)

The pressure on the source and sink is determined by the efficiency of the process that depends among the other things, on the type of technology applied. It is clearly evident from Fig. 1.1 that, efficiency improvement in Technology would possibly lead to reduced pressure on the resource base, both on the source and sink resulting in increased production of goods and services. In the Indian sub-continent, the selection of technologies based on the criteria of lowest initial capital investment has resulted in few technologies that are poor in quality and created increasing pressure on the natural resource base (Maudgal, 1995). The technology development in India needs rapid changes in its approach (Fig. 1.2). There is a need to catch up with the rest of the world through leapfrogging by adopting a strategy combining indigenous development of technology and judicious technology transfer.

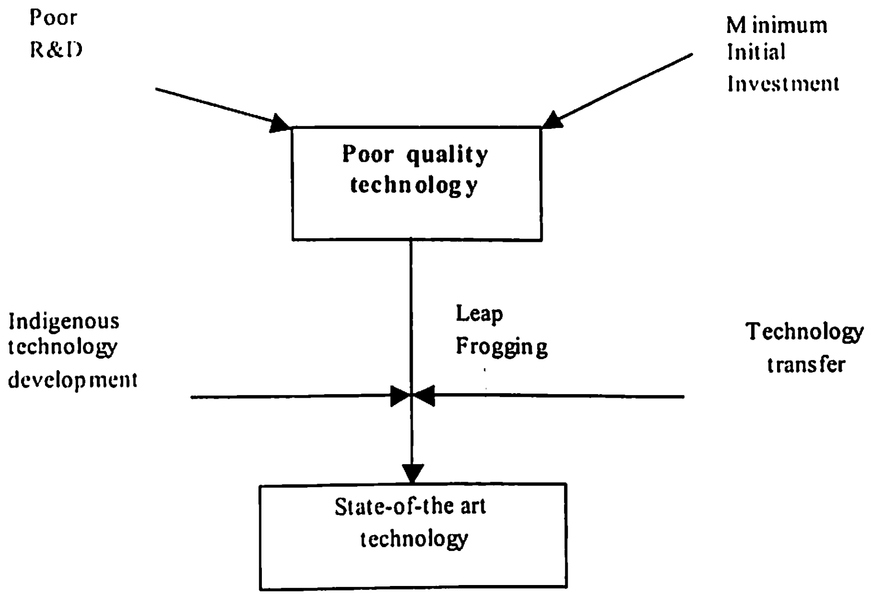


Fig. 1.2: Scope of technology development in India (Source: Tare and Chaudhari, 1995)

There are three stages in the development of technology (Tare and Chaudhari, 1995) as shown in Fig. 1.3. Emerging technologies are those that have not crossed beyond laboratory and pilot scale testing. Innovative technologies include any fully developed technology of which insufficient cost or performance data exists to allow its routine use. The Innovative technology need full scale testing. Available technologies are the ones that are fully proven and available for routine commercial or private use. The cost, availability, reliability, developmental nature, and limitations of treatment capacity, if it were a treatment technology, are the key factors that determine the preferential choices of the available technologies.

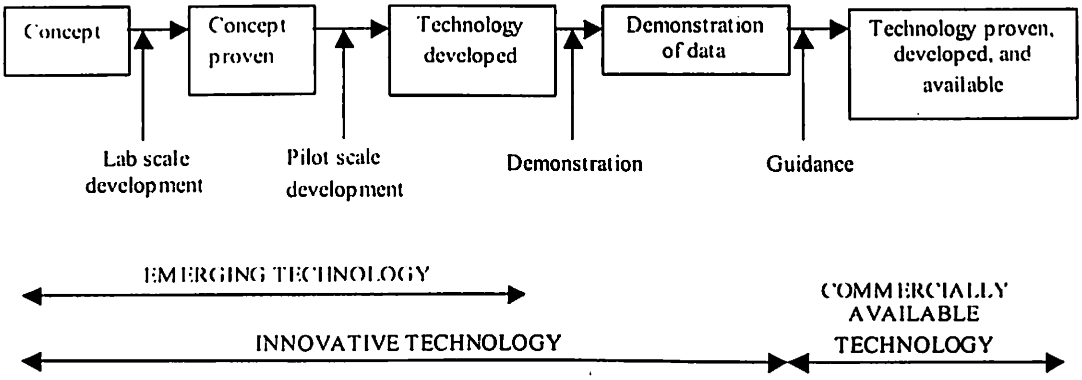


Fig. 1.3: Various stages in the development of technology (Source: Tare and Chaudhari, 1995)

A few guidelines are also available (Tare and Chaudhari, 1995) for evaluating the technologies, preferably emerging, for practice and are given as follows:

- availability of process parameter data for design purpose
- availability of vendors willing to sell technology or parts therein
- availability of trained technicians or training facility
- robustness or delicacy of the process
- environmental compatibility
- availability of material in market
- side effects and by-products of pre-treatment and post-treatment

A close examination of the available water/wastewater treatment technologies reveals that there are some technologies that can be studied in detail for further and continuous improvements. Adsorption is one such technique that has a lot of potential in this regard. The advantages it holds are:

- no sludge handling as in chemical precipitation
- no electricity requirement for its operation

- versatility in its effectiveness and wide range of usage for water and gaseous pollutants
- portable nature of the adsorption modules for commercial uses

Further studies in adsorption are useful on account of the following reasons:

- adsorption is a system specific treatment technique suitable under a set of operating conditions and source materials being tried.
- the batch/bench scale tests, mostly reported in literature cannot be extended for the large-scale purposes on techno-economic grounds.
- hence, there is a lot of scope for conducting studies in this emerging area incorporating modeling, preparation of adsorbent, and scale-up criteria.

In order to understand the implications of an appropriate technology with minimum waste emissions and maximum efficiency of product preparation (Fig. 1.1), a screening of the process technology is essential that can result in a process, which gives minimum pollutant emissions or in other words, a pollution prevention approach. The technology that is screened can be of any type mentioned in Fig. 1.3. Life Cycle Assessment (LCA) is one of such tools that quantifies the amount of waste emissions discharged into environment on account of material changes in the entire life cycle of a material. The conversion of a raw material to a finished product (or service) involves mass and energy inputs. LCA gives complete account of these changes during the material conversion. Few details of LCA are discussed in the next section.

1.1.3 Life Cycle Assessment (LCA)

Life Cycle Assessment (LCA) is an approach to analyze the environmental implications of product and service systems (Chubbs and Steiner, 1998). LCA is a methodology, which has its roots in the late 1960s and early 1970s when a number of studies were conducted to predict the impacts of the utilization of the world's raw material and energy resources (Marano and Rogers, 1999). An LCA framework can be used to assess potential improvement activities to identify when a change results, in effect, in the shifting of environmental burdens among media (for air, water, land) or to another stage of the life cycle (Aelion et al., 1995; Curran, 1995). Methodologies have been developed incorporating process performance, economics, and life cycle inventory data to synthesize process systems that meet life cycle impact-improvement targets at lowest possible cost (Marano and Rogers, 1999).

The LCA is an objective process to:

- evaluate the environmental loads associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to environment
- assess the impact of those energy and materials used and released to the environment and
- evaluate and implement opportunities to affect environmental improvements.

The assessment includes the entire life cycle of the product, process or activity, encompassing:

- extracting and processing of raw materials
- manufacturing, transportation and distribution
- use, re-use, maintenance and
- recycling and final disposal.

LCA comprises of the following four steps:

- **Scope and Goal definition:** It defines the aim, system boundaries, the target audience and the data requirements involved in the system.
- **Inventory analysis:** It estimates the environmental loads associated with the entire life cycle of a product or process.
- **Impact assessment:** It characterizes the effects on human health and on the environment of the loads identified in the inventory step.
- **Improvement assessment:** It lists the process or product modifications aimed at reducing the environmental loads and/or their effects.

1.1.3.1 Life Cycle Inventory Analysis (LCIA)

Life Cycle Inventory Analysis (LCIA) is the second step of the LCA. It deals with the identification and quantification of energy and materials used, wastes released to, and resources depleted from, the environment. LCIA is conducted by both mass- and energy-balance approaches to assess the release of loads to environment. The main components involved in the LCIA are:

- **Environmental load:** The Environmental load or burden generated by a product during any aspect of life cycle is the amount of certain species or radiation that, upon release to the environment (or depletion from the environment), is capable of producing a harmful effect. Harmful effects include resource depletion and deterioration of human and ecological health.
- **Environmental impact:** It is a quantification of the harmful effects of the environmental load.
- **Mass Eco-vector:** It is a multi-dimensional vector whose dimensions correspond to particular loads. Each category in this eco-vector involves several released chemical

compounds, groups of compounds or other environmental loads. The elements are expressed as mass/mass of material stream (kg/kg of material stream etc.)

- **Energy Eco-vector:** It is a multi-dimensional vector whose dimensions correspond to particular loads. Each category in this eco-vector involves several released chemical compounds, groups of compounds or other environmental loads. The elements are expressed as mass/energy of material stream (kg/kJ of energy stream etc.)
- **Waste Eco-vector:** Outlet streams designated as waste streams have eco-vectors with negative values in their loads. The negative loads associated with waste streams are added to the loads of the products, for balancing the environmental loads. Each eco-vector element must be balanced around the process.

Assigning environmental loads to a product is only an approximate science because every aspect of the life of the product, small or large, intended or not, contributes to the product's loads. The challenge remains to account for as many of these aspects as possible, while focusing on the ones that contribute the most to the overall environmental load.

The function of wastewater systems is essentially wastewater collection and reduction of waterborne pollutants (Suh and Rousseaux, 2001). LCIA can be applied to these systems to assess the quantity of removed pollutants (COST, 2001) and to assess the possible reduction in wastewater flow rates (COST, 2001). The environmental impacts of different sludge handling methods can be assessed (COST, 2001) and the energy balance in the functioning of wastewater treatment plant also can be studied (COST, 2001) using LCA. LCIA can be applied to the materials that are developed and used in wastewater treatment. For example, if an indigenous adsorbent is prepared for wastewater treatment, LCIA can be applied to estimate the environmental loads released due to this activity.

1.2 An overview of wastewater treatment

The waste management can usually be done (i) at the source and (ii) at the final disposal point. The waste management that is done at the source is referred to as *waste minimization*. This can be achieved in a number of ways (Parwana, 1999). There are several options for waste management (Babu and Gupta, 1997). They depend upon the type and phase of the wastes. The applicability of the treatment options in waste management is given in Table 1.4 (Tchobanoglous et al., 1987). The practices discussed under waste management are applicable for handling and managing the liquid waste i.e., wastewater. The primary technique used for reducing the concentrations of liquid pollutants is dilution, which is a natural treatment technique. This helps the rivers to purify themselves due to ingression of pollutants. However, it cannot be considered as a commercial treatment option due to heavy demand for dilution water. The dilution, however, occurs within the wastewater collection system (both domestic and industrial) itself. In the wastewater collection system, the wastewater generated from different sections having different concentrations and different flow rates will be mixed together. This will dilute the high concentrations to low concentrations. The diluted and normalized concentrations will be treated at the Effluent Treatment Plant (ETP), a common collection and treatment point. This approach is known as *end-of-pipe treatment*. The minimization of wastewater generation can be achieved when water harvesting and recycling options are practiced. The water that is currently harvested and/or recycled in the country is comparatively less than that is untreated. Hence, *end-of-pipe treatment* technique is essential to treat the large quantities of wastewater.

Table-1.4: Applicability of treatment options in waste management

Operation/process	# Functions performed	$ Type of wastes	@ Forms of wastes
Physical treatment			
Aeration	Se	1,2,3,4	L
Ammonia stripping	VR, Se	1,2,3,4	L
Carbon sorption	VR, Se	1,3,4,5	L, G
Centrifugation	VR, Se	1,2,3,4,5	L
Distillation	VR, Se	1,2,3,4,5	L
Encapsulation	St	1,2,3,4,6	L, S
Evaporation	VR, Se	1,2,5	L
Filtration	VR, Se	1,2,3,4,5	L, G
Reverse osmosis	VR, Se	1,2,4,6	L
Vapor scrubbing	VR, Se	1,2,3,4	L
Chemical treatment			
Calcination	VR	1,2,5	L
Ion exchange	VR, Se, De	1,2,3,4,5	L
Neutralization and oxidation	De	1,2,3,4	L
Precipitation	VR, Se	1,2,3,4,5	L
Reduction	De	1,2	L
Solvent extraction	Se	1,2,3,4,5	L
Sorption	De	1,2,3,4	L
Thermal treatment			
Incineration	VR, De	3,5,6,7,8	S, L, G
Pyrolysis	VR, De	3,4,6	S, L, G
Biological treatment			
Activated sludge process, Aerated lagoons, Anaerobic digesters, Anaerobic filters, waste stabilization ponds	De	3	L

 # Functions : VR - Volume reduction; Se - Separation; De - Detoxification and St - Storage
$ Waste types : 1 - inorganic chemical without heavy metals; 2 - inorganic chemical with heavy metals;
3 - organic chemical without heavy metals; 4 - organic chemical with heavy metals; 5 - radiological; 6 - biological; 7 - flammable and 8 - explosive
@ Waste forms : S - solid; L - liquid and G - gas

A wastewater treatment system is composed of a combination of treatment techniques. These treatment techniques are broadly classified under two categories (Metcalf & Eddy, 1993; Peavy et al., 1985) based on:

- nature of treatment techniques or unit operations
    - physical treatment
    - chemical treatment

    - biological treatment
    - Advanced treatment
- type of treatment given to wastewater
    - primary treatment
    - secondary treatment
    - tertiary treatment

The details of the function and the unit operations in each of the treatment mode are given in Table-1.5.

Table 1.5: Wastewater treatment techniques-functions and unit operations

S.No.	Treatment technique	Function	Typical unit operations
1	Physical	Change is brought about by means of or through the application of Physical forces.	Screening, Comminution, Flow equalization, Mixing, Flocculation, Sedimentation, Flotation, Filtration.
2	Chemical	Change is brought about by means of or through Chemical reactions.	Chemical precipitation, Gas removal, Disinfection.
3	Biological	Biological conversion of dissolved and colloidal organics into biomass that can be removed by sedimentation.	Activated sludge process (Suspended growth), Trickling Filter, Rotating Biological Discs (Attached growth), Facultative ponds, Anaerobic digesters, Aerobic digesters.
4	Advanced	Removal of fine suspended solids and other pollutants not removed by the above three techniques.	Adsorption, Reverse Osmosis, Electro dialysis, Ion exchange, Nitrification-Denitrification, Phosphorous removal.

The other type of classification viz., based on type of treatment given to wastewater, is usually referred to when dealing with the facilities available or to be designed at the ETPs. The design details of the unit operations pertaining to both the classifications are available in literature (Kiely, 1998; Metcalf & Eddy, 1993; Peavy et al., 1985). The functions of each of the treatment types covered under the second classification are as follows:

- primary treatment: removal of suspended solids from the wastewater.

- secondary treatment: biological conversion of dissolved and colloidal organics into biomass that can be subsequently removed by filtration.
- tertiary treatment: further removal or suspended solids and/or removal of nutrients.

From Tables 1.4 and 1.5, it is evident that adsorption technique is widely used in wastewater treatment for tertiary treatment. Due to the easy handling, availability of novel adsorbents (Mohammad et al., 1999), applicability for a wide range of pollutants, and scope for improvement in the technology and/or cost, adsorption studies for wastewater treatment are gaining attention of the researchers. A number of investigators have studied different novel adsorbents for their applications in wastewater treatment. The compiled details are available in literature (Mohammad et al., 1999; Rai et al., 1998; De and De, 1994).

Modeling of the design parameters for the unit operations is often performed either to predict pollutant removal efficiency/kinetic constants, or for process control and monitoring. For example, a water or wastewater treatment process consists of a sequence of complex physical and chemical unit operations. The process control of these plants is usually accomplished through examining the quality of water/wastewater at several stages in the plant and adjusting the processes through an operator's experience (Zhang and Stanley, 1999). Results from models can be utilized to control such situations more effectively. For example, the amount of alum to be added for removal of turbidity from raw water is modeled for its consumption in different months of the year and is used (Chatterjee, 2003). This practice has reduced the consumable cost on the plant and subsequent operating costs to remove the excess alum that has been added earlier. An overview of available modeling approaches is discussed in the next section.

1.3 An overview of modeling approaches

A model is a representation of the significant attributes of a real prototype, but is simpler, and is easier to build, change or operate (Gupta et al., 2003). For example, assuming an output variable (y) as a function of one or more input variables such as A, B, C,. etc., the relationship between the dependent and independent variables can be modeled as-

$$y = f(A, B, C, \ldots) \tag{1.1}$$

The number of different variables in a model and the nature of the relationships between them are determined by the complexity of the system. The aim in modeling is to minimize the number of variables and keep the relationships as simple as possible, while retaining a sufficiently accurate and workable representation of the environment system (Gupta et al., 2003). The cause and effect relationships are transformed to mathematical forms in models.

In modeling, the flow of information is broken down into the following two stages (Babu, 2004):

- the model is compared with the real process and it is taken to be adequate if the discrepancy is negligible.
- the expectations are compared with the indications of the model.

Modeling of environmental processes and contaminant transport (Bhatia, 2003; Kiely, 1998) is a very important aspect in Environmental engineering applications. The scope of engineering problems that can be addressed by modeling is very wide (Babu, 2004; Babu and Ramakrishna, 2003g, b; 2002a; 2000; 1998a; Ramakrishna and Babu, 1999b; 1998). Modeling the mechanism of pollutant fate in environment is one of the hot topics for modeling in Environmental engineering applications. It can be modeling for surface water quality (Bhatia, 2003) or for groundwater quality (Keshari, 2003) or for wastewater treatment (Kiely, 1998). The developed models are then simulated with respect to space and/or time to understand the fate of pollutant in the environment.

The different types of models that are generally adopted for engineering applications can be broadly classified (Babu, 2004) into the following categories:

- physical model
- mathematical model

Each of these models are briefly discussed as follows:

1.3.1 Physical modeling

Physical modeling for any engineering application is usually based on proposing empirical relations using large amount of experimental data. There are several approaches of developing empirical relations (Babu, 2004) with emphasis to generalization based on dimensionless groups or similarity. The approaches that are used due to the nature of problem that is considered in the present study are:

- Dimensional analysis for the relevant dimensional and non-dimensional parameters
- Regression techniques based on method of least squares
- Artificial Neural Networks

A number of applications are available in literature pertaining to empirical modeling. Physical modeling based on regression technique is widely used. Few of the applications are- modeling of site sensitivity indices for treatment, storage and disposal facility earmarked for hazardous waste treatment and disposal (Babu and Ramakrishna, 2000; 2003g, b; Ramakrishna and Babu, 1999b), modeling for estimation of electric power generation based on calorific value of solid waste (Ramakrishna and Babu, 1998), determination of kinetics of adsorption (Mohammad et al., 1997; Patnaik and Das, 1995; Khanna and Malhotra, 1977); estimation of equilibrium time of adsorption (Bhargava and Killedar, 1991); prediction of removal efficiency of Cr (VI) under the specific range of the operating parameters tested (Manju and Anirudhan, 1997; Raji and Anirudhan, 1997).

Artificial Neural Networks (ANNs) is an application of soft computing and is an example of *black-box* type of model development (Babu, 2004). The black-box principle is found to be extremely useful when one system has to be replaced with another functioning in a similar manner. A lot of information is available in literature pertaining to the concept, formulation, and application of the above approaches in physical modeling (Babu, 2004; Modi and Seth, 2000; Hassoun, 1998; Behera, 1997; Holman, 1994; Picton, 1994).

Each of the above techniques are briefly explained as follows:

1.3.1.1 Dimensional analysis

Dimensional analysis is a mathematical technique, which makes use of the study of dimensions as an aid to the solution of several engineering problems. Each physical phenomenon can be expressed by an equation, composed of variables (or physical quantities) that may be dimensional and non-dimensional quantities. The Dimensional analysis helps in determining a systematic arrangement of the variables in the physical relationship and combining dimensional variables to form non-dimensional parameters (Modi and Seth, 2000). When equations are developed in terms of non-dimensional parameters, they show the significance of each parameter. For example, the dimensionless parameters such as Reynolds Number, Mach Number, Froude Number, Weber Number, and Euler Number are significant parameters in describing the fluid flow phenomenon. Similarly the efficiency of a system is another dimensionless parameter relating input with output.

The two methods that are generally used in the Dimensional analysis are:

- Rayleigh method
- Buckingham π-method.

The principles and applications regarding the above two methods are discussed elsewhere (Modi and Seth, 2000).

1.3.1.2 Regression analysis

This is based on the method of least squares and minimizes the sum of the squares of the deviation with respect to the mean value (Holman, 1994). The regression of a dependent variable y on an independent variable x can be expressed in a simple linear form as:

$$y = a + bx \tag{1.2}$$

where, a and b are coefficients indicating the intercept and slope which are minimized.

The analytical approach of solving for a and b is available in literature (Holman, 1994).

1.3.1.3 Artificial neural networks

The ANN is a rapidly evolving technique that has invaded a large number of fields in science and engineering. A unique feature of ANN is their ability to relate experimental input and output data without the need for the knowledge of the physical relation between the input and output variables. A very important feature of these networks is their adaptive nature, where "learning by example" replaces "programming" in solving problems (Hassoun, 1998). The neural networks can yield solutions to complex phenomena where the relationships and rules are not known. The details of the ANN, the non-linear functions of ANN and the related mathematical treatment are documented in the literature (Babu, 2004; Hassoun, 1998; Behera, 1997; Picton, 1994; Khanna, 1990).

1.3.2 Mathematical modeling

Mathematical modeling is based on physical principles such as conservation of mass, momentum, energy etc. The sequential steps involved in the mathematical modeling (Bhatia, 2003; Kiely, 1998) are shown in Fig. 1.4. While formulating a conceptual model, processes occurring in the system are evaluated to investigate significant processes that are governing contaminant transport (i.e., objective) in the system domain for a particular problem. The adoption of the appropriate dimensionality is another important aspect in the model development. The trade-offs among accuracy, cost and effort with respect to the model development, model use and data requirements dictate the final architecture of the model. It is generally observed that (Keshari, 2003) the efficiency and accuracy in modeling a system is probably more affected by the formulation of a proper and appropriate conceptual model than by the choice of a particular numerical method or code.

The following information is essential (Gupta et al., 2003) to develop and apply for the model:

- equations describing the physical processes
- region of flow
- boundary conditions
- initial conditions
- material properties
- method of solution

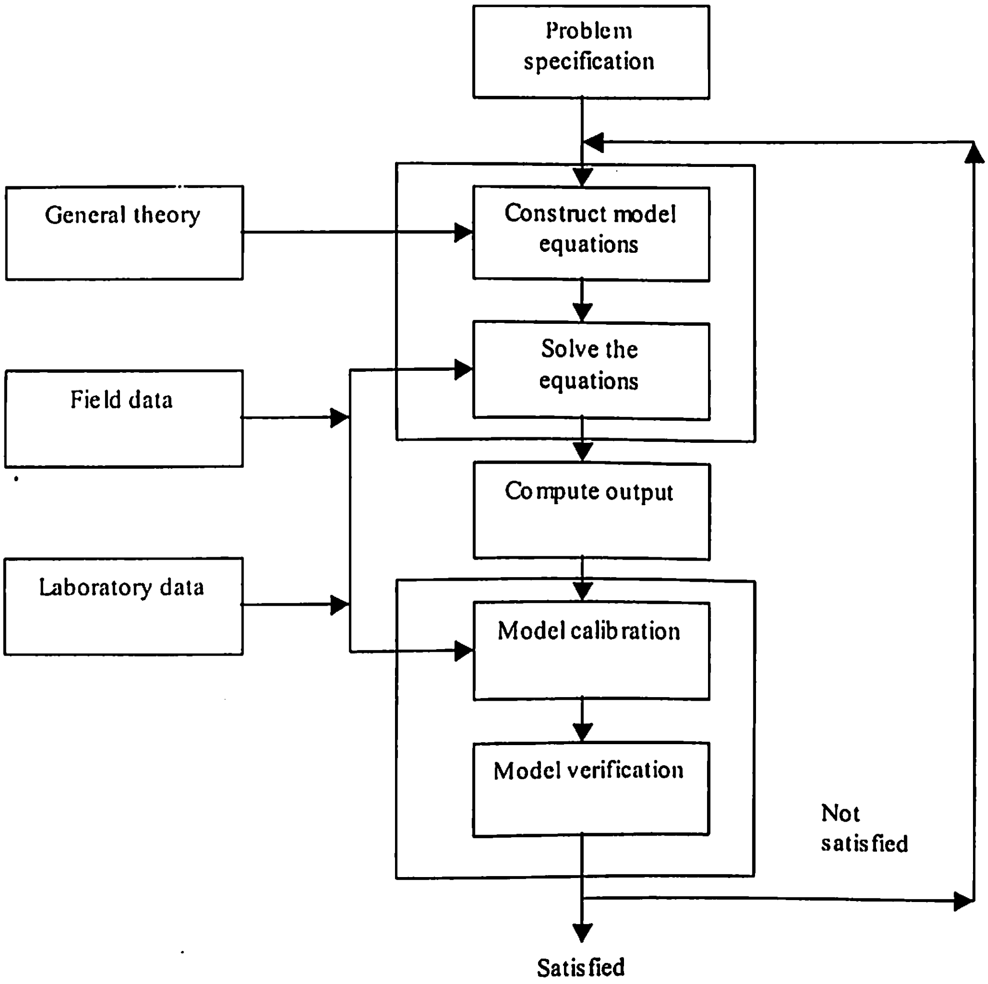


Fig. 1.4: Simplified flow sheet of modeling (Source: Bhatia, 2003)

The region of flow may involve one, two or three dimensions. The flow and transport equations are based on the principle of conservation of mass/momentum/energy. Boundary conditions are used to define the value of the dependent variable(s) along the boundaries of the region to be modeled. Initial conditions provide the state of the system at the start of simulation. Material properties such as density, porosity, dispersion coefficient etc. must be defined over the region. The model equations developed are solved using the initial & boundary conditions and material properties. The model can be solved either analytically or numerically. When a numerical algorithm is implemented in a computer code to solve one or more model equations, the resulting computer code can be considered as *generic code*. When the material properties, boundary conditions and grid dimensions of the generic model are specified to represent a particular geographical area, the resulting model is called a *site-specific model.*

The mathematical models are primarily classified based into three categories (Babu, 2004) such as:

- variation of various independent variables
- state of the process
- type of the process

The interconnection details of these models (Babu, 2004) are shown in Fig. 1.5. The complete mathematical model shown in Fig. 1.5, should possess the following information (Babu, 2004):

- the basic process variables
- relationships between the basic variables under static or steady-state conditions
- constraints
- optimality criteria
- objective functions
- relationships between the basic variables under dynamic or steady-state conditions.

A number of examples are available in literature pertaining to mathematical modeling. Streeter-Phelps model for dissolved oxygen balance in rivers (Peavy et al., 1985), modeling for wastewater treatment using activated sludge process (Kiely, 1998), modeling for resource utilization (Babu and Ramakrishna, 2002a), modeling of water balance in landfills (Kiely, 1998; Tchobanoglous et al., 1987), groundwater modeling (Gupta et al., 2003; Keshari, 2003; Sharma and Bhatnagar, 2003), seawater intrusion in multi-layered coastal aquifers (Rastogi and Ukarande, 2003), modeling of estuaries (Metcalf & Eddy, 1993), Gaussian model of plume dispersion (Peavy et al., 1985), are some of the examples of mathematical modeling in Environmental engineering applications.

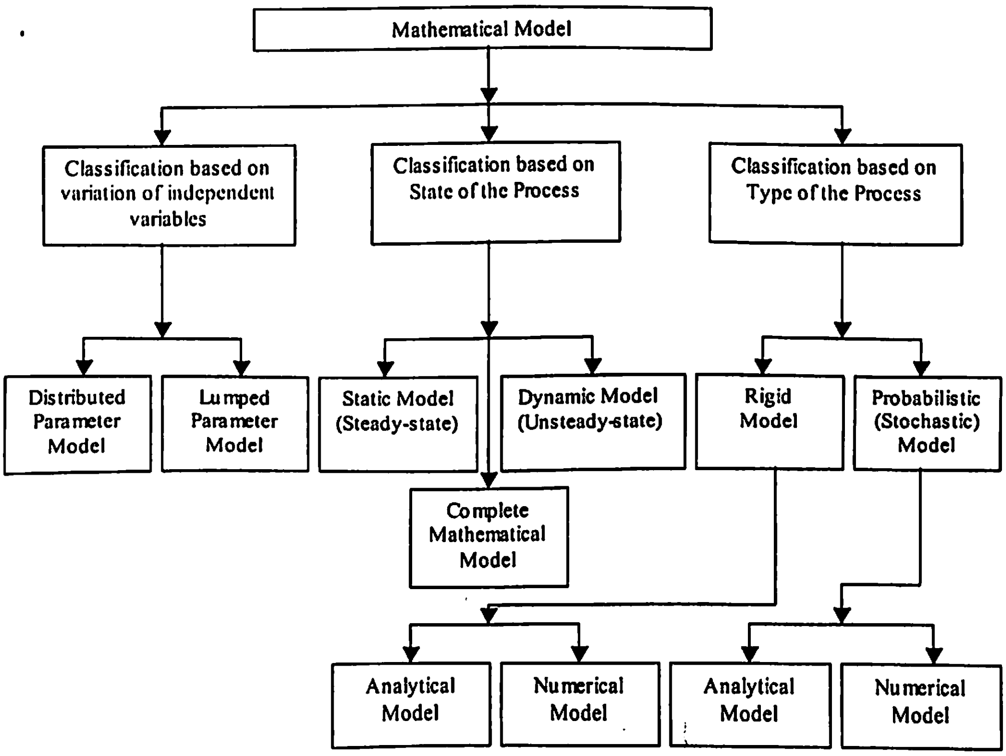


Fig. 1.5: Classification of mathematical modeling (Source: Babu, 2004)

1.4 Gaps in past studies

Activated carbon is widely used for contaminated water treatment (Rai et al., 1998; Sai et al., 1997; Tare and Chaudhari, 1995; Peavy et al., 1985). In spite of having advantages in terms of effectiveness and efficiency in the removal of pollutants especially from wastewater (Rengaraj et al., 1999), the commercial activated carbon is costly (Mall and Kumar, 1997). Hence there is a need to develop novel and cheaper adsorbents (Babu and Ramakrishna, 2001). The selection of adsorbents is based on their characteristic properties. Several investigators (Rao et al., 2000; Rao et al., 1999; Rai et al., 1998; Namasivayam, 1995; De and De, 1994) tried a number of low cost novel adsorbents. The novel adsorbents can be broadly classified into two categories:

- based on the raw material of adsorbent
- based on the pollutant for which they have been studied

Since a large number of novel adsorbents are being prepared from these materials using several methodologies, it becomes necessary to study the similarities in (i) the characteristics of adsorbents (ii) performance of the adsorbents. However no such studies are reported in literature. The studies are however limited to only draw comparisons (i) for the uptake of same adsorbate (Mohan and Karthikeyan, 1999; Shrichand et al., 1994) and/or (ii) with that of Commercial Activated Carbon (CAC) (Rao and Bhole, 2001; Rao and Bhole, 2000; Sekar and Murthy, 1998; Swamy et al., 1998; Mall and Kumar, 1997; Ramu et al., 1992; Gajghate and Saxena, 1991; Khagesan et al., 1991).

The modeling studies on adsorption reported in literature focused on:

- assessing the performance trends from the experimental data of the same investigator (Mall and Kumar, 1997; Manju and Anirudhan, 1997; Mohammad et al., 1997 etc).
- fitting the experimental data to the isotherm models (Bhole et al., 2002; Rao and Bhole, 2001; Rao and Bhole, 2000; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Mohammad et al., 1997; Raji et al., 1997; Patnaik and Das, 1995 etc).

- determining thermodynamic constants from experimental data (Manju and Anirudhan, 1997; Mohammad et al., 1997; Raji et al., 1997 etc).
- developing breakthrough curves using fixed-bed adsorption column and validating the Homogeneous Surface Diffusion Model (HSDM) with the experimental data (Markovska et al., 2001; Basheer and Najjar, 1996).
- modifying the mass transfer models by varying the assumptions in its development for more accurate prediction (Yao and Tien, 1994; Buzanowski and Yang, 1989; Liaw et al., 1979).

The regulatory standards [viz., Bureau of Indian Standards (BIS) formerly known as Indian Standards Institution (ISI)] are supposed to give guidelines for preparation and analysis aspects of most of the engineering applications. It is surprising to note that, there is no separate BIS code for defining the suitability of activated carbon for wastewater treatment. Only two BIS codes are available in India on this subject viz., for water treatment (IS 2752:1995) and for decolorization purposes (IS 8366:1989). In the absence of a relevant BIS code, comparison of adsorbent characteristics with permissible limits cannot be performed. The approaches to compare the adsorbent characteristics under such circumstances need to be addressed. However such approaches are not available in literature.

Adsorption as a phenomenon is complex due to highly random geometry of the packing material used as adsorbent bed. The underlying physical aspects have not been completely understood and hence adsorption modeling becomes a big challenge. Various investigators have used both analytical and empirical approaches for adsorption modeling. But unfortunately, the resultant predictions of these models for operating conditions other than those considered for development of these models is not very satisfactory. This may be attributed to incomplete understanding of adsorption phenomenon.

A close look at the literature available on adsorption studies revealed that there is an unanimity with reference to spontaneity of adsorption under a wide range of operating conditions for various materials with respect to free energy change (i.e., ΔG^0 negative). Further, the results reported by the investigators when compared on a common basis with respect to the adsorbate (pollutant) /adsorbent/specific characteristic property (i.e., macro level), inconsistent trends in the results are observed and hence, it is extremely difficult to compare any indigenous data with that already published in literature. Assuming that the results may be accurate and adequate for the specific study (i.e., micro level), development of a model incorporating available heterogeneous data of adsorption batch studies is extremely useful for comparison purposes. This model may reveal few interesting aspects either to understand (i) the adsorption phenomenon or (ii) the effectiveness of novel adsorbents. Incidentally, no such studies are reported in literature. For modeling purpose, the database reported in the literature is assumed as accurate at micro level. The first step in any model development starts with identification of affecting parameters and making use of dimensional analysis and regression approaches. Subsequently, the model is improved either by relaxing certain assumptions or using another approach that gives relatively better results than those obtained from dimensional analysis and regression approaches.

Prediction of Pollutant Removal Efficiency (PRE) is an important aspect in wastewater treatment. The variation of PRE depends on several factors such as adsorbent characteristics, contact time, adsorbate concentration etc. Several adsorbent preparation methodologies are being used in adsorption studies for different novel adsorbents. The database that is used for comparison becomes heterogeneous due to the change in preparation methodology and adsorbent. The prediction of PRE for such heterogeneous database will be an important study from the user's viewpoint.

The application of Artificial Neural Networks (ANNs), a black box tool for modeling complex mechanisms (Babu, 2004; Hassoun, 1998; Behera, 1997), is limited in adsorption studies (Basheer and Najjar, 1996). The Back-Propagation Network (BPN) is one of several networks that is widely used for predicting the output and is successfully applied to a wide range of problems (Babu, 2004; Basheer and Najjar, 1996).

It is proved in literature that, existing analytical models such as HSDM can predict the PRE with better accuracy. However, there is a need to have a closer look at HSDM to identify the reasons why it is not giving satisfactory predictions for the entire range of experimental data reported in literature. Studies pertaining to the relative efficiency of analytical model in PRE prediction over the empirical models are not available in literature.

Very few applications are available in literature on LCIA (McDougall and White, 1998) alone but a wide range of applications based on complete LCA are available addressing issues in waste management such as, highway waste management (Contadini et al., 2000), wastewater treatment (Suh and Rousseaux, 2001), solid waste management (Finnveden, 1998), resources management (Turkulainen et al., 2000), effective management of building materials (Paulsen, 2001) etc. Incidentally, no studies are reported in the usage of LCIA for preparation of an adsorbent.

1.5 Scope of present study

The present study focuses on understanding the physical phenomenon occurring in adsorption by modeling using dimensional analysis, regression analysis, ANN, and analytical approaches. The analysis taken up in the present study covers wide range of operating conditions and huge amount of data collected from various literature sources for removal of various pollutants from wastewater. However, only the batch studies of adsorption are considered in this study since they are simple in operation and less complicated than continuous column studies for modeling purposes. The following objective is identified for the thesis work:

- modeling the adsorption mechanism for wastewater treatment from literature data using analytical-, regression-, and neural network- approaches.

The scope of the thesis work covering the above objective is very wide and is as follows:

- carrying out comparative studies of adsorbents based on their precursor material, preparation methodology and their performance pertaining to adsorbate removal.
- development of a ranking model for identifying the adsorbents for their designated purpose based on the available BIS codes.
- validating the applicability of regression and ANN approaches for batch studies of adsorption.
- modeling for prediction of PRE from batch studies of adsorption using both dimensional and dimensionless groups.
- identifying the dominant design variables and model parameters of HSDM and finding the methods or models for accurate estimation of these parameters.

- validation of HSDM using the above corrected parameters and carrying out parametric study.
- for the experimental data generated in the preparation of an adsorbent from sawdust:
  - performing LCIA studies using mass balance approach.
  - establishing suggestions for reduction of waste emissions to the environment.

1.6 Organization of Thesis Report

The thesis is organized as follows:

Chapter-2 deals with Literature review. A brief introduction to adsorption, few technical aspects of adsorption covering commercial methods of adsorbent preparation, isotherm studies etc., past work in adsorption modeling, the various modeling approaches studied, and LCIA are discussed in this chapter.

Chapter-3 deals exclusively on Problem Formulation. The objectives are set based on past studies on adsorption and the modeling studies to be conducted are formulated. Comparative studies on different types of adsorbents reported in literature, applicability of -regression modeling in adsorption, -dimensional analysis for modeling in adsorption, -ANN for adsorption modeling and, –LCIA in adsorbent preparation from its precursor material are identified. Analytical modeling of adsorption system based on component balance is also identified for study.

Chapter-4 focuses on the Results and Discussions. The results obtained from the studies conducted based on problems formulated in the previous chapter are discussed in detail. Comparative studies of adsorbents are carried out based on BIS codes, raw material categories of adsorbent, adsorbent preparation methodologies etc.; regression and neural network modeling for prediction of pollutant (or adsorbate) removal efficiency from a heterogeneous database compiled from literature; discritization of Homogeneous Surface Diffusion Model (HSDM) for batch studies of adsorption- its validation and an exhaustive parametric study; and application of LCIA on adsorbent preparation are carried out and are discussed in detail.

Chapter-5 deals with the summary and conclusions obtained from the thesis.

The codes developed in this study and other relevant information are given in Appendices.

CHAPTER
2

LITERATURE REVIEW

It is evident from the discussion in Chapter-1 that, adsorption is a widely used technique for water/wastewater treatment. The literature review pertaining to adsorption technique, mechanism, and models are discussed in this chapter.

2.1 Adsorption

Adsorption is defined as the accumulation of substances at the interface between two phases (Peavy et al., 1985). In water and wastewater treatment, the interface is between the liquid and solid surfaces. The adsorbent most commonly used in water and wastewater treatment is activated carbon.

Activated carbon treatment of wastewater is usually considered as a tertiary technique (Table-1.5) for water that has already received normal biological treatment (Babu et al., 2000). The function of treatment in this case is to remove a portion of the remaining particulate and dissolved organic matter (Metcalf & Eddy, 1993).

The adsorption operation is one in which molecules leave the solution and are held on the solid surface by bonding. The distribution of the solute (adsorbate) between the phases results from its relative affinity for each phase. This in turn, relates to the nature of forces existing between molecules of adsorbate and those of the adsorbent phases. If the bonds are weak, the process is reversible and is called Physical adsorption. If the bonds are strong, process is irreversible and is called Chemical adsorption. Physical adsorption is the process that occurs most frequently in the removal of wastewater constituents by activated carbon (Metcalf & Eddy, 1993).

2.1.1 Isotherms

The quantity of adsorbate (q) that can be taken up by an adsorbent is a function of both the concentration of adsorbate (C) and the temperature. The amount adsorbed is determined as a function of C and at a constant temperature T and the resulting function is called an adsorption isotherm. The isotherm equations that are available in literature are compiled and given in Table 2.1. However, the isotherms developed by Freundlich and Langmuir are most commonly used for wastewater treatment (Metcalf & Eddy, 1993). Each of these two isotherms has two constants in their general forms (Singh and Srivastava, 2001; Patnaik and Das, 1995; Singh and Rawat, 1993a; Ramu et al., 1992), indicating:

- adsorption capacity: a of Langmuir equation and K_f of Freundlich equation
- energy of adsorption: b of Langmuir equation
- intensity of adsorption: $(1/n)$ of Freundlich equation

Table-2.1: Adsorption isotherms

S.No.	Name of the Isotherm	Mathematical form	Remarks
1	Linear	$q = KC$	Linear variation of q with C.
2	Freundlich	$q = K_f C^{1/n}$	▪ Empirical consideration. ▪ Heterogeneous surface energy. ▪ Formation of several molecular layers.
3	Langmuir	$q = \dfrac{abC}{1+bC}$	▪ Fixed number of adsorption sites are available on the adsorbent surface. ▪ All the sites have same energy. ▪ Monolayer formation. ▪ Adsorption is reversible.

K = Linear isotherm constant.

The Freundlich constant, n also indicates the degree of favorability of adsorption (Treybal, 1981). The Freundlich constant, n should have values lying in the range of *1 to 10* for classification as favorable adsorption (Rao and Bhole, 2001; Raji et al., 1997).

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor, R_L. It indicates the nature of isotherm and is defined by,

$$R_L = \frac{1}{1+bC_0} \qquad (2.1)$$

where, C_o = initial adsorbate concentration, mg/L

if $R_L > 1 \Rightarrow$ isotherm is unfavorable

if $R_L = 1 \Rightarrow$ isotherm is linear

if $R_L < 1 \Rightarrow$ isotherm is favorable

if $R_L > 1 \Rightarrow$ isotherm is irreversible

The mathematical proof of the separation factor concept is given in Appendix-C. The generalized Langmuir isotherm (Goyal et al., 1999) is given by

$$q_e = \frac{a(bC_e)^n}{(1+bC_e)^n} \qquad (2.2)$$

The above equation reduces (Goyal et al., 1999) to conventional Langmuir and Freundlich isotherms respectively under specific conditions such that,

$$q_e = K_f (C_e)^n \tag{2.3}$$

where, $K_f = a(b^n)$ (2.4)

where, K_f and n are Freundlich constants while a and b are Langmuir constants, while q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration at equilibrium (mg/L) respectively.

2.1.2 Mechanism of adsorption

The adsorption mechanism is explained through a set of sequential steps (Rai et al., 1998; Namasivayam, 1995; Metcalf & Eddy, 1993; Montgomery, 1985) as follows:

1. Transport of adsorbate from bulk solution phase to the boundary layer or a surface film surrounding the adsorbent particle and transport of adsorbate across the boundary layer to the exterior surface of the adsorbent particle. This is termed as film diffusion (or external mass transfer).
2. Diffusion of solute through the internal pores of the adsorbent and/or along the pore-wall surface. This is termed as intra-particle diffusion (or internal mass transfer).
3. Uptake of the adsorbate molecules by the active surface, the physical or chemical binding of adsorbate at the surface of the adsorbate.

The thickness of the stagnant aqueous film that surrounds the adsorbent depends on the flow regime maintained in the system. The rate of adsorption then depends on the rate at which the molecules move or diffuse in solution or the rate at which the molecules can reach the available surface by diffusing through the film and pore. The adsorbates can either diffuse in the adsorbed state along the pore surface (surface diffusion) or within the fluid contained in the pores (pore diffusion). In surface diffusion, molecules migrate along the surface when adjacent adsorption site is available and the molecule has the energy to leave the site it is presently occupying (Hand et al., 1983). It is observed that, surface diffusion is greater than the pore diffusion and hence can be neglected.

It is generally accepted that the step 3 in the mechanism of adsorption as mentioned above, i.e., uptake of the adsorbate molecules by the active surface, is very rapid and does not represent the rate-determining step in the uptake of organic/inorganic compounds. For the remaining two steps in the overall transport, three distinct cases occur (Mohan et al., 2001):

Case I: external transport > internal transport

Case II: external transport < internal transport

Case III: external transport ≈ internal transport.

In cases I and II, the rate is governed by film and particle diffusion, respectively. In case III, the transport of ions to the boundary may not be possible at a significant rate, thereby, leading to the formation of a liquid film with a concentration gradient surrounding the adsorbent particles.

Usually, external transport is the rate-limiting step in systems, which has: (i) poor mixing (ii) dilute concentration of adsorbate (iii) small particle size and (iv) high affinity of adsorbate for adsorbent. In contrast, the intra-particle step limits the overall transfer for those systems that have: (i) high concentration of adsorbate (ii) good mixing (iii) large particle size of adsorbent and (iv) low affinity of adsorbate for adsorbent.

Development of mathematical model in adsorption is based on the above steps of the adsorption mechanism. The available mathematical models in adsorption are discussed in Sec. 2.2.

2.1.3 Different adsorbents used in contaminated water treatment

Activated carbon is widely used for contaminated water treatment (Rai et al., 1998; Sai et al., 1997; Tare and Chaudhari, 1995; Peavy et al., 1985). In spite of having advantages in terms of effectiveness and efficiency in the removal of pollutants especially from wastewater (Rengaraj et al., 1999), the commercial activated carbon is costly (Mall and Kumar, 1997). Hence there is a need to develop novel and cheaper adsorbents. The selection of adsorbents is based on their characteristic properties. The effectiveness of the adsorbents however, is dependent on few operating parameters. The affecting parameters of adsorption along with the significance are summarized (Rai et al., 1998) in Table-2.2.

Table-2.2: Typical affecting parameters of adsorption

Factors	Description
Surface area	Measures available surface area for adsorption
Pore size distribution	Governs penetration of contaminants of various molecular sizes into the pores, which affects amount of usable area
Particle size distribution	Affects rate of adsorption
Hardness	Resistance to attrition during handling
Moisture content	Describes physical nature of material
Ash content	Describes physical nature of material
Surface properties	Nature and level of surface functional groups influence the capacity and specificity of adsorption
Loss of adsorptive capacity	Key factor in governing the process economics
Agitation speed	Key factor in governing the diffusion rate
Porosity	Indicates the available pore spaces
Ignition temperature	Useful when thermal activation/regeneration is employed
pH	Indicates the chemical nature of the material
Interferences	Presence of any other elements/compounds which may affect the efficient functioning of adsorbent

Several investigators (Rao et al., 2000; Rao et al., 1999; Rai et al., 1998; Namasivayam, 1995; De and De, 1994) tried a number of low cost novel adsorbents in their studies. The novel adsorbents can be broadly classified into two categories:

- based on the raw material of adsorbent
- based on the pollutant for which they have been studied

Tables 2.3 and 2.4 give the compilation of a partial list of investigators who have used the novel adsorbents in their studies. From Tables-2.3 and 2.4, it is to be noted that investigators are using a number of novel adsorbents.

Table-2.3: List of ivestigators based on raw material of the adsorbent

S.No.	Raw material of adsorbent	Investigators	
1	Industrial wastes	Khanna and Malhotra, 1977 Ramu et al., 1992 Kurian and Rajenthiran, 1995 Mall and Kumar, 1997 Mall and Upadhyay, 1998 Singh et al., 1998 Sekhar and Chakravarthy 2000 Prasad et al., 2000a, b	Gupta and Tiwari, 1985 Singh and Rawat, 1993a, b Patnaik and Das, 1995 Srivasatava et al., 1997a, b Swamy et al., 1998 Lee et al., 1998 Rao and Bhole, 2001 Singh and Rawat, 1993
2	Agricultural wastes	Kumar and Dara, 1980 Singh et al., 1993 Tiwari et al., 1995 Muthukumaran et al., 1995 Raji and Anirudhan, 1997 Manju and Anirudhan, 1997 Rao and Bhole, 2000 Singh and Srivastava, 2001	Khagesan et al., 1991 Shrichand et al., 1994 Kurian and Rajenthiran, 1995 Mohammad et al., 1997 Raji et al., 1997 Ajmal et al., 1998 Verma and Shukla, 2000 Ansari et al., 2000

2.1.4 Preparation of activated carbon

Activated carbon is prepared industrially from a number of raw materials (Sai et al., 1997; Hassler, 1974) such as- pinewood, bituminous coal, coconut shell etc. A variety of industrial equipment is used in the preparation of activated carbon from above raw materials. They include- shaft kilns, rotary kilns, moving grate stokers, multiple hearth furnaces, vertically stacked and connected crucibles, spaced perforated plates, dual pulse jet combustion systems, and fluidized beds (Sai et al., 1997).

Table-2.4: Novel adsorbents studied for their use in wastewater treatment

Adsorbents	Studied for the removal of
Crushed coconut shell, Rice straw, Rice husk ash, Fly ash, Sawdust, Granular amorphous peat, Ricehulls treated with zinc chloride, Bituminous coal, Coal, China clay, Lignite, Lime, Activated carbon, Modified acacia bark, *Chrolella vulgaris*, Rice husk powder, Waste tea and coffee powder, Exhausted coffee nuts, Walnut shells, Blast furnace flue dust, Fly ash regenerated with acid, Bagasse, Coconut jute carbon, Acacia arabica bark, Waste tea leaves carbon, Rice husk carbon, Carbonaceous waste slurry of fertilizer plant, Road dust.	Cr^{+6}
Fly ash, Sawdust, Modified acacia bark, *Chlorella vulgaris*, Coconut coir dust, Blast furnace slag, Ground nut hull treated with EDTA, Waste tyre rubber, Commercial activated carbon, Fly ash regenerated with acid, Polymerized grafted tin oxide gel, Jute, Montmorillonite, Kaolinite, Serpentine, Coal, Fly ash and Cement matrix; Waste tea leaves.	Pb^{+2}
Fly ash, Sawdust, Bituminous coal, Coconut shell, Raw rice husk, Chitosan, Hair, Modified acacia bark, Coconut coir dust, Rubber from scrap tyre, Groundnut hull treated with EDTA, Waste tea/ coffee powder, Exhausted coffee nuts, Walnut shells, Peanut skin, Coconut husk hull, Waste tyre rubber, Wollastonite, Montmorillonite, Kaolinite, Serpentine, Waste tea leaves.	Cd^{+2}
Pyrrhotite pyrite, Wool fibers modified with polyethyl amine, Coal, Waste rubber, Hair, Modified acacia bark, Tannery hair, Maize starch bark, Modified cellulose, Cattle hair, Chemically modified cotton, Waste tyre rubber, Sawdust, Jute, Modified cotton N-amino-deoxy cellulose, Foamed natural rubber.	Hg^{+2}
Granular amorphous peat, Fly ash, Alumino-silicates, Cowdung, Peat, Modified acacia bark, Coconut coir dust, Wollastonite, China clay, Fly ash-China clay, Peanut skin, Coconut husk hull, Sawdust, Jute, Serpentine, Coal, Fly ash, and cement matrix, Chitosan.	Cu^{+2}
Granular amorphous peat, Fly ash, Clay, Coconut coir dust, Blast Furnace slag, China clay, Coal, Fly ash, and cement matrix, Waste tea leaves.	Zn^{+2}
Granular amorphous peat, Fly ash, Modified acacia bark, Coconut coir dust, Peanut skin, Coconut husk hull, Wollastonite, China clay.	Ni^{+2}

The manufacture of activated carbon involves two main processes:

- physical activation
- chemical activation

2.1.4.1 Physical activation

This process comprises of two stages, viz.,

- carbonization of the precursor material (or raw material) and
- activation of the residual char.

Carbonization of the precursor material is achieved by subjecting it to temperatures in the range of 800-1000°C in the absence of air. During carbonization, the volatile component is almost eliminated. Activation of the residual char is performed to enhance the pore structure by partial gasification of the char in steam, carbon dioxide or air. The carbonized material reacts in a partial and controlled fashion with a gas such as CO_2, steam or a mixture of both at high temperatures, usually above 800 °C. In this controlled oxidation process, the activating agents essentially burn the most reactive parts of the carbonaceous skeleton.

The most important reactions in gasification with CO_2 and steam are (Sanchez et al., 2002):

$$C + H_2O \Rightarrow CO + H_2 \text{ -29 kcal} \quad (2.5)$$

$$C + CO_2 \Rightarrow 2CO \text{ -39 kcal} \quad (2.6)$$

Other reactions involved in this process are:

$$CO + H_2O \Rightarrow CO_2 + H_2 \text{ +10 kcal} \quad (2.7)$$

$$C + 2\,H_2 \Rightarrow CH_4 \text{ - 17.87 kcal} \quad (2.8)$$

Since reactions (2.5) and (2.6) are endothermic, activation of the carbonized material is readily achieved with an external supply of energy. The rate of gasification with steam is decreased by the presence of H_2, which becomes strongly adsorbed in the active sites of the carbon surface, which is in turn reflected in a decrease in the activation rate. In industrial applications, often the flue gas is used to substitute CO_2 and is mixed with steam for activation. However, it has been reported (Sai et al., 1997) that usage of steam alone as an activating gas enhances the activation compared to a mixture of steam and CO_2 or pure CO_2.

Activation of carbon occurs (Sai et al., 1997) in a series of processes, broadly classified as carbonization and activation. During carbonization, most of the non-carbon elements such as hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material. The freed atoms of elementary carbon are grouped into sheets of condensed aromatic ring systems with a degree of planar structure. The mutual arrangement of these aromatic sheets is irregular and leaves free interstices between them. They become filled with tarry matter or the products of deposition or blocked partially by the disorganized carbon. In the first stage of activation, when burn-off is not higher than 10%, this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation, at the second stage, carbon of the aromatic sheets is burnt. When the burn-off is less than 50%, a micro-porous activated carbon is obtained and at a burn-off greater than 75%, a macro-porous activated carbon is obtained. When the burn-off is in the range 50% to 75%, the product obtained is of mixed structure and contains both micro- and macro-pores. Development of macropores due to coalescence or widening of micro-pores under fast reaction conditions result in a reduction of surface area of the adsorbent.

Pores in activated carbon have numerous sizes and shapes. Pore sizes have been classified into three types:

- micropores (pore diameter less than 20 nm)
- mesopores (pore diameter 20-200 nm) and
- macropores (pore diameter greater than 200 nm)

The micropores contribute maximum to the surface area while, the meso and micropres serve as 'roads' and 'streets' leading to micropores (KCPL, 2004). A lower degree of activation yields an activated carbon with a high proportion of micro pores, whereas with increasing degree of activation the portion of mesopores and macropores increases (Degel, 1990). A typical flow sheet of Physical activation process is given (KCPL, 2004) in Fig. 2.1. A sketch of the activated carbon showing the development of pores is given in Fig. 2.2.

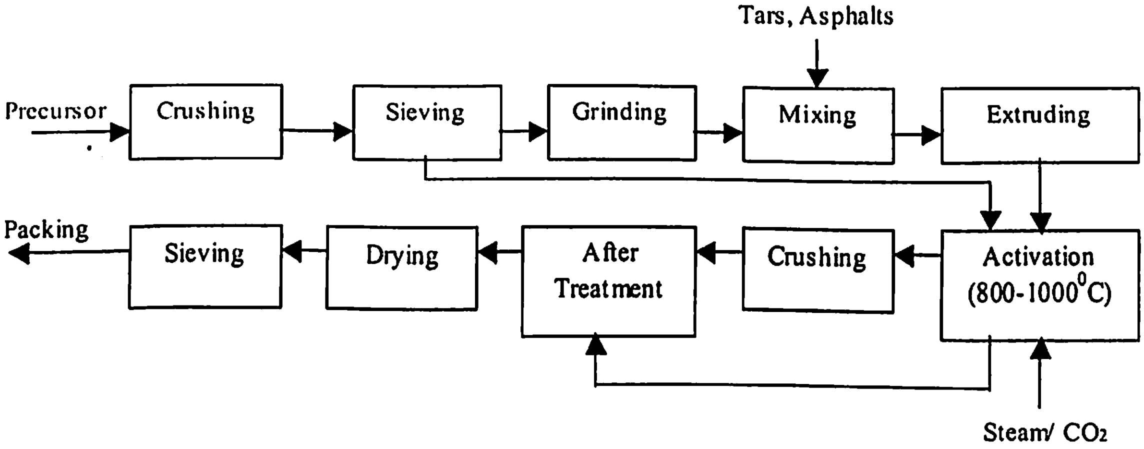


Fig. 2.1: Typical flow sheet for manufacturing activated carbon using physical activation
(Source: KCPL, 2004)

2.1.4.2 Chemical activation

Chemical activation refers to the carbonization of the precursor after addition of substances such as phosphoric acid, NaOH, KOH, $ZnCl_2$, etc., that restricts the formation of tar and resulting in a porous carbonized product. The advantage of chemical activation method is that, it lowers the adsorbent preparation temperature, which may cause an increase in product yield and a control of pore size distribution. The common feature of all substances used in the chemical activation process reveals that the dehydrating agents influence pyrolytic decomposition and inhibit formation of tar, thus enhancing higher yield of activated carbon. It can be achieved using one-step activation or two-step activation (Kurakane et al., 2002):

- **One-step activation:** Impregnation of the chemical used for activation (NaOH, KOH, $ZnCl_2$, etc.) is carried out on the precursor material. The sample is dried, heated to high temperatures and activated using gases described above under physical activation.
- **Two-step activation:** In the first step, carbonization of precursor material is carried out at high temperatures in inert (N_2) atmosphere. In the second step, the char and the chemical are mixed and heated under the same temperature as in previous step. The residual sample is washed with acid and distilled water.

Kurakane et al. (2002) studied the above two types of chemical activation treatment using NaOH on Loy Yang Low Ash coal (from Victoria, Australia), which is a low rank coal. They observed that, the yield of activated carbon was decreased with increasing relative amount of added NaOH. Especially in the one-step preparation, the yield remarkably decreased in a slight addition of NaOH. But the weight loss in the one-step preparation was lower compared with the two-step preparation when the relative amount of added NaOH was the same.

A typical flow sheet of chemical activation process using zinc chloride/phosphoric acid is given (KCPL, 2004) in Fig. 2.3. When activation is performed, the pores developed are usually bottle-shaped in case of chemical activation and cone-shaped in case of physical activation. As the internal surface area of the narrow–mouthed bottle-shaped pores is not available to adsorbates of larger size than the mouth, the cone-shaped pores may contribute to useful effective surface area (Sai et al., 1997).

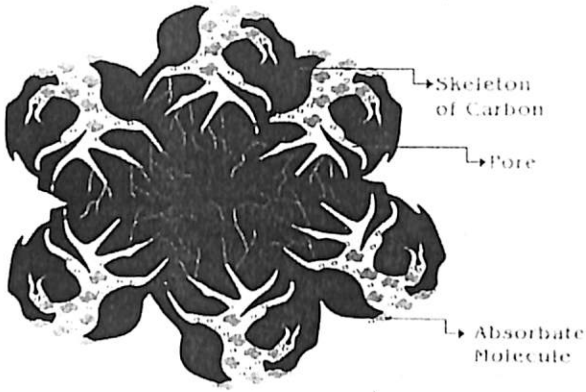


Fig. 2.2: Sketch of activated carbon (Source: KCPL, 2004)

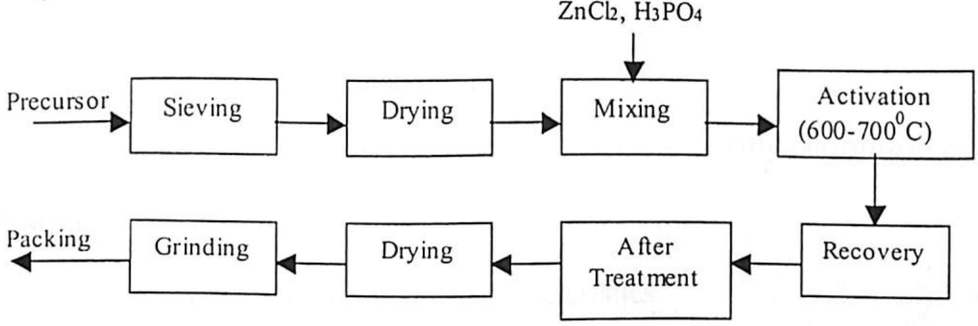


Fig. 2.3: Typical flow sheet for manufacturing activated carbon using chemical activation
(Source: KCPL, 2004)

The size and shape of adsorbent particle are important for increased adsorption. Though smaller size of particle may produce larger surface area, they may burn out easily during activation at high temperatures and faster reaction rates resulting in lesser surface area (Sai et al., 1997). The variation of shape factor of the adsorbent particle is also studied (Wang, 1999) for its influence on adsorption capacity. Wang (1999) studied the effects of three shapes- planar, cylindrical/fibrous, and spherical. He concluded that, the spherical geometry is most favorable for adsorption due to the minimum surface energy (minimum surface area per unit volume ratio) for the sphere. The planar geometry is found out to be the most unfavorable of the three geometrical shapes studied.

Based on their applications, activated carbon is classified as liquid phase carbons characterized by their macropores and vapor phase carbons characterized by their micropores. Liquid phase carbons are generally applicable to water treatment and vapor phase carbons are used to remove undesirable organic vapors from effluent gas streams. Chemical activation is predominantly used for making powdered activated carbon while physical activation is used for making granular activated carbons. Commercially, wood, peat, lignite, hardcoal, oil products, charcoal, and coconut shells are used as precursors in physical activation (Degel, 1990).

2.1.5 Experimental studies

The experimental studies in water/wastewater treatment are usually performed to evaluate the following:

- physical, chemical, and bacteriological characteristics
- process parameters
- performance of treatment units etc.

The first option among the above is a routine operation in the laboratories where the water/wastewater is tested. The second option is primarily a research activity where the optimum process parameters are systematically investigated. Determining the kinetics (rate constants) of biological treatment units is one of the examples under this option. The third option can be studied both at field and research laboratories by collecting field samples and/or taking inputs from either first or second option.

The experimental studies can be classified as:

- batch studies (or bench scale studies)
- continuous studies

- pilot studies

The batch studies are usually done at bench scale. Settling column test for discrete or flocculent settling, determining adsorption isotherm constants, determining equilibrium time of adsorption etc. are examples of batch studies. Column studies of adsorption for determination of breakthrough curves, study of the quality of water from a sand filter etc. are examples of continuous studies. Here, the samples are collected and tested over a long periods of time on a continuous basis for a continuous flow. The pilot studies take inputs from the batch and continuous studies. The pilot plant (model) will be established on a relatively larger scale to that of laboratory scale but to a relatively smaller scale from that of a field or commercial scale (prototype). These are primarily run with the objectives of establishing the techno-economic feasibilities of the model studies.

2.2 Past studies in adsorption modeling

The adsorption experimental studies are performed either as batch studies or continuous flow (or column) studies. The results are analyzed using simple empirical models (regression techniques) or analytical models. Since the adsorption mechanism is very complex depending on several dimensional and dimensionless parameters, black-box techniques such as ANN can be used for modeling purposes. The past work reported on adsorption modeling using the above approaches is discussed below:

2.2.1 Regression models

2.2.1.1 Batch studies

The batch adsorption studies are usually conducted in conical flasks or beakers in the laboratory. A fixed quantity (W) of the adsorbent is added at a known pH to a known concentration (C_0) and volume (V) of adsorbate. The contents are stirred at constant temperature (T) at a constant rpm (ω) for a specific contact time (t_c) and filtered. The filtrate is analyzed for the concentration of the adsorbate (C_f). The final adsorbate concentration (C_f) is determined by repeating the tests for different values of the operating parameters viz., W, V, C_0, t_c, pH , T, and ω. The effect of each parameter on the adsorbate removal is studied and the optimum values of the operating parameters are determined from the results. The results are modeled for estimation of the following:

- equilibrium time
- isotherm constants
- thermodynamic constants

The adsorbent's performance is calculated by calculating the dimensionless parameters such as, adsorbate (or Pollutant) Removal Efficiency (PRE) and the amount adsorbed for which it is used. The following expressions are used for this purpose:

$$\text{PRE (\%)} = \left(\frac{C_0 - C_f}{C_0}\right)100 \qquad (2.9)$$

$$\text{Amount adsorbed} = \frac{V(C_0 - C_f)}{W} \qquad (2.10)$$

Equilibrium time

The equilibrium time (t_{eq}) is the contact time corresponding to stabilized solute concentration in bulk solution. However estimation of such an equilibrium time may work out to be a long time for practical conditions. The pollutant (adsorbate) removal curve becomes asymptotic after certain contact time indicating the stabilized concentration of the adsorbate (C_e) in bulk solution. Identification of the appropriate equilibrium time from such plot needs some judgment. Bhargava and Killedar (1991) suggested a rational methodology to estimate the most appropriate and practical equilibrium time in batch adsorption studies. They suggested three criteria for such purposes:

- an eye judgment when the curve appears nearly asymptotic to the time axis.
- an arbitrary cut-off value of the slope (say 2%) of the curve.
- an arbitrary cut-off point of say 95% of maximum removal for a given variable.

Bhargava and Killedar (1991) conducted experiments for the removal of fluoride and modeled the results for estimation of optimum equilibrium time. Studies pertaining to modeling of equilibrium time are scarce. Few investigators (Rahman and Saad, 2003; Prasad et al., 2000a; Ajmal et al., 1998; Patnaik and Das, 1995; Singh et al., 1993; Grover and Narayanaswamy, 1982) however modeled the variation of PRE with contact time for their studies. This is an empirical model and is of the form,

$$PRE = kt^{m} \qquad (2.11)$$

where, k and m are constants that can be determined by regressing the above equation and t is the contact time.

The above equation indicates that the PRE curves are non-linear with respect to contact time. Ricordel et al., (2001) reported an empirical model for predicting amount adsorbed (q) as a function of contact time (t) and is given by:

$$q = \frac{q_e kt}{1 + kt} \tag{2.12}$$

The above equation can be rearranged to a linear form of $y = mx + c$ type and as follows:

$$\frac{1}{q} = \frac{1}{q_e} + \left(\frac{1}{q_e k}\right)\left(\frac{1}{t}\right) \tag{2.13}$$

The experimental data is plotted as ($1/q$) vs. ($1/t$), which gives a straight line having a slope of ($1/q_e k$) and an intercept of ($1/q_e$). The constants q_e (maximum amount of adsorbate adsorbed) and k can be determined from the intercept and slope respectively.

Isotherm constants

Investigators used either Langmuir (Karthikeyan et al., 2002; Al-Qodah, 2000; Raji and Anirudhan, 1997; Singh and Rawat, 1997; Kumaraswamy et al., 1995; Tiwari et al., 1995; Singh and Rawat, 1994; Singh and Rawat, 1993a, b; Singh et al., 1993) or Freundlich isotherms (Rahman and Saad, 2003; Sivabalan et al., 2003; Das and Patnaik, 2001; Ansari et al., 2000; Chandrasekhar and Chakravarthy, 2000; Verma and Shukla, 2000; Rengaraj et al., 1999; Anirudhan and Sreedhar, 1998; Manju and Anirudhan, 1997; Mohammad et al., 1997; Dimitrova, 1996; Raji and Anirudhan, 1996; Muthukumaran et al., 1995; Patnaik and Das, 1995; Shrichand et al., 1994; Ramu et al., 1992; Khagesan et al., 1991; Periasamy et al., 1991; Grover and Narayanaswamy, 1982) or both (Meena and Rajagopal, 2003; Tseng et al., 2003; Bayat, 2002; Bhole et al., 2002; Johnson et al., 2002; Rao and Bhole, 2002; Rao et al., 2002; Mohan et al., 2001; Rao and Bhole, 2001; Singh and Srivastava, 2001; Somani et al., 2001; Banat et al., 2000; Prasad et al., 2000a, b; Rao and Bhole, 2000; Singh and Srivastava, 1999; Raji et al., 1997; Swamy et al., 1998; Ajmal et al., 1998; Mall and Upadhyay, 1998; Singh et al., 1998; Mall and Kumar, 1997; Raji and Anirudhan, 1997; Kurian and Rajenthiran, 1995; Himesh and Mahadevaswamy, 1994; Singh et al., 1993) to study their results for suitability of adsorption.

Each of these two isotherms has two constants in their general form (Table-2.1). These constants are useful in predicting the concentration profiles through analytical modeling in either batch studies or adsorption columns. They are also required for determining the thermodynamic constants. These isotherm equations are linearized (regression model) to determine the constants. The linearized form of the Freundlich isotherm is:

$$\ln q = \ln K_f + \frac{1}{n}\ln C \tag{2.14}$$

When a graph is plotted between ln$q$ and ln$C$, the slope and intercepts will give $(1/n)$ and lnK_f respectively from which the Freundlich isotherm constants n and K_f can be obtained.

Similarly the Langmuir isotherm can be regressed as:

$$\frac{1}{q} = \frac{1}{b} + \left(\frac{1}{ab}\right)\left(\frac{1}{C}\right) \tag{2.15}$$

When a graph is plotted between $1/q$ and $1/C$, the slope and intercepts will give $(1/ab)$ and $(1/b)$ respectively from which the Langmuir isotherm constants a and b can be obtained. The Langmuir constants are also used to estimate the separation factor (given in Eq. 2.1) for understanding whether the isotherm is favorable or not for a particular system.

Thermodynamic constants

The thermodynamic constants viz., free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) are used to predict the exothermicity/endothermicity and spontaneity of adsorption (Singh and Srivastava, 1999; Raji et al., 1997).

A positive value of ΔH^0 indicates endothermic nature of adsorption (Singh and Srivastava, 1999; Singh and Rawat, 1994) while a negative value indicates exothermic nature of adsorption (Singh and Srivastava, 2001). A positive value of ΔS^0 indicates more affinity for the adsorbent and increased randomness at solid-liquid interface (Raji et al., 1997) while a negative value indicates reduction in free movement of ions at the interface (Das and Patnaik, 2001). A negative value of ΔG^0 indicates the feasibility of the adsorption process and spontaneous nature (Raji et al., 1997). It is evident from the literature that though the results are conflicting with reference to exothermicity (ΔH^0 is negative) and endothermicity (ΔH^0 is positive), there is an unanimity with reference to spontaneity (ΔG^0 being negative) under a wide range of operating conditions for various materials.

2.2.1.2 Column studies

Column type continuous flow studies are advantageous over batch studies because rate of adsorption depends upon the concentration of the solute in the solution being treated (Singh and Srivastava, 2001). For column operation, the adsorbent is continuously in contact with a fresh solution. Subsequently, the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant. In contrast, the concentration of solute in contact with a specific quantity of adsorbent steadily decreases as adsorption proceeds thereby decreasing the effectiveness of the adsorbent for removing the solute in batch treatment.

Some investigators (Sivabalan et al., 2003; Das and Patnaik, 2001; Singh and Srivastava, 2001; Singh and Srivastava, 1999; Mall and Upadhyay, 1998; Swamy et al., 1998; Muthukumaran et al., 1995; Tiwari et al., 1995; Singh et al., 1994; Singh et al., 1993) who performed batch studies also performed column studies. The procedure adopted in general by these investigators is as follows: The column is packed with the adsorbent. The adsorbate flow rate and bed depth are varied through the column. Breakthrough curves are generated from which the breakthrough and exhaustive capacities are calculated. Activated carbon is also used as an adsorbent to estimate the effectiveness of the other adsorbents used (Singh et al., 1994). The column test results are analyzed using Bed-Depth Service Model (BDST) to estimate adsorptive capacity, critical bed depth, and rate constant (Das and Patnaik, 2001; Mall and Upadhyay, 1998; Swamy et al., 1998; Tiwari et al., 1995).

2.2.2 Analytical models

The analytical models available in adsorption studies are primarily of two types:

- Estimation of mass transfer over a porous adsorbent particle: This is usually done for batch studies to estimate the mass transfer from the liquid to solid and within the solid.
- Prediction of adsorbate concentration history profiles in the fixed-bed columns: This is useful in understanding the movement of adsorbate front across the adsorbent column.

Determination of appropriate isotherm equation and its constants is essential for both the above models. This information will indicate how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Al-Qodah, 2000). Different models for the adsorption process of gaseous or liquid components have been proposed in the literature. The differences in the mathematical models of adsorption processes arise from different representation of the equilibrium behavior, different expressions of the mass transfer inside and outside the adsorbent particle and from how the axial dispersion is taken into account in the material balance for the adsorbate in the fixed bed column. Also various numerical techniques have been used for the solution of the fixed bed adsorber models. The details of the past studies on these models for both the batch and column studies are briefly discussed below:

2.2.2.1 Simple model for batch studies

Singh et al., (1993) presented a simple model based on mass balance in batch studies of adsorption. The details are as follows:

Consider V liters of adsorbate solution used in adsorption studies where its concentration is reduced from C_0 to C_1 mg/L after a specific contact time, t. The amount of adsorbent used is W g and the solute loading changes from q_0 to q_1 mg/g of adsorbent. When a fresh adsorbent is used, $q_0 = 0$ and the mass balance equates the adsorbate removed from the liquid to that adsorbed by the solid.

i.e., $V(C_0 - C_1) = W(q_1 - q_0) = W q_1$ (2.15)

If the system is allowed to come to equilibrium,

$$\begin{aligned} C_1 &= C_e \\ q_1 &= q_e \end{aligned} \tag{2.16}$$

Assuming the system follows Langmuir isotherm model,

$$\frac{W}{V} = \frac{(C_0 - C_e)}{(abC_e/1 + aC_e)} \tag{2.17}$$

If the system follows Freundlich isotherm model,

$$\frac{W}{V} = \frac{(C_0 - C_e)}{K_f C_e^{1/n}} \tag{2.18}$$

Singh et al., (1993) predicted the adsorbent dose (*W*/*V*) from the model and verified with their experimental data. Langmuir isotherm model found to be suitable for their experimental data. They compared the adsorbent dose used in the experiments to that obtained from the model. An error ranging from –5% to +21% for five experimental values (different values of C_0) was reported, which was attributed to the probable approximation in obtaining the Langmuir isotherm constants. This may be mainly due to the experimental errors involved at various stages such as (i) weighing the adsorbent (ii) dilutions to bring the desired concentrations of adsorbate (iii) estimation of final adsorbate concentration by analytical chemistry methods, and so on. Errors may also occur due to approximation in the regressed data for determining the isotherm constants.

Batch studies are useful for estimation of the parameters that indicate the feasibility of adsorption. However, data from column studies is needed to establish the design parameters of adsorption column. Hence, there is a need to examine the response of adsorbents under continuous studies both experimentally and theoretically.

But due to the errors involved in experimentation as mentioned above, the focus should be on theoretical modeling by appropriately understanding the physical phenomena occurring in adsorption. The following section deals with the literature reported on theoretical studies in adsorption.

Al-Qodah (2000) studied the adsorption of reactive dyes on shale oil ash during a series of batch adsorption experiments. The adsorption isotherm data were fitted to Langmuir isotherm. The models for predicting the performance of batch adsorbers are usually based on either liquid film resistance or pore diffusion resistance. Models based on any one of these will have a limitation in understanding the actual adsorption mechanism. He used a successfully proven model based on the combination of the two resistances. The model equations are numerically solved using implicit scheme of finite difference method in conjunction with Crank and Nicholson method. The model and experimental results are compared.

McKay (1985a, b) used a mass transport model based on external mass transfer and homogeneous solid phase diffusion for agitated batch reactors. McKay (1985b) analyzed the model incorporating dimensionless time and dimensionless distance using Crank and Nicholson method. He performed experimental studies for adsorption of dyes onto activated carbon and applied the developed model.

Flora et al. (1998) studied modeling of powdered activated carbon for the uptake of elemental mercury vapors. He studied Homogeneous Surface Diffusion Model (HSDM) for his batch studies assuming Langmuir isotherm represents the equilibrium behavior between the activated carbon surface and the gas phase. He solved the model equations using orthogonal collocation and applied his experimental data to the model.

Kaguei et al. (1989) studied the available analytical models describing the rate of adsorption onto porous adsorbent particle. He studied the variation of equilibrium time with respect to contact time. He conducted experiments for the adsorption of chloroform on activated carbon in a batch reactor and compared the results with the numerical solutions obtained by the models.

Hand et al. (1983) developed few user-oriented solutions to the HSDM that are applicable to batch studies. They presented correlations and graphical solutions for estimating the diffusivity from the experiments.

2.2.2.2 Column studies

The Homogeneous Surface Diffusion Model (HSDM) is used and analyzed by several researchers (Slaney and Bhamidimarri, 1998; Basheer and Najjar, 1996). Models for the heterogeneous diffusion model have been developed that assume macropore and micropore diffusion occurring in series or in parallel. Yao and Tien (1994; 1993; 1992a, b) presented two approximate expressions for the rate of solute uptake by spherical adsorbent pellets. They used these expressions for adsorption calculations of batch, continuous flow stirred tank and fixed bed systems. Robinson et al. (1994) presented a full description of the mass transfer mechanisms for zeolite adsorption and ion exchange in wastewater treatment. The dynamics of a fixed bed is described by a set of convection diffusion equations, coupled with source terms due to adsorption and diffusion inside the adsorbent particles. Prediction of the breakthrough curves is based on correctly formulating the mathematical model for a fixed bed adsorber.

Slaney and Bhamidimarri (1998) used HSDM to predict the Penta-Chloro Phenol (PCP) adsorption breakthrough curves in the fixed beds. The diffusion and convection model equations were solved using orthogonal collocation in conjunction with Runge-Kutta technique. The experimental results on the adsorption of PCP in activated carbon columns proved that the HSDM can predict the column performance satisfactorily and therefore can be used in the design of fixed beds for removal of PCP.

2.2.3 Artificial neural network modeling

Very few studies are available for application of Artificial Neural Network (ANN) modeling in water/wastewater treatment/adsorption studies. Basheer and Najjar (1996) used Back-Propagation Network (BPN) model to predict the breakthrough curves of fixed-bed adsorbers. Close agreement is observed between the breakthrough curves predicted by the developed BPN model and those obtained from the HSDM. For prediction purposes, the breakthrough curve is discritized to have times corresponding to 1, 5, 25, 50, 75, and 90% removal of adsorbate. The model is used with three inputs (weight of adsorbate in column, initial concentration of adsorbate, and particle radius) and six outputs (discritized times). The model is trained and tested using 31 and 5 sets of data respectively from column studies. Two other studies are also available that primarily concern with process control of a water treatment plant involving a combination of physical and chemical unit operations (Zhang and Stanley, 1999) and optimizing a process operation in paper and pulp industry (Lanoutte et al., 1999).

BPN classifiers have the ability to learn the classifications of a set of training examples, and can often successfully generalize this knowledge to classify new cases of known failure types. They have been successfully applied to a wide variety of problems such as pattern classification problems in a number of fields, which include classification of sonar targets (Gorman and Sejnowski, 1988), speech recognition (Lippmann, 1989) and sensor interpretation (McAvoy et al., 1989), failure state recognition in chemical plants (Babu and Shailesh, 2000; Ungar et al., 1990; Venkatasubramanian et al., 1990;

Ferrada et al., 1989; Venkatasubramanian and Chan, 1989; Watanabe et al., 1989; Hoskins and Himmelblau, 1988; Hoskins et al., 1988). Other applications of ANN include dynamic modeling and control of chemical process systems (Bhat and McAvoy, 1989), diagnosis using BPN model (Kramer and Leonard, 1990), ANN model for the equilibria prediction in ternary mixture extraction (Babu and Karthik, 1997), for the estimation of heat transfer parameters in trickle bed reactors using radial basis functional networks (Babu and Sangeetha, 1998). Basheer and Najjar (1996) discussed a number of other applications of BPN model in Civil Engineering.

2.2.4 Life cycle inventory analysis

Removing pollutants from waste is the most important aspect in waste management. Very few applications are available in literature on Life Cycle Inventory Analysis (LCIA) (McDougall and White, 1998) alone but a wide range of applications based on complete Life Cycle Assessment (LCA) are reported in literature addressing issues in waste management such as, highway waste management (Contadini et al., 2000), wastewater treatment (Suh and Rousseaux, 2001), solid waste management (Finnveden, 1998), resources management (Turkulainen et al., 2000), effective management of building materials (Paulsen, 2001) etc. Incidentally, no studies are reported in the usage of LCIA for preparation of an adsorbent.

Adsorption is one of the proven techniques for treatment of both liquid and gaseous pollutants (Peavy et al., 1985). Commercial Activated Carbon (CAC) prepared from charcoal is widely used for adsorption of pollutants (Metcalf & Eddy Inc., 1993; Peavy et al., 1985). As discussed in earlier sections, a number of non-conventional adsorbents are being attempted by several investigators in order to develop an alternative to the CAC satisfying techno-economic requirements. The investigators attempted a number of methodologies [Nominal treatment (N), Physical treatment (P), Thermal treatment (T), Chemical treatment (C), and combinations of all these options] to prepare adsorbent from different raw materials. The adsorbent with thermal treatment is found to have more effective surface area than developed from chemical treatment (Sai et al., 1997). The LCIA can help in studying the quantity and location of waste emissions leaving into environment during the conversion of a raw material into an useful product. This will help in identifying the approaches to reduce the waste emissions, if possible, and/or recycling them for some other use. This measure will minimize the waste emission discharged into environment. Further the cost aspects during the material conversion can be understood by performing mass and energy balance over the material conversion system.

CHAPTER
3

PROBLEM FORMULATION

The problems are formulated for the Thesis work after a detailed study of the available literature (Chapter-2) and the scope of work identified (Chapter-1) for addressing the gaps. The problem formulation is divided into the following categories based on the nature of objectives addressed:

- comparative study on adsorbents
- modeling for predicting process performance
- laboratory investigations in adsorption batch studies

The Freundlich isotherm is applicable for dilute concentrations (Treybal, 1981) that are used in wastewater treatment and hence is chosen as basis for comparative studies of different adsorbents reported in literature. Information pertaining to the Freundlich isotherm constants are collected, compiled, compared, and analyzed with specific objectives as mentioned in the following sections. The results and discussions of these studies are addressed in Chapter-4.

3.1 Comparative study on adsorbents

3.1.1 Based on the raw (precursor) material used

Different raw (precursor) materials are reported in literature (Bhole et al., 2002; Rao and Bhole, 2002; Rao et al., 2002; Das and Patnaik, 2001; Singh and Srivastava, 2001; Ansari et al., 2000; Chandrasekhar and Chakravarthy, 2000; Prasad et al., 2000b; Verma and Shukla, 2000; Singh and Srivastava, 1999; Ajmal et al., 1998; Anirudhan and Sreedhar, 1998; Mall and Upadhyay, 1998; Swamy et al., 1998; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Raji and Anirudhan, 1997; Raji et al., 1997; Raji and Anirudhan, 1996; Muthukumaran et al., 1995; Shrichand et al., 1994; Singh et al., 1993; Ramu et al., 1992; Khagesan et al., 1991; Periasamy et al., 1991; Grover and Narayanaswamy, 1982; Khanna and Malhotra, 1977) for preparation of novel adsorbents. For the comparative study, they are broadly classified into three categories viz., Agricultural Wastes (AW), Industrial Wastes (IW), and Mineral Wastes (MW). The information pertaining to the values of Freundlich constants reported for the novel adsorbents prepared from these raw materials is collected and compiled. The database is analyzed to study the effect of raw material with respect to Freundlich isotherm constants.

3.1.2 Based on adsorbent preparation methodology

Physical and chemical activation are the two common commercially adopted methodologies (KCPL, 2004). Rengaraj et al., (1999), for example, conducted studies using chemical activation while Sai et al. (1997) discussed the advantages of fluidized beds for physical activation. Literature review (Bhole et al., 2002; Rao and Bhole, 2002; Rao et al., 2002; Das and Patnaik, 2001; Singh and Srivastava, 2001; Ansari et al., 2000;

Chandrasekhar and Chakravarthy, 2000; Prasad et al., 2000b; Verma and Shukla, 2000; Singh and Srivastava, 1999; Ajmal et al., 1998; Anirudhan and Sreedhar, 1998; Mall and Upadhyay, 1998; Swamy et al., 1998; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Raji and Anirudhan, 1997; Raji et al., 1997; Raji and Anirudhan, 1996; Muthukumaran et al., 1995; Shrichand et al., 1994; Singh et al., 1993; Ramu et al., 1992; Khagesan et al., 1991; Periasamy et al., 1991; Grover and Narayanaswamy, 1982; Khanna and Malhotra, 1977) shows that, a number of methodologies are being adopted to prepare novel adsorbents from their raw material. The different methodologies reported in literature are studied for recommending the better methodology for adsorbent preparation. The recommendation is based on the compliance of Freundlich isotherm constants from the experimental data available for the adsorbents. The adsorbent preparation methodologies reported in literature are studied and are categorized based on the predominant method of operation involved. The database is analyzed to study the effects with respect to the Freundlich isotherm constants.

3.1.3 Based on functional dependency of Freundlich isotherm constants

A wide spread in the data pertaining to Freundlich isotherm constants is noticed in literature. It is important to know the reason behind the above inconsistency so as to make use of the literature data in analysis of adsorption as a process. The Freundlich constant, n should have values lying in the range of 1 to 10 for classification as favorable adsorption (Rao and Bhole, 2001; Raji et al., 1997). A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent (Ramu et al., 1992), while a higher value for K_f indicates high rate of adsorbate removal (Ajmal et al., 1998; Ramu et al., 1992). The functional dependency of Freundlich isotherm constants (K_f and n) on Temperature

(T) is studied for the data available in literature (Bhole et al., 2002; Rao and Bhole, 2002; Rao et al., 2002; Das and Patnaik, 2001; Singh and Srivastava, 2001; Ansari et al., 2000; Chandrasekhar and Chakravarthy, 2000; Prasad et al., 2000b; Verma and Shukla, 2000; Rengaraj et al., 1999; Singh and Srivasatava, 1999; Ajmal et al., 1998; Anirudhan and Sreedhar, 1998; Mahadevaswamy et al., 1998; Mall and Upadhyay, 1998; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Raji and Anirudhan, 1997; Raji et al., 1997; Raji and Anirudhan, 1996; Himesh and Mahadevaswamy, 1994; Shrichand et al., 1994; Singh et. al., 1993; Ramu et al., 1992; Khagesan et al., 1991; Periasamy et al., 1991; Grover and Narayanaswamy, 1982; Khanna and Malhotra, 1977).

3.1.4 Based on available Bureau of Indian Standards (BIS) codes

The characteristics of the adsorbents reported in literature are compared with those prescribed in Bureau of Indian Standards (BIS) codes (IS 2752:1995 and IS 8366:1989) to study their compliance. A compilation of the adsorbent characteristics reported in literature revealed that, the range of characteristics that are examined is varying for the novel adsorbents. This led to comparison of the adsorbent characteristics reported to that prescribed in relevant BIS codes. Two BIS codes viz., IS 2752:1995 and IS 8366:1989 are available for classification of adsorbents for their use in specific purposes based on their physico-chemical characteristics.

IS 2752:1995 (originally published in 1963 and revised in 1978, 1989, and 1995) defines the activated carbon for two specific purposes viz.,

- Respirator carbons and Solvent recovery (Type-1)
- Water treatment (Type-2)

IS 8366:1989 (originally published in 1977 and revised in 1989) defines the activated carbon for three specific purposes viz.,

- Decolorizing vegetable oils, fats, and waxes (Type-1)
- Decolorizing sugar solutions, corn sugar solutions etc. (Type-2)
- Decolorizing pharmaceuticals (Type-3)

The activated carbons of Type-2 under IS 2752:1995 are suitable for water treatment. For comparison of adsorbent characteristics that are reported in literature, the Type-2 under IS 2752:1995 can be considered. The Type-3 under IS 8366:1989 is for decolorization of pharmaceuticals. The wastewater from pharmaceuticals causes pollution and needs to be treated. Decolorization of pharmaceuticals can be considered as a treatment option. Activated carbon defined in Type-3 under IS 8366:1989 is suitable for the above purpose and hence considered for comparison.

Data available in literature is collected pertaining to the physico-chemical characteristics of several adsorbents (Rao and Bhole, 2001; Singh and Srivastava, 2001; Ansari et al., 2000; Prasad et al., 2000a, b; Rao and Bhole, 2000; Chandrasekhar and Chakravarthy 2000; Verma and Shukla, 2000; Ajmal et al., 1998; Lee et al., 1998; Mall and Upadhyay, 1998; Sekar and Murthy, 1998; Singh et al., 1998; Swamy et al., 1998; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Mohammad et al., 1997; Raji and Anirudhan, 1997; Raji et al., 1997; Srivasatava et al., 1997a, b; Kurian and Rajenthiran, 1995; Muthukumaran et al., 1995; Patnaik and Das, 1995; Tiwari et al., 1995; Shrichand et al., 1994; Singh and Rawat, 1993a, b; Singh and Rawat, 1993; Singh et al., 1993; Ramu et al., 1992; Gajghate and Saxena, 1991; Khagesan et al., 1991; Gupta and Tiwari, 1985; Kumar and Dara, 1980; Khanna and Malhotra, 1977). The database comprises of information pertaining to 65 different materials comprising 28 and 26 adsorbents prepared from two different types of precursor materials (viz., AW & IW) and 11 datasets for Commercial Activated Carbon (CAC) respectively. The above database is analysed for the range of physico-chemical characteristics that are reported and making a comparative study with those prescribed in the BIS codes.

3.1.5 Based on the suitability of adsorbent for a specific use: Model development

For assessing the suitability (or ranking) of an adsorbent for a specific purpose based on its physico-chemical characteristics, the data for the characteristics prescribed by the relevant BIS codes (IS 2752:1995 and IS 8366:1989) must be available. In the absence of the relevant data, ranking becomes difficult. A Linear Ranking Model for Adsorbents (LRMA) is developed with a four-scale ranking approach. The LRMA is illustrated with a data source (Rengaraj et al., 1999) where the information pertaining to the relevant physico-chemical characteristics is fully available.

3.1.6 Comparative studies with Commercial Activated Carbon (CAC)

The adsorption studies using Commercial Activated Carbon (CAC) are generally expected to give better results compared to the novel adsorbents due to their comparatively high surface area that is achieved due to the systematic activation given to the material during its preparation. The results obtained using CAC in adsorption studies are compared using the following approaches:

3.1.6.1 Based on Linear Ranking Model of Adsorbents (LRMA)

A Linear Ranking Model of Adsorbents (LRMA) is developed for ranking adsorbents based on their physico-chemical characteristics (Sec. 3.1.5). The database that is available for CAC (Rao and Bhole, 2001; Rao and Bhole, 2000; Sekar and Murthy, 1998; Swamy et al., 1998; Mall and Kumar, 1997; Ramu et al., 1992; Gajghate and Saxena, 1991; Khagesan et al., 1991) is used for fitting into LRMA.

3.1.6.2 Based on Freundlich isotherm constants

This is based on the study of the performance of CACs with respect to Freundlich isotherm constants. The database available in literature pertaining to the Freundlich constants obtained using CAC (Rao and Bhole, 2001; Rao and Bhole, 2000; Sekar and Murthy, 1998; Swamy et al., 1998; Mall and Kumar, 1997; Ramu et al., 1992; Gajghate and Saxena, 1991; Khagesan et al., 1991) is collected and analyzed.

3.2Modeling based on the process performance

Pollutant Removal Efficiency (PRE) is the important parameter in determining the adsorption efficiency. The adsorption efficiency of an adsorbent with respect to PRE can be assessed by modeling the experimental data. This modeling can be (i) empirical, based on regression and/or dimensional analysis approaches (ii) based on ANN and (iii) analytical (or numerical), covering the study of pollutant transport either for batch studies (on the surface of the adsorbent particle) or for column studies.

The data available in literature is used in the present study to model the prediction of PRE using:

- Regression technique
- Regression in conjunction with dimensional analysis technique
- Artificial neural networks
- Analytical technique

The detailed description under each of the above categories is discussed as follows:

3.2.1 Regression technique for adsorption modeling

The regression technique is used to first study its suitability for adsorption modeling and subsequently used to predict the PRE of adsorbents.

3.2.1.1 Applicability

Regression techniques are widely used for physical modeling. They are used for adsorption modeling (Bhole et al., 2002; Rao and Bhole, 2001; Rao and Bhole, 2000; Mall and Kumar, 1997; Manju and Anirudhan, 1997; Mohammad et al., 1997; Raji et al., 1997; Patnaik and Das, 1995), any engineering application (Babu and Ramakrishna, 2003g, b; 2000; Ramakrishna and Babu, 1999b) etc. The application of regression techniques in adsorption studies is discussed in Chapters-1 and 2.

In the above applications, Least Squares Method (LSM) is used as a best-fit approach for predicting the trends of results from experimental data. The adsorption mechanism is very complex and a proper understanding of the physics of the system is required for accurate modeling. For example, the efficiency of adsorption depends on several parameters and is predominantly material (adsorbent/adsorbate) specific. The parameters that are generated using experimental results should be adequate to develop an appropriate regression (physical) model for projecting a complete representation of adsorption mechanism. The data available in literature with respect to removal of fluoride from contaminated water comprising of both homogeneous (Bhargava, 2002) and heterogeneous (Bhargava, 2002; Mariappan and Vasudevan, 2002) in terms of adsorbent is collected. The applicability of regression technique for adsorption is studied using the above data. A Physical Model is developed based on affecting parameters using Multiple

Regression (PMMR) to predict the removal of fluoride from contaminated water by adsorption.

3.2.1.2 Isotherm constants

The Isotherm constants, which depend on temperature, are important in understanding the adsorption mechanism. It is hence desirable to predict the isotherm constants for the adsorption system to assess the suitability of the adsorbents. A model is developed for this purpose in terms of the Freundlich isotherm constants and temperature reported in literature discussed in Sec. 3.1.3.

3.2.2 Adsorption modeling using dimensional analysis and regression technique

Regression is a simple empirical technique based on data regression to obtain a linear relation between one dependant variable and one (or more) independent variable(s). Available experimental data is used for regression. Such regression will show a representative relationship only if all the affecting variables are studied in the experiments, from which the data is collected. There may be some other affecting parameters that might not have been studied in those stages of experimentation.

Dimensional analysis can be used to identify all the affecting parameters that are not taken into account using a simple regression. Hence dimensional analysis in conjunction with regression is used in the present study for modeling the PRE in batch studies. The operating parameters that are significant in affecting the PRE in adsorption batch studies are identified. The following dimensional- and dimensionless-operating parameters of adsorption are identified that affect the prediction of PRE:

- material of adsorbate (dimensionless)
- adsorbent (dimensionless)

- pH (dimensionless)
- contact time, t_c (dimensional, T)
- equilibrium time, t_{eq} (dimensional, T)
- adsorbent dose, C_d (dimensional, ML^{-3})
- initial concentration of adsorbate, C_0 (dimensional, ML^{-3})

A functional relation is developed incorporating the above parameters and PRE (η) such that,

$$\eta = f(material,\ adsorbate,\ pH,\ t_c,\ t_{eq},\ C_d,\ C_0) \tag{3.1}$$

Considering only the dimensional groups, Eq. (3.1) reduces to,

$$\eta = f(t_c,\ t_{eq},\ C_d,\ C_0) \tag{3.2}$$

taking the dimensions and performing dimensional analysis, Eq. (3.2) reduces to,

$$\eta = f_1(t_c/t_{eq})^{\alpha}\ (C_d/C_0)^{\beta} \tag{3.3}$$

When the adsorption studies run till equilibrium time, $t_c = t_{eq}$ and hence, Eq. (3.3) becomes,

$$\eta = f_2\ (C_d/C_0)^{\gamma} \tag{3.4}$$

where f_1 and f_2 are functional constants and α, β, γ are exponential constants.

The database is tested using the model equations given by Eqs. (3.3) and (3.4).

3.2.3 Artificial neural network modeling

The basic information pertaining to Artificial Neural Networks (ANNs) is discussed widely in literature (Babu, 2004; Hassoun, 1998; Basheer and Najjar, 1997; Behera, 1997). Modeling of ANN using Back-Propagation Network (BPN) is discussed in this section. Multi-layered networks are used for BPN.

A multi-layered neural network contains an input layer, one or more hidden layers, and an output layer as shown in Fig. 3.1. The network receives input as X vector (or x_1, x_2, ...x_p) while the output is stored in Y vector (or y_1, y_2, ..., y_n). The output of the network is calculated using an activation function and weights associated with each node (w). During the forward pass of the training, an input pattern is applied to the network that is propagated through the network in forward direction producing a set of outputs for the network. In BPN, the output obtained from the network (y^o) is compared with the desired output (y^d) for the input vector and the error (e^r) is calculated. This error is then propagated in the backward direction and the weights are adjusted accordingly to move the response closer to the desired response. The algorithm of BPN (Behera, 1997) is discussed below:

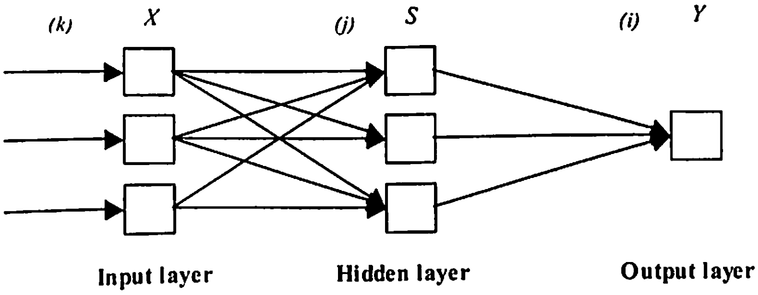


Fig. 3.1: Typical multi-layered network

Algorithm for BPN

Step: 1 (Initiation)

- Initialize the weights.
- Activate the network using the sigmoid function: $f(x)=\dfrac{1}{1+e^{-x}}$ (3.5)
- Compute the response using forward pass technique.

Step: 2 (Forward pass)

Calculate the actual output of the network using the following equations:

1. Output at hidden node (s) for the input vector $\boldsymbol{x}$: $$s_j = \frac{1}{1+e^{-h_j}} \tag{3.6}$$

   Where, $$h_j = \sum_{k=1}^{p} w_{jk} x_k \tag{3.7}$$

2. Output at output node (y) for the input from hidden node (s): $$y_i = \frac{1}{1+e^{-g_i}} \tag{3.8}$$

   Where, $$g_i = \sum_{j=1}^{m} w_{ij} s_j \tag{3.9}$$

Step: 3 (Backward pass)

- Compute the error from the network: $$e^r = y^d - y^a \tag{3.10}$$
- Compute: $$\delta^i = y^a(1-y^a)(y^d - y^a) \tag{3.11}$$

  This is used to distribute the error at the output unit back to the preceding layers.
- Update the weights connecting the hidden layer to output layer using:

  $$w_{ij}(t+1) = w_{ij}(t) + \sigma\delta^i s_j, \tag{3.12}$$

  where, σ is the learning rate for the network.
- Compute: $$\delta_j = s_j(1-s_j) w_{jk} \delta_j x_k \tag{3.13}$$
- Update the weights connecting input layer to hidden layer:

  $$w_{jk}(t+1) = w_{jk}(t) + \sigma\delta_i\delta_j x_k \tag{3.14}$$

After all the δ factors have been determined, the weights for all layers are adjusted simultaneously.

Step: 4 (Repetition)

- Repeat Steps **2** and **3** for all given patterns in the training set.

- Continue the runs till the error is less than or equal to a tolerance limit defined by the user.

3.2.3.1 Application

The major limitation observed in the regression and dimensional analysis approaches is in combining both dimensional and dimensionless parameters that affect PRE. ANN model is hence used for prediction of PRE from adsorption studies since it is of a black box nature, which can yield solution due to its ability to relate experimental input and output data without the need for the knowledge of the physical relation between the input and output variables.

In the application of ANN to the current problem, the model equation given in Eq. (3.1) is used. A database of 514 data points is developed comprising of the information of all the parameters listed in Eq. (3.1) from literature (Sekar and Murthy, 1998; Mall and Kumar, 1997; Raji and Anirudhan, 1997; Raji et al., 1997; Kurian and Rajenthiran, 1995; Muthukumaran et al., 1995; Patnaik and Das, 1995; Tiwari et al., 1995; Shrichand et al., 1994; Singh and Rawat 1993a, b; Singh and Rawat, 1993; Singh et al., 1993; Bhoyar et al., 1992; Periasamy et al., 1991; Kumar and Dara, 1980). The dimensionless groups such as material, adsorbate, and pH are also included in the ANN analysis. Each of the items in the above groups is given a number and the database is normalized. Likewise, the database for the dimensional groups is also normalized. The details of the databases are given in Appendices-D and E.

The BPN of ANN is used for modeling studies. A code is developed in C++, which is given in Appendix-G. It is applied for three different cases that are previously studied (Sec. 3.2.2) using regression and dimensional analysis approaches:

- Applicability of ANN for adsorption batch studies is tested using a case study of predicting the removal of fluoride where a heterogeneous database is used (Sec. 3.2.1.1).
- Modeling of adsorption isotherm constants (Sec. 3.2.1.2).
- Prediction of PRE for adsorption batch studies by incorporating the affecting dimensional and dimensionless parameters (Sec. 3.2.2).

3.2.4 Analytical modeling

The analytical model studied is based on mass transfer approach for batch system (Flora et al., 1998), whose details are as follows:

The rate of change of amount adsorbed (q) in a batch reactors is calculated from the mass balance across the adsorbent particle and is given by:

$$\frac{\partial q}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \tag{3.15}$$

or

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial r^2} + 2D\left(\frac{1}{r}\right)\left(\frac{\partial q}{\partial r}\right) \tag{3.15}$$

where, r is the radius of the particle and D is the diffusion coefficient.

The amount of adsorbate transferred from solution is equal to the amount adsorbed. Hence,

$$V\frac{dc_b}{dt} = -W\frac{dq_{avg}}{dt} \tag{3.16}$$

where, $q_{avg} = \frac{3}{r_p^3}\int_0^{r_p} q(r,t)r^2 dr$ (3.17)

W is the mass of adsorbent and V is the volume of adsorbate used in batch adsorption studies.

The initial and boundary conditions with the assumption that the adsorption process is better understood using Langmuir isotherm, are given by:

$$q(r, t = 0) = 0 \tag{3.18}$$

$$c_b(t = 0) = c_0 \tag{3.19}$$

$$\frac{\partial q}{\partial r}(r = 0, t > 0) = 0 \tag{3.20}$$

$$\frac{\partial q}{\partial r}(r = r_p, t > 0) = \left(\frac{k_f}{\rho D}\right)(c_b - c_s) \tag{3.21}$$

$$q\left(r = r_p, t > 0\right) = \frac{q_{\max} b c_s}{1 + b c_s} \tag{3.22}$$

where, c_b and c_s are the bulk and equilibrium concentration of adsorbate respectively, while ρ is the adsorbent particle density and k_f is mass transfer coefficient. The following parameters are introduced for non-dimensionalization:

$$C = \frac{c}{c_0} \tag{3.23a}$$

$$Q = \frac{q}{q_0} \tag{3.23b}$$

$$\theta = \left(\frac{Dt}{r_p^2}\right) \tag{3.23c}$$

$$x = \frac{r_0}{r_p} \tag{3.23d}$$

$$\text{Biot number, } Bi = \left(\frac{k_f r_p c_0}{D \rho q_0}\right) \tag{3.23e}$$

Distribution parameter, $\lambda = \frac{Wq_0}{Vc_0}$ (3.23f)

where, $q_0 = \frac{q_{\max} bc_0}{1 + bc_0}$ (3.23g)

Rewriting the model equations in terms of dimensionless parameters,

$$\frac{\partial Q}{\partial \theta} = \left(\frac{1}{x^2}\right)\frac{\partial}{\partial x}\left(x^2 \frac{\partial Q}{\partial x}\right) \tag{3.24}$$

$$\frac{\partial Q}{\partial \theta} = \frac{\partial^2 Q}{\partial x^2} + 2\left(\frac{1}{x}\right)\left(\frac{\partial Q}{\partial x}\right) \tag{3.24a}$$

$$\frac{dC_b}{d\theta} = -\lambda \frac{dQ_{avg}}{d\theta} \tag{3.25}$$

$$Q_{avg} = 3\int_0^1 Q(x,\theta)x^2 dx \tag{3.26}$$

$$Q(x,\theta = 0) = 0 \tag{3.27}$$

$$C_b(\theta = 0) = 1 \tag{3.28}$$

$$\frac{\partial Q}{\partial x}(x = 0, \theta > 0) = 0 \tag{3.29}$$

$$\frac{\partial Q}{\partial x}(x = 1, \theta > 0) = Bi(C_b - C_s) \tag{3.30}$$

$$Q(x = 1, \theta > 0) = \frac{(1 + bc_0)C_s}{1 + bc_0 C_s} \tag{3.31}$$

Eq. (3.24a) is solved using the initial and boundary conditions given by Eqs. (3.27)-(3.31). The model equations are discritized using implicit scheme of Finite Difference Method in conjunction with Simpson's 1/3rd rule (Appendix-F). A code is developed in C language and is given in Appendix-H. The model is validated (Flora et al., 1998) and tested (Al-Qodah, 2000) with published data.

3.3 Laboratory investigations in batch studies of adsorption

The laboratory investigations in adsorption studies are conducted for: (i) preparation of adsorbent from sawdust (ii) analyzing the laboratory data using mass balance approach in LCIA and (iii) batch studies to assess the effect of agitation in the adsorbate removal. The details of each of these are discussed as follows:

3.3.1 Preparation of adsorbent from sawdust

The sawdust that is locally available is collected. Its local, scientific and botanical names are *Jhaati*; *Prosopis*, and *Spicijera* respectively. An adsorbent is prepared from it in the laboratory. The characteristic properties of adsorbent prepared are analyzed.

3.3.2 Analyzing the laboratory data using Life Cycle Inventory Analysis (LCIA)

The LCIA is applied to identify and quantify the materials involved in the preparation of the adsorbent from sawdust in the laboratory. The waste-and non-waste emissions in the process are carefully studied using mass balance approach. Suggestions are floated to minimize the waste load from the process of preparation of adsorbent from sawdust.

3.3.2.1 Mass balance approach in Life Cycle Inventory Analysis (LCIA)

Consider a single-product process (Fig.3.2) with two inputs IP_1 and IP_2 that are converted to useful product P_1 and a waste release of W_1 into the atmosphere. All input and waste streams in a system or subsystem must be allocated the respective non-waste output streams. When an output stream becomes an input stream to the next process step, it carries the environmental loads onto the next output streams (Aelion et al., 1995).

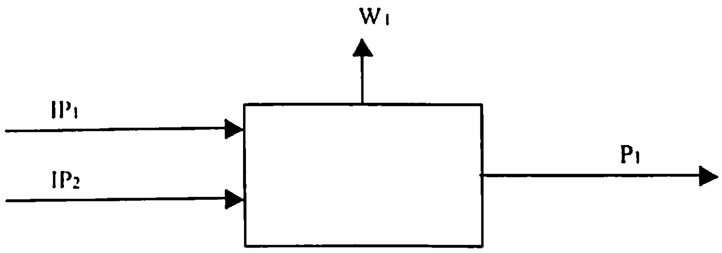


Fig. 3.2: Typical single-product process

The manufacturing process, for example, consists of many periods of operation (eg. startup, shutdown, maintenance etc.). It is reasonable to expect that activities during these operating periods also involve loads that contribute to the overall environmental load. In addition, manufacturing processes do not always operate as intended.

For example, in any batch processing industry, a small number of batches each year will not meet the product quality standards, leading to the discarding or the possible reprocessing of these batches. In other processes that involve perishable goods, occasional discarding of out-of-date material frequently is required. Finally accidents also contribute to pollution, due to chemical release as well as the use and ultimate disposal of other chemicals aimed to contain accident. Thus, the total environmental load or Total Production Load (TPL) assessed in the complete Environmental LCI is a combination of:

- steady-state production load
- off-specification production load and
- load due to accidental losses

3.3.3 Experimental batch studies of adsorption

The batch studies are conducted in the laboratory using Laboratory Activated Carbon (LAC). The operating parameters identified for this purpose are: weight of adsorbent, volume of adsorbate, pH, initial concentration of adsorbate, contact time, constant temperature (30^0C) and constant agitation speed. The adsorption studies are run for removal of Zn^{+2} from synthetic wastewater. The stock solution is prepared from zinc sulphate salt (4.4 g) dissolved in one liter of Triple Distilled Water (TDW) for a concentration of 1000 mg/L of zinc. It is diluted to the required concentration. The pH of the adsorbate solution is adjusted using 0.1 N H_2SO_4 and 0.1N NaOH. A known amount of adsorbent (LAC) is transferred into a beaker where the adsorbate of known initial concentration and volume is allowed to contact for a specific contact time. During this period, the beaker is subjected to agitation. The concentration of Zn^{+2} in the solution after the specific contact time is determined by testing the filtrate using Atomic Absorption Spectrophotometer (AAS) where, the concentration of Zn^{+2} is determined at a wavelength of 213.8 nm.

CHAPTER
4

RESULTS AND DISCUSSION

As mentioned in problem formulation (Chapter-3), the studies are conducted based on (i) comparative study of novel adsorbents (ii) process performance and (iii) laboratory investigations in batch studies of adsorption. The results and discussions based on the above studies are given as follows:

4.1Comparative studies of novel adsorbents

Different novel adsorbents are reported in literature (Sec. 3.1) in adsorption studies. A comparative study is conducted pertaining to several aspects of these novel adsorbents as detailed in Chapter-3. The results of the studies are discussed in the following six sections:

4.1.1 Based on the raw (precursor) material used

The information pertaining to different raw (precursor) materials being used in the preparation of novel adsorbents is collected from literature (as referred in Sec. 3.1.1). The Raw Material Categorization Database (RMCD) is compiled with respect to the raw material of the adsorbent. The RMCD contains 75, 18, and 8 data points pertaining to AW, IW, and MW respectively. The suitability of the raw materials for adsorption studies is assessed *vis-à-vis* Freundlich isotherm constants. The available data pertaining to the two Freundlich constants viz., K_f and n are collected for the adsorbents prepared from these raw materials. The ranges of the values of the Freundlich constants for AW, IW, and MW categories in the database are given in Table-4.1.

Table-4.1: Range of values of Freundlich constants in RMCD

Raw Material Category	Data Points	Freundlich constants			
		K_f		n	
		Max.	*Min.*	*Max.*	*Min.*
AW	75	204.17	1.08×10^{-6}	25	0.013
IW	18	48.97	4×10^{-7}	7.16	0.102
MW	8	555.57	0.154	3.12	0.443

The data given in Table-4.1 shows that, the investigators prefer AW based raw materials (74.25%) as novel adsorbents followed by IW based raw materials (17.82%). The available database is sorted based on n value below 1 and beyond 10. Results are given in Table-4.2.

Table-4.2: Sorted RMCD based on n values

Raw Material Category	Freundlich constant, n			
	Data Points for $n<1$	% of total RMCD	Data Points for $n>10$	% of total RMCD
AW	17	22.66	4	5.33
IW	3	16.66	0	0.00
MW	2	25.00	0	0.00

The segregated database after eliminating the data points below and beyond the above limits of n consists of 54, 15, and 6 data points pertaining to AW, IW, and MW categories respectively. The above segregated database is further sorted based on K_f values since a higher value for K_f indicates high rate of adsorbate removal (Ajmal et al., 1998; Ramu et al., 1992). In order to compare the relative variation of the K_f values in these categories, frequency distribution of the K_f values is used and is given in Table-4.3.

Table-4.3: Frequency distribution of K_f values in sorted RMCD

Frequency Range	Percentage of the frequency distribution		
	AW	IW	MW
> 100	5.55	--	--
50-100	14.82	--	--
30-50	11.11	20.00	--
20-30	5.55	6.66	--
10-20	29.63	--	--
1-10	27.78	20.00	--
<1	5.55	53.33	100.00

From Table-4.3, it is clearly evident that, adsorbents prepared from AW category are showing high K_f values compared to that of the other two categories. The adsorbents prepared from MW category are showing very low K_f values. From the above analysis of this study (Babu and Ramakrishna, 2003a), it is concluded that, the order of preference of raw material category for preparation of novel adsorbents with respect to the Freundlich isotherm constants is, AW>IW>MW.

4.1.2 Based on adsorbent preparation methodology

Several methodologies are being followed in the preparation of novel adsorbents from their raw materials. The suitability of the adsorbent preparation methodology *vis-à-vis* Freundlich isotherm constants is assessed. The values of Freundlich constants for the novel adsorbents prepared from AW, IW, and MW are collected from literature. This database is analyzed in the present study (Babu and Ramakrishna, 2003a) to understand the effects of adsorbent preparation methodology on the Freundlich constants.

The adsorbent preparation methodologies reported in literature are studied and they are categorized based on the predominant method of operation involved. The following categories are identified in this analysis:

- Nominal Treatment (N)
- Physical Treatment (P)
- Chemical Treatment (C)
- Thermal Treatment (T)
- Physical-Chemical Treatment (PC)
- Chemical-Thermal Treatment (CT)
- Physical-Thermal Treatment (PT)

The detailed activities considered for N, P, C, and T categories are given in Table-4.4. The remaining three combinations listed above (PC, CT, and PT) are simply the combinations of these individual categories in that order.

Table-4.4: Categorization of adsorbent preparation methodologies

Treatment category	**Activities considered**
Nominal Treatment	Normal drying either at low temperature (<105^{0}C) or sun drying, grounding and sieving, washing with only distilled water.
Physical Treatment	Oven drying to 105^{0}C, washing with acid for removal of impurities.
Chemical Treatment	Acidification and impregnation of the sample.
Thermal Treatment	Thermal cracking of the sample at very high temperatures with or without activation.

The available Adsorbent Preparation Methodologies Database (APMD) is segregated as per the above categories and the corresponding Freundlich constants are compiled. The APMD is divided into clusters based on the method of preparation and the corresponding K_f and n values. The adsorbent preparation methodologies fitted to this APMD are: N, P, C, and CT. The available data points are very less for T, PC, and PT categories to draw any observations and hence ignored. The details of the sorted APMD are given in Table-4.5. The database given in Table-4.5 is subsequently sorted based on n value viz., for $n < 1$ and $n > 10$. The details of the sorted database are given in Table-4.6.

Table-4.5: Range of values of Freundlich constants in APMD

Category	Data points	Freundlich constants			
		K_f		n	
		Max.	*Min.*	*Max.*	*Min.*
N	21	141.12	4×10^{-7}	7.155	0.102
P	19	555.57	0.094	4.85	0.443
C	35	63.09	1.08×10^{-6}	3.33	0.342
CT	26	550	0.187	25	0.13

Table-4.6: Sorted APMD based on n values

Category	Freundlich constant, n			
	Data Points for $n < 1$	% of APMD	Data Points for $n > 10$	% of APMD
N	4	19.05	Nil	--
P	10	52.63	Nil	--
C	7	20.00	Nil	--
CT	2	7.69	4	15.38

The database is further screened for high values of K_f. It is observed that, the C and CT categories are showing relatively high values of K_f values than that of N and P categories. The K_f values are compared in these categories using frequency distribution, which is given in Table-4.7.

Table-4.7: Frequency distribution of K_f values in sorted APMD

Frequency Range	Percentage of the frequency distribution			
	N	P	C	CT
> 100	5.88	--	--	10.00
50-100	--	--	14.29	20.00
30-50	5.88	22.22	3.57	25.00
20-30	--	11.11	7.14	10.00
10-20	--	11.11	46.43	5.00
1-10	17.65	33.33	25.00	25.00
<1	70.58	22.22	3.57	5.00

The following observations are drawn from Table-4.7:

- The adsorbents prepared by N category are showing very low K_f values (70.58% of the database show values less than 1).
- The adsorbents prepared by P category are also showing low K_f values (22.22% of the database show values less than 1).
- The K_f values of N category are mostly lying (88.23%) in the range of less than 10.

- Majority of the K_f values (77.77%) for the adsorbents prepared by P category are lying in the range of less than 30.
- The percentage range of K_f values lying less than a value of 10 is in the following order: N (88.23%), P (55.55%), C (28.57%), and CT (30.00%). It indicates that the rate of adsorbate removal is high in the adsorbents prepared by the C and CT categories compared to those from N and P categories.
- The percentage of the data points for which the K_f values lying in the range of 20-100 is higher for CT category (55%) than that for C category (25%), which is almost double. It indicates that the adsorbents prepared by the CT category are showing relatively higher adsorbate removal compared to that from C category.
- The adsorbents prepared from CT category are hence showing better values for Freundlich constants compared to that from N, P, and C categories.

The above observation of adsorbents prepared by CT category showing better results indicate that some sort of cracking and/or activation at high temperatures is essential for adsorbent to give satisfactory values of adsorption. This observation is consistent with that reported in literature (Rengaraj et al., 1999; Sai et al., 1997). It is further noticed that, the entire database of CT and C comprises of AW category of adsorbents only. This indicates that the adsorbents developed from AW are showing better results of adsorption than the other two categories viz., IW and MW. This is consistent with the earlier observation that, adsorbents prepared from AW category are relatively better than that from IW and MW categories.

4.1.3 Based on functional dependency of Freundlich isotherm constants

As discussed in Sec. 3.1.3, a wide spread in the values of Freundlich isotherm constants reported in literature is noticed. The reason for the possible wide spread is studied by modeling the prediction of each of the isotherm constants as a function of temperature. The information pertaining to these constants for several adsorbents is collected and is segregated into four databases (DB-1 to DB-4). The database comprising of 120 data points (DB-1) is first sorted out with respect to the reported values of Freundlich constants, K_f and n. The lower limit of n is taken as 0.9 instead of 1 considering an allowance for experimental/graphical errors in determining the isotherm constants. Further, the room temperature is assumed to be 30 ^{0}C unless otherwise mentioned in the literature. A Model based on Linear Regression (LRM) technique is developed for prediction of K_f and n with respect to T. Standard Deviation (SD) based on the expected value (Babu, 1993) is chosen to identify the accuracy of the above model, which is given in Eq. 4.1:

$$SD = \sqrt{\frac{\sum_{1}^{z}\left[\frac{y_{expected} - y_{calculated}}{y_{expected}}\right]^2}{z-1}} \tag{4.1}$$

The results indicated that, the Freundlich constant, n is reported to have values in the range of 0.9 to 10 for 94 data points (comprising 87 data points of 43 different novel adsorbents) out of 120 data points (comprising 110 data points of 51 different novel adsorbents). The details of the results are given in Table-4.8. A wide spread in the values for the Freundlich isotherm constants is observed (Table-4.8). The 94 data points for which, the n values are lying in the range 0.9 to 10, are separated from DB-1 considered as second database (DB-2) and LRM is applied. The reduction of SD value for DB-2 compared to that of DB-1 (Table-4.9) indicates a relative reduction in the variations in the values of the databases.

Table-4.8: Range of Freundlich isotherm constants and temperature in the database

S.No.	Database type	Range	K_f	n	T	Total data points
1	DB-1	Max	727.05	25	70	120
		Min	1×10^{-7}	0.06	20	
2	DB-2	Max	727.05	7.813	70	94
		Min	3×10^{-6}	0.91	20	
3	DB-3	Max	52.72	4.655	60	12
		Min	1×10^{-7}	1.01	20	
4	DB-4	Max	13.90	5.49	70	14
		Min	0.06	0.91	25	

Table-4.9: SD values for LRM

S.No.	Parameters	Model	Standard Deviation for			
			DB-1	DB-2	DB-3	DB-4
1	K_f vs. T	LRM	104.93	86.661	5.7168	1.0846
2	n vs. T	LRM	3.463	1.261	0.4048	0.3629

Since, it is evident from the above observations that, the variations in the database is due to spreading in the range of data points, the DB-2 is screened for clustering based on the type of adsorbate. Two datasets for removal of Cr^{+6} (DB-3) and Pb^{+2} (DB-4) comprising of 12 and 14 data points each (maximum data points available in the database) are identified and the databases are sorted with respect to K_f and n values. It is observed that, the SD value is reducing from DB-1 to DB-4 indicating that, the erratic prediction of functional relationship is due to the wide spread in the database. Incidentally, majority of the data points in the databases correspond to the novel adsorbents (Fig. 4.1) indicating that a lot of studies are currently being conducted using novel adsorbents. It is to be noted that, while sorting the database on Freundlich constant (n), the lower limit is considered as 0.9 instead of 1 as mentioned earlier. However, the number of data points that lie in the range of 0.9 and 1 are marginal as given below for different types of databases:

- three data points in DB-2 i.e., a database comprising 94 data points.
- one data point in DB-4 i.e., a database comprising 14 data points exclusively for Pb^{+2}.

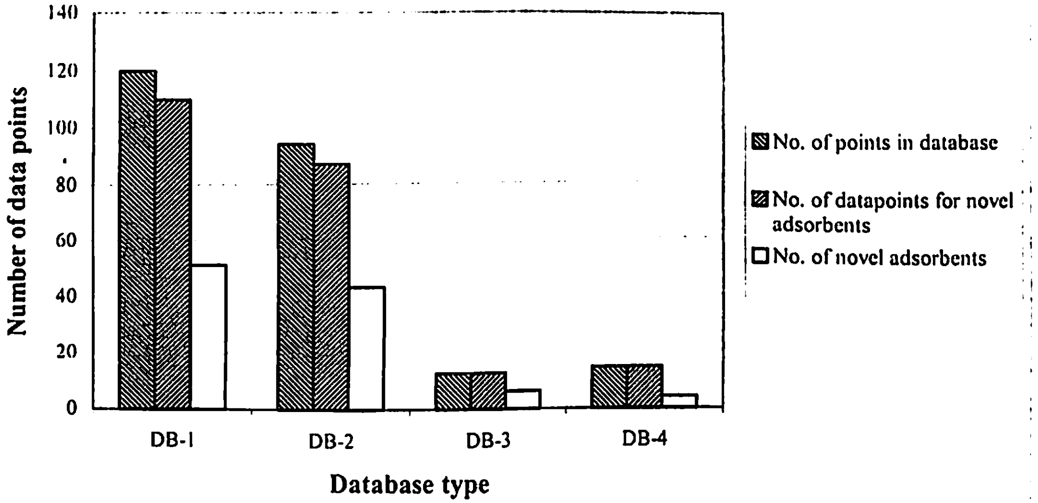


Fig. 4.1: Distribution of data points in the databases

This study indicated that (Babu and Ramakrishna, 2003f), majority (94 out of 120 considered) of the data points show n values in the range of 0.9-10, indicating favorable adsorption. However, there is a huge wide spread in the values reported for isotherm constants indicating that the variation is due to the preferential nature of a specific adsorbent to an adsorbate. The adsorbents with high affinity to an adsorbate showed a very high value for K_f as is evident from the earlier studies (Sec. 4.1.1 and 4.1.2). The high SD values for K_f vs. T and n vs. T indicate that, though the isotherm constants depend upon temperature, estimating them as a function of temperature is erratic. Further, as the size of the database reduces, the erratic prediction also reduces indicating the reduction in the spread of the values.

4.1.4 Based on available Bureau of Indian Standards (BIS) codes

A compilation of the adsorbent characteristics reported in literature revealed that, the range of characteristics that are examined is varying for the novel adsorbents. A study is hence conducted to compare adsorbent characteristics reported to that prescribed in relevant BIS codes. The present analysis is focussed on a comparative study for the suitability of activated carbons for water/wastewater (contaminated water) treatment based on their physico-chemical characteristics. The details of the analysis are as follows:

As discussed in Sec. 3.1.4, two BIS codes viz., IS 2752:1995 and IS 8366:1989 are available for classification of adsorbents for their use in specific purposes based on their physico-chemical characteristics. The physico-chemical characteristics that are covered under the above two BIS codes are given in Table-4.10. Barring moisture and ash contents, the characteristic properties prescribed by the BIS are different for both the water treatment and decolorization purposes (Table-4.10).

The activated carbons of Type-2 under IS 2752:1995 are suitable for water treatment. For comparison of adsorbent characteristics that are reported in literature, the Type-2 under IS 2752:1995 can be considered. The Type-3 under IS 8366:1989 is for decolorization of pharmaceuticals. The wastewater from pharmaceuticals causes pollution and needs to be treated. Decolorization of pharmaceuticals can be considered as a treatment option. Activated carbon defined in Type-3 under IS 8366:1989 is suitable for the above purpose and hence considered for comparison.

Table-4.10: Characteristics prescribed under IS 2752:1995 and IS 8366:1989

Characteristic	
IS 2752:1995	IS 8366:1989
1. Moisture, % by mass	1. Moisture, % by mass
2. Ash, % by mass	2. Ash, % by mass
3. Adsorption capacity for carbon tetra chloride, % by mass	3. Matter soluble in water, % by mass
4. Hardness number	4. Matter soluble in acid, % by mass
5. Retentivity index, % by mass	5. pH
6. Adsorption capacity in terms of iodine number	6. De-colorizing power, mg/g
7. Half dechlorination value, cm	7. Oil retention, % by mass
8. Surface area, m^2/g	8. Filterability, minutes
	9. Particle size
	10. Iron as Fe, % by mass
	11. Sulphate as SO_4
	12. Chloride as Cl^-, % by mass
	13. Cyanogen compounds

4.1.4.1 Database development

As discussed in Sec. 3.1.4, a database corresponding to a total of sixty-five (65) different materials reported is compiled. This total comprises of 26 and 28 different materials of IW, AW and 11 different types of CAC respectively. The physico-chemical characteristics reported in literature are given in Table-4.11.

Table-4.11: Characteristics reported in literature

S. No.	Characteristic	S. No.	Characteristic
1	Apparent density	14	Calcium (CaO)
2	Porosity	15	Sulphur
3	Cation exchange capacity	16	MgO
4	Surface area	17	MnO
5	Particle size	18	FeO
6	Moisture content	19	Loss on ignition
7	Ash content	20	Fe_2O_3
8	Decolorizing power	21	Combustible matter
9	Matter soluble in water	22	Specific gravity
10	Matter soluble in acid	23	Phenol number
11	Bulk density	24	Iodine number
12	Silica	25	pH
13	Alumina		

From Tables-4.10 and 4.11, it is noticed that:

- The investigators have examined more characteristics than those prescribed under BIS codes.

- Data for most of the characteristics described in Table-4.10 is surprisingly missing.

To quantify the above information, the frequency of reporting each of the physico-chemical characteristics in literature is compiled. From this database, the characteristics that are more frequently reported are identified and are given below:

- bulk density (24.62%)
- moisture content (24.62%)
- ash content (24.62%)
- particle size (72.31%)
- surface area (32.31%)
- silica (26.15%)
- alumina (24.62%)

The figures in the parenthesis indicate the percentage of the number of materials for which the data is available out of the total 65 materials. The following aspects are observed when the above information is compared with the characteristics prescribed by the BIS codes (Table-4.10):

- The characteristics such as moisture content, ash content, particle size, and surface area are prescribed in the BIS codes.
- The characteristics such as bulk density, silica, and alumina are not prescribed in the BIS codes but are frequently reported in literature.

The information available for particle size and Iodine number are not considered for the comparative study purpose due to insufficient and inadequate data. Based on the above observations, the physico-chemical characteristics that are selected for the comparative study are as follows:

- Type-2 under IS 2752:1995

    - moisture content, %
    - ash content, %
    - surface area, m^2/g
- Type-3 under IS 8366:1989
    - moisture content, %
    - ash content, %
    - decolorizing power, mg/g
    - matter soluble in water, %
    - matter soluble in acid, %
    - pH

The permissible limits of the above characteristics as per IS 2752:1995 and IS 8366:1989 are given in Table-4.12.

4.1.4.2 Compliance studies

The database is examined with the above selected list of characteristics and their prescribed limits as per the relevant BIS codes. For the three characteristics selected under IS 2752:1995, the results are expressed in the following sequence:

- compliance of one of the characteristics
- compliance of any two characteristics
- compliance of all three characteristics
- no compliance of any of the characteristics
- no compliance based on partial data reported
- data not reported for any of the characteristics

The results of the six characteristics selected for comparison as per IS 8366:1989 are also expressed in similar lines.

Table-4.12: Permissible limits of the selected characteristics as per IS 2752:1995 and IS 8366:1989

Characteristic	IS 2752:1995		IS 8366:1989		
	A	B	C	D	E
Moisture, %, Max.	5	5	15	15	15
Ash content, %, Max.	5	6	60	40	20
Matter soluble in water, %, Max.	NA	NA	--	1.5	0.5
Matter soluble in acid, %, Max.	NA	NA	6	6	2.5
pH	NA	NA	5-8	5-8	6.5-7.5
Decolorizing power, mg/g, Min.	NA	NA	50	70	205
Surface area, m^2/g, Min.	900	550	NA	NA	NA

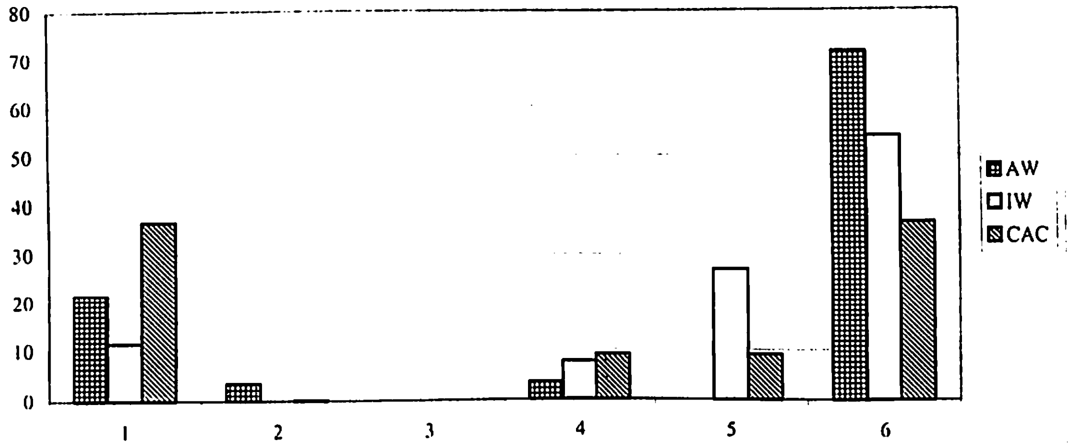
NA: Not available

IS 2752:1995:
A = Respiratpr carbons and solvent recovery;
B = Water treatment

IS 8366:1989:
C = Decolorizing vegetable oils, fats, and solvent recovery;
D = Decolorizing sugar solutions, corn sugar solution etc.;
E = Decolorizing pharmaceuticals

The compliance of the data with the two BIS codes under each of the above sequences is recorded. The percentage share of compliance is calculated based on the compliance data for each sequence of the category and the total number of materials under each of the three categories. The results are given in Fig. 4.2 for percentage compliance under IS 2752:1995.

Similarly the percentage overall compliance is computed based on the compliance data for each sequence and the total number of materials available under all the three categories (i.e., 65). Table-4.13 shows the percentage overall compliance for the activated carbon of all the above three categories under IS 2752:1995 and IS 8366:1989.



Note:
1: Compliance of one of the characteristics;
2: Compliance of any two of the characteristics;
3: Compliance of any two of the characteristics;
4: No Compliance of any of the characteristics;
5: No Compliance based on partial data reported;
6: Data not reported for any of the characteristics.

Fig. 4.2: Percentage share of compliance under IS 2752:1995 with respect to category of activated carbon

Table-4.13: Percentage compliances under the BIS codes

S.No.	Parameter	Percentage compliance under	
		IS 2752:1995	IS 8366:1989
1	Compliance of one of the characteristics	20.00	15.38
2	Compliance of any two of the characteristics	3.08	7.69
3	No Compliance of any of the characteristics	6.15	3.08
4	No Compliance based on partial data reported	12.31	6.15
5	Data not reported for any of the characteristics	58.46	67.69

The following observations are made from Fig. 4.2 and Table-4.13:

- There is no compliance for any two of the characteristics for the activated carbons prepared from IW.
- None of the activated carbons from the categories under study are fully complying under both the BIS codes.
- More than 50% of the data is not fully reported (53.85% and 71.43%) under IW and AW.
- The overall percentage share for the activated carbons of all three categories together also shows that the information about relevant characteristics for the activated

carbons missing (fully and not complying based on partial data reported) is as high as 70.77% and 73.85% under IS 2752:1995 and IS 8366:1989 respectively.

As it is noticed earlier, the BIS codes prescribed certain characteristics for classification of activated carbon based on physico-chemical characteristics. However, the investigators have been examining for few additional characteristics and at the same time not reporting few characteristics prescribed by the BIS codes. For example, the characteristics such as bulk density, silica, and alumina are being reported more frequently (24.26%) but they are not required as per the BIS codes. There are few more characteristics that are being examined less frequently by the investigators (Table-4.14). Reporting of such information is creating a gap between that prescribed by the BIS codes and studied by the investigators. There is a need to reduce this gap. The available database is compiled for the characteristics that are reported for each of three categories (viz., IW, AW, and CAC) under study and is given in Table-4.14.

The following observations are made from Table-4.14:

- All the 25 characteristics are reported over the entire database for the activated carbons prepared from IW. However, very few characteristics are reported for activated carbon from AW.
- The information pertaining to characteristics such as decolorizing power, matter soluble in water, matter soluble in acid, pH, and Iodine number is missing for CAC. These characteristics are prescribed in BIS codes (Table-4.10). The investigators might have felt the need to examine for the above 25 characteristics (either fully or partly) for the raw material they used. But, they are in fact not prescribed in the relevant BIS codes.

Table-4.14: Characteristics reported in literature for each of the categories of activated carbon

S. No.	Characteristic	Activated carbon from IW	Activated carbon from AW	Commercial activated carbon
1	Apparent density	✓	×	×
2	Porosity	✓	✓	×
3	Cation exchange capacity	✓	✓	×
4	Surface area	✓	✓	✓
5	Particle size	✓	✓	✓
6	Moisture content	✓	✓	✓
7	Ash content	✓	✓	✓
8	Decolorizing power	✓	✓	×
9	Matter soluble in water	✓	✓	×
10	Matter soluble in acid	✓	✓	×
11	Bulk density	✓	✓	✓
12	Silica	✓	×	✓
13	Alumina	✓	×	✓
14	Calcium (CaO)	✓	×	✓
15	Sulphur	✓	×	×
16	MgO	✓	×	✓
17	MnO	✓	×	×
18	FeO	✓	×	×
19	Loss on ignition	✓	×	×
20	Fe_2O_3	✓	×	✓
21	Combustible matter	✓	×	×
22	Specific gravity	✓	✓	×
23	Phenol number	✓	✓	×
24	Iodine number	✓	✓	×
25	PH	✓	✓	×

Note: ✓ = Reported; × = Not reported.

In view of the above aspects, there appears to be a need to prescribe a set of characteristics separately for the activated carbons prepared from each of the raw material category viz., IW, AW etc.

It may also be noted that, the BIS codes are presently available for classifying the activated carbons for water treatment, decolorization, solvent recovery and respiratory purposes. But there is no specific BIS code available for classifying the activated carbons for their use in wastewater treatment. In fact, the present study is carried out assuming that the activated carbon of Type-3 under IS 8366:1989 is suitable for wastewater treatment (decolorization of pharmaceuticals wastewater) due to the absence of a separate BIS code for the purpose. Since a number of investigators are working on low-cost novel adsorbents, the requirement of a separate BIS code for suitability of activated carbons for wastewater treatment is desirable. All the activated carbons selected under the present study are giving encouraging results for the treatment of contaminated water. This trend is observed despite their very poor compliance with reference to the IS 2752:1995 and IS 8366:1989. In view of this anomaly, there is a need to re-examine the limits prescribed under the relevant BIS codes as well.

The conclusions drawn from the above study (Babu and Ramakrishna, 2003e) are as follows:

- A separate BIS code is desirable for defining the suitability of activated carbon for wastewater treatment.
- Identification of characteristics for the activated carbon prepared from a specific raw material category is required.
- A standard/common method should be prescribed for the preparation of activated carbon that is commercially available.
- A possible re-examination of the characteristics selected and prescribed under IS 2752:1995 and IS 8366:1989 is needed.

4.1.5 Based on the suitability of adsorbent for a specific use: Model development

It is observed from the earlier discussion (Sec. 4.1) that, a wide variety of novel adsorbents are being studied by investigators using different preparation methodologies. As is observed earlier, a number of factors affect the adsorbate removal efficiency of adsorbent. In such cases, assessing the suitability or ranking the adsorbent for its specific purpose of usage gains importance. Suitability of adsorbent can be assessed by the following approaches:

- Preparation methodology
- Characteristics of adsorbent
- Process performance
- Comparative studies using CAC

The first two approaches are discussed above (Sec. 4.1.2 and 4.1.4) and the last two approaches will be discussed later (Sec. 4.2 and 4.1.6). For assessing the suitability of an adsorbent for a specific purpose, information pertaining to all the relevant characteristics should be available. As is seen from Sec. 4.1.3, the complete information pertaining to all the relevant characteristics is seldom available in literature. In this section, the approaches for assessing the suitability or ranking of adsorbate is discussed using reported data where complete information is available for all the relevant characteristics. A four scale Linear Ranking Model is developed in the present study (Babu and Ramakrishna, 2003d) for ranking the suitability of Adsorbents (LRMA) based on compliance of the adsorbent characteristics with respect to the BIS codes.

The data reported by Rengaraj et al., (1999) is used for illustrating the above LRMA. Rengaraj et al., (1999) prepared six different activated carbons viz., Rubber Seed Carbon (RSCC), Polyseed Carbon (POSCC), Myrobalan Carbon (MWC), Cashew nut Sheath Carbon (CSC), Palm Tree Flower Carbon (PTFC), and Pongam Seed Carbon (POSCC) using six standard procedures of preparing activated carbon viz., Acid process, Sulphate process, Carbonate process, Chloride process, Dolomite process, and Pyrolytic process from the respective AW. They examined selected characteristics of the activated carbon. A sample of CAC is also subjected to similar tests for comparison. The available information is compiled for each of the above activated carbons and are compared with their permissible limits prescribed under IS 2752:1995 and IS 8366:1989. The frequency of the specific activated carbon complying with the permissible limits is determined. The percentage of compliance is calculated with respect to the frequency of compliance for the prescribed limits and the maximum possible chances of compliance of the material. For example, the maximum possibility of compliance for each of the activated carbon is six times for each of the characteristics since there are six different methods of preparation. So, there will be a maximum of 36 and 18 possible chances of compliance for the activated carbons prepared from AW under IS 8366:1989 and IS 2752:1995 respectively. The results of the compliance are shown in Fig. 4.3.

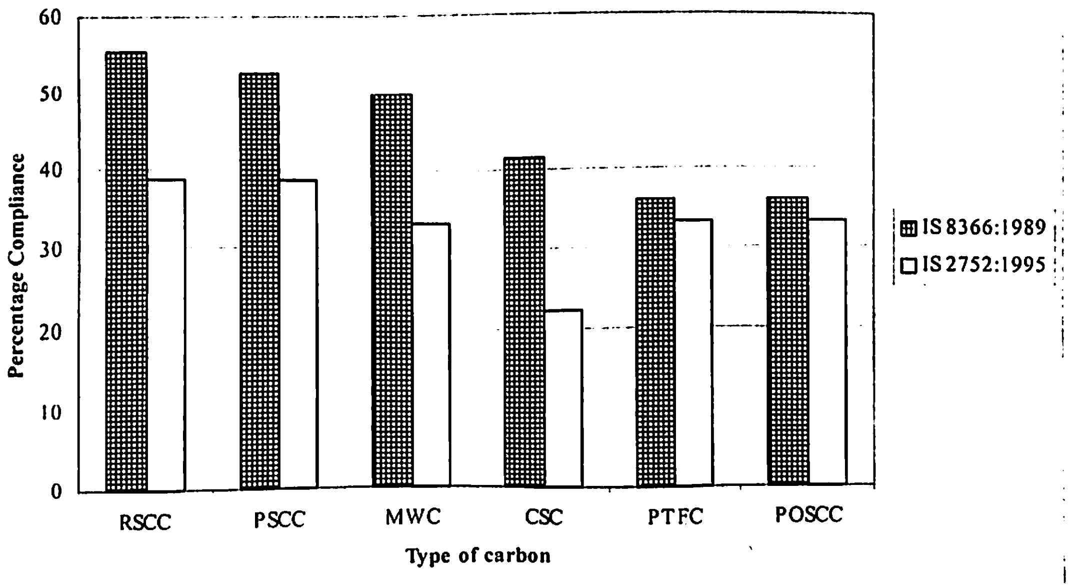


Fig. 4.3: Compliance of the physico-chemical characteristics with respect to BIS codes

It is evident from Fig. 4.3 that, the activated carbons under study are not fully complying with the guidelines prescribed under IS 2752-1995 and IS 8366-1989. The LRMA is proposed for the relative ranking of the activated carbons under study based on the frequency of their complying with the standards. Four ranks are proposed viz., Very

Good, Good, Fair and Poor. They are linearly distributed with regard to percentage compliance and are given in Table-4.15.

Table-4.15: Proposed ranks under Linear Ranking Model

S. No.	Range of percentage compliance	Rank
1	≥ 75	Very Good
2	50 – 74	Good
3	25 – 49	Fair
4	< 25	Poor

All the six activated carbons tested are more suitable (Good to Fair) for decolorization of pharmaceuticals than for water treatment (Fair to Poor). The CSC is ranked Poor as it has a compliance of only 22.22%. The above ranking model can be modified by increasing the levels of scale of ranking and can be used to assess the relative suitability of the activated carbons. The model developed in this study (Babu and Ramakrishna, 2003d) helps in a systematic assessment of the suitability/classification of an activated carbon for a specific purpose and can be applied where information is fully available for the relevant characteristics.

4.1.6 Comparative studies with Commercial Activated Carbon (CAC)

4.1.6.1 Based on Linear Ranking Model of Adsorbents (LRMA)

The data reported by Rengaraj et al. (1999) is used for the suitability of CAC to the LRMA developed (Sec. 3.1.6.1). Rengaraj et al. (1999) studied the characteristics of a CAC sample for comparison with the characteristics of the six activated carbons they prepared (Sec. 4.1.5). The characteristics of CAC reported are compared in this study (Babu and Ramakrishna, 2003d) with the permissible limits prescribed under IS 2752:1995 and IS 8366:1989. The frequency of CAC complying with the permissible limits is determined using the same procedure as discussed under Sec. 4.1.5. The percentage of compliance is calculated with respect to the frequency of compliance for the prescribed limits and the maximum possible chances of compliance of the material. Results indicated that, CAC is showing a compliance of 33.33% under both IS 8366:1989 and IS 2752:1995 respectively. The LRMA indicates that the suitability of the CAC studied can be classified as Fair for its usage based on the percentage compliance. This suggests that, the CAC that is available commercially is not giving excellent compliance with respect to the available BIS codes. This indicates a probable revision of either the limits prescribed by BIS codes or the preparation methodology of CACs.

4.1.6.2 Based on Freundlich isotherm constants

It should be noted from the earlier studies (Secs. 4.1.4 and 4.1.6.1) that there are few anomalies pertaining to the results using CAC in adsorption. This necessitated in studying the performance of CACs with respect to Freundlich isotherm constants. The database available in literature (Bhole et al., 2002; Rao and Bhole, 2002; Rao et al., 2002; Swamy et al., 1998; Mall and Kumar, 1997; Ramu et al., 1992; Khagesan et al., 1991) pertaining to the usage of CAC in the experimental studies is considered. The experimental data pertaining to the Freundlich constants obtained using CAC is collected. Eleven data points are obtained with the following ranges for the Freundlich constants:

K_f: Max.: 727.05; Min.: 1.86×10^{-5}.

n: Max.: 3.56; Min.: 0.588.

The CAC database is sorted for the upper and lower limits of n values as 10 and 1 respectively. Three data points are found to be less than one and the rest of the eight data points are found to be less than 10. The K_f values of this CAC database are sorted using frequency distribution.

The adsorbents prepared by Chemical and Thermal treatment (CT) approach (Sec. 4.1.2) are giving encouraging results with respect to K_f values. It is to be noted that, the adsorbents are given chemical and thermal treatment with or without activation in CT category. CAC is usually prepared (Sai et al., 1997; Hassler, 1974) by heating the raw material at high temperatures and activating it using inert gases such as Steam or N_2. Due to the similarity in adsorbent preparation approach (thermal treatment with/without activation), the frequency distribution of CAC and CT category are compared for studying the trends. The details are given in Table-4.16.

Table-4.16: Frequency distribution comparison for CAC and CT category databases

Frequency Range	Percentage of the frequency distribution	
	CAC	CT
> 100	12.50	10.00
50-100	--	20.00
30-50	12.50	25.00
20-30	--	10.00
10-20	12.50	5.00
1-10	25.00	25.00
<1	37.50	5.00

The results of CT database are relatively better than that of CAC (Table-4.16). The range of K_f values less than 20 is relatively higher for CAC (75%) than that of CT (35%). It indicates that, the adsorbents prepared from CT category show higher adsorbate removal than that from CAC. The limitation however in this comparison is the size of the database. The CAC database is relatively smaller (only 8 data points) than that of CT category database (20 data points). It should be noted that, the comparison being made is with respect to the parameter, which is identified as indicative of the effectiveness of the adsorbent.

The analysis of the above comparative study (Babu and Ramakrishna, 2003a) highlights the drawback of either not following or not adopting the standard procedure for preparing CAC. Earlier studies (Sec. 4.1.4) based on the comparison of the characteristics of CAC and different novel adsorbents being reported in literature with the available BIS codes, also indicated that the need for prescribing a standard/common method for the preparation of CAC.

4.2Based on the process performance

4.2.1 Regression technique for adsorption modeling

This section deals with the results obtained from regression technique. This technique is used for two different cases in adsorption. It is first used to test its suitability for adsorption modeling and is further used to model the isotherm constants of novel adsorbents. The results are discussed below:

4.2.1.1 Applicability

The applicability of regression technique for adsorption is studied using a case study. A Physical Model is developed based on the affecting parameters in conjunction with Multiple Regression (PMMR) to predict the removal of fluoride from contaminated water by adsorption. A compiled database available in literature consisting of twenty-one data points (Bhargava, 2002) pertaining to the same adsorbent (homogeneous with reference to the adsorbent) is collected. The database has three independent variables viz., initial concentration of the adsorbate, adsorbent dose, and contact time, .and one dependent variable viz., PRE. The PMMR is developed in the present study using MATLAB (Rudrapratap, 1999) and Microsoft Excel. The PMMR is developed using the database and validated by comparing the predicted data with that of the actual data. The accuracy of the prediction is determined using Standard Deviation (SD) calculated with reference to the actual data. The SD used in the present study is determined using Eq. 4.1. The results indicated that the predicted data is in close agreement with that of actual data and gave a SD of 0.157.

Another database consisting of twenty-seven data points (Mariappan and Vasudevan, 2002) that are generated for another adsorbent but for the same pollutant is added to the initial database of twenty-one data points totaling to forty-eight data points. The second database of twenty-seven data points comprises of non-linear data points generated during the batch studies of adsorption. The combined data (forty-eight data points) thus developed is heterogeneous, which is fitted in the PMMR to verify the validity of the model for heterogeneous and non-linear adsorption data. Interestingly, it is found that the model predictions for this combined data is relatively erratic and a SD of 0.361 is recorded. This corresponds to an increase of 130% than that for a homogeneous data.

The PRE predicted using the PMMR is compared with that of the actual value reported and is given in Fig. 4.4. Many of the calculated values are in resemblance with those of actual values except for a small zone of database. This zone corresponds to the equilibrium values of adsorption, having approximately the same value. The physics of adsorption system could not be adequately explained by the dimensional variables considered in PMMR and gave highly deviating values for this zone. Such types of equilibrium adsorption values are not available in the first data set and hence the deviation is comparatively lesser resulting in a lower SD value. The results (Babu and Ramakrishna, 2002b) showed that the physical modeling based on affecting dimensional variables in conjunction with regression techniques does not always ensure good prediction unless and until all the affecting variables or affecting dimensionless groups are identified. The success of physical modeling is highly dependent on the thorough understanding and complete knowledge of the physical phenomenon that is taking place in the given system and hence, regression techniques showed the limitation in accurately predicting the output due to incomplete understanding of physical phenomena.

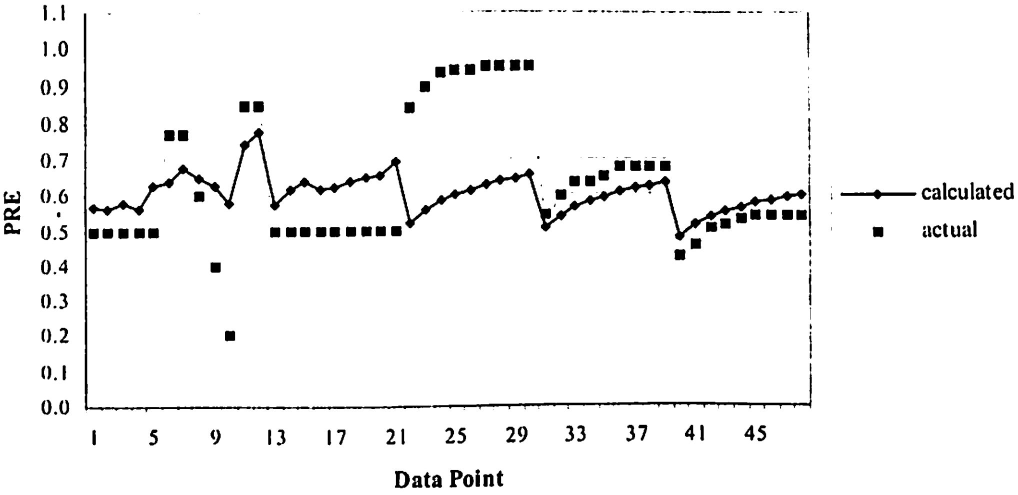


Fig. 4.4: Comparison of PRE for multiple variable regressed heterogeneous data

4.2.1.2 Isotherm constants

The functional dependency of the Freundlich isotherm constants is modeled as a function of temperature using reported data (as referred in Sec. 4.1.3). For this purpose, four different databases (DB-1 to DB-4) are used comprising 120, 94, 12, and 14 data points respectively. They are fitted to regression based LRM and it is observed that huge errors are obtained in the prediction of K_f vs. T and n vs. T respectively. The above databases (DB-1 to DB-4) are subjected to regression using a model based on Normalized Sum-of-Squares (MNSS), which indicates the weighted error in the database and is given by (Hanslip and Buffham, 2002):

Squares (MNSS), which indicates the weighted error in the database and is given by (Hanslip and Buffham, 2002):

$$\text{Sum of squares, } S^2 = \sum_{i=1}^{N} (M_i - M_{model})^2 \tag{4.2}$$

$$\text{Normalized sum of squares, } s = \frac{\sqrt{nS^2}}{\sum M_i} \tag{4.3}$$

In this approach, lesser value of s indicates a good fit.

Comparison of LRM and MNSS

The results obtained from MNSS and LRM (Sec. 4.1.3) are compared (Table-4.17). It is evident from Table-4.17, that the SD values of MNSS are comparatively lesser than that in LRM. This indicates that,

- the data points are widely spread in the database and
- the deviations in the errors are canceling out leaving a small error in the database

Table-4.17: Comparative results of SD for MNSS and LRM

S.No.	Parameters	Model	Standard Deviation for			
			DB-1	DB-2	DB-3	DB-4
1	K_f vs. T	LRM	104.93	86.661	5.7168	1.0846
		MNSS	2.578	2.798	0.7914	0.3000
2	n vs. T	LRM	3.463	1.261	0.4048	0.3629
		MNSS	1.223	0.554	0.4514	0.4323

High values of SD are obtained for K_f vs. T (Table-4.17) for both DB-1 and DB-2 under LRM. Interestingly, the SD value for these two databases is drastically reduced using MNSS. This led to a close examination of K_f values in the databases. The K_f values are compiled in four clusters: (i) values greater than 100 (ii) values lying between 100 and 10 (both limits including) (iii) values less than 10 and up to 1 (including 1) and (iv) values less than 1. The results are plotted in Fig. 4.5 for all the databases. The value of K_f exceeds 100 for 11 data points and is less than 1 for 33 data points in DB-1 as can be seen in Fig. 4.5. In case of DB-2, the K_f value exceeds 100 for 5 data points and is less than 1 for 21 data points. Interestingly, the K_f values in DB-3 and DB-4 are less than 100. The spread in the K_f values is reduced from DB-1 to DB-4, which is evident from Fig. 4.5. This explains the reason (Babu and Ramakrishna, 2003f) for very high values of SD in DB-1 and DB-2 using LRM. In the case of MNSS, the wide spread in the K_f values got nullified resulting in comparatively lower values of SD for DB-1 and DB-2.

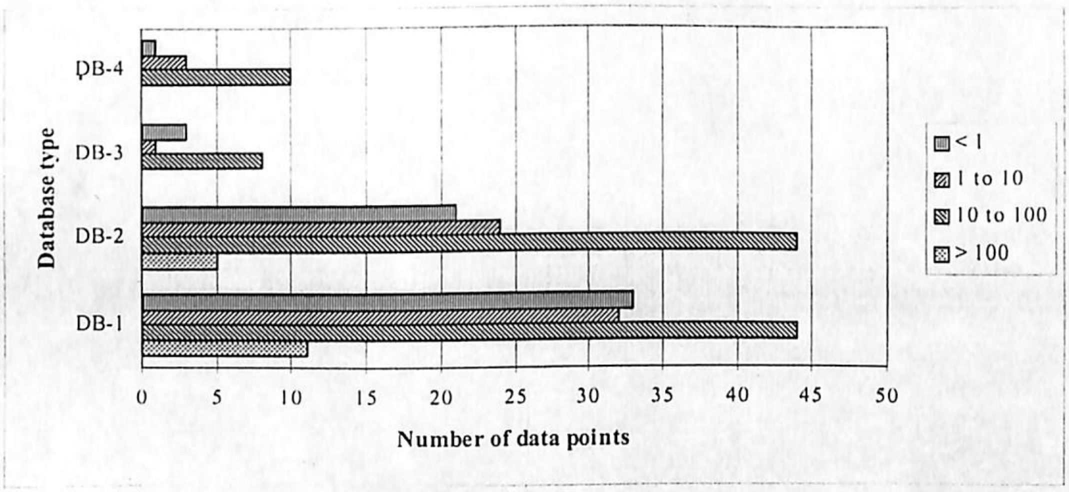


Fig. 4.5: Distribution of K_f values in the databases

4.2.2 Adsorption modeling using dimensional analysis and regression

The results obtained from the earlier studies (Sec. 4.2.1) indicated that, regression approach has a limitation in understanding the trends of the data unless all the affecting parameters are identified. This led to a detailed study of the operating parameters that are significant in affecting the specific objective of adsorption studies. Further, the above case study considered relatively a small database (48 data points). Prediction of PRE is considered as the objective and Equations 3.3 and 3.4 are used for this purpose (Sec. 3.2.2).

A database is compiled from literature covering eight different adsorbates (pollutants) studied over 24 different materials. The details of the database are given in Table-4.18, where the database is modeled to the linearized forms of Eqs. (3.3) and (3.4) and the model constants, f_1, f_2 and exponents α, β, and γ are determined using LSM of Regression technique (LSMM). The results are compared using another Model developed from Method of Averages (MOAM). The accuracy of the model (LSMM and MOAM) prediction is evaluated using Standard Deviation (SD) given by Eq. 4.1.

The results of the study given in Table 4.19 show a huge variation in the accuracy of the predictions for all the combinations. A high value of SD (0.9306 to 1.0265) for Eq. (3.3) indicates that, the PRE prediction using LSMM is erratic. Very high values of SD ranging from 2.0707 to 987.5323 and 4.7 to 5.8039 obtained for MOAM and LSMM for Eq. (3.4) respectively also indicate the PRE prediction by these two models is highly erratic. The value of the model constants f_1 and β for the data points of few pollutants are becoming equal thus making one of three equations developed from either of these two (LSMM and MOAM) models redundant. Hence the SD for these data points could not be calculated.

The above study highlighted the following aspects:

- The model developed for PRE prediction should include all the affecting parameters. The models developed (LSMM and MOAM) are however an improvement over the limitation encountered in the previous case (Sec. 4.2.1), where regression approach for a partial set of dimensional parameters is not found sufficient to predict the adsorption mechanism. In these models, out of the seven parameters identified to be affecting the PRE, three parameters are ignored considering-

- only dimensional parameters and
- the limitation in the dimensional analysis to combine the dimensionless parameters with dimensional parameters in developing a physical model.

The models hence gave erratic predictions for the PRE.

- Another limitation that is encountered is in the LSMM approach. The adsorption experimental data in batch studies is generally non-linear and becomes asymptotic with increase of time (abscissa). The linearized LSMM and MOAM could not represent this asymptotic behavior of the experimental trends. This is identical to the observation noticed in the previous study (Sec. 4.2.1).
- Modeling using Eq. (3.3) [M-2 model] should have given better results for prediction than that using Eq. (3.4) [M-1 model]. This is because, Eq. (3.3) has a parameter indicating variation of time (t_c / t_{eq}) taken in the adsorption process, which is considered to be unity in Eq. (3.4). The variation of time parameter in the model will offer more data points (experimental results) for modeling and hence reducing the bias. However, the results are not in agreement with this modeling logic and showed the contradictory trends. The M-2 model considers $t_c = t_{eq}$. This will give only one point for the entire experimental run and will lie on the asymptote (since it is equilibrium time). The points that are compiled similarly will have similar saturation (equilibrium) state. The data points for M-1 model will have two trends (Fig. 4.6) viz., Linear Rising Trend (LRT) and Asymptotic Trend (AT). The LRT will indicate the rapidity of adsorption and the AT will indicate the convergence to the equilibrium state. The affinity of a specific adsorbate towards an adsorbate depends on many factors including characteristics of adsorbent and operating parameters (Table-2.2).

The slope of the LRT will thus indicate the affinity or uptake of adsorbate by an adsorbent, which may be varying for a given adsorbate-adsorbent system. Since the database collected is heterogeneous with respect to the material, the variations in the trends of the data points might have been reflected in the large variations of SD for M-1model compared to that of M-2 model.

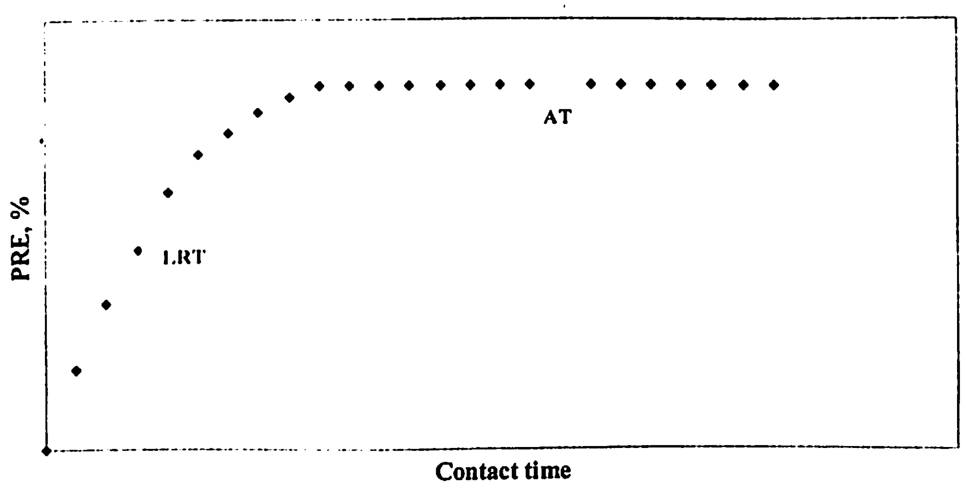


Fig. 4.6: Typical trend of adsorption batch experiment results

Table-4.18: Summary of the variation of the operating parameters in batch studies of adsorption

Item	Data available in literature								Overall
Number of materials attempted	6	8	10	6	7	1	2	3	43
Pollutant removed	Zn^{+2}	Cu^{+2}	Pb^{+2}	Cd^{+2}	Cr^{+6}	Hg^{+2}	COD	Color	Zn^{+2}, Cu^{+2}, Pb^{+2}, Cd^{+2}, Cr^{+6}, Hg^{+2}, COD, Color
pH	6.5 – 7.0	5.8 – 7.0	5.0 – 6.5	5.0 – 6.5	2.0 – 7.0	5.5	5.0	1.0 – 9.0	1.0-9.0
Equilibrium time, hrs	0.5 – 24	0.5 – 24	0.5 –24	0.5 – 24	1.5 – 24	3	8	3 – 4	0.5-24
Contact time, min	10 – 1440	20 – 1440	10 – 1440	30 – 1440	90 – 1440	30 – 180	480	30 – 240	10-1440
Adsorbate concentration, mg/L	10 – 200	10 – 100	20 – 1000	20 – 80	2 – 100	50 – 500	400 – 1500	89.193 – 100	2-1500
Adsorbent dose, g/L	10 – 100	10 – 100	0.1 – 40	0.1 – 10	0.2 – 150	20	20 – 30	3.33 – 50	0.1-150
Pollutant removal efficiency, %	9.17 – 99.7	40.6 – 99.80	8.52 – 99.35	40.0 – 98.70	20.0 – 99.9	15.0 – 78.0	38.0 – 78.0	2.0 – 91.8	2.0-99.9

Table-4.19: **Empirical models developed for the batch studies of adsorption using low cost adsorbents**

Pollutant	**Least squares method model, LSMM**			**Least squares method model, LSMM**			**Method of averages model, MOAM**		
	$\eta = f_2 (C_o/C_d)^\gamma$	**Data points**	**SD**	$\eta = f_1 (t_c/t_{eq})^\alpha (C_o/C_d)^\beta$	**Data points**	**SD**	$\eta = f_1 (t_c/t_{eq})^\alpha (C_o/C_d)^\beta$	**Data points**	**SD**
Zn^{+2}	$f_2 = 0.2372$; $\gamma = 0.6744$	19	1.0162	**	48	# .	$f_1 = 0.0193$; $\alpha = 6.2452$; $\beta = -1.4454$	48	102.3884
Cu^{+2}	$f_2 = 0.4568$; $\gamma = 0.8040$	17	1.0265	**	21	#	**	21	#
Pb^{+2}	$f_2 = 0.7565$; $\gamma = 0.9659$	39	0.9306	$f_1 = 2.8268$; $\alpha = 0.4544$; $\beta = 0.4819$	90	4.7	$f_1 = 0.2943$; $\alpha = 0.2115$; $\beta = -0.1939$	90	0.3527
Cd^{+2}	$f_2 = 0.7577$; $\gamma = 0.9136$	28	0.9460	--	--			--	
Cr^{+6}	$f_2 = 0.5861$; $\gamma = 0.8838$	59	0.8771	**	24	#	$f_1 = 1$; $\alpha = 0.0405$; $\beta = -0.0152$	24	2.0707
Hg^{+2}	--	--	--	**	24	#	$f_1 = 672.8217$; $\alpha = 12.8110$; $\beta = -0.0975$	24	987.5323
COD	$f_2 = 0.3779$; $\gamma = 0.7634$	14	0.9729	--	--	--	--	--	--
Color	--	--	--	$f_1 = 606.3170$; $\alpha = 0.3640$; $\beta = 1.7283$	82	5.8039	$f_1 = 41.5240$; $\alpha = 0.1932$; $\beta = 1.1933$	82	3.4386

** Same coefficients for f_1 and β

\# Could not be calculated

4.2.3 Artificial neural network modeling

The results from regression- and dimensional analysis- approaches reveal (Sec. 4.2.1 and 4.2.2) that,

- combining two different trends (linear and asymptotic) of the same experimental data yielding erratic results in the prediction by regression technique.
- limitation in combining dimensionless (eg. material of adsorbent, pH, adsorbate) parameters with dimensional parameters for establishing an effective model using dimensional analysis.
- the wide range in the values of the parameters in the databases in addition to the above two aspects is leading to erratic prediction of results.
- identification of another approach that overcomes these limitations is needed.

It should be noted from the above conclusions that, the model that is needed for prediction of results from adsorption studies should be of a black box model. The black box model can yield solution due to its ability to relate experimental input and output data without the need for the knowledge of the physical relation between the input and output variables. For example, there is a limitation in regression approach to- (i) combine both the dimensional and dimensionless parameters that affect PRE (ii) combine different trends of experimental data and (iii) accurately predict the trends due to wide variations of the parameters in the database. ANN has the ability to overcome such limitations. The Back-Propagation Network (BPN) of ANN is used for modeling studies. It is applied for three different cases that are previously studied using regression and dimensional analysis approaches:

- Applicability of ANN for adsorption batch studies is tested using a case study of predicting the removal of fluoride where a heterogeneous database is used (Sec 4.2.1.1).
- Modeling of adsorption isotherm constants (Sec. 4.2.1.2).
- Prediction of PRE for adsorption batch studies by incorporating the affecting dimensional and dimensionless parameters (Sec. 4.2.2).

The details of each of these applications are discussed below:

4.2.3.1 Applicability

The applicability of ANN for adsorption batch studies is tested using a case study containing heterogeneous data (Sec. 4.2.1.1). Data available from literature (Bhargava, 2002; Mariappan and Vasudevan, 2002) pertaining to removal of fluoride from adsorption batch studies is collected. Two sets of data points are collected viz., of twenty-one points consisting of homogeneous data with respect to adsorbent (Bhargava, 2002) and of forty-eight points (heterogeneous data, including the above twenty-one points) (Bhargava, 2002; Mariappan and Vasudevan, 2002). The databases are normalized in the range 0 to 1 using Eq. 4.4 given below for mapping and prediction using BPN:

$$Y_{norm} = \frac{y - Y_{\min}}{Y_{\max} - Y_{\min}} \qquad (4.4)$$

where, Y_{norm} is the normalized value

y is the original value

Y_{max} is the maximum value

Y_{min} is the minimum value

The above two databases are fitted into a Physical Model developed based on Multiple Regression technique (PMMR). The model results are verified for their accuracy using Standard Deviation (SD) calculated using Eq. 4.1. The SD obtained (Sec. 4.2.1.1) is less for homogeneous data (SD of 0.157) compared to that of heterogeneous data (SD of 0.361). A three layer BPN is developed in C++ and is used to verify the accuracy of PMMR's prediction. The BPN is trained and tested with normalized data of forty-two and six data points respectively from the database. The learning parameters adopted in the present study are given in Table-4.20.

Table-4.20: Learning parameters used in BPN

S. No.	Learning parameter	Range
1	Number of Neurons in Hidden Layer (NNHL)	3, 5
2	Learning Rate (LR)	0.5, 0.7
3	Number of Epochs (NE)	10000, 20000 to 100000 @ 20000 epochs
4	Error Tolerance (ET)	0.01

A SD of 0.26 is observed for the following combination of learning parameters:

- NNHL: 3
- LR: 0.7
- Epochs: 20000 and
- ET: 0.01.

The SD value obtained is encouraging compared to that using PMMR for heterogeneous data (SD of 0.361). The present study (Babu and Ramakrishna, 2002b) showed that encouraging results are obtained using ANN compared to the PMMR for the heterogeneous data of adsorption batch studies. Hence, BPN model of ANN can be applied for modeling the adsorption studies.

4.2.3.2 Isotherm constants

Langmuir and Freundlich isotherms are used in adsorption studies to understand the extent and degree of favorability of adsorption. The two isotherms depend on temperature and they have two constants (Table-2.1) each in their general form. The results of the previous study (Sec. 4.1.3 and 4.1.6.2) indicated that,

- no satisfactory trends obtained for understanding the trends for n and K_f, the Freundlich constants with Temperature (T).
- the accuracy of prediction, verified using SD, is relatively better for MNSS than for LRM. This is because of the difference in basic principle of the model formulations.
- a wide range of values is observed for these three (n, K_f, and T) parameters in the database causing an erratic prediction by the regression (physical) models.

BPN of ANN is applied to the above problem in modeling for isotherm constants in this study. The modeling is carried out based on Generalized Langmuir equation that is discussed below:

Model based on Generalized Langmuir Equation

The Generalized Langmuir equation is given by (Goyal et al., 1999):

$$q_e = \frac{a(bC_e)^n}{(1+bC_e)^n} \tag{4.6}$$

Eq. 4.6 reduces to Langmuir equation for n=1, which is given by:

$$q_e = \frac{a(bC_e)}{(1+bC_e)} \tag{4.7}$$

and Freundlich equation (Goyal et al., 1999):

$$q_e = K_f(C_e)^n \tag{4.8}$$

$$K_f = a(b^n) \qquad (4.9)$$

A model is developed based on Generalized Langmuir equation and a functional dependency of the parameter K_f with n, and the two Langmuir constants is studied. Since, these constants are dependent on temperature, a function is proposed such that, K_f depends on n, Langmuir constants, and T. Mathematically the function is written as,

$$K_f = f(n, a, b, T) \qquad (4.10)$$

where, K_f and n are Freundlich constants while a and b are Langmuir constants, while q_e and C_e are the amount of adsorbed (mg/g) and the adsorbate concentration at equilibrium (mg/L) respectively. From the entire database of 120 experimental data points collected from literature (Sec. 3.1.3, 3.1.6.2, and 3.2.1.2), the data reported to be following both the isotherms is separated. It is found that 39 data points (comprising 34 data points pertaining to 10 novel adsorbents) are lying under this condition in the database. It is observed from literature that few investigators reported that their experimental results are following both Freundlich and Langmuir isotherms. Since the results of the earlier study (Sec. 4.1.3, 4.1.6.2, and 4.2.1.2) on modeling the Freundlich isotherm constants are not quite encouraging, an alternate approach is considered including both the isotherm constants in this study.

Model based on Artificial Neural Networks: Back-Propagation Network (BPN)

A three-layer Back-Propagation Network (BPN) is developed (Appendix-G) and used to predict K_f with 33 data points for training and the rest six data points for testing. The accuracy of the results is verified by calculating SD using Eq. 4.1. The range of the variables lying in the database used for BPN model is given in Table-4.21.

Table-4.21: Range of values used for BPN model

S.No.	Parameter	Maximum	Minimum
1	Langmuir constant, a	333.33	0.0092
2	Langmuir constant, b	2.58	0.00109
3	Freundlich constant, n	25	0.4428
4	Freundlich constant, K_f	727.05	0.06
5	Temperature, T	70	25

The results of the study (Babu and Ramakrishna, 2003f) show that, a SD of 1.8676 is observed for three neurons in hidden layer at a LR of 0.7. The K_f value is predicted from the same database using multiple regression technique for verification. The SD obtained (157.85) is very high compared to that (1.8676) using neural network modeling. This observation showed that, neural network modeling yields encouraging results compared to that of regression modeling. In the present case, an improvement in prediction to the extent of 98.8% is observed using neural network modeling. However, the SD value obtained using neural network modeling also is little higher indicating the (i) wide range of variations for the values in the database and (ii) probable limitations that might have been faced in generating the experimental data on adsorption isotherms. The wide range of variations for the values in the database indicates that the adsorption phenomenon is system specific and depends upon the affinity of an adsorbate to an adsorbent. This led to the occurrence of variations in the relative affinities of the adsorbent-adsorbate combinations considered in the database and is ascertained in the results obtained for the present modeling studies.

4.2.3.3 Prediction of Pollutant Removal Efficiency (PRE) for heterogeneous database

The successful application of ANN to heterogeneous adsorption data (Sec. 4.2.3.1) indicated that, ANN model could be used for modeling in adsorption studies. Hence, the ANN model is applied to predict the PRE from a large heterogeneous database consisting of heterogeneous data points. It may be noted that, previous attempts to develop a Model using Regression and Dimensional Analysis approaches (RDAM) for prediction of PRE are not successful (Sec. 4.2.1 and 4.2.2). The BPN is chosen for applying to this problem. The database is further increased to that previously used and 513 data points pertaining to eight different pollutants is compiled. The objective here is to include as many different materials as possible that are employed for the removal of one or more of the eight pollutants under study. The dimensionless parameters (viz., material of adsorbent, pollutant, and pH) that could not be incorporated in the earlier RDAM are incorporated in the Neural Network Model (NNM) while retaining the dimensional parameters of the RDAM. Each of the dimensionless parameters (viz., material of adsorbent, pollutant) is assigned separate numbers while the range of pH is taken from 0-14. The details of these numbers assigned and the range of the database for the dimensional parameters are given in Appendices-D and E. The values of all the seven independent parameters (both dimensionless and dimensional) are normalized using Eq. (4.4).

The available 513 data points are divided such that, 440 data points are used for training the network and the remaining are used for its testing. The variables adopted for the learning sequence are:

- Error Tolerance (ET)
- Learning Rate (LR)
- Number of epochs (NE)
- Number of hidden layers
- Number of Neurons in the Hidden Layer (NNHL)

The BPN is systematically trained and tested using three combinations of learning parameters and one hidden layer (Table-4.22). A systematic approach is adopted to identify the optimum learning parameters for the network using elimination technique as per the following priority:

- NNHL
- LR
- NE

Table-4.22: Combinations of learning parameters studied

Learning parameter	Combinations		
	I	II	III
Number of epochs	10000, 15000, 20000, 40000	10000, 15000, 20000, 40000	10000, 15000, 20000, 40000
Number of neurons in hidden layer	5, 7, 9, 10, 12, 14, 15, 20, 25	5	5
Learning rate	0.3, 0.5, 0.7	0.3, 0.5, 0.7	0.3, 0.5, 0.7
Error tolerance	0.01	0.001	0.1

The results obtained from each of the steps adopted are carried forward in the subsequent analysis. The percentage errors in the results are calculated using the formula:

$$Error(\%) = \frac{Testdata - Obtaineddata}{Testdata} x100 \qquad (4.5)$$

The SD is calculated using the formula given in Eq. 4.1. The tests are performed using the combinations given in Table-4.22. The LR is varied as 0.3, 0.5, and 0.7 for all the above combinations. The other learning parameters are retained. The results obtained (Babu et al., 2003) are categorized in the following sequence to apply the elimination technique:

- identification of optimum number of neurons in the hidden layer
- identification of optimum value of learning rate
- identification of optimum number of epochs

The details of each of the above are discussed as follows:

Identification of optimum number of neurons in the hidden layer

The variation of SD is compared with respect to NNHL for each of the three LRs. It is noticed that,

- as the LR is increased, the SD value is becoming lesser. In other words, the learning and prediction of the ANN is effective.
- among the number of neurons attempted in the hidden layer, the SD value for 14 neurons is consistent (range: 2.5-3.0) for three epochs viz., 10000, 15000, and 20000. The SD value is even low (1.58) for 40000 epochs for the 14 neurons.

If the NNHL is more, the network becomes complicated. Results probably indicate that, the present problem (predicting the PRE of adsorbents) is not too complex to have a complicated network routing. Hence, the results can be satisfactorily achieved by keeping the number of neurons in the hidden layer at an optimum value of 14.

Identification of optimum value of learning rate

The combinations-II and -III are attempted in order to study the effect of ET on LR. For this purpose, the NNHL are kept constant at 5 while the variation of the SD value is studied for each of the three LRs viz., 0.3, 0.5, and 0.7 respectively. The accurate prediction of the output depends on ET. In general, the lesser the ET, the more accurate is the prediction. Four different epochs are attempted for understanding the variation of SD with respect to ET. The number of times the SD value reduced for a specific learning rate, for an ET from 0.01 to 0.001 is recorded. Inferences drawn from this observation are as follows:

- For a LR of 0.7, the SD value is reduced for an ET from 0.01 to 0.001 on one-out-of-four occasions (Epochs: 20000) and is found to be almost constant on two occasions (Epochs: 10000 and 40000).
- For a LR of 0.5, the SD value is reduced for an error tolerance from 0.01 to 0.001 on one-out-of-four occasions (Epochs: 40000) and is found to be constant on one occasion (Epochs: 20000).
- For a LR of 0.3, higher values of the SD are observed for an ET from 0.01 to 0.001 on three-out-of-four occasions (Epochs: 10000, 20000 and 40000).

Based on the results obtained for the reduction of SD value pertaining to a reduction in ET from 0.01 to 0.001, the following conclusions are drawn:

- The LRs of 0.3 and 0.5 can be ignored.
- The LR of 0.7 can be adopted.

Interestingly, similar observation is also drawn from Table-4.23. It may be noted that, three different LRs viz., 0.3, 0.5, and 0.7 are considered in the present study. The LRs of 0.3 and 0.7 are chosen such that they can represent the conditions above and below the LR of 0.5. Keeping the SD values obtained for the LR of 0.5 as zero condition, the percentage changes of the other two learning rates are calculated with respect to that of 0.5. A positive value indicates a high SD value compared to that obtained for a learning rate of 0.5. Similarly, a negative value indicates a low SD value compared to that obtained for a learning rate of 0.5. A large number of negative values (Table-4.23) for the LR change from 0.5 to 0.7 indicate that the LR of 0.7 is giving encouraging results in terms of low SD values compared to that obtained for a LR of 0.5. Similarly, a series of negative values ranging from –36% to –62.73% are observed for 14 neurons in the hidden layer for all the four epochs. Results given in Table-4.23 also confirm that a LR of 0.7 and 14 neurons are giving encouraging results. This inference confirms that there is a maximum decrease of SD value up to 62.73% at 40000 epochs. This shows that a higher LR given to the ANN in the present case is resulting in lesser SD values.

Table-4.23: Percentage change of Standard Deviation for learning rates of 0.3 and 0.7 over 0.5 with respect to number of nodes in hidden layer

NNHL	10,000 epochs		15,000 epochs		20,000 epochs		40,000 epochs	
	0.3	0.7	0.3	0.7	0.3	0.7	0.3	0.7
5	41.65	-2.81	54.33	5.06	42.62	-8.10	-0.57	-37.79
7	4.81	-31.26	5.26	-8.17	1.87	-35.87	1.58	-35.70
9	55.73	8.22	136.51	47.46	2.81	-34.11	-2.31	-35.03
10	-0.38	-35.51	-0.40	-31.50	-2.47	-36.76	-0.85	-3.46
12	2.95	-34.62	13.13	11.63	4.49	-29.98	0.02	0.28
14	-4.0	-37.48	-0.65	-36.0	0.16	-37.18	0.58	-62.73
15	2.14	-3.87	-1.35	-37.31	-5.20	-1.29	-0.94	2.52
20	-6.94	-7.30	8.45	7.02	2.28	-36.51	-2.52	-47.93
25	114.36	33.53	2.63	2.74	2.42	-38.33	99.86	100.31

NNHL: Number of Nodes in Hidden Layer

Identification of optimum number of epochs

Epochs are usually increased in ANN to make the network repeatedly understand the trends of the data. There can be a point beyond which even ANN cannot understand the trends despite increasing the epochs. This may even result in higher error values. From the earlier discussions, it is observed that, a LR of 0.7 is giving encouraging results. Hence the analysis is focused exclusively for the results obtained for the LR of 0.7 to understand the variation of SD value with regard to the NE and given in Fig. 4.7. In order to understand how many epochs each set of neurons is consuming before converging to a minimum SD value, 5 sets of neurons viz., 5, 7, 10, 14, and 15 are selected based on the results obtained and discussed earlier.

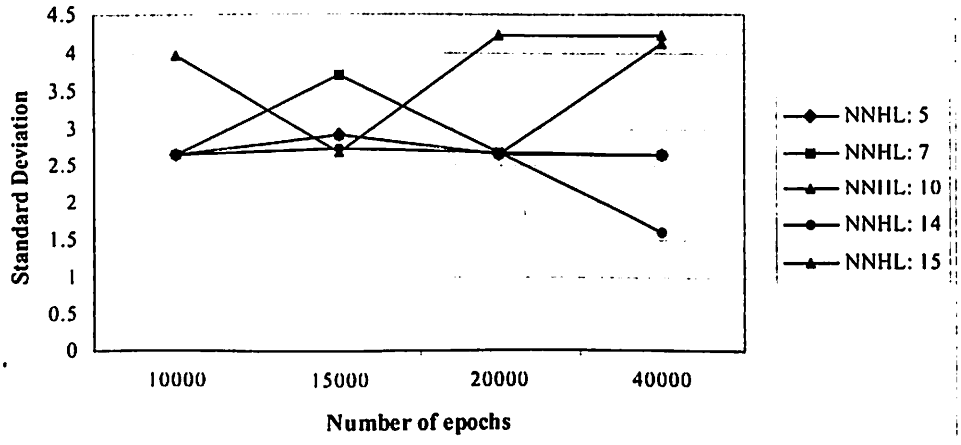


Fig. 4.7: Effect of number of epochs on Standard Deviation for number of neurons in hidden layer at a learning rate of 0.7

The following observations are made from Fig. 4.7:

- The SD values of 14 neurons follow a consistent range (2.67-2.74) for the first three sets of epochs (i.e., 10000, 15000, and 20000) while it is even lower (1.58) for 40000 epochs.
- The SD values of 5 neurons follow a consistent range (2.66-2.92) for all the four different epochs.
- The SD value of 14 neurons at 40000 epochs (1.58) is lower than that of 5 neurons (2.66) at the same set of epochs.
- The SD values for other neurons considered are relatively not encouraging.

It can be concluded from the present study (Babu and Ramakrishna, 2003b) that successful results can be obtained by using 14 neurons in the hidden layer of the BPN for the present problem. It can thus be concluded that, the following learning parameters are found to give optimum results for prediction of PRE for the heterogeneous data from adsorption batch studies:

- Number of hidden layers: 1
- ET: 0.001
- NNHL: 14
- LR: 0.7
- NE: 40000

4.2.4 Analytical modeling

To predict the adsorbate removal as a function of time, the system is modeled analytically using component mass balance. As discussed in Sec. 2.2.2.1, Homogeneous Surface Diffusion Model (HSDM) is widely used for this purpose assuming a simultaneous contribution of external mass transfer coefficient (k_f) and diffusion coefficient (D) at the surface of the adsorbent. The use of this model requires input data from batch studies such as isotherm constants, k_f and D etc. In this study, HSDM is used for predicting concentration profiles from batch studies. The experimental data reported in literature (Flora et al., 1998; Al-Qodah, 2000) is used for this purpose. A computer code in C language is developed for estimating the relevant parameters required as inputs in the model. The details of the study are given below:

4.2.4.1 Software development for predicting parameters from batch studies of adsorption

Determination of the isotherm constants and empirical models for predicting PRE from experimental data will be useful in analyzing the output from batch studies. Further, determination of mass transfer coefficients from batch experiments is essential for simulation studies. The results based on closed batch studies are used for this purpose (Traegner and Suidan, 1989). The values of k_f and D are then found by minimizing the difference between experimental data and model prediction (Chen and Lin, 2001; Al-Qodah, 2000; McKay, 1984a). The procedure for above error minimization is available in literature (Bautista et al., 2000; Traegner and Suidan, 1989). McKay (1984a) reported that the k_f value obtained in his experimental studies is used as an estimate in the simulation of the model and is tested using a best-fit approach over a wide range of experiments.

Determination of diffusion coefficient based on uptake approach is documented in literature (Rengaraj et al., 1999; Buzanowski and Yang, 1989). Another method based on Linear Driving Force (LDF) approach and given by Buzanowski and Yang (1989), Liaw et al. (1979) is considered for software development (Eq. 5 and 6 of Table-4.24) for calculation of k_f and D. A third approach given by Kaguei et al. (1989) for determining the mass transfer approach is also considered for comparison (Eq. 9 and 10 of Table-4.24). The third approach assumes that the rate of change of mass accumulation on the surface of adsorbent is proportional to the change of concentration in liquid phase. Another model suggested by McKay and Allen (1980) for prediction of external mass transfer coefficient is also used. Mohan et al. (2001) and Srivastava et al., (1997a), reported the use of this model in their studies. The above four approaches will give an indication of the range of mass transfer coefficients that are best suited for batch adsorption experiments. The mass transfer coefficients obtained from the above models can be used as initial guess values in simulation and can be adjusted to fit to the actual experimental values.

The software that is developed is hence an attempt to make it comprehensive in its coverage, and user friendly in usage. For this purpose, few requirements are identified and are given as follows:

- Langmuir isotherm constants
- Calculation of Separation Factor
- Mass balance on the surface of adsorbent and check for actual adsorbent dose
- Freundlich isotherm constants
- Mass balance on the surface of adsorbent and check for actual adsorbent dose
- Prediction of Pollutant Removal Efficiency (PRE) using a non-linear model
- Prediction of amount adsorbed on adsorbent
- Estimation of mass transfer coefficients using the above discussed four different models
- Estimation of thermodynamic parameters

The code is developed in C language using the model equations available in literature (Rengaraj et al., 1999; Raji et al., 1997; Buzanowski and Yang, 1989; Kaguei et al., 1989; Singh et al., 1993; McKay and Allen, 1980; Liaw et al., 1979). The model equations used in developing the code are given in Table-4.24. The code is given in Appendix-I. The execution of the code is divided into the following three parts based on the input data requirement:

- Determination of mass transfer coefficients and physical model for predicting PRE
- Determination of isotherm constants
- Determination of thermodynamic constants

Table-4.24: Model equations used in the software developed

Eq.No.	Equation	Purpose
1	$PRE = \left(\frac{C_0 - C}{C_0}\right)$	Calculation of PRE from experimental data
2	$PRE = kt^m$	Empirical model to predict PRE at any time *t*
3	$q = \left(\frac{V}{W}\right)(C_0 - C)$	Calculation of amount adsorbed on adsorbent
4	$q = \frac{q_e kt}{1 + kt}$	Empirical model to predict amount adsorbed at any time *t*
5	$\frac{dq_{avg}}{dt} = \frac{3k_f}{r}(q_e - q_{avg})$	Estimation of external mass transfer coefficient using LDF approach
6	$D = \frac{k_f r}{5}$	Estimation of diffusion coefficient using LDF approach
7	$\left(1 - \frac{q}{q_e}\right) = \frac{6}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{r^2}\right)$	Estimation of diffusion coefficient using uptake approach
8	$k_f = \frac{5D}{r}$	Estimation of external mass transfer coefficient using uptake approach
9	$\frac{\partial q_{avg}}{\partial t} = \frac{3k_f}{\rho r}(C - C_e)$	Estimation of external mass transfer coefficient using alternate LDF approach
10	$D = \frac{k_f r}{5}$	Estimation of diffusion coefficient using alternate LDF approach
11	$\frac{C}{C_0} = \left(\frac{1}{1 + K_L(W/V)}\right) + \frac{K_L(W/V)}{1 + K_L(W/V)}\exp\left(\frac{-(1 + K_L(W/V))}{K_L(W/V)}k_f S_s t\right)$	McKay and Allen model (1980) to calculate external mass transfer coefficient
12	$S_s = \left(\frac{6}{d}\right)\left(\frac{1}{\rho}\right)\left(\frac{W}{V}\right)$	Specific surface of adsorbate
13	$K_L = (ab)$	Langmuir constant (from Eq. No. 15)
14	$D = \frac{k_f r}{5}$	Estimation of diffusion coefficient using external mass transfer coefficient
15	$q_e = \frac{abC_e}{1 + bC_e}$	Langmuir isotherm
16	$R_L = \frac{1}{1 + bC_0}$	Separation factor based on Langmuir isotherm
17	$q_e = K_f C_e^{1/n}$	Freundlich isotherm

Table-4.24 (Contd...)

Eq.No.	Equation	Purpose
18	$\frac{W}{V}=\frac{(C_0-C_e)}{(abC_e/1+aC_e)}$	Mass balance on batch reactor-Checking suitability of Langmuir isotherm
19	$\frac{W}{V}=\frac{(C_0-C_e)}{K_f C_e^{1/n}}$	Mass balance on batch reactor-Checking suitability of Freundlich isotherm
20	$K_c=\frac{q_e}{C_e}$ $\Delta G=-RT\ln K_c$ $\ln K_c=\frac{\Delta S}{R}-\frac{\Delta H}{RT}$	Thermodynamic parameters based on Equilibrium constant
21	$b=b_0 e^{-\left(\frac{\Delta H}{RT}\right)}$ $\ln\left(\frac{1}{b}\right)=\frac{\Delta G}{RT}$ $\Delta S=\frac{\Delta H-\Delta G}{T}$	Thermodynamic parameters based on Langmuir isotherm constant

The details covered under each of the three parts is given as follows:

The first part of the code deals with taking the experimental data pertaining to the concentration of adsorbate at different contact times as input and calculates the PRE using Eq. 1. The physical model for predicting PRE is developed using Eq. 2. The amount adsorbed is calculated from the experimental data entered (for Eq. 1) and adsorbent dose using Eq. 3. The empirical model for prediction of amount adsorbed at equilibrium is developed using Eq. 4. The external mass transfer coefficient (LT^{-1}) is calculated from the LDF approach (Eq. 5) and subsequently, the diffusion coefficient (L^2T^{-1}) are be calculated using Eq. 6. The diffusion coefficient (L^2T^{-1}) is calculated from the uptake approach (Eq. 7) and subsequently, the external mass transfer coefficient (LT^{-1}) is calculated using Eq. 8. The external mass transfer coefficient (LT^{-1}) is calculated from alternate LDF approach (Eq. 9) and subsequently, the diffusion coefficient (L^2T^{-1}) is calculated using Eq. 10. Similarly the external mass transfer coefficient (LT^{-1}) is calculated from the McKay and Allen model (Eq. 11) and subsequently, the diffusion coefficient (L^2T^{-1}) is calculated using Eq. 14. The specific surface of adsorbent and Langmuir constant are calculated using Eq. 12 and 13 for their use in Eq. 11. For comparison purposes, each of the above described four models for determination of mass transfer coefficients is given a nomenclature (Table-4.25). The detailed procedure executed in the code is schematically shown as a flow sheet in Fig.4.8.

The second part of the code deals with calculation of the Langmuir and Freundlich isotherm constants (Eq. 15 and 17) based on a set of C_e and q_e values from experimental data. The code simultaneously checks for the separation factor, R_L (Eq. 16) and the mass balance based on both Langmuir and Freundlich isotherms (Eq. 18 and 19).

The third part of the code deals with calculation of thermodynamic constants calculated in two different approaches (Eq. 20 and 21). For this the experimental data pertaining to a variation of at least two different operating temperatures is required. Regression based on method of least squares (Holman, 1994) is used in the code for developing the empirical models.

The code is validated with the data available in literature (Siddique, 2003; Al-Qodah, 2000; Raji et al., 1997). The mass transfer coefficients are determined from experimental data reported (Al-Qodah, 2000) using four different approaches (Table-4.24). The mass transfer coefficient values obtained by each of the four models (Table-4.25) for the same experimental data are compared with the actual values reported (Al-Qodah, 2000) and are given in Table-4.26. It is noted that, the prediction of mass transfer coefficients from McKay and Allen model (1980) and Kaguei et al. model (1989) are relatively closer to the actual value reported (Table-4.26) and hence can be considered reliable. The predicted values of mass transfer coefficients from these models are used in the simulation studies.

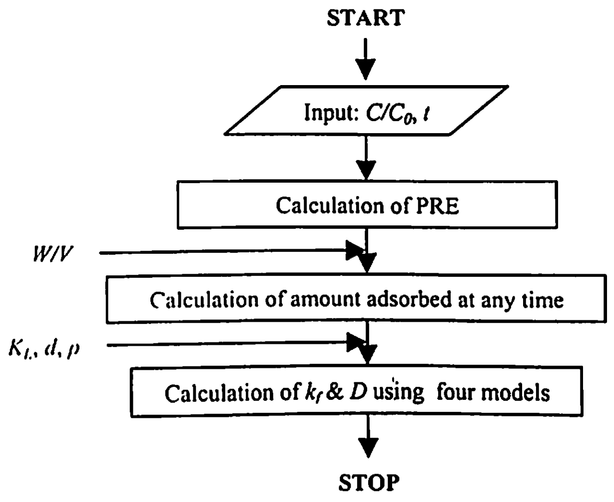
Table-4.25: Nomenclature of models used for estimation of mass transfer coefficient values

S.No.	Model Equation	Reference
1	$\frac{dq_{avg}}{dt} = \frac{3k_f}{r}(q - q_{avg})$	Buzanowski and Yang, 1989
2	$\left(1 - \frac{q}{q_e}\right) = \frac{6}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{r^2}\right)$	Liaw et al., 1979
3	$\frac{\partial q_{avg}}{\partial t} = \frac{3k_f}{\rho r}(C - C_e)$	Kaguei et al., 1989
4	$\frac{C}{C_0} = \left(\frac{1}{1 + K_L(W/V)}\right) + \frac{K_L(W/V)}{1 + K_L(W/V)}\exp\left(\frac{-(1 + K_L(W/V))}{K_L(W/V)} k_f S_s t\right)$	McKay and Allen, 1980

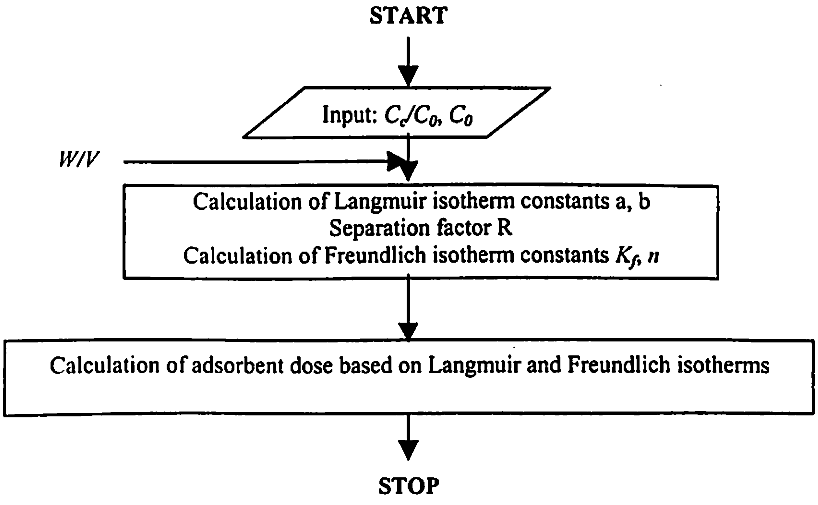
Table-4.26: Comparison of mass transfer coefficient values

S.No.	W/V, kg/m^3	Experimental data (Al-Qodah, 2000)		Buzanowski and Yang, 1989		Liaw et al., 1979		Kaguei et al., 1989		McKay and Allen, 1980	
		k_f	D	k_f	D	k_f	D	k_f	D	k_f	D
1	0.5	2.5	1.0	0.00217	0.00043	0.01230	0.00240	3.54	0.707	3.138	0.627
2	1.0	2.5	1.1	0.00567	0.00110	0.01878	0.00375	4.96	0.991	3.865	0.773
3	2.0	2.5	1.0	0.01250	0.00250	0.02700	0.00540	6.16	1.230	5.560	1.112

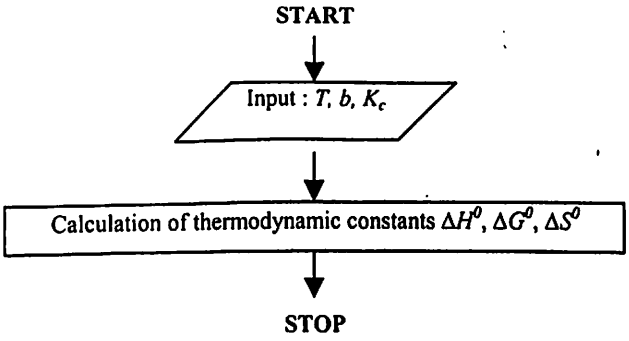
k_f: External mass transfer coefficient, m/s (x10^{-6})
D: Diffusion coefficient, m^2/s (x10^{-10})



(a): Determination of physical models and mass transfer coefficients



(b): Determination of isotherm constants



(c): Determination of thermodynamic constants

Fig. 4.8: Flow chart showing calculation of values from different models

4.2.4.2 *Simulation of Homogeneous Surface Diffusion Model (HSDM)*

The Homogeneous Surface Diffusion Model (HSDM) available in literature (Flora et al., 1998) is discritized using pure implicit scheme of Finite Difference Method and Simpson's 1/3rd rule. The code is developed in C language and is given in Appendix-H. For validating the simulation model, experimental data available in literature (Flora et al., 1998) is considered. The HSDM is run with the input parameters (Table-4.27) and the results obtained are compared with the actual experimental data (Flora et al., 1998). The results are shown in Figs. 4.9-4.11. Flora et al. (1998) conducted his experiments for three different initial concentrations of adsorbate viz., 110 μg/m^3, 352 μg/m^3, and 1017 μg/m^3 respectively. From Figs. 4.9-4.11, it is noted that the simulation results are in good agreement with the actual experimental data.

Table-4.27: Model input parameters for simulation (Flora et al., 1998)

S.No.	Parameter	Value
1	Particle density, kg/m^3	500
2	Particle radius, m	372 x 10^{-6}
3	Volume of adsorbate, m^3	0.0125
4	Mass of adsorbent, kg	0.0001
5	External mass transfer coefficient (k_f), m/s	12 x 10^{-2}
6	Diffusion coefficient (D), m^2/s	2.29 x 10^{-11}
7	Langmuir constant (b), m^3/kg	6.15 x 10^6
8	Langmuir constant (a), kg/kg	123 x 10^{-6}

The simulation model performance is verified using another set of experimental data (Al-Qodah, 2000). The input parameters used for simulation are given in Table-4.28. Al-Qodah (2000) varied initial concentrations (C_o) and adsorbent dose (W/V) for his experiments.

Al-Qodah (2000) calculated the mass transfer coefficients for each of his experimental runs. Comparative studies are carried out for changes in adsorbent dose keeping initial concentration of adsorbate constant i.e., $W/V = 0.5, 1.0, 2.0$ for $C_o = 200$ mg/L.

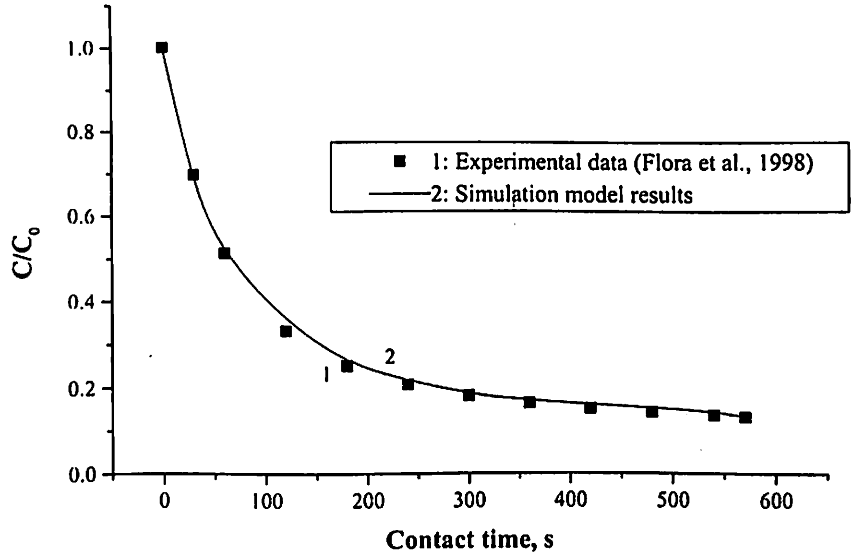


Fig. 4.9: Comparison of simulation results with experimental data for an initial concentration (C_o) of 110 µg/m^3

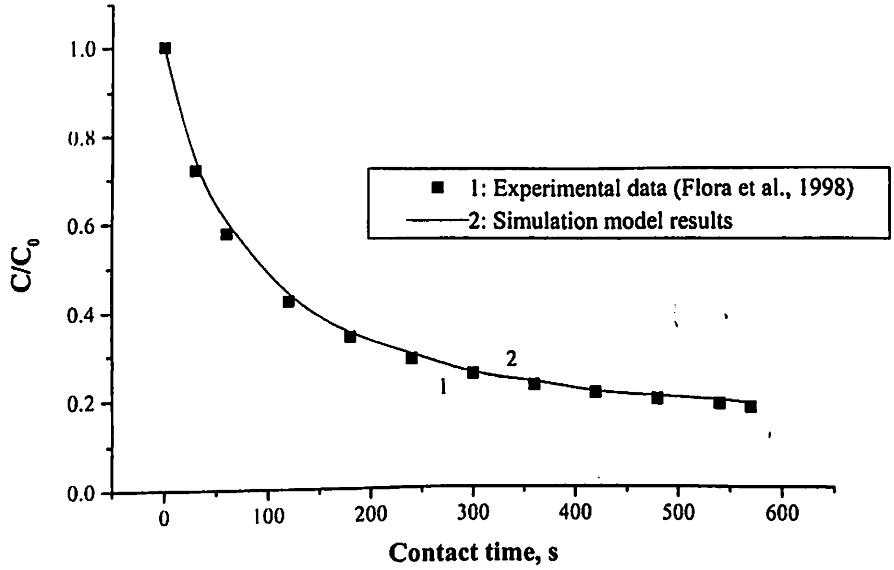


Fig. 4.10: Comparison of simulation results with experimental data for an initial concentration (C_o) of 352 µg/m^3

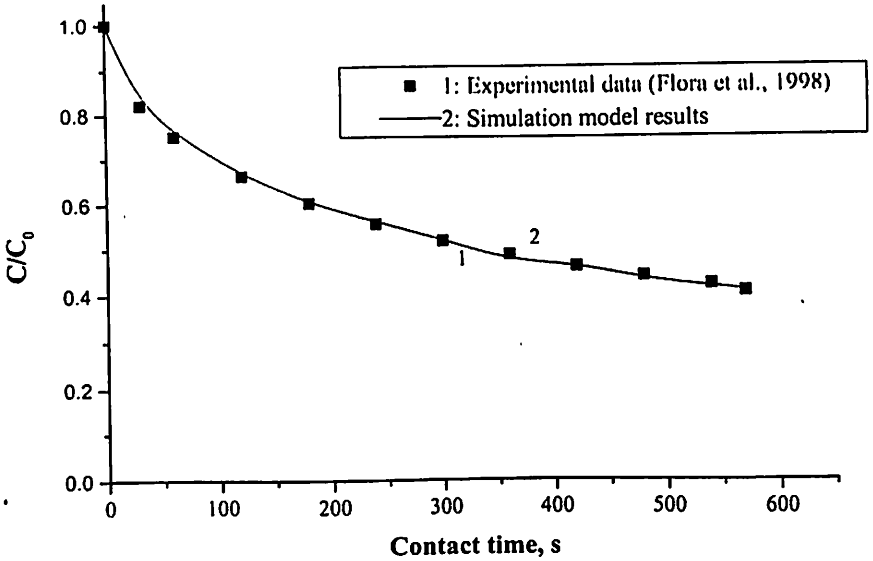


Fig. 4.11: Comparison of simulation results with experimental data for an initial concentration (C_o) of 1017 µg/m^3

Table-4.28: Model input parameters for simulation (Al-Qodah, 2000)

S.No.	Parameter	Value
1	Particle density, kg/m^3	841
2	Particle diameter, m	200 x 10^{-6}
3	Volume of adsorbate, m^3	1.0
4	Mass of adsorbent, kg	1.0
5	External mass transfer coefficient (k_f), m/s	2.5 x 10^{-6}
6	Diffusion coefficient (D), m^2/s	1.10 x 10^{-10}
7	Langmuir constant (b), m^3/kg	30.478
8	Langmuir constant (a), kg/kg	0.2275

The results for comparative studies are given in Fig. 4.12-4.14. Al-Qodah (2000) reported k_f and D values of 2.5x10^{-6} m/s and 1.0x10^{-10}m^2/s for W/V=0.5 kg/m^3 and 2.0 kg/m^3. For W/V = 1 kg/m^3, the k_f and D values are 2.5x10^{-6} m/s and 1.10x10^{-10} m^2/s respectively. Simulation is carried out with these values and an under-prediction of experimental data points is noted in all three cases of W/V values. Assuming an error in reported values, the k_f and D values are calculated from McKay and Allen model. The k_f values are 3.138 x 10^{-6}, 3.865 x 10^{-6}, and 5.562 x 10^{-6} m/s and D values are 0.627x10^{-10}

m^2/s, 0.773 x 10^{-10} and 1.112 x10^{-10} m^2/s respectively for *W/V*=0.5, 1.0, and 2.0 kg/m^3. Similarly, the mass transfer coefficient values obtained from Kaguei et al. model are- 3.537 x 10^{-6}, 4.959 x 10^{-6}, and 6.157 x 10^{-6} m/s for k_f and 0.991 x 10^{-10}, 0.707 x 10^{-10}, and 1.231 x 10^{-10} m^2/s for *D* respectively. These values are used as inputs in the model and the simulated results obtained are shown in Fig. 4.12-4.14. The errors are reduced compared to those obtained from actual (reported) values of k_f and *D* used. The predicted k_f and *D* values from the above two models are showing encouraging results (Fig. 4.12-4.14).

This study indicated the closeness with which the McKay and Allen model and Kaguei et al. model can predict the mass transfer coefficients for a given set of experimental values.

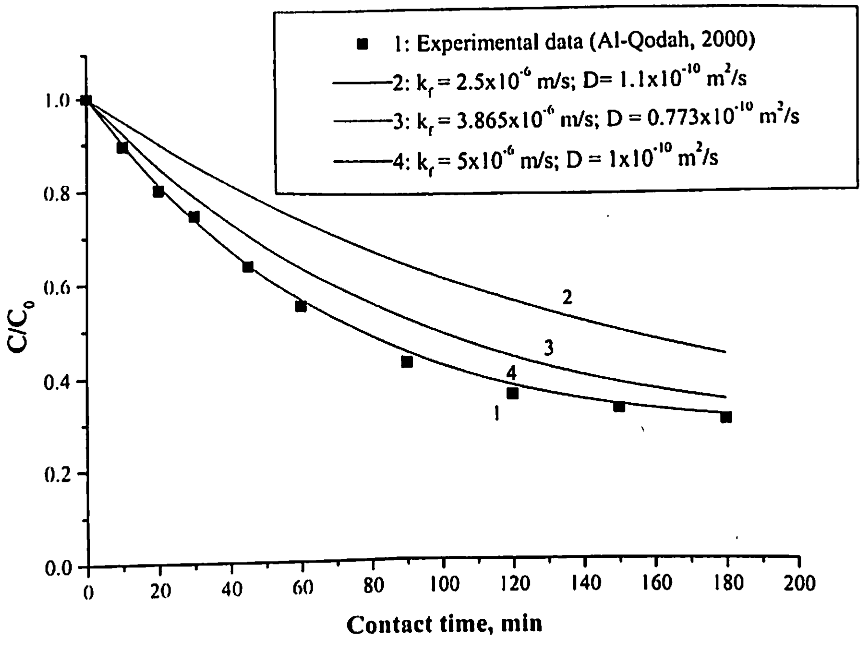


Fig. 4.12: Validation of simulation results for *W/V*=1.0 kg/m^3

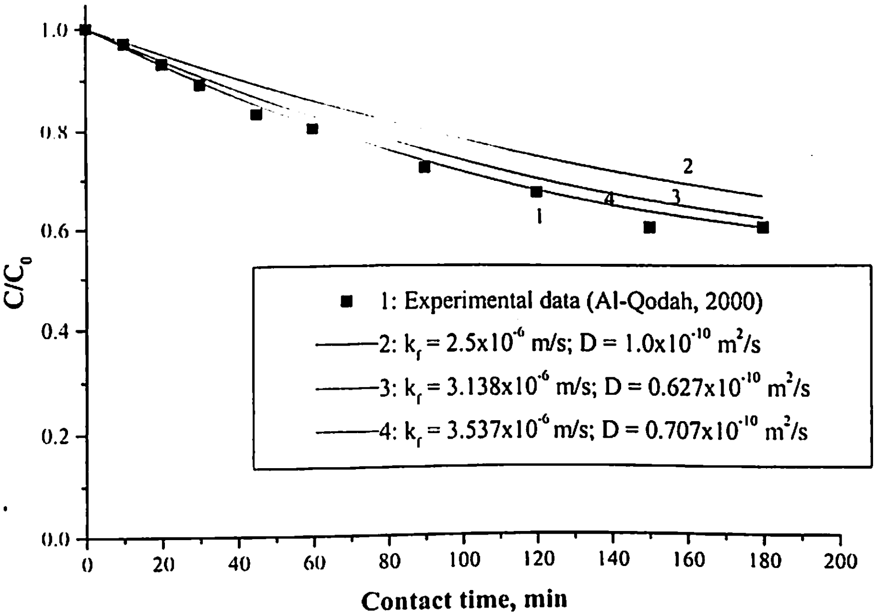


Fig. 4.13: Validation of simulation results for *W/V* = 0.5 kg/m^3

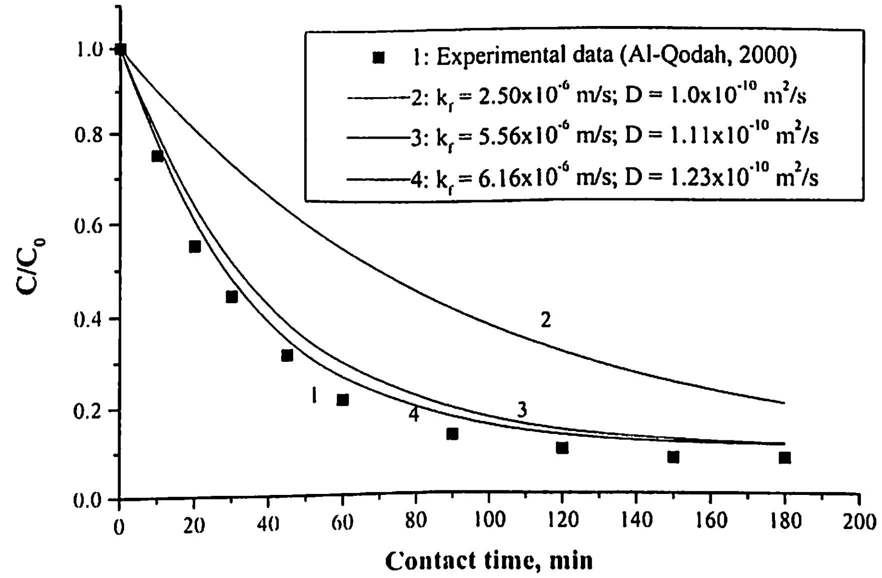


Fig. 4.14: Validation of simulation results for *W/V* = 2.0 kg/m^3

4.2.4.3 Parametric study

The following parameters are identified that affect the simulation model developed for batch studies:

- external mass transfer coefficient, k_f, m/s
- diffusion coefficient, D, m^2/s
- initial concentration of adsorbate (C_0), g/L or kg/m^3
- adsorbent dose (W/V), g/L or kg/m^3
- adsorbent particle density (ρ), kg/m^3
- particle diameter (d), m

An exhaustive parametric study is conducted with a set of combinations listed in Table-4.29. For this purpose, the ranges of parameters are primarily identified (Table-4.29) based on their ranges used and successfully validated with experimental data of Al-Qodah (2000). Additional ranges of these parameters that are reported in literature (Flora et al., 1998) are also studied. A total of 81 combinations are used and simulation runs are carried out from the ranges listed in Table-4.29.

Table-4.29: Ranges of parameter values used in parametric study

S.No.	Variable Parameter	Ranges of values	Unit
1	External mass transfer coefficient, k_f	0.5×10^{-6}; 2.5×10^{-6}; 5.0×10^{-6}; 10.0×10^{-6}	m/s
2	Diffusion coefficient, D	1.0×10^{-10}; 2.5×10^{-10}; 5.0×10^{-10}; 10.0×10^{-10}	m^2/s
3	Initial concentration of adsorbate, C_0	50; 250; 500	mg/L
4	Adsorbent dose, W/V	1.0; 0.1	kg/m^3
5	Adsorbent particle density, ρ	500; 841	kg/m^3
6	Particle diameter, d	100; 200	m

The study of the several combinations given Figs. 4.15–4.23 revealed that, the equilibrium time is reduced with increase in either C_0 or k_f. This is understandable since, increase of C_0 increases amount of adsorbate available for adsorption and increase of k_f indicates the rapid release of adsorbate from liquid. This has resulted in achieving equilibrium in shorter durations at higher values of these two parameters. Further, the rapid release of adsorbate from the liquid resulted in a steep slope of the linear portion of the curves while the lower values of k_f showed a relative flatter slope (Figs. 4.18-4.20). Hence, the linear portion of the curve is shifting close to the axis indicating a steep slope or rapid adsorption while the curve is shifting away from the axis indicating a slower adsorption. For example, it can be observed from Figs. 4.18-4.20 that, an increase in initial concentration of adsorbate (50 mg/L, 250 mg/L, and 500 mg/L) keeping the other parameters fixed showed decrease in equilibrium time (beyond 180 min, 160 min, and 80 min respectively). It should also be noted from these figures that, the time taken for achieving equilibrium under lower k_f is relatively more with respect to the higher values of k_f. Similar trends are observed for both the parametric values of W/V studied i.e., 1.0 and 0.1 kg/m^3).

The typical results obtained from the parametric study are discussed in this section. The results obtained from the above combinations are classified into the following categories for analysis:

- Variation of k_f with respect to adsorbent dose
- Variation of D with respect to adsorbent dose
- Variation of C_0 with respect to adsorbent dose

Variation of k_f with respect to adsorbent dose: The variation of k_f with respect to adsorbent dose (i.e., W/V) is studied for a wide range of parameters keeping D, d, ρ, and C_0 as constants (Figs. 4.24-4.25). It is observed that the trends of adsorbate removal curves are similar for a specific value of C_0 and W/V values. The adsorbate removal is increasing with increase of k_f value indicating the increased release rate of the adsorbate from the liquid. The amount adsorbed (q) on the adsorbent is increased (Figs. 4.24-4.25) with decrease of W/V values. This is clear from Eq. 4.11, which indicates the higher accumulation of adsorbate when the W/V value is reduced. For example, the amount adsorbed increased from 164.43 mg/g to 199.10 mg/g when W/V is reduced for an initial concentration of 250 mg/L of adsorbate (Fig. 4.24). Similarly, the amount adsorbed increased from 45.47 mg/g to 121.80 mg/g when W/V is reduced from 1.0 kg/m^3 to 0.1 kg/m^3 for an initial concentration of 50 mg/L of adsorbate (Fig. 4.25) This is important since, the efficiency of adsorbent is judged from its dosage into the system and the corresponding accumulation of adsorbate on adsorbent. In view of this aspect, study of W/V values for less than 1.0 is useful. The study showed that, the adsorption system is dependent on W/V value and the accumulation is inversely proportional to the ratio of W/V value. The effect of k_f with respect to particle radius and density are studied (Fig. 4.26 and 4.27). Adsorbate removal increased with decrease in particle size. This indicates the availability of higher specific surface of the adsorbent (Eq. 4.12) when the particle size is reduced. Further, the adsorbate removal is reduced with decrease of particle density. This also indicates the availability of higher specific surface on the adsorbent (Eq. 4.12). The lower values of particle diameter (100 μm) and density (500 kg/m^3) together resulted in higher adsorbate removal (Fig. 4.28) validating the above assumption.

$$q = \left(\frac{V}{W}\right)(C_0 - C) \tag{4.11}$$

$$S_s = \left(\frac{6}{d}\right)\left(\frac{1}{\rho}\right)\left(\frac{W}{V}\right) \tag{4.12}$$

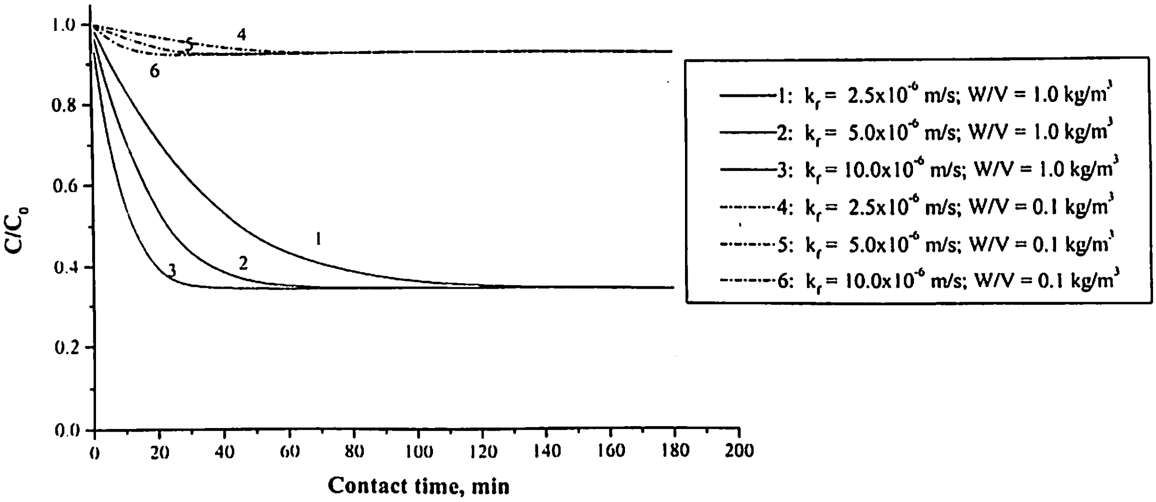


Fig. 4.15: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V*
Operating parameters: $D = 5\times10^{-10}$ m²/s; $C_0 = 250$ mg/L; $\rho = 500$ kg/m³; $d = 100\mu$m.

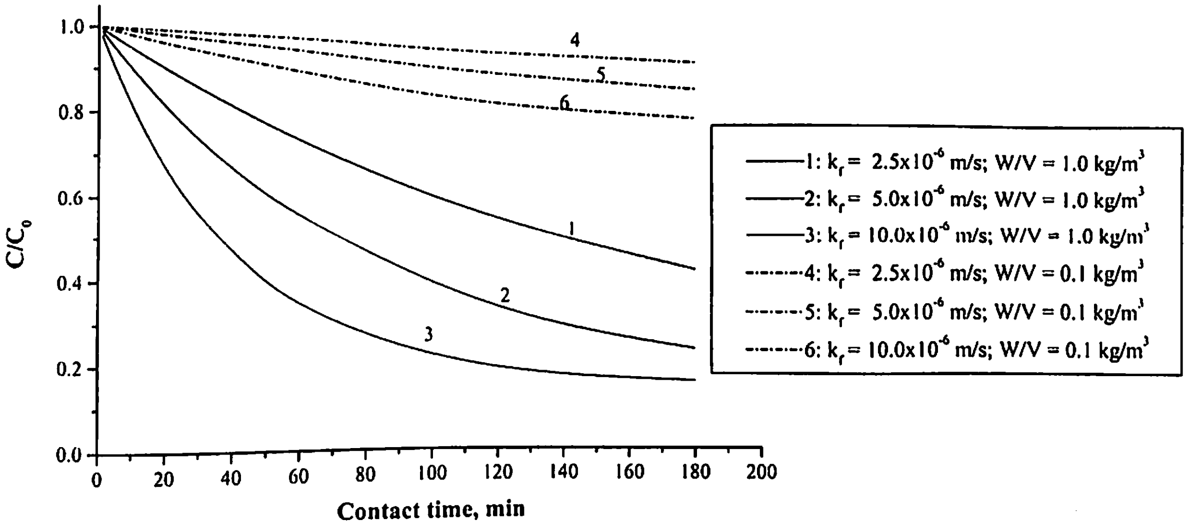


Fig. 4.16: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V*
Operating parameters: $D = 0.5\times10^{-10}$ m²/s; $C_0 = 50$ mg/L; $\rho = 841$ kg/m³; $d = 200\mu$m.

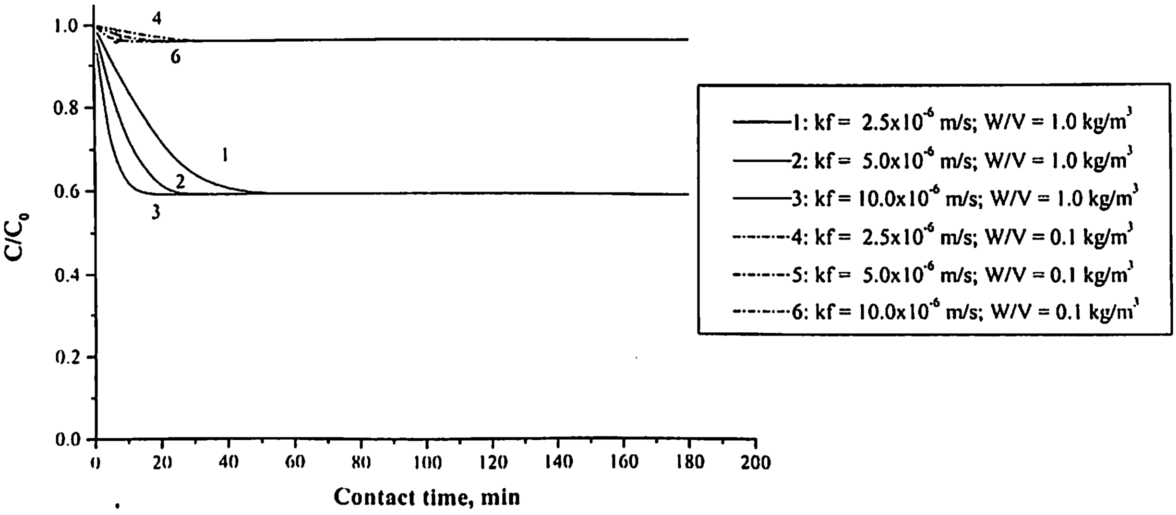


Fig. 4.17: Effect of contact time on adsorbate removal for various parameter values of k_f and W/V
Operating parameters: $D = 5\times10^{-10}$ m²/s; $C_0 = 500$ mg/L; $\rho = 500$ kg/m³; $d = 100$µm.

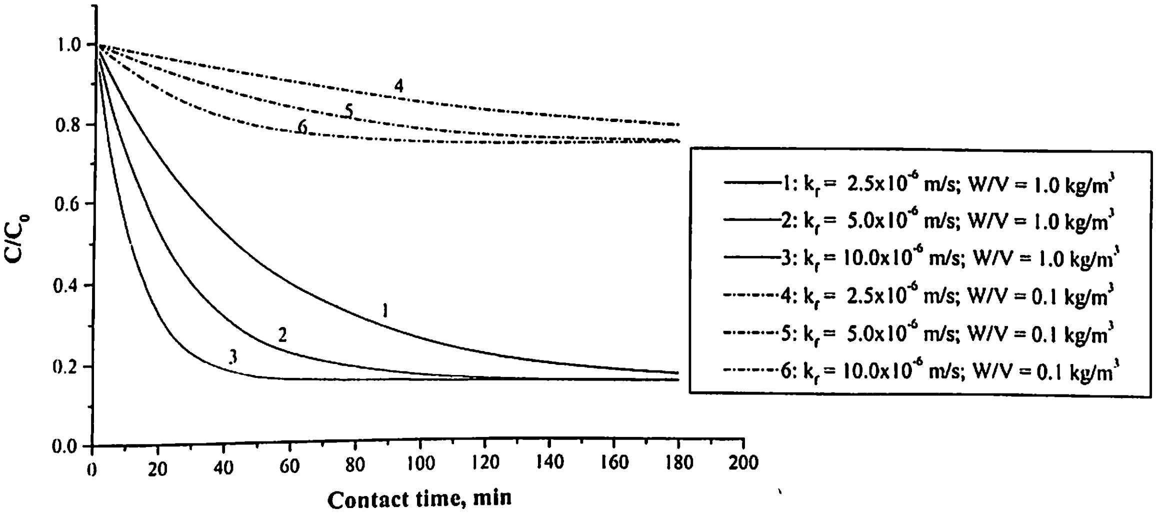


Fig. 4.18: Effect of contact time on adsorbate removal for various parameter values of k_f and W/V
Operating parameters: $D = 2.5\times10^{-10}$ m²/s; $C_0 = 50$ mg/L; $\rho = 500$ kg/m³; $d' = 100$µm.

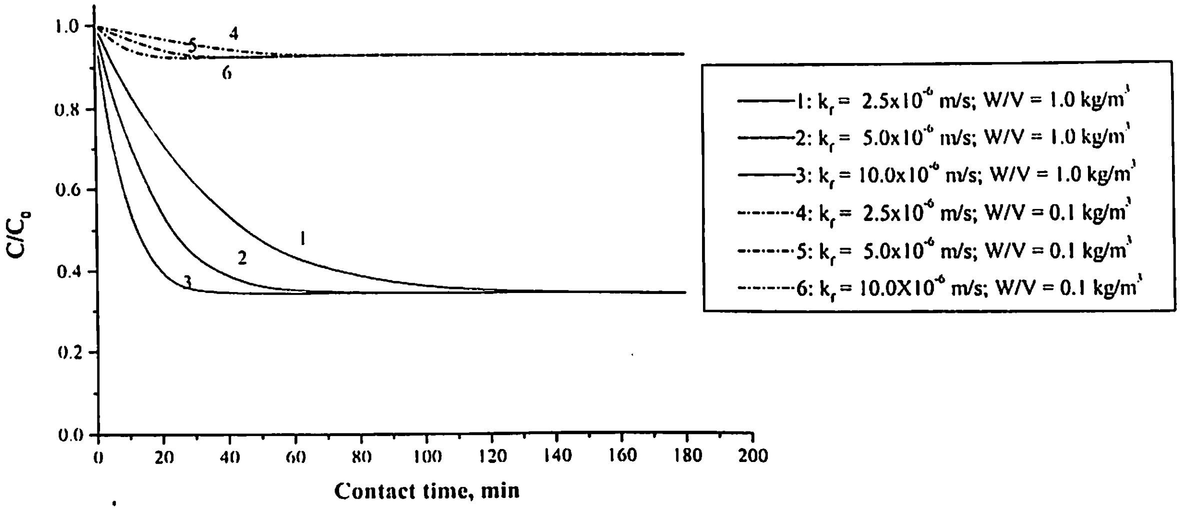


Fig. 4.19: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 2.5\times10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

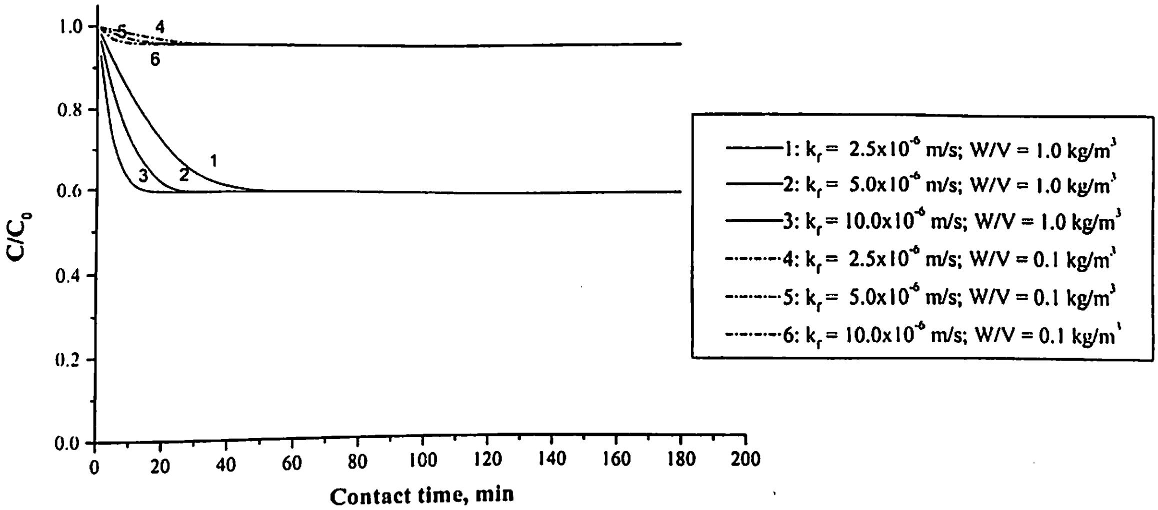


Fig. 4.20: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 2.5\times10^{-10}$ m^2/s; $C_0 = 500$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

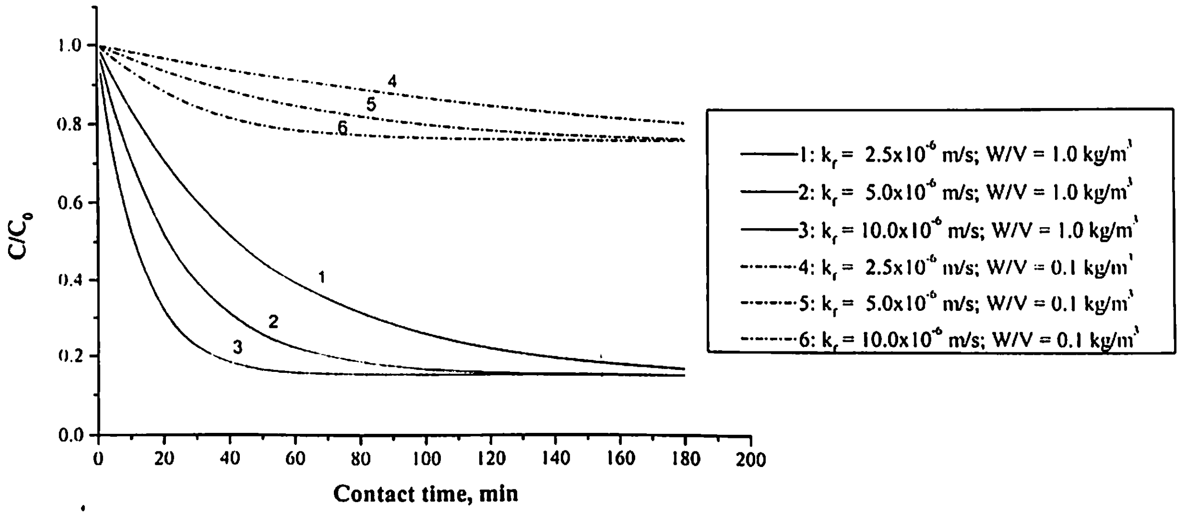


Fig. 4.21: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 10\text{x}10^{-10}$ m^2/s; $C_0 = 50$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

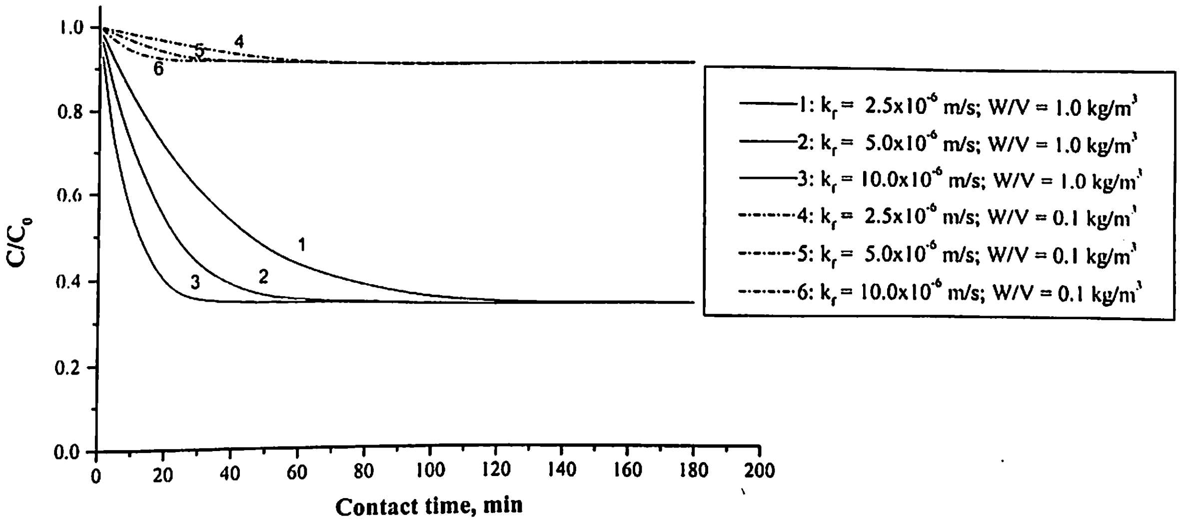


Fig. 4.22: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 10\text{x}10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

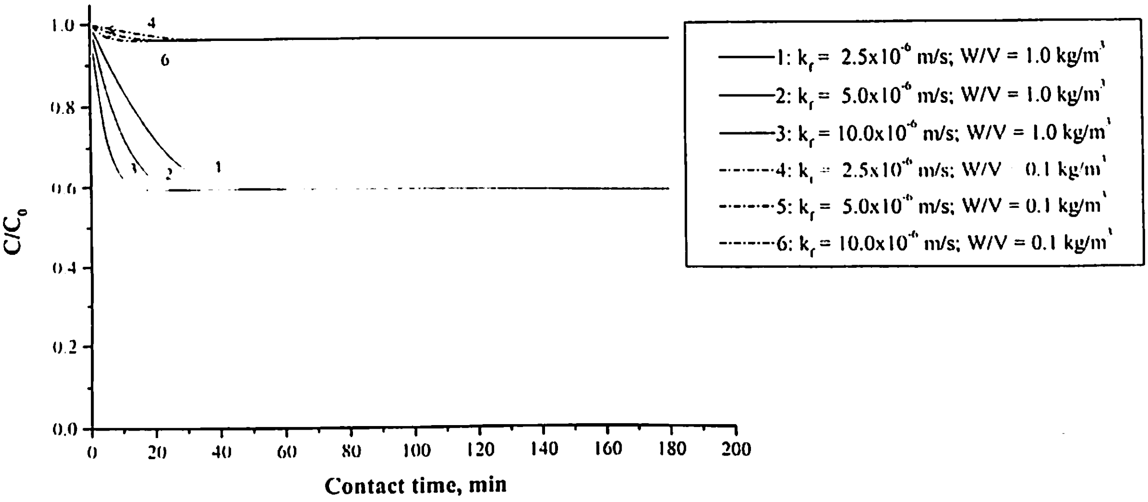


Fig. 4.23: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 10\times10^{-10}$ m^2/s; $C_0 = 500$ mg/L; $\rho = 500$ kg/m^3; d = 100μm.

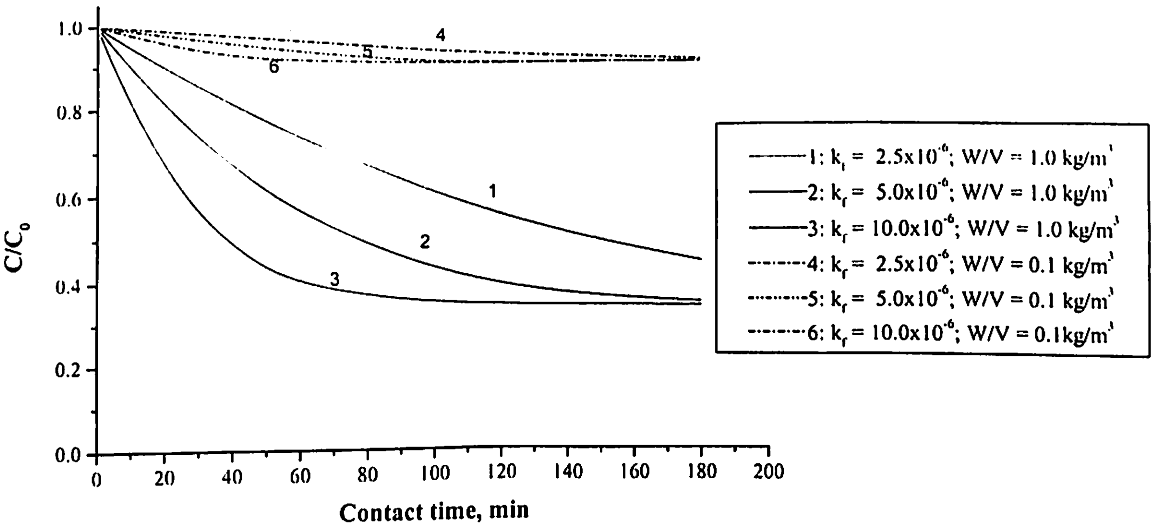


Fig. 4.24: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V* Operating parameters: $D = 0.5\times10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $\rho = 841$ kg/m^3; $d = 200$μm.

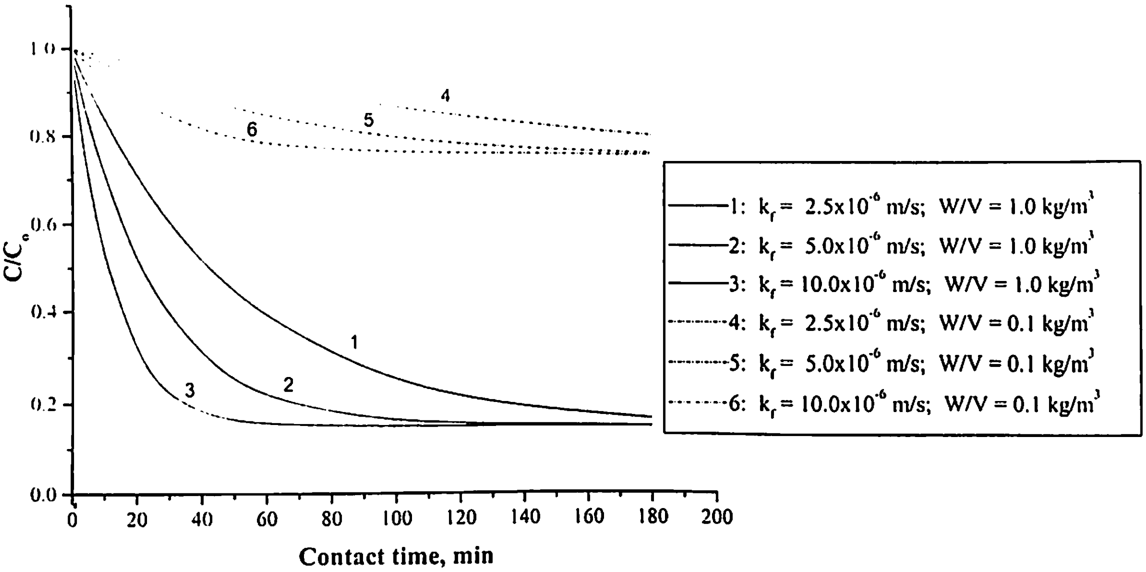


Fig. 4.25: Effect of contact time on adsorbate removal for various parameter values of k_f and *W/V*
Operating parameters: $D = 5\times10^{-10}$ m²/s; $C_0 = 50$ mg/L; $\rho = 500$ kg/m³; $d = 100\mu$m.

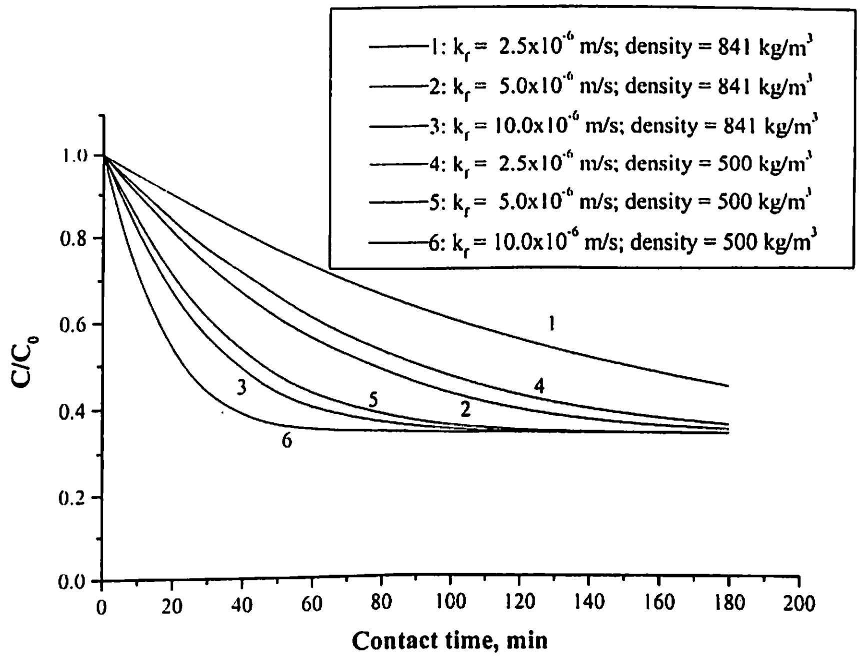


Fig. 4.26: Effect of contact time on adsorbate removal for various parameter values of k_f and ρ
Operating parameters: $D = 0.5\times10^{-10}$ m²/s; $C_0 = 250$ mg/L; $W/V = 1.0$ kg/m³; $d = 200\mu$m.

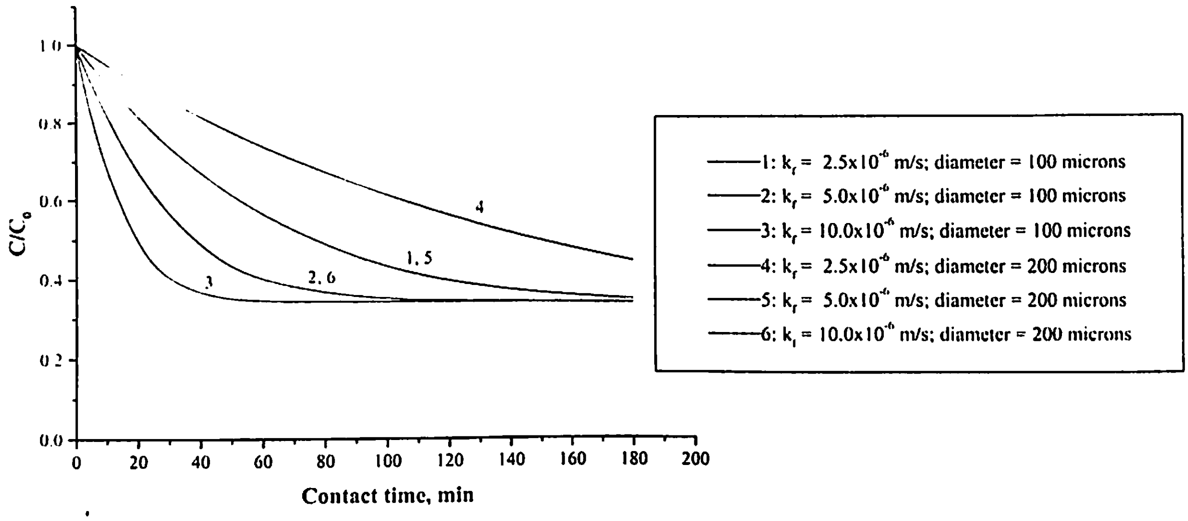


Fig. 4.27: Effect of contact time on adsorbate removal for various parameter values of k_f and d
Operating parameters: $D = 0.5\times10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $W/V = 1.0$; $\rho = 841$ kg/m^3

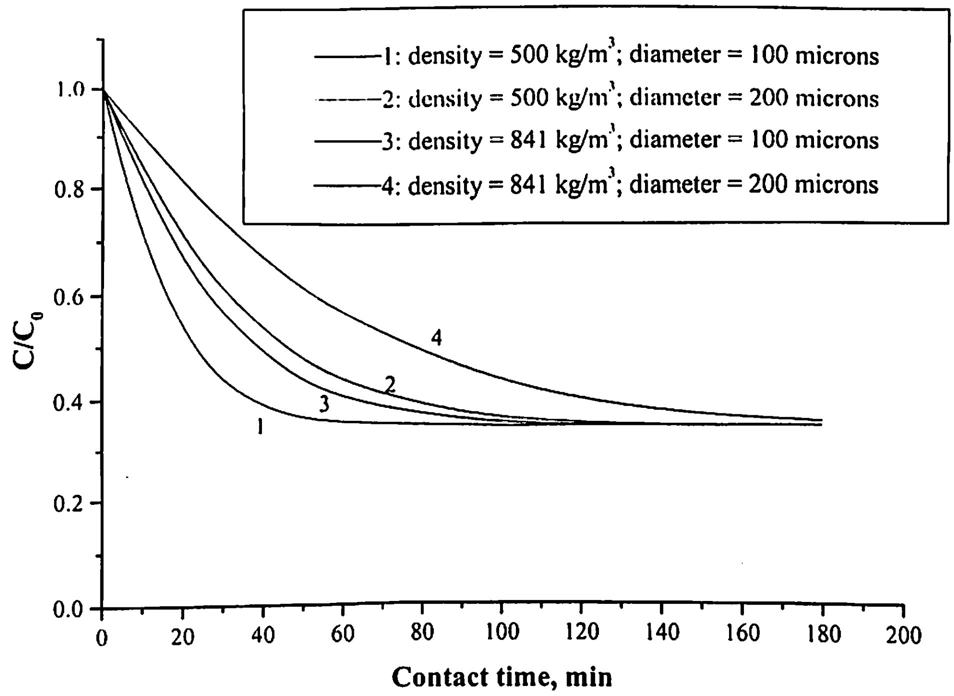


Fig. 4.28: Effect of contact time on adsorbate removal for various parameter values of ρ and d
Operating parameters: $k_f = 2.5\times10^{-6}$ m/s; $D = 5\times10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $W/V = 1.0$ kg/m^3

Variation of D with respect to adsorbent dose: The variation of D with respect to adsorbent dose (i.e., W/V) is studied for a wide range of parameters keeping k_f, d, ρ, and C_0 as constants (Figs. 4.29-4.30). It is observed that, adsorption is independent with respect to the variations of D. This indicates that, external mass transfer (i.e., k_f) is the dominant parameter in adsorbate removal of the system considered. This is in accordance with the analysis of the parametric study conducted for variation of k_f. Further, it is noted that, the accumulation is increasing with decrease in W/V value (Fig. 4.29 and 4.30). About 199.11 mg/g of adsorbate is accumulated for W/V of 0.1 kg/m^3 as against 164.44 mg/g for a W/V of 1.0 kg/m^3 (Fig. 4.30).

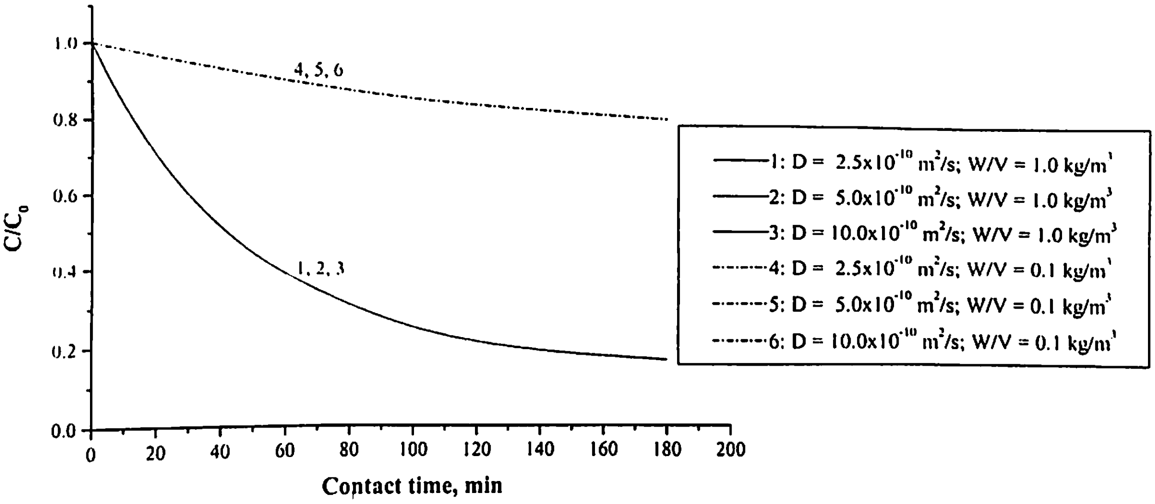


Fig. 4.29: Effect of contact time on adsorbate removal for various parameter values of D and W/V
Operating parameters: $k_f = 2.5\text{x}10^{-6}$ m/s; $C_0 = 50$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

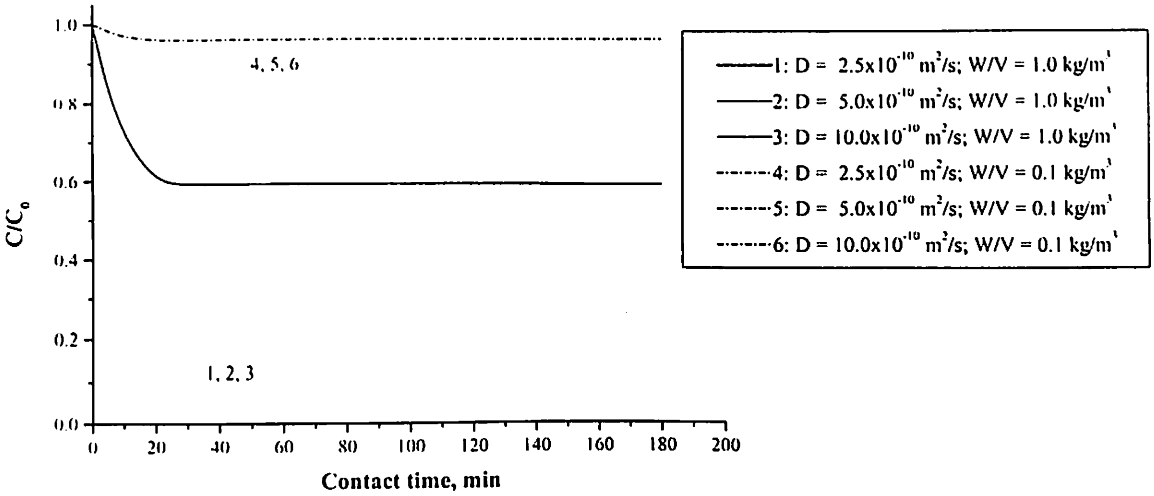


Fig. 4.30: Effect of contact time on adsorbate removal for various parameter values of D and W/V
Operating parameters: $k_f = 5.0\times10^{-6}$ m/s; $C_0 = 250$ mg/L; $\rho = 500$ kg/m^3; $d = 100\mu$m.

Variation of C_0 with respect to adsorbent dose: The study pertaining to the variation of C_0 (Fig. 4.31 and 4.32) indicates that the percentage removal of adsorbate is decreasing with increase of initial concentration for both values of W/V considered and the amount adsorbed on the adsorbate is increasing with decrease of W/V. With the increase of initial concentration, more amount of adsorbate is available for transfer from liquid onto the adsorbent and hence there is an increase in accumulation of adsorbate on adsorbent.

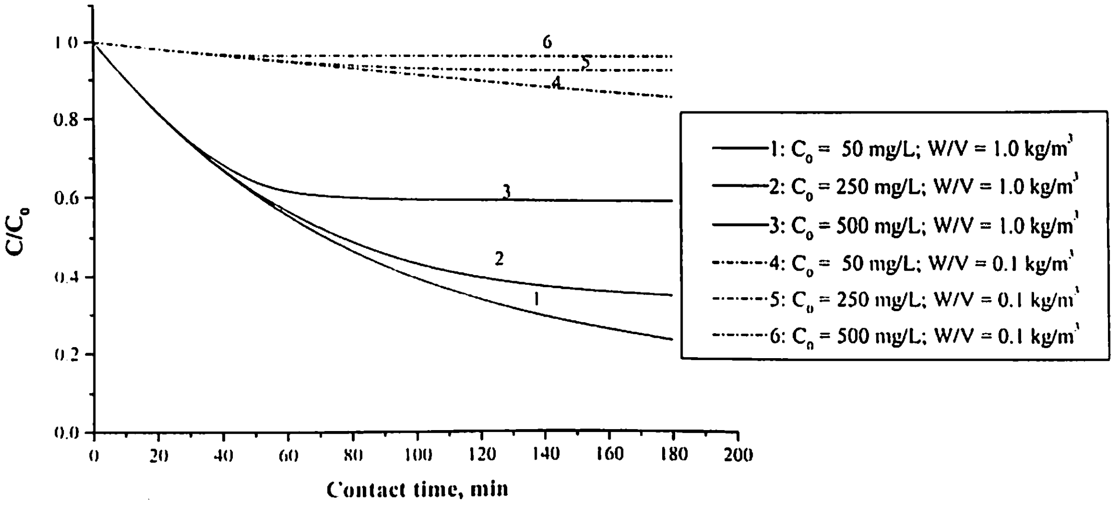


Fig. 4.31: Effect of contact time on adsorbate removal for various parameter values of C_0 and W/V
Operating parameters: $k_f = 2.5\times10^{-6}$ m/s; $D = 5\times10^{-10}$ m^2/s; $d = 100$ μm; $\rho = 500$ kg/m^3.

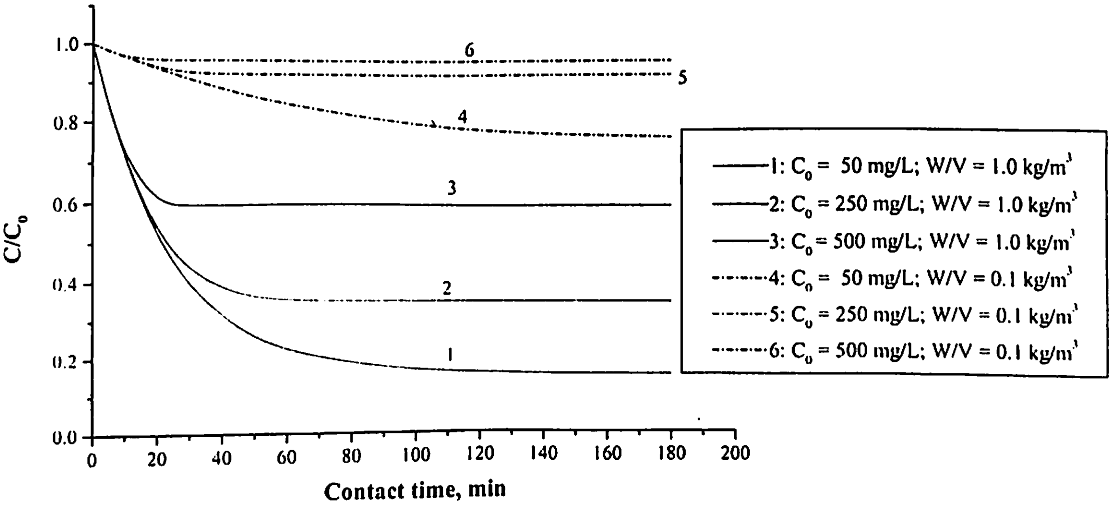


Fig. 4.32: Effect of contact time on adsorbate removal for various parameter values of C_0 and W/V
Operating parameters: $k_f = 5\times10^{-6}$ m/s; D = 5×10^{-10} m^2/s; $d = 100$ μm; $\rho = 500$ kg/m^3.

From the results obtained and above discussion, it is evident that, the parameters such as, k_f, D, C_0, and W/V on adsorption are inter-dependent for a given set of adsorbent characteristics such as particle diameter and adsorbent particle density. A study probing into a relation among all these parameters will be useful in the light of the above inference, which is discussed in the next section.

4.2.4.4 Relation between Biot number and Distribution parameter

The simulation model developed in this study has a group of dimensionless parameters, including Biot number (Bi) and Distribution parameter (λ) etc. The Biot number (Bi) depends on mass transfer coefficients, adsorbent characteristics, and adsorption parameters and is mathematically expressed as (Flora et al., 1998):

$$Bi = \left(\frac{k_f}{D}\right)\left(\frac{r}{\rho}\right)\left(\frac{C_0}{q_0}\right) \tag{4.14}$$

where, k_f = external mass transfer coefficient

D = diffusion coefficient

r = radius of adsorbent particle

ρ = adsorbent particle density

C_0 = initial concentration of adsorbate

q_0 = amount adsorbed for $C = C_0$ (from isotherm equation) and is calculated as-

$$q_0 = \frac{(abC_0)}{1+bC_0} \quad \text{for Langmuir isotherm} \tag{4.15}$$

The distribution parameter (λ) depends on adsorption parameters (Eq. 4.16) and W/V value and is mathematically expressed as:

$$\lambda = \left(\frac{W}{V}\right)\left(\frac{q_0}{C_0}\right) \tag{4.16}$$

combining Eqs. 4.14 and 4.16, we have

$$(Bi)(\lambda)=\left(\frac{k_f}{D}\right)\left(\frac{r}{\rho}\right)\left(\frac{W}{V}\right) \tag{4.17}$$

Eq. 4.17 indicates that, *Bi* is inversely proportional to λ and the product of $[(Bi)(\lambda)]$ is a constant.

The values of *Bi* and λ are calculated from the parameters studied (Table-4.29) and are plotted. The slope of the plot (Fig. 4.33) yielded a slope of 0.002, a constant value, for W/V = 1.0 kg/m^3 and is the same as per the calculated value (Table-4.30). The *Bi* and λ are calculated for a W/V value of 0.1 kg/m^3 and the resulting slope is equal to 0.0002 (Fig. 4.33 and Table-4.30).

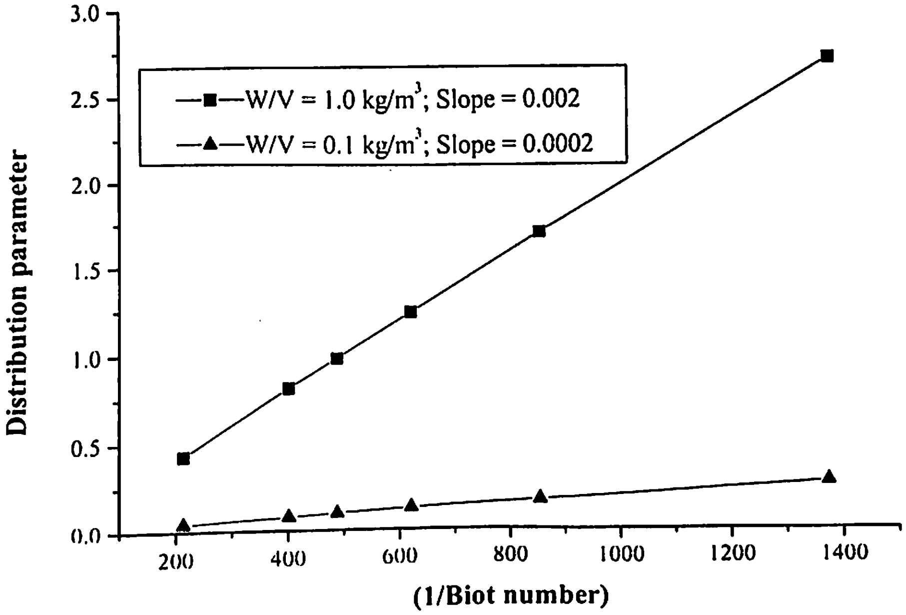


Fig. 4.33: Plot of Biot number vs. Distribution parameter

Table-4.30: Calculated values of (Bi)(λ)

S.No.	Biot number (Bi)	Distribution parameter (λ)		(Bi)(λ)	
		W/V = 1.0 kg/m^3	W/V=0.1 kg/m^3	W/V = 1.0 kg/m^3	W/V=0.1 kg/m^3
1	7.28×10^{-4}	2.725	0.2725	0.00198	0.000198
2	1.17×10^{-3}	1.712	0.1712	0.00200	0.000200
3	1.61×10^{-3}	1.245	0.1245	0.00200	0.000200
4	2.05×10^{-3}	0.976	0.0976	0.00200	0.000200
5	2.49×10^{-3}	0.806	0.0806	0.00200	0.000200
6	4.68×10^{-3}	0.427	0.0427	0.00199	0.000199

The above study showed the inter-dependence of Biot number and distribution parameter, the two dimensionless parameters used in the simulation model. Based on the encouraging results obtained in this study, an analysis is carried out based on the three functional groups involved in the Biot number for their inter-dependence.

4.2.4.5 Study of the functional groups in Biot number

As discussed above, the Biot number comprises of three functional groups, which are dimensional viz.,

- mass transfer coefficients, $\left({}^{k_f}\!/\!_{D}\right)$ with dimensions of (L^{-1})
- adsorbent characteristics, $\left({}^{r}\!/\!_{\rho}\right)$ with dimensions of (L^4M^{-1})
- adsorption parameters $\left({}^{C_0}\!/\!_{q_0}\right)$ with dimensions of (ML^{-3})

The inter-dependence of these three functional groups is studied using a selected range of values (Table-4.31). The values for each of the six parameters in the functional groups are chosen such that they will give the value identified for the analysis. The ranges of these values are selected based on the values adopted for initial parametric study (Table-4.29). The results are plotted in Figs. 4.34-4.36.

Table-4.31: Range of values studied for inter-dependence of functional groups in Biot number

S.No.	Values of the independent functional groups		Values of the dependent functional group	
	Functional group	*Value*	*Functional group*	*Value*
1	q_0/C_0	0.804	k_f/D	0.25×10^4; 1.0×10^4; 2.0×10^4; 3.0×10^4; 4.0×10^4.
	ρ/r	1×10^7		
2	q_0/C_0	0.804	ρ/r	1.0×10^6; 5.0×10^6; 1.0×10^7; 2.0×10^7.
	k_f/D	2.0×10^4		
3	ρ/r	1.0×10^7	q_0/C_0	0.220; 0.291; 0.977; 1.245; 1.713.
	k_f/D	2.0×10^4		

Effect of k_f/D: The value of k_f is kept same (2.5×10^{-6} m/s) for the ratio of $k_f/D = 0.25 \times 10^4$ m^{-1} and 1.0×10^4 m^{-1}. The trends of adsorbate removal indicate (Fig. 4.34) that the effect of reduction in D value for the above ratios is negligible. The k_f value is then increased for $k_f/D = 2.0 \times 10^4$ m^{-1} onwards ($k_f = 5.0 \times 10^{-6}$, 6×10^{-6}, and 10×10^{-6} m/s respectively) while there is a marginal reduction of D value for $k_f/D = 3.0 \times 10^4$ m^{-1}. The trends show increased adsorbate removal for the last three combinations. This could be largely attributed to the increase of k_f value in the k_f/D ratios since the effect of D is found negligible in the first two cases. It is evident from the results that, k_f is dominant compared to D in this analysis.

Effect of ρ/r: The adsorbent particle density is doubled (500 and 1000 kg/m^3) in the first two combinations while the particle radius is reduced 2.5 times (500 and 200 μm). This indicates that ρ/r value is increased 5 times. Since the changes made in adsorbent particle density and particle radius are almost same (i.e., 2 and 2.5), a similar trend of adsorbate removal (Fig. 4.35) is obtained. Further, in the second combination, particle radius is decreased resulting in availability of higher specific surface of adsorbent. The adsorbate removal is hence increased with decrease in particle size. In the third and fourth combinations, radius of adsorbent is kept constant (50 μm) while the particle density is doubled (500 and 1000 kg/m^3). The relatively higher adsorbate accumulation in the third combination compared to that of the fourth is due to the availability of more specific surface of the adsorbent (Eq. 4.12) since the density is decreased. The results obtained are in agreement with those discussed earlier (Sec. 4.2.4.3). Hence, it is concluded that, lower values of adsorbent particle density *(ρ)* and particle diameter *(d)* favor adsorbate removal in adsorption.

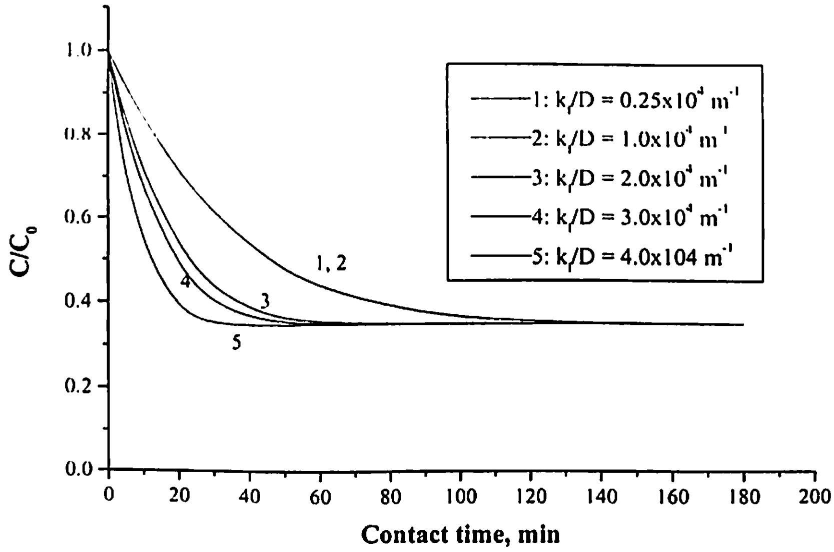


Fig. 4.34: Effect of contact time on adsorbate removal for various parameter values of k_f/D
Operating parameters: C_0 = 250 mg/L; W/V = 1.0 kg/m^3; d = 100 μm; ρ = 500 kg/m^3.

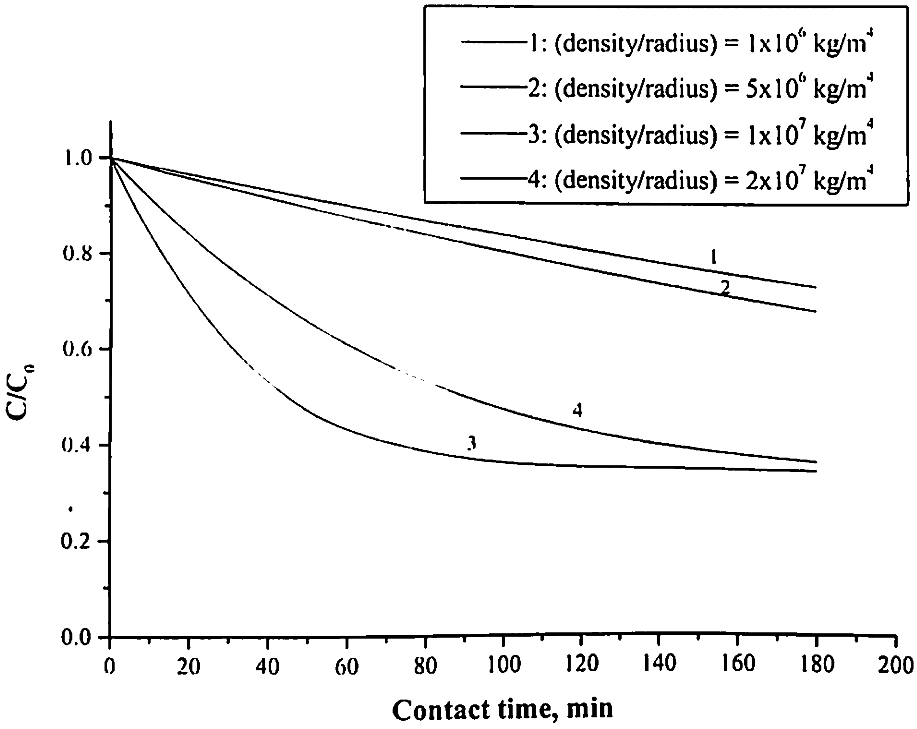


Fig. 4.35: Effect of contact time on adsorbate removal for various parameter values of ρ/r
Operating parameters: $k_f = 2.5\times10^{-6}$ m/s; $D = 5\times10^{-10}$ m^2/s; $C_0 = 250$ mg/L; $W/V = 1.0$.

Effect of q_0/C_0: This study is conducted with five different adsorbate concentrations viz., 100, 150, 200, 750, and 1000 mg/L respectively. The corresponding values of q_0 are calculated using Eq. 4.15. It should be noted that, the percentage adsorbate removal is increasing with decrease in q_0/C_0 value (Fig. 4.36). The value of q_0 calculated from Eq. 4.15 is increasing with increase of C_0. It indicates that, the accumulation of adsorbate is increasing with increase of C_0. The results obtained are in agreement with this assumption.

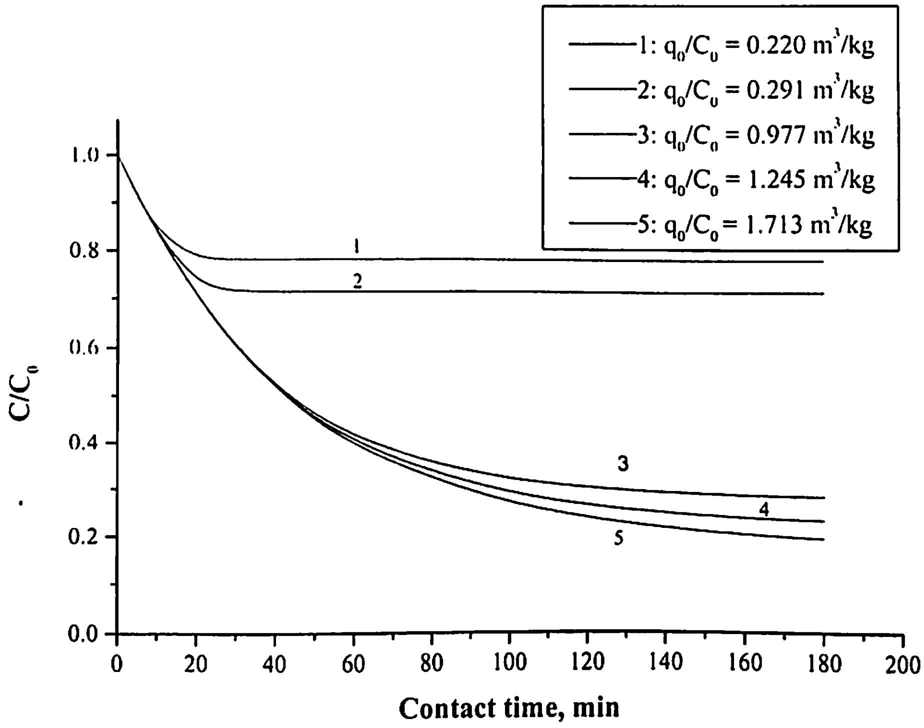


Fig. 4.36: Effect of contact time on adsorbate removal for various parameter values of q_0/C_0 Operating parameters: $k_f = 2.5\times10^{-6}$ m/s; $D = 5\times10^{-10}$ m²/s; ρ =500 kg/m³; d = 100 μm; W/V = 1.0 kg/m³.

4.3 Laboratory investigations in batch studies of adsorption

The laboratory studies are carried out in the lab for (i) preparation of an adsorbent from sawdust (ii) analyzing the laboratory data using LCIA and (iii) sample runs to fit the experimental adsorption data into the available empirical models. The details of each of the above are given below:

4.3.1 Preparation of adsorbent from sawdust

An adsorbent is prepared in the laboratory using sawdust, which is purchased locally. The following procedure is adopted:

1. Initial sieving of the sawdust to remove any impurities in it.

2. Washing with single distilled water (SDW) and acid (10% solution of 0.02N H_2SO_4) separately, to remove inorganic and greasy particles.
3. Drying the sample in oven at 105-110^{0}C for 24 hours for removal of moisture.
4. Thermal treatment of the sample in a muffle furnace at a temperature maintained at 400^{0}C for one hour.
5. Washing with SDW and acid (10% solution of 0.02N HCl) separately, to remove inorganic and ash particles.
6. Drying the sample in oven at 105-110^{0}C for 24 hours. The dried sample is stored for its use as adsorbent.

The information available at each of the above stages is recorded using a datasheet prepared for the purpose. The sawdust samples (designated as sample sets) after initial cleaning are kept in metal trays (capacity: 750 cc - 1500 cc) for drying and heating in furnace. The detailed information at each and every step of the experiment is collected using a Datasheet. A total of twelve sample sets are subjected to these tests. The sample information for one of the sample sets is given in Table-4.32. The summation of the quantities for all the twelve sets is given in the last column of Table-4.32. The item listed against S.No. 6 in Table-4.32 is the final product. The final samples are tested for their characteristic properties. The results are given in Table-4.33.

4.3.2 Analyzing the laboratory data using Life Cycle Inventory Analysis (LCIA)

The LCIA is applied to identify and quantify the materials involved in the investigations carried out in the laboratory for preparing adsorbent from sawdust. The mass balance approach of LCIA is considered in the present study.

Table-4.32: Experimental data for preparation of adsorbent from sawdust

S.No	Item Description	Data for a Sample set	Total of 12 sample sets
1	Weight of sieved samples, g	200	2461.2
2	Weight of sample after Distilled water and H_2SO_4 wash, g	612	7231.4
3	Weight of sample after oven drying, g	160	1794.4
4	Weight of sample after furnace burning, g	38	488.2
5	Weight of sample after HCl wash, g	77	1024.2
6	Weight of sample after oven drying, g	22	324.5
7	Distilled water used in Phase-I, mL	1520	21090
8	H_2SO_4 used in Phase-I, mL	80	1110
9	Distilled water used in Phase-II, mL	289	4719
10	HCl used in Phase-II, mL	15	249
11	Weight of raw sawdust, g	332	3255

Table-4.33: Characteristic properties of adsorbent prepared from sawdust

S.No.	Parameter	Value
1	Bulk density, g/cc	0.392
2	Moisture content, %	3.31
3	pH	6.5-7.3*
4	Particle size	37μm

* range

4.3.2.1 Mass balance approach in Life Cycle Inventory Analysis (LCIA)

For applying LCIA, few items involved in the conversion of sawdust into an adsorbent are selected based on their significance with respect to environmental aspects. The details are given in Table-4.34. A wide range of environmental aspects such as consumption of natural resources, renewable raw material; generation of solid, liquid and gaseous emissions are addressed even in a simple process such as conversion of sawdust into an adsorbent. The above-identified aspects justify the application of LCIA, whose basic principle is based on the identification and quantification of energy and materials used, and waste released to- and resources depleted from- the environment (Aelion et al., 1995).

The activities involved in the steps described under laboratory investigations are divided into two phases, viz., activities involved under items 1-4 (Sec. 4.3.1) as Phase-I and rest as Phase-II. The liquid input, i.e., both SDW and acid are taken as one unit. Seven items are considered for generating mass eco-vector for the LCIA.

Table-4.34: Justification of items selected for LCIA

Item description	Justification
Sawdust	Renewable raw material
Single distilled water	Natural resource
Acid	Non-renewable material
Sawdust rejects	Solid waste
Loss of moisture on drying	Air emissions
Wastage of single distilled water	Liquid discharge/Natural resource
Wastage of acid	Liquid discharge

The material balance calculations are performed using the primary data generated in the laboratory assuming that the mass density of both the acid solutions, H_2SO_4 and HCl used in the study are taken equal to that of water as very low concentrations of acid are used. The calculations are performed using a simple and systematic approach. The information obtained from laboratory experiments is used in developing the material balance diagram (Fig.4.37).

The eco-vector is computed for the raw material consumption and waste releases with respect to the primary raw material assuming steady state production. The Total Production Load (TPL) under steady-state condition is calculated using the respective raw materials for each item. The stages regarding discarding out-of-date materials and risks are negligible in this particular case. The TPL is calculated for the production data only. The TPL per unit of the product is given in Table-4.35. The TPL is calculated based on the mass of final product and the material balance data for the items. For example, TPL per unit of product for SDW is equal to (21090+4719)/324.5 = 79.535 units. The TPL per unit of product is calculated similarly for the other items.

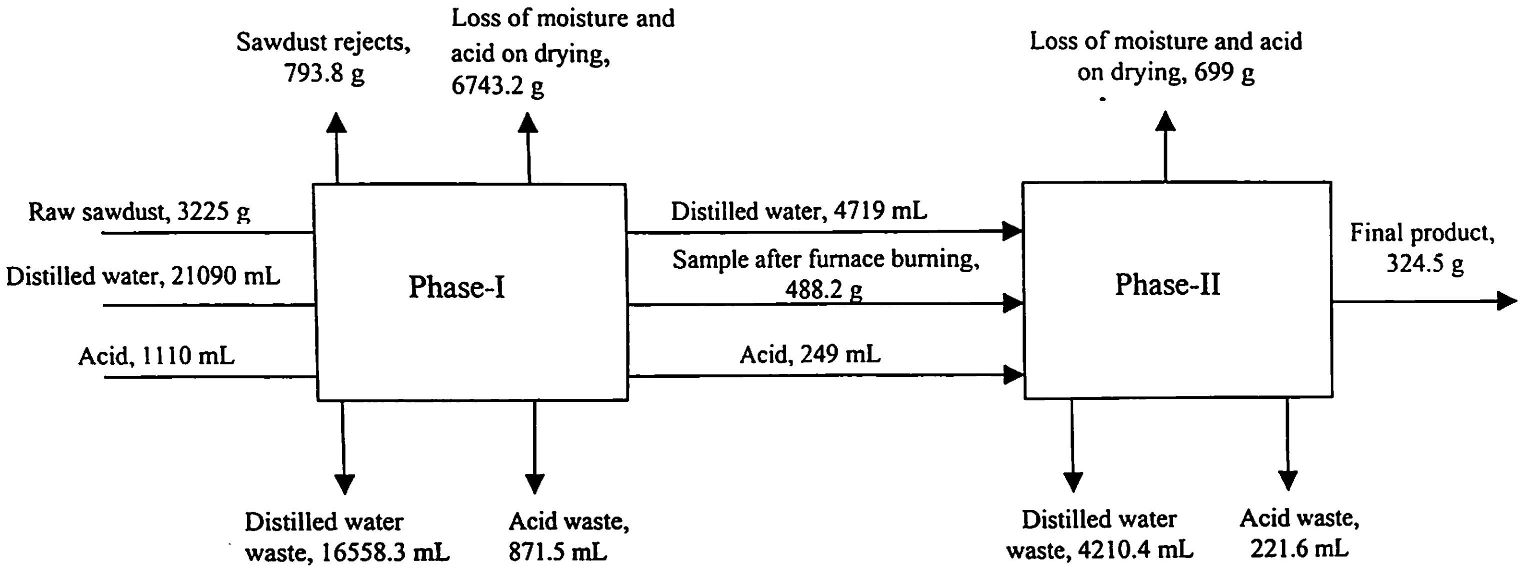


Fig. 4.37: Material balance for adsorbent preparation

Assuming the material eco-vectors are same for the product i.e., adsorbent prepared from sawdust, the eco-vector for the product is also calculated and given in the last column of Table-4.35. It can be thus understood from Table-4.35 that 11.535 kg of raw material is required and 79.535 kg of SDW is consumed for preparation of one kg of adsorbent.

Table-4.35: Total Production Load under steady-state condition

Item description	Raw materials, kg		Waste releases, kg		Total Production Load (TPL), kg	TPL per unit of product, kg/kg
	Phase-I	*Phase-II*	*Phase-I*	*Phase-II*		
Sawdust	3,255	488.2	--	--	3,743.2	11.535
Single distilled water	21,090	4,719	--	--	25,809	79.535
Acid	1,110	249	--	--	1,359	4.188
Sawdust rejects	--	--	793.5	--	793.5	2.445
Loss of moisture on drying	--	--	6,743.2	699.7	7,442.9	22.937
Wastage of single distilled water	--	--	16,588.8	4,210.4	20,769.2	64.000
Wastage of acid			871.4	221.6	1,093	3.368

The waste-and non-waste emissions in the process are carefully studied. The following suggestions are floated to minimize the waste load from the process of preparation of adsorbent from sawdust:

- The rejects from sawdust are of the order of 2.4453 kg per kg of the finished product. The rejects can be used as supplementary fuel.
- The SDW wastage is accounting for 64 kg per kg of finished product. This is presently discharged into drain. This can be diverted for gardening purpose that can save the load on natural resource (water) consumption. The SDW wastage is accounting to a total of 80% of total SDW consumed under both the phases and 95% of total liquid wastes.
- The loss of moisture and acid retained in the sawdust by oven drying and furnace heating (approximately 23 kg of finished product) is leading to air pollution. This

cannot be controlled since the amount of moisture and acid absorbed during the respective washes depends upon specific material that is being used.

The above study (Babu and Ramakrishna, 2003c) indicates that LCIA can be successfully applied to adsorbent preparation. It is to be noted here that, for applying LCIA, a large amount of experimental data covering each and every change undergone in the process is essential. This necessitates for systematic recording of data using a datasheet that is carefully designed based on the sequence of steps in the operation. The data that is available in literature pertaining to novel adsorbents is not sufficient for applying LCIA. However, LCIA can be applied to adsorbent preparation if the relevant data pertaining to its preparation is available as illustrated in the above study.

4.3.3 Experimental batch studies of adsorption

Batch studies are conducted in the laboratory using Laboratory Activated Carbon (LAC) for the removal of Zn^{+2} from synthetic wastewater. The operating conditions are given in Table-4.36 and the experimental results are shown in Fig. 4.38.

Table-4.36: Details of the operating parameters studied

S.No.	Parameter	Unit	Range
1	Weight of adsorbent	g	0.1, 0.05
2	Initial concentration of adsorbate	mg/L	10
3	Volume of adsorbate	mL	25
4	Temperature	^0C	30
5	Agitation speed	rpm	Constant
6	pH	Nil	6

It can be noted from Fig. 4.38 that, adsorption reached equilibrium at 24-hours and the PRE at equilibrium condition is 99.2% and 93.8% for 0.1 g and 0.05 g of LAC respectively.

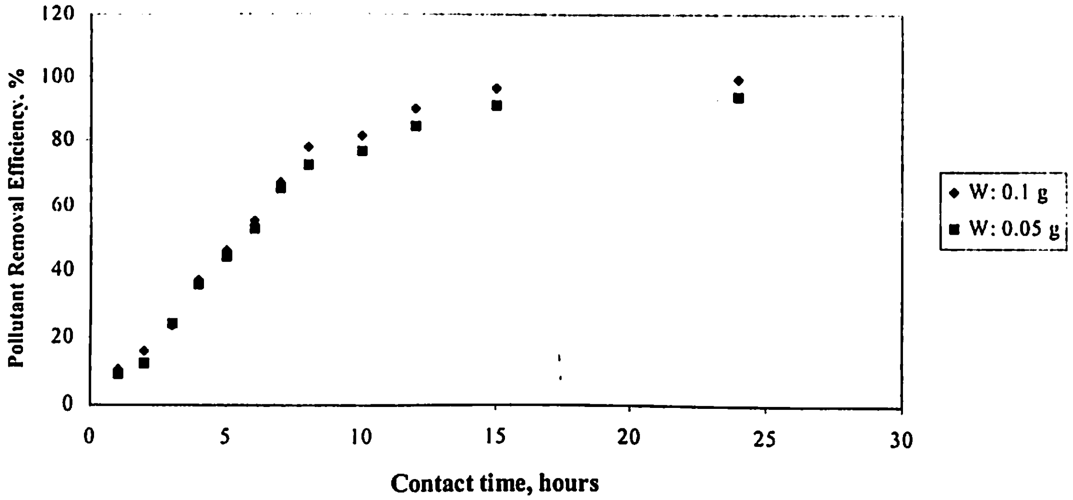


Fig. 4.38: Equilibrium time of adsorption for Zn^{+2} on laboratory activated carbon

The removal curves are smooth indicating a possibility of monolayer coverage on the outer surface of the adsorbent (Manju and Anirudhan, 1997). The accumulation of adsorbate is relatively higher for lower *W/V* value i.e., 0.31 mg/g for *W/V*= 2 g/L against 0.02 mg/g for *W/V*= 4g/L.

CHAPTER
5

SUMMARY, CONCLUDING REMARKS AND FUTURE SCOPE OF WORK

This chapter deals with the brief summary of the studies conducted in the Thesis. The contributions that are achieved through this study are highlighted and the scope for further studies in this subject is discussed.

5.1 Summary and Conclusions

A wastewater treatment system is composed of a combination of treatment techniques including Adsorption. A number of investigators have studied different novel adsorbents for their applications in wastewater treatment in an attempt to find an alternative to commercial activated carbon, which is costlier. The selection of adsorbents is based on their characteristic properties. Isotherm studies are used to judge the suitability of adsorbents for a specific application. Modeling of the adsorption system will help in assessing the performance of the adsorbent under a wide range of operating conditions. The Thesis study is taken with an objective of modeling of adsorption for wastewater treatment from literature data using analytical-, regression-, and neural network-approaches using data reported in literature. The salient aspects of the results obtained from the above study, which considered only the batch studies of adsorption, are explained as follows:

The information available in literature pertaining a number of novel adsorbents is collected and compiled. The compiled database is analyzed with respect to the characteristics of the adsorbents, their preparation methodologies, precursor materials etc. It is found from the comparative studies that,

- there is no separate BIS code for defining the suitability of activated carbons for wastewater treatment and hence a separate BIS code is desirable.
- the researchers are examining for more characteristics than that prescribed in the available BIS codes.
- identification of characteristics for the activated carbon prepared from a specific raw material category (eg. industrial wastes/by-products, agricultural wastes, mineral wastes etc.) is desirable.
- a standard/common method should be prescribed for the preparation of commercially available activated carbon.
- a possible re-examination of the characteristics selected and prescribed under IS 2752:1995 and IS 8366:1989 is desired.
- the adsorbents prepared from agricultural wastes are relatively effective than those prepared from industrial wastes and mineral wastes.
- majority of the adsorbents are prepared from simple physical treatment to the precursor material and it is observed that this preparation methodology is not

effective for adsorbate removal. In comparison, better results are obtained when some sort of cracking and/or activation at high temperatures is provided to the adsorbent.

It is to be noted, that the choice of selecting an adsorbent is possible from two different aspects viz., precursor material and adsorbent preparation methodology. In order to judge the suitability of an adsorbent based on its characteristic properties, a linear ranking model is developed. This model will help in identifying the adsorbents for their designated purpose based on the compliance of characteristics of adsorbent with respect to those prescribed under the available BIS codes.

In the process of doing the above data analysis, different regression models are developed and the above conclusions are based on the results obtained from some of these models. Modeling is carried out to determine the Pollutant (adsorbate) Removal Efficiency (PRE) from adsorption batch experiments and to determine the inter-dependence of isotherm constants. For this purpose, regression modeling and neural network modeling are used for a database that is compiled from literature. The following three cases are studied for modeling by regression and/or dimensional analysis approaches:

- applicability of regression modeling for a case study using relevant dimensional parameters.
- modeling of isotherm constants using regression analysis. Two models viz., Linear Regression Model (LRM) and Model based on Normalization of Sum of Squares (MNSS) are developed for modeling the Freundlich isotherm constants (K_f & n) vis-à-vis the Temperature (T).

- modeling using selected dimensional parameters from the identified seven dimensional and dimensionless parameters, which are affecting PRE in adsorption batch studies.

The studies indicated that,

- physical modeling based on affecting dimensional variables in conjunction with regression techniques does not always ensure good prediction unless and until all the affecting variables or affecting dimensionless groups are identified. The success of physical modeling is highly dependent on the thorough understanding and complete knowledge of the physical phenomenon that is taking place in the given system. Regression techniques showed the limitation in accurately predicting the output due to incomplete understanding of physical phenomena in the cases that are studied.
- wide spread in the values for adsorption isotherm constants is reported for several adsorbate-adsorbent systems ranging from, for example, 1×10^{-7} to 727.05 for K_f, the Freundlich constant. The wide ranges in the values of the parameters in the database is leading to erratic prediction of results by Least Squares Model (LSM) of regression technique.
- combining dimensionless (eg. material of adsorbent, pH, adsorbate) parameters with dimensional parameters is a limitation in establishing an effective model using dimensional analysis.
- combining two different trends (linear and asymptotic) of the same experimental data could not be properly represented by regression technique.
- identification of another approach that overcomes the limitations encountered by this method is needed.

Hence, neural network modeling is taken up as an improvement over the regression modeling. The Back-Propagation Network (BPN) model is used for this purpose. In the first step, the BPN model is tested with a heterogeneous database of 48 data points. The PRE is predicted and is compared with that predicted from regression modeling. The results showed that, a Standard Deviation (SD) of 0.26 is obtained for the BPN model as against a SD of 0.361 for the regression model. This indicates that BPN model is more suitable for predicting the results from the adsorption studies. The BPN model is then tested with a heterogeneous database comprising of 513 data points for predicting the PRE. The model is tested with a set of learning parameters such as learning rate, error tolerance, number of neurons in hidden layer, and number of epochs. The learning parameters are varied systematically and an optimum combination of the learning parameters that result in obtaining a minimum standard deviation is determined. The optimum combination is as follows:

- number of hidden layers: 1
- error tolerance: 0.001
- number of neurons in the hidden layer: 14
- learning rate: 0.7
- number of epochs: 40000

The BPN model is used to model the adsorption isotherm constants. A generalized Langmuir isotherm equation is used for this purpose and a relationship between the Langmuir and Freundlich among the isotherm constants is modeled as $K_f = f(n, a, b, T)$. A SD of 1.8676 is observed for three neurons in hidden layer at a learning rate of 0.7 for BPN model. The K_f value is predicted from the same database using multiple regression technique for verification. The SD obtained (157.85) is very high compared to that (1.8676) using neural network modeling.

The adsorption system is analytically modeled using the Homogeneous Surface Diffusion Model (HSDM) for batch studies of adsorption. The model is validated using experimental data (Flora et al., 1998) and is tested with another set of experimental data (Al-Qodah, 2000). The model results are in good agreement with that of the data used for validation (Flora et al., 1998). However, the results are not completely in agreement with that of the data used for testing (Al-Qodah, 2000) and giving under-predicted values. To address this problem, four existing models are identified from literature for calculating the external mass transfer coefficient (k_f) and diffusion coefficient (D). The k_f and D are calculated from Al-Qodah (2000) data using the above four models. Codes are developed in C language to determine (i) the adsorbate removal using HSDM and (ii) the mass transfer coefficients from the above four models using experimental data. The code developed for calculating the k_f and D also calculates some other parameters that are obtained from adsorption batch studies such as, prediction of PRE, determination of mass accumulation on adsorbent, isotherm constants, and thermodynamic constants such as enthalpy and entropy changes using experimental data. The k_f and D values obtained from two of the available models are close to those reported by Al-Qodah (2000) and are used in the model for simulation. The results are encouraging. The present study proved that, (i) keeping all other design variables constant, the parameters k_f and D are found to be the dominant design variables for adsorption studies for accurately estimating the adsorbate removal (ii) accurate estimation of the mass transfer coefficients is an important aspect in the simulation of analytical model for reliable results. An exhaustive parametric study is conducted comprising of 81 combinations of the values of k_f and D, initial concentration of adsorbate (C_0), particle density (ρ), particle diameter (d), and adsorbent dose (W/V). The results show that,

- the equilibrium time is reduced with increase in either C_0 or k_f.
- the linear portion of the adsorbate removal curve is shifting close to the axis indicating a steep slope or rapid adsorption while the curve is shifting away from the axis indicating a slower adsorption.
- the time taken for achieving equilibrium under lower k_f is relatively more with respect to the higher values of k_f.
- the adsorbate removal is increasing with increase of k_f value indicating the increased release rate of the adsorbate from the liquid.
- the amount adsorbed (q) on the adsorbent is increased with decrease of W/V values.
- adsorbate removal increased with decrease in particle size.
- adsorbate removal is reduced with decrease of particle density.
- adsorption is independent with respect to the variations of D.
- the percentage removal of adsorbate is decreasing with increase of initial concentration for both values of W/V considered and the amount adsorbed on the adsorbate is increasing with decrease of W/V.

The effect of Biot number (Bi) on distribution parameter (λ) is studied and it is found that Bi is inversely proportional to λ and the product of $[(Bi)(\lambda)]$ is a constant. This constant value is equal to 0.002 for a W/V value of 1.0 kg/m^3 and 0.0002 for a W/V value of 0.1 kg/m^3. The results are verified both analytically and graphically.

The inter-dependence of the three functional groups (viz., mass transfer coefficients, adsorbent characteristics, and adsorption parameters) in the Biot number is studied using a selected range of values. The results indicate that,

- k_f is dominant compared to D in the analysis.
- lower values of adsorbent particle density *(ρ)* and particle diameter *(d)* favor adsorbate removal in adsorption.
- accumulation of adsorbate is increasing with increase of C_0.

Life Cycle Inventory Analysis (LCIA) using material balance approach is carried out for the experimental data pertaining to preparation of adsorbent from saw dust. The eco-vector is computed for the raw material consumption and waste releases with respect to the primary raw material assuming steady state production. The Total Production Load under steady-state condition is calculated using the respective raw materials for each item. It is concluded that, 11.535 kg of raw material (saw dust) is required and 79.535 kg of SDW is consumed for preparation of one kg of adsorbent. The waste-and non-waste emissions in the process are studied and suggestions are floated to minimize the waste emissions. The data that is available in literature pertaining to novel adsorbents is not sufficient for applying LCIA. However, LCIA can be applied to adsorbent preparation if the relevant data pertaining to its preparation is available as illustrated in the above study.

5.2 Major Contributions of present study

The following are the contributions that are achieved through the present study:

- The data analysis conducted in this study revealed that, there is no separate BIS code for defining the suitability of activated carbons for wastewater treatment and hence a separate BIS code is desirable. A possible re-examination of the characteristics selected and prescribed under IS 2752:1995 and IS 8366:1989 is desired.

- Establishing the fact that, the adsorbents prepared from agricultural wastes are relatively effective than those prepared from industrial wastes and mineral wastes.
- Combining dimensionless (eg. material of adsorbent, pH, adsorbate) parameters with dimensional parameters is a limitation in establishing an effective model using dimensional analysis.
- Combining two different trends (linear and asymptotic) of the adsorption experimental data is not properly represented by regression technique.
- ANN modeling to the adsorption gives improved prediction than those of the regression modeling.
- It is proved in literature that, existing analytical models such as HSDM can predict the adsorbate removal efficiency with better accuracy. To understand their efficiency relative to empirical models, the HSDM is taken up for batch studies and analyzed using literature data. The model is validated and an exhaustive parametric study is conducted using 81 combinations of six parameters that effect the adsorbate removal.
- The effect of Biot number (Bi) on Distribution parameter (λ) is studied and it is found that Bi is inversely proportional to λ and the product of $[(Bi)(\lambda)]$ is a constant, which is proved both analytically and graphically.
- The inter-dependence of the three functional groups (viz., mass transfer coefficients, adsorbent characteristics, and adsorption parameters) in the Biot number is studied using a selected range of values.

- Development of a code that calculates the mass transfer coefficients, prediction of PRE, determination of mass accumulation on adsorbent, isotherm constants, verification of adsorbent dose based on mass balance on adsorbent, and thermodynamic constants using the models available in literature.
- LCIA using material balance approach is carried out for the experimental data pertaining to preparation of adsorbent from saw dust.
- Methodologies are developed for usage pertaining to few scenarios that are often encountered at the user level in adsorption studies viz., selection of adsorbent, selection of adsorbent preparation methodology, ranking of adsorbents, comparison of adsorbent characteristics, analysis of adsorbate removal, application of LCIA in adsorption, and parametric study showing the significance of each parameter and the relevant dimensional and non-dimensional parameters on adsorbate removal efficiency.

5.3 Future scope of work

The accomplishments that are achieved through this study revealed that, there are a few areas in adsorption studies where further studies are needed. The details are discussed below:

- There is no BIS code presently available for identifying the suitability of adsorbent for wastewater treatment and the investigators are examining for a wide range of characteristics of adsorbents. There is a lot of scope in this area for identifying the proper characteristics for judging the suitability of adsorbent in wastewater treatment. Further, specific extensive studies can be taken up for compiling the variations in the characteristics based on a specific precursor material, adsorbent preparation methodology, process performance etc. Such studies will help in disseminating the data to a wide range of users interested in adsorption studies.

- The results obtained in the Thesis showed that the results from ANN modeling are relatively better than that of regression modeling. In the present study, only Back-Propagation Network is considered. The study can be conducted using different architectures of ANN.
- The parametric study conducted is limited to only batch studies. Similar studies can be extended to column studies and occurrence of inter-dependence of any specific dimensional and non-dimensional groups can be studied.
- LCIA based on mass balance approach is used in this study. The LCIA studies can be applied to wide ranges of precursor materials and adsorbent preparation methodologies. This data will help in establishing a methodology for adsorbent preparation with minimum pollutant emissions.

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APPENDICES

A	CRITERIA FOR CLASSIFICATION OF INLAND SURFACE WATER AS PER IS: 2291
B	MAXIMUM PERMISSIBLE LIMITS FOR EFFLUENT DISCHARGES
C	DERIVATION OF ISOTHERM EQUATIONS
D	DISCRETIZATION OF HOMOGENEOUS SURFACE DIFFUSION MODEL (HSDM) FOR A BATCH ADSORBER SYSTEM TO PREDICT THE ADSORBATE REMOVAL EFFICIENCY USING PURE-IMPLICIT SCHEME OF FINITE DIFFERENCE METHOD
E	DETAILS OF THE DATA POINTS USED FOR TRAINING AND TESTING THE BACK-PROPAGATION NETWORK
F	NUMBERS ASSIGNED TO MATERIALS AND POLLUTANTS IN BACK-PROPAGATION NETWORK
G	CODE DEVELOPED FOR BACK-PROPAGATION NETWORK
H	CODE DEVELOPED FOR HOMOGENEOUS SURFACE DIFFUSION MODEL BASED ON PURE-IMPLICIT SCHEME OF FINITE DIFFERENCE METHOD AND SIMPSON'S $1/3^{RD}$ RULE
I	CODE DEVELOPED FOR DETERMINING ADSORPTION PARAMETERS FROM BATCH STUDIES

Appendix-A

CRITERIA FOR CLASSIFICATION OF INLAND SURFACE WATER AS PER IS: 2291

Parameter	Max./Min.	A	B	C	D	E
Dissolved Oxygen, mg/L	Min.	6	5	4	4	--
BOD, mg/L	Max.	2	3	3	--	--
Total Dissolved Solids, mg/L	Max.	500	--	1500	--	2100
Chloride as Cl^-, mg/L	Max.	250	--	600	--	500
Color, Hazen units	Max.	10	300	300	--	--
Sodium Absorption Ratio	Max.	--	--	--	--	26
Boron, mg/L	Max.	--	--	--	--	2
Sulphates, mg/L	Max.	400	--	400	--	1000
Nitrates, mg/L	Max.	20	--	50	--	--
Free ammonia as N, mg/L	Max.	--	--	--	12	--
pH	--	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.0-8.0
Arsenic, mg/L	Max.	0.05	0.20	0.20	--	--
Iron, mg/L	Max.	0.3	--	50	--	--
Fluorides, mg/L	Max.	1.5	1.5	1	--	--
Lead, mg/L	Max.	0.1	--	0.1	--	--
Copper, mg/L	Max.	1.5	--	1.5	--	--
Zinc, mg/L	Max.	15	--	15	--	--
Conductivity at 25^{0}C, μΩ/cm	Max.	--	--	--	1	2.25
Total Coliform bacteria (MPN/100 mL)	Max.	50	500	5000	--	--

A: Drinking water without conventional treatment but after disinfection
B: Outdoor bathing, organized
C: Drinking water with conventional treatment followed by disinfection
D: Propagation of wildlife and fisheries
E: Irrigation, industrial cooling etc.

Appendix-B

MAXIMUM PERMISSIBLE LIMITS FOR EFFLUENT DISCHARGES

Parameter	Into inland surface waters IS: 2490 (1974)	Into public sewers IS: 3306 (1974)	On land for irrigation purposes IS: 3307 (1974)
pH	5.5-9.0	5.5-9.0	5.5-9.0
BOD_5	30	350	100
COD	250	--	--
Suspended solids	100	600	200
TDS (inorganic)	2100	2100	2100
Temperature (^0C)	40	45	--
Oil & Grease	10	20	10
Cyanides	0.2	2	0.2
Sulphides	2	--	--
Fluorides	2	15	--
Pesticides	--	--	--
Arsenic	0.2	0.2	0.2
Cadmium	2	1	--
Chromium $^{(+6)}$	0.1	2	--
Copper	3	3	--
Lead	0.1	1	--
Mercury	0.01	0.01	--
Nickel	3	3	--
Selenium	0.05	0.05	--
Zinc	5	15	--
Chlorides	1000	1000	600
Boron	2	2	2
Sulphates	1000	1000	1000
Sodium (%)	--	60	60
Total residual chorine	1	--	--
Phenolic compounds	1	5	--
Ammoniacal Nitrogen	50	50	--

DERIVATION OF ISOTHERM EQUATIONS

The most simple assumption (Stumm, 1992) is that the adsorption sites, S on the surface of the solid (adsorbent) become occupied by an adsorbate from the solution, A. Implying a 1:1 stoichiometry,

$$S+A \leftrightarrow SA \text{ or} \tag{1}$$

where, S = surface site of adsorbents, mol L^{-1}

A = adsorbate in solution

SA = adsorbate on surface sites, mol L^{-1}

Applying mass law to Eq. (1),

$$\frac{[SA]}{[S][A]} = k_{ads} \tag{2}$$

The maximum concentration of surface sites, S_T is given by

$$S_T = [S]+[SA] \tag{3}$$

Thus,

$$[SA] = S_T - [S] \tag{4}$$

$$[S] = S_T - [SA] \tag{5}$$

From Eqs. (2) & (5)

$$\frac{[SA]}{[S_T - [SA]][A]} = k_{ads} \tag{6}$$

On re-arranging Eq. (6),

$$[SA] = S_T \frac{k_{ads}[A]}{1+k_{ads}[A]} \tag{7}$$

If we define the surface concentration,

$\tau = [SA]/$mass adsorbent, and

$\tau_{max} = S_T/$mass adsorbent, we get from Eq. (7)

$$\tau = (\tau)_{\max} \frac{(k_{ads})[A]}{1+(k_{ads})[A]} \tag{8}$$

Eq. (8) is the Langmuir equation. However, it can also be written in conventional form as

$$q_e (or) \frac{x}{M} = \frac{abC_{eq}}{1 + bC_{eq}} \tag{9}$$

where, q_e is the amount adsorbed at equilibrium, mg/g

x is the amount of adsorbate adsorbed, mg

M is the mass of the adsorbent, g

C_{eq} is the equilibrium concentration of the adsorbate, mg/L

b & a are Langmuir constants, L/mg and mg/g respectively

The Langmuir isotherm can also be written (Stumm, 1992) as

$$\frac{\theta}{1-\theta} = k_{ads}[A] \tag{10}$$

where, $\theta = [SA]/S_T$

An empirical factor known as, *Separation factor*, R_L, indicating the shape of the Langmuir isotherm is defined as,

$$R_L = \frac{1}{1+bC_0} \tag{11}$$

where, C_0 is the initial concentration of the adsorbate, mg/L

b is the Langmuir constant, L/mg

The isotherm and hence the adsorption is considered favorable or unfavorable based on R_L values such that

$R_L > 1$: Unfavorable

$R_L = 1$: Linear

$0<R_L<1$: Favorable

$R_L = 0$: Irreversible

This can be explained considering the Langmuir isotherm given in Eq. (10) and comparing with Eq. (11). The Eq. (10) can be re-written as:

$$\frac{1}{1 + k_{ads}[A]} = \theta = R_L \tag{12}$$

Here, $b = k_{ads}$ and $[A] = C_0$ [see Eq. (11)]

When $R_L = \theta = 0$, $[SA] = 0$ or no adsorption

$R_L = \theta = 1$, $[SA] = S_T$ or maximum adsorption i.e., all the adsorption sites are occupied.

Hence, R_L or θ value should lie between 0 & 1 to understand the extent of adsorption.

The Freundlich Isotherm is expressed in a similar way in a general form,

$$q_e = (x/M) = k_f\,(C_e)^{(1/n)} \qquad (13)$$

where, k_f and n are Freundlich constants. The term n indicates the degree of favorability of adsorption and should have values lying in the range of *1 to 10* for classification as *favorable* adsorption.

The adsorption isotherms can however (Goyal et al., 1999) be described by the general Langmuir isotherm equation

$$q_e = \frac{a(bC_e)^n}{(1+bC_e)^n} \qquad (14)$$

when $n=1$, the Eq. (14) reduces to Eq. (9), the general form of Langmuir equation.

At lower concentrations, $(bC_e)^n$ is very small and can be neglected. Then, Eq. (14) reduces to:

$$q_e = a(bC_e)^n \qquad (15)$$

or

$$q_e = a(b^n)(C_e)^n \qquad (16)$$

Eq. (16) can be written as,

$$q_e = k_f\,(C_e)^n \qquad (17)$$

where, $k_f = a(b^n)$ (18)

Eq. (*17*) is the Freundlich equation, which is given by Eq. (*13*).

DETAILS OF THE DATA POINTS USED FOR TRAINING AND TESTING THE BACK-PROPAGATION NETWORK

Data points used for training the network:	440
Data points used for testing the network:	73

Range of the operating parameters for each of the eight pollutants

Chromium			**Mercury**		
Parameter	*Minimum*	*Maximum*	*Parameter*	*Minimum*	*Maximum*
Equilibrium time, hours	1.5	24	Equilibrium time, hours	3	3
Contact time, min	30	1440	Contact time, min	30	180
Adsorbate concentration, mg/L	2	150	Adsorbate concentration, mg/L	50	500
Adsorbent dose, g/L	0.2	150	Adsorbent dose, g/L	20	20
Zinc			**Cadmium**		
Parameter	*Minimum*	*Maximum*	*Parameter*	*Minimum*	*Maximum*
Equilibrium time, hours	0.5	24	Equilibrium time, hours	0.5	24
Contact time, min	10	1440	Contact time, min	30	1440
Adsorbate concentration, mg/L	10	200	Adsorbate concentration, mg/L	20	70
Adsorbent dose, g/L	10	100	Adsorbent dose, g/L	0.1	10
Copper			**Lead**		
Parameter	*Minimum*	*Maximum*	*Parameter*	*Minimum*	*Maximum*
Equilibrium time, hours	0.5	24	Equilibrium time, hours	0.5	24
Contact time, min	20	1440	Contact time, min	10	1440
Adsorbate concentration, mg/L	10	100	Adsorbate concentration, mg/L	20	1000
Adsorbent dose, g/L	10	100	Adsorbent dose, g/L	0.1	40
Color			**COD**		
Parameter	*Minimum*	*Maximum*	*Parameter*	*Minimum*	*Maximum*
Equilibrium time, hours	3	4	Equilibrium time, hours	8	8
Contact time, min	30	240	Contact time, min	480	480
Adsorbate concentration, mg/L	89.1993	1000	Adsorbate concentration, mg/L	400	1500
Adsorbent dose, g/L	3.33	50	Adsorbent dose, g/L	20	30

NUMBERS ASSIGNED TO MATERIALS AND POLLUTANTS IN BACK-PROPAGATION NETWORK

Material	Number assigned
Steam activated coconut carbon	1
Chemically activated coconut shell carbon	2
Blast furnace flue dust	3
Rice husk ash	4
Activated bagasse carbon	5
Activated coconut jute carbon	6
Raw bagasse	7
Chemically modified sawdust	8
Bagasse fly ash	9
Commercial activated carbon	10
Chemically treated used tea leaves	11
Commercial activated carbon	12
Fly ash	13
Acidic sludge activated carbon	14
Commercial coconut shell activated carbon	15
Groundnut husk carbon	16
Black cotton soil amended with dried sewage sludge and refuse compost	17
Acacia bark	18
Laurel bark	19
Bijasal bark	20
Teak	21
Bituminous coal	22
Bituminous coal treated with MnO_2	23
Bituminous coal treated with H_2O_2	24
Chemically modified sawdust	25

Pollutant	Chromium	Mercury	Zinc	Cadmium	Copper	Lead	COD	Color
Number assigned	1	2	3	4	5	6	7	8

Appendix-F

DISCRITIZATION OF HOMOGENEOUS SURFACE DIFFUSION MODEL (HSDM) FOR A BATCH ADSORBER SYSTEM TO PREDICT THE ADSORBATE REMOVAL EFFICIENCY USING PURE-IMPLICIT SCHEME OF FINITE DIFFERENCE METHOD

Model Equations

$$\frac{\partial q}{\partial t}=\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \qquad (1)$$

or

$$\frac{\partial q}{\partial t}=D\frac{\partial^2 q}{\partial r^2}+2D\left(\frac{1}{r}\right)\left(\frac{\partial q}{\partial r}\right) \qquad (1)$$

$$V\frac{dc_b}{dt}=-W\frac{dq_{avg}}{dt} \qquad (2)$$

where, $q_{avg}=\frac{3}{r_p^3}\int_0^{r_p} q(r,t)r^2dr$ (3)

Initial and Boundary conditions

$$q(r,t=0)=0 \qquad (4)$$

$$c_b(t=0)=c_0 \qquad (5)$$

$$\frac{\partial q}{\partial r}(r=0,t>0)=0 \qquad (6)$$

$$\frac{\partial q}{\partial r}(r=r_p,t>0)=\left(\frac{k_f}{\rho\, D}\right)(c_b-c_s) \qquad (7)$$

$$q(r=r_p,t>0)=\frac{q_{\max}bc_s}{1+bc_s} \qquad (8)$$

The following parameters are introduced for non-dimensionalisation:

$$C = \frac{c}{c_0} \tag{9a}$$

$$Q = \frac{q}{q_0} \tag{9b}$$

$$\theta = \left(\frac{Dt}{r_p^2} \right) \tag{9c}$$

$$x = \frac{r_0}{r_p} \tag{9d}$$

$$B_i = \left(\frac{k_f r_p c_0}{D\rho \; q_0} \right) \tag{9e}$$

$$\lambda_b = \frac{W q_0}{V c_0} \tag{9f}$$

$$\text{where, } q_0 = \frac{q_{\max} b c_0}{1 + b c_0} \tag{9g}$$

Rewriting the model equations in terms of dimensionless parameters,

$$\frac{\partial Q}{\partial \theta} = \left(\frac{1}{x^2} \right) \frac{\partial}{\partial x} \left(x^2 \frac{\partial Q}{\partial x} \right) \tag{10}$$

which can be reduced as,

$$\frac{\partial Q}{\partial \theta} = \frac{\partial^2 Q}{\partial x^2} + 2 \left(\frac{1}{x} \right) \left(\frac{\partial Q}{\partial x} \right) \tag{10a}$$

$$\frac{dC_b}{d\theta} = -\lambda \frac{dQ_{avg}}{d\theta} \tag{11}$$

$$Q_{avg} = 3 \int_0^1 Q(x,\theta) x^2 dx \tag{12}$$

$$Q(x,\theta=0)=0 \tag{13}$$

$$C_b(\theta=0)=1 \tag{14}$$

$$\frac{\partial Q}{\partial x}(x=0,\theta>0)=0 \tag{15}$$

$$\frac{\partial Q}{\partial x}(x=1,\theta>0)=B_i(C_b-C_s) \tag{16}$$

$$Q(x=1,\theta>0)=\frac{(1+bc_0)C_s}{1+bc_0C_s} \tag{17}$$

Eq. (10) is solved using the initial and boundary conditions given by Eqs. (13)-(17). Finite Difference Method using pure implicit scheme (Babu, 2004) is applied to Eq. (10) and the Tri-Diagonal Matrix Approach (TDMA) can be used to solve the matrix (Ghoshdastidar, 1998) formed in the dicritization.

Equations (10) and (11) are simultaneously solved with the initial and boundary conditions given in Eqs. (13-17) using pure-implicit scheme of Finite Difference Method in conjunction with Simpson's 1/3rd rule.

Solving the model equations using Pure-Implicit scheme of Finite Difference Method

We know that, $\frac{\partial Q}{\partial \theta}=\frac{\partial^2 Q}{\partial x^2}+2\left(\frac{1}{x}\right)\left(\frac{\partial Q}{\partial x}\right)$ (10a)

Discretization results in,

$$\frac{Q_i^{p+1}-Q_i^p}{\Delta\theta}=\frac{Q_{i+1}^{p+1}-2Q_i^{p+1}+Q_{i-1}^{p+1}}{(\Delta x)^2}+\left(\frac{2}{x_i}\right)\left(\frac{Q_{i+1}^{p+1}-Q_{i-1}^{p+1}}{2\Delta x}\right) \tag{18}$$

At the outer boundary (x=1, i=m).

Applying image-point technique for Eq. (16), we obtain:

$$Q_{m+1}^{p+1} = 2\Delta x Bi(C_b - C_s)^p + Q_{m-1}^{p+1} \tag{19}$$

From Eq.s (9) and (10):

$$\frac{Q_m^{p+1} - Q_m^p}{\Delta\theta} = \frac{2\Delta x Bi(C_b - C_s)^p + Q_{m-1}^{p+1} - 2Q_m^{p+1} + Q_{m-1}^{p+1}}{(\Delta x)^2} + \left(\frac{2}{1}\right)Bi(C_b - C_s)^p \tag{20}$$

Rearranging the terms:

$$\left(\frac{-2\Delta\theta}{(\Delta x)^2}\right)Q_{m-1}^{p+1} + \left(1 + \frac{2\Delta\theta}{(\Delta x)^2}\right)Q_m^{p+1} = Q_m^p + \left(1 + \frac{1}{\Delta x}\right)2Bi(C_b \_ C_s)^p \tag{21}$$

At center (x=0; $\frac{\partial Q}{\partial x} = 0$)

Substituting the value of x=0 in Eq. (10a) results an infinite value. The second term of RHS giving infinite value can be re-written as:

i.e., $\left(\frac{2}{x}\right)\frac{\partial Q}{\partial x}$ as $\left(\frac{2\partial Q}{\partial x}\Big/x\right)$

Applying L-Hospital's rule for $x \to 0$:

$$Lt\left(\frac{\partial Q}{\partial x}\Big/x\right) = \frac{\partial^2 Q}{\partial x^2} \tag{22}$$

Substituting Eq. (22) in Eq. (10a):

$$\frac{\partial Q}{\partial \theta} = 3\frac{\partial^2 Q}{\partial x^2} \tag{23}$$

Discretizing,

$$\frac{Q_i^{p+1} - Q_i^p}{\Delta\theta} = 3\left(\frac{Q_{i+1}^{p+1} - 2Q_i^{p+1} + Q_{i-1}^{p+1}}{(\Delta x)^2}\right) \tag{24}$$

for i=1 at center, Eq. (24) reduces to:

$$\frac{Q_1^{p+1} - Q_1^p}{\Delta\theta} = 3\left(\frac{Q_2^{p+1} - 2Q_1^{p+1} + Q_0^{p+1}}{(\Delta x)^2}\right) \tag{25}$$

From image-point technique, $Q_0^{p+1} = Q_2^{p+1}$ (26)

From Eq.s (25) and (26):

$$\frac{Q_1^{p+1} - Q_1^p}{\Delta\theta} = 3\left(\frac{2Q_2^{p+1} - 2Q_1^{p+1}}{(\Delta x)^2}\right) = 6\left(\frac{Q_2^{p+1} - Q_1^{p+1}}{(\Delta x)^2}\right) \tag{27}$$

Rearranging the terms:

$$\left(1 + \frac{6\Delta\theta}{(\Delta x)^2}\right)Q_1^{p+1} + \left(\frac{-6\Delta\theta}{(\Delta x)^2}\right)Q_2^{p+1} = Q_1^p \tag{28}$$

Between center and surface i.e., i=2 to m-1:

From Eq. (18) we have, $\frac{Q_i^{p+1} - Q_i^p}{\Delta\theta} = \frac{Q_{i+1}^{p+1} - 2Q_i^{p+1} + Q_{i-1}^{p+1}}{(\Delta x)^2} + \left(\frac{2}{x_i}\right)\left(\frac{Q_{i+1}^{p+1} - Q_{i-1}^{p+1}}{2\Delta x}\right)$

Substituting i for 2 to m-1, and re-arranging the terms, we have:

$$\left(\frac{\Delta\theta}{x_i\Delta x} - \frac{\Delta\theta}{(\Delta x)^2}\right)Q_{i-1}^{p+1} + \left(1 + \frac{2\Delta\theta}{(\Delta x)^2}\right)Q_i^{p+1} + \left(\frac{-\Delta\theta}{x_i\Delta x} - \frac{\Delta\theta}{(\Delta x)^2}\right)Q_{i+1}^{p+1} = Q_i^p \tag{29}$$

The Eq.s, (21), (28), & (29) can be arranged in matrix form as:

$$\begin{bmatrix} b_1 & c_1 & 0 & 0 & 0 \\ a_1 & b_2 & c_2 & 0 & 0 \\ 0 & a_2 & b_3 & c_3 & 0 \\ 0 & 0 & a_3 & b_4 & c_4 \\ 0 & 0 & 0 & a_4 & b_5 \end{bmatrix}^p \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \\ Q_4 \\ Q_5 \end{bmatrix}^{p+1} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ d_4 \\ d_5 \end{bmatrix}^p \tag{30}$$

or simply in the form,

$[Z]^p[q]^{p+1}=[D]^p$ (31)

The above model matrix assumes that there are five equations to be solved (i.e., i=0, 1,2,3,4). The last value i.e., i=4, corresponds to the surface condition and is referred as i=m in the above discretisation. Similar type of matrix can be obtained depending on the interval for discretisation, i.e, Δx. The values of a, b, c, & d in Eq. (30) correspond to the following values obtained from discretisation [Eq.s, (21), (28), & (29)]:

$$b_1 = \left(1 + \frac{6\Delta\theta}{(\Delta x)^2}\right);\ c_1 = \left(\frac{-6\Delta\theta}{(\Delta x)^2}\right) \quad .\ (32)$$

$$a_i = \left(\frac{\Delta\theta}{x_i\Delta x} - \frac{\Delta\theta}{(\Delta x)^2}\right);\ b_i = \left(1 + \frac{2\Delta\theta}{(\Delta x)^2}\right);\ c_i = \left(\frac{-\Delta\theta}{x_i\Delta x} - \frac{\Delta\theta}{(\Delta x)^2}\right) \quad (33)$$

$$a_m = \left(\frac{-2\Delta\theta}{(\Delta x)^2}\right);\ b_m = \left(1 + \frac{2\Delta\theta}{(\Delta x)^2}\right) \quad (34)$$

$$d_1 = Q_i^p;\ d_i = Q_i^p;\ d_m = Q_m^p + \left(1 + \frac{1}{\Delta x}\right)2Bi(C_b - C_s)^p \quad (35)$$

Determination of Q values using Tri-Diagonal Matrix Approach (TDMA)

For calculating the set of 'C' values expressed in a matrix form, [A]=[B][C], several approaches are available like Gaussian Elimination method, Inverse method etc. The TDM Approach is useful when the values matrix form a specific bandwidth such that the upper and lower triangular elements become zero. In this approach, few constants are calculated that are actually obtained during the matrix multiplication. Using these values the unknown values of the array (i.e., [C] in the above example) are calculated. The following are the steps involved in this approach (Ghoshdastidar, 1998):

$$\beta_0 = b_0 \text{[from Eq. (32)]} \quad (36)$$

For i = 1 to m:

$$\beta_i = b_i - \frac{a_i c_{i-1}}{\beta_{i-1}} \tag{37}$$

$$\gamma_0 = \frac{d_0}{\beta_0} \tag{38}$$

For i = 1 to m:

$$\gamma_i = \frac{d_i - a_i \gamma_{i-1}}{\beta_i} \tag{39}$$

$$Q_m = \gamma_m \tag{40}$$

For i = 1 to m:

$$Q_{m-1} = \gamma_{m-1} - \frac{c_{m-1} Q_m}{\beta_{m-1}} \tag{41}$$

$$[Z]^p[q]^{p+1}=[D]^p \tag{31}$$

In the present problem, [Z] comprises of values calculated as [a], [b], & [c] (Eqs. 32-34) and [D] comprises of values calculated as [d] using Eq. 35. Substituting the above values in TDMA, we get the values of ‘Q’ expressed as [q] in Eq. 31. The Q values obtained are used to calculate the average ‘Q’ value using Simpson’s 1/3rd rule.

Simpson’s 1/3rd rule for solving Eq. (12)

We have, $Q_{avg} = 3\int_0^1 Q(x,\theta)x^2 dx$ (12)

It can be written as,

$$Q_{avg} = 3\int_0^1 f(x)dx$$

where, $f(x) = Q(x,\theta)x^2$. Simpson’s 1/3rd rule can be applied to Eq. (12).

Assuming 10 equal parts for example:

$$\int_0^1 f(x)dx = \frac{h}{3}[(f_0 + f_{10}) + 4(f_1 + f_3 + f_5 + f_7 + f_9) + 2(f_2 + f_4 + f_6 + f_8)] \tag{42}$$

where the step interval, h = (1/10) =0.1 (for 10 equal parts)

Calculation of C_b value using Q_{avg}

We have, $\frac{dC_b}{d\theta} = -\lambda \frac{dQ_{avg}}{d\theta}$ (11)

Above equation can be discritized as,

$$\frac{C_b^{p+1} - C_b^p}{\Delta\theta} = (-\lambda)\frac{Q_{avg}^{p+1} - Q_{avg}^p}{\Delta\theta} \tag{43}$$

from which, the concentration of adsorbate in bulk solution can be obtained for $p+1$ (future) time interval as, $C_b^{p+1} = C_b^p - \lambda(Q_{avg}^{p+1} - Q_{avg}^p)$.

Appendix-G

CODE DEVELOPED FOR BACK-PROPAGATION NETWORK

```
// backprop.cpp
//layer.cpp
// compile for floating point hardware if available
#include <stdio.h>
#include <iostream.h>
#include <stdlib.h>
#include <math.h>
#include <time.h>
#include "layer.h"


inline float squash(float input)
// squashing function
// use sigmoid -- can customize to something
// else if desired; can add a bias term too
//
{
if (input < -50)
      return 0.0;
else  if (input > 50)
            return 1.0;
      else return (float)(1/(1+exp(-(double)input)));

}


inline float randomweight(unsigned init)
{
int num;
// random number generator
// will return a floating point
// value between -1 and 1

if (init==1)       // seed the generator
      srand ((unsigned)time(NULL));

num=rand() % 100;

return 2*(float(num/100.00))-1;
}

// the next function is needed for Turbo C++
static void force_fpf()
{
      float x, *y;
      y=&x;
      x=*y;
}

// ------------------------------------------
//                        input layer
//------------------------------------------
input_layer::input_layer(int i, int o)
{
```

```
num_inputs=i;
num_outputs=o;

outputs = new float[num_outputs];
if (outputs==0)
      {
      cout << "not enough memory\n";
      cout << "choose a smaller architecture\n";
      exit(1);
      }
}

input_layer::~input_layer()
{
delete [num_outputs] outputs;
}

void input_layer::calc_out()
{
//nothing to do, yet
}



// -----------------------------------------
//                        output layer
//------------------------------------------



output_layer::output_layer(int i, int o)
{

num_inputs=i;
num_outputs=o;
weights = new float[num_inputs*num_outputs];
output_errors = new float[num_outputs];
back_errors = new float[num_inputs];
outputs = new float[num_outputs];
expected_values = new float[num_outputs];
if ((weights==0)||(output_errors==0)||(back_errors==0)
      ||(outputs==0)||(expected_values==0))
      {
      cout << "not enough memory\n";
      cout << "choose a smaller architecture\n";
      exit(1);
      }

}

output_layer::~output_layer()
{
delete [num_outputs*num_inputs] weights;
```

```
delete [num_outputs] output_errors;
delete [num_inputs] back_errors;
delete [num_outputs] outputs;

}


void output_layer::calc_out()
{

int i,j,k;
float accumulator=0.0;


for (j=0; j<num_outputs; j++)
      {

      for (i=0; i<num_inputs; i++)

            {
            k=i*num_outputs;
            if (weights[k+j]*weights[k+j] > 1000000.0)
                  {
                  cout << "weights are blowing up\n";
                  cout << "try a smaller learning constant\n";
                  cout << "e.g. beta=0.02    aborting...\n";


                  exit(1);
                  }
            outputs[j]=weights[k+j]*(*(inputs+i));
            accumulator+=outputs[j];
            }
      // use the sigmoid squash function
      outputs[j]=squash(accumulator);
      accumulator=0;
      }

}


void output_layer::calc_error(float & error)
{
int i, j, k;
float accumulator=0;
float total_error=0;

for (j=0; j<num_outputs; j++)
     {
      output_errors[j] = expected_values[j]-outputs[j];
      total_error+=output_errors[j];
      }

error=total_error;

for (i=0; i<num_inputs; i++)
      {
      k=i*num_outputs;
      for (j=0; j<num_outputs; j++)
```

```
                {
                back_errors[i]=
                      weights[k+j]*output_errors[j];
                accumulator+=back_errors[i];
                }
        back_errors[i]=accumulator;
        accumulator=0;
        // now multiply by derivative of
        // sigmoid squashing function, which is
        // just the input*(1-input)
        back_errors[i]*=(*(inputs+i))*(1-(*(inputs+i)));
        }

}

void output_layer::randomize_weights()
{
int i, j, k;
const unsigned first_time=1;

const unsigned not_first_time=0;
float discard;

discard=randomweight(first_time);

for (i=0; i< num_inputs; i++)
        {
        k=i*num_outputs;
        for (j=0; j< num_outputs; j++)
                weights[k+j]=randomweight(not_first_time);
        }
}

void output_layer::update_weights(const float beta)
{
int i, j, k;

// learning law: weight_change =
//              beta*output_error*input

for (i=0; i< num_inputs; i++)
        {
        k=i*num_outputs;
        for (j=0; j< num_outputs; j++)
                weights[k+j] +=
                        beta*output_errors[j]*(*(inputs+i));
     }

}

void output_layer::list_weights()
{
int i, j, k;

for (i=0; i< num_inputs; i++)
        {
        k=i*num_outputs;
        for (j=0; j< num_outputs; j++)
                cout << "weight["<<i<<","<<
                        j<<"] is: "<<weights[k+j];
```

```
      }

}

void output_layer::list_errors()
{
int i, j;

for (i=0; i< num_inputs; i++)
      cout << "backerror["<<i<<
            "] is : "<<back_errors[i]<<"\n";

for (j=0; j< num_outputs; j++)
      cout << "outputerrors["<<j<<
                  "] is: "<<output_errors[j]<<"\n";

}


void output_layer::write_weights(int layer_no,
            FILE * weights_file_ptr)
{
int i, j, k;

// assume file is already open and ready for
// writing

// prepend the layer_no to all lines of data
// format:
//          layer_no    weight[0,0] weight[0,1] ...
//          layer_no    weight[1,0] weight[1,1] ...
//          ...

for (i=0; i< num_inputs; i++)
      {
      fprintf(weights_file_ptr,"%i ",layer_no);
      k=i*num_outputs;
    for (j=0; j< num_outputs; j++)
      {
      fprintf(weights_file_ptr,"%f ",
                  weights[k+j]);
      }
    fprintf(weights_file_ptr,"\n");
    }


}

void output_layer::read_weights(int layer_no,
            FILE * weights_file_ptr)
{
int i, j, k;


// assume file is already open and ready for
// reading

// look for the prepended layer_no
// format:
//          layer_no    weight[0,0] weight[0,1] ...
```

```
//          layer_no    weight[1,0] weight[1,1] ...
//          ...
while (1)
      {

      fscanf(weights_file_ptr,"%i",&j);
      if ((j==layer_no)|| (feof(weights_file_ptr)))
            break;
      else
            {
            while (fgetc(weights_file_ptr) != '\n')
                  {;}// get rest of line
            }
      }

if (!(feof(weights_file_ptr)))
      {
      // continue getting first line
      i=0;
      for (j=0; j< num_outputs; j++)
                  {

                  fscanf(weights_file_ptr,"%f",
                              &weights[j]); // i*num_outputs = 0
            }
      fscanf(weights_file_ptr,"\n");



      // now get the other lines
      for (i=1; i< num_inputs; i++)
            {
            fscanf(weights_file_ptr,"%i",&layer_no);
            k=i*num_outputs;
      for (j=0; j< num_outputs; j++)
            {
            fscanf(weights_file_ptr,"%f",
                  &weights[k+j]);
          }

      }
    fscanf(weights_file_ptr,"\n");
    }

else cout << "end of file reached\n";

}
void output_layer::list_outputs()
{
int j;

for (j=0; j< num_outputs; j++)
      {
      cout << "outputs["<<j
            <<"] is: "<<outputs[j]<<"\n";
      }
```

```
}


// -----------------------------------------
//                      middle layer
//------------------------------------------


middle_layer::middle_layer(int i, int o):
      output_layer(i,o)
{

}

middle_layer::~middle_layer()
{
delete [num_outputs*num_inputs] weights;
delete [num_outputs] output_errors;
delete [num_inputs] back_errors;
delete.[num_outputs] outputs;
}


void middle_layer::calc_error()
{
int i, j, k;
float accumulator=0;

for (i=0; i<num_inputs; i++)
      {
      k=i*num_outputs;
      for (j=0; j<num_outputs; j++)
            {
            back_errors[i]=
                  weights[k+j]*(*(output_errors+j));
            accumulator+=back_errors[i];
            }
      back_errors[i]=accumulator;
      accumulator=0;
      // now multiply by derivative of
      // sigmoid squashing function, which is
      // just the input*(1-input)
      back_errors[i]*=(*(inputs+i))*(1-(*(inputs+i)));
      }

}

network::network()
{
position=0L;
}

network::~network()
{
int i,j,k;
i=layer_ptr[0]->num_outputs;// inputs
j=layer_ptr[number_of_layers-1]->num_outputs; //outputs
k=MAX_VECTORS;
```

```
delete [(i+j)*k]buffer;
}

void network::set_training(const unsigned & value)
{
training=value;
}

unsigned network::get_training_value()
{
return training;
}


void network::get_layer_info()
{
int i;

//-----------------------------------------
//
//    Get layer sizes for the network
//
// -----------------------------------------



cout << " Please enter in the number of layers for your network.\n";
cout << " You can have a minimum of 3 to a maximum of 5. \n";
cout << " 3 implies 1 hidden layer; 5 implies 3 hidden layers : \n\n";

cin >> number_of_layers;

cout << " Enter in the layer sizes separated by spaces.\n";
cout << " For a network with 3 neurons in the input layer,\n";
cout << " 2 neurons in a hidden layer, and 4 neurons in the\n";
cout << " output layer, you would enter: 3 2 4 .\n";
cout << " You can have up to 3 hidden layers,for five maximum entries
:\n\n";

for (i=0; i<number_of_layers; i++)
      {
      cin >> layer_size[i];
      }

// -----------------------------------------------------
// size of layers:
//           input_layer            layer_size[0]
//           output_layer           layer_size[number_of_layers-1]
//           middle_layers          layer_size[1]
//                            optional: layer_size[number_of_layers-3]
//                            optional: layer_size[number_of_layers-2]
//
//-----------------------------------------------------


}

void network::set_up_network()
{
int i,j,k;
//-----------------------------------------------------
```

```
// Construct the layers
//
// ---------------------------------------------------


layer_ptr[0] = new input_layer(0,layer_size[0]);

for (i=0;i<(number_of_layers-1);i++)
      {
      layer_ptr[i+1] =
      new middle_layer(layer_size[i],layer_size[i+1]);
      }

layer_ptr[number_of_layers-1] = new
output_layer(layer_size[number_of_layers-2],layer_size[number_of_layers-
1]);

for (i=0;i<(number_of_layers-1);i++)
      {
      if (layer_ptr[i] == 0)
            {
            cout << "insufficient memory\n";
            cout << "use a smaller architecture\n";
            exit(1);
            }
      }

//---------------------------------------------------
// Connect the layers
//
//---------------------------------------------------
// set inputs to previous layer outputs for all layers,
//    except the input layer

for (i=1; i< number_of_layers; i++)
      layer_ptr[i]->inputs = layer_ptr[i-1]->outputs;



// for back_propagation, set output_errors to next layer
//          back_errors for all layers except the output
//          layer and input layer


for (i=1; i< number_of_layers -1; i++)
      ((output_layer *)layer_ptr[i])->output_errors =
            ((output_layer *)layer_ptr[i+1])->back_errors;

// define the IObuffer that caches data from
// the datafile
i=layer_ptr[0]->num_outputs;// inputs
j=layer_ptr[number_of_layers-1]->num_outputs; //outputs
k=MAX_VECTORS;

buffer=new
      float[(i+j)*k];
if (buffer==0)
      {
      cout << "insufficient memory for buffer\n";
```

```
        exit(1);
        }
}

void network::randomize_weights()
{
int i;

for (i=1; i<number_of_layers; i++)
        ((output_layer *)layer_ptr[i])
                ->randomize_weights();
}


void network::update_weights(const float beta)
{
int i;

for (i=1; i<number_of_layers; i++)
        ((output_layer *)layer_ptr[i])
                ->update_weights(beta);
}


void network::write_weights(FILE * weights_file_ptr)
{
int i;

for (i=1; i<number_of_layers; i++)
        ((output_layer *)layer_ptr[i])
                ->write_weights(i,weights_file_ptr);
}


void network::read_weights(FILE * weights_file_ptr)
{
int i;

for (i=1; i<number_of_layers; i++)
        ((output_layer *)layer_ptr[i])
                ->read_weights(i,weights_file_ptr);
}


void network::list_weights()
{
int i;

for (i=1; i<number_of_layers; i++)
        {
        cout << "layer number : " <<i<< "\n";
        ((output_layer *)layer_ptr[i])
                ->list_weights();
        }
}

void network::list_outputs()
{
int i;
```

```
for (i=1; i<number_of_layers; i++)
      {
      cout << "layer number : " <<i<< "\n";
      ((output_layer *)layer_ptr[i])
            ->list_outputs();
      }
}

void network::write_outputs(FILE *outfile)
{
int i, ins, outs;
ins=layer_ptr[0]->num_outputs;
outs=layer_ptr[number_of_layers-1]->num_outputs;
float temp;

fprintf(outfile,"for input vector:\n");

for (i=0; i<ins; i++)
      {
      temp=layer_ptr[0]->outputs[i];
      fprintf(outfile,"%f  ",temp);
      }


fprintf(outfile,"\noutput vector is:\n");

for (i=0; i<outs; i++)
      {
      temp=layer_ptr[number_of_layers-1]->
      outputs[i];
      fprintf(outfile,"%f  ",temp);

      }

if (training==1)
{
fprintf(outfile,"\nexpected output vector is: \n");

for(i=0;i<outs;i++)
      {
       temp =((output_layer*)(layer_ptr[number_of_layers-1]))-
>expected_values[i];
       fprintf(outfile,"%f  ",temp);
      }
}
fprintf(outfile, "\n----------------\n");

}

void network::list_errors( )
{
 int i;
for(i =1;i<number_of_layers;i++)
      {
      cout<<"layer number :  "<<i<<"\n";
      ((output_layer *)layer_ptr[i])->list_errors();
      }
}

int network::fill_IObuffer(FILE *inputfile)
```

```
{
//this routine fills memory with
//an array of input, output vectors
//up to a maximum capacity of
// MAX_INPUT_VECTORS_IN_ARRAY
//the return value is the number of read vectors

int i,k,count, veclength;
int ins,outs;

ins =layer_ptr[0]->num_outputs;
outs=layer_ptr[number_of_layers-1]->num_outputs;
if(training ==1)
      veclength = ins+outs;
else
      veclength = ins;
count=0;
while ((count<MAX_VECTORS)&&(!feof(inputfile)))
      {
      k=count*(veclength);
      for(i=0;i<veclength;i++)
            {
            fscanf(inputfile,"%f",&buffer[k+i]);
            }
      fscanf(inputfile,"\n");
      count++;
      }
if(!(ferror(inputfile)))
      return count;
else
      return -1; //error condition
}

void network::set_up_pattern(int buffer_index)
{
//read one vector into the network
int i,k;
int ins, outs;

ins=layer_ptr[0]->num_outputs;
outs=layer_ptr[number_of_layers-1]->num_outputs;
if(training==1)
      k=buffer_index*(ins+outs);
else
      k=buffer_index*ins;
for(i=0;i<ins;i++)
      layer_ptr[0]->outputs[i]=buffer[k+i];
if(training==1)
{
      for(i=0;i<outs;i++)
      ((output_layer *)layer_ptr[number_of_layers-1])-
>expected_values[i]= buffer[k+i+ins];
}

}
  void network::forward_prop()
{
int i;
for(i=0;i<number_of_layers;i++)
{
```

```
layer_ptr[i]->calc_out(); //polymorphic function
}
}

void network::backward_prop(float &toterror)
{
int i;
//error for the output layer
((output_layer*)layer_ptr[number_of_layers-1])-> calc_error(toterror);

//error for the middle layer(s)
for (i=number_of_layers-2;i>0;i--)
{
((middle_layer*)layer_ptr[i])-> calc_error();
}

}
#define TRAINING_FILE   "training.dat"
#define WEIGHTS_FILE    "weights.dat"
#define OUTPUT_FILE     "output.dat"
#define TEST_FILE "test.dat"


void main()
{

float error_tolerance=0.1;
float total_error=0.0;
float avg_error_per_cycle=0.0;
float error_last_cycle=0.0;
float avgerr_per_pattern=0.0; // for the latest cycle
float error_last_pattern=0.0;
float learning_parameter=0.02;
unsigned temp, startup;
long int vectors_in_buffer;
long int max_cycles;
long int patterns_per_cycle=0;

long int total_cycles, total_patterns;
int i;


// create a network object
network backp;


FILE * training_file_ptr, * weights_file_ptr, * output_file_ptr;
FILE * test_file_ptr, * data_file_ptr;

// open output file for writing
if ((output_file_ptr=fopen(OUTPUT_FILE,"w"))==NULL)
            {
            cout << "problem opening output file\n";
            exit(1);
            }

// enter the training mode : 1=training on     0=training off
cout << "----------------------------------------------------\n";
cout << "   Backpropagation \n";
cout << "----------------------------------------------------\n";
```

```
cout << "Please enter 1 for TRAINING on, or 0 for off: \n\n";
cout << "Use training to change weights according to your\n";
cout << "expected outputs. Your training.dat file should contain\n";
cout << "a set of inputs and expected outputs. The number of\n";
cout << "inputs determines the size of the first (input) layer\n";
cout << "while the number of outputs determines the size of the\n";
cout << "last (output) layer :\n\n";

cin >> temp;
backp.set_training(temp);

if (backp.get_training_value() == 1)
      {
      cout << "--> Training mode is *ON*. weights will be saved\n";
      cout << "in the file weights.dat at the end of the\n";
      cout << "current set of input (training) data\n";
      }
else
      {
      cout << "--> Training mode is *OFF*. weights will be loaded\n";
      cout << "from the file weights.dat and the current\n";
      cout << "(test) data set will be used. For the test\n";
      cout << "data set, the test.dat file should contain\n";
      cout << "only inputs, and no expected outputs.\n";
      }

if (backp.get_training_value()==1)
      {
      // ----------------------------------------
      //    Read in values for the error_tolerance,
      //    and the learning_parameter
      // ----------------------------------------
      cout << " Please enter in the error_tolerance\n";
      cout << " --- between 0.001 to 100.0, try 0.1 to start --\n";
      cout << "\n";
      cout << "and the learning_parameter, beta\n";
      cout << " --- between 0.01 to 1.0, try 0.5 to start -- \n\n";
      cout << " separate entries by a space\n";
      cout << " example: 0.1 0.5 sets defaults mentioned :\n\n";

      cin >> error_tolerance >> learning_parameter;
      //-----------------------------------------
      // open training file for reading
      //-----------------------------------------
      if ((training_file_ptr=fopen(TRAINING_FILE,"r"))==NULL)
            {
            cout << "problem opening training file\n";
            exit(1);
            }
      data_file_ptr=training_file_ptr; // training on

      // Read in the maximum number of cycles
      // each pass through the input data file is a cycle
      cout << "Please enter the maximum cycles for the simulation\n";
      cout << "A cycle is one pass through the data set.\n";
      cout << "Try a value of 10 to start with\n";

      cin >> max_cycles;

      }
```

```
else
      {
      if ((test_file_ptr=fopen(TEST_FILE,"r"))==NULL)
            {
            cout << "problem opening test file\n";
            exit(1);
            }

      data_file_ptr=test_file_ptr; // training off
      }



// the main loop
//
// training: continue looping until the total error is less than
//          the tolerance specified, or the maximum number of
//          cycles is exceeded; use both the forward signal propagation
//          and the backward error propagation phases. If the error
//          tolerance criteria is satisfied, save the weights in a file.
// no training: just proceed through the input data set once in the
//          forward signal propagation phase only. Read the starting
//          weights from a file.
// in both cases report the outputs on the screen


// intialize counters
total_cycles=0; // a cycle is once through all the input data
total_patterns=0; // a pattern is one entry in the input data



// get layer information
backp.get_layer_info();

// set up the network connections
backp.set_up_network();

// initialize the weights
if (backp.get_training_value()==1)
      {
      // randomize weights for all layers; there is no
      // weight matrix associated with the input layer
      // weight file will be written after processing
      // so open for writing
      if ((weights_file_ptr=fopen(WEIGHTS_FILE,"w"))
                  ==NULL)
            {
            cout << "problem opening weights file\n";
            exit(1);
            }
      backp.randomize_weights();
      }
else
      {
      // read in the weight matrix defined by a
      // prior run of the backpropagation simulator
      // with training on
      if ((weights_file_ptr=fopen(WEIGHTS_FILE,"r"))
```

```
                  ==NULL)
            {
            cout << "problem opening weights file\n";
            exit(1);
            }
      backp.read_weights(weights_file_ptr);
      }



// main loop
// if training is on, keep going through the input data
//         until the error is acceptable or the maximum number of
cycles
//         is exceeded.
// if training is off, go through the input data once. report outputs
// with inputs to file output.dat

startup=1;
vectors_in_buffer = MAX_VECTORS; // startup condition
total_error = 0;


while (                  ((backp.get_training_value()==1)
                  && (avgerr_per_pattern
                              > error_tolerance)
                  && (total_cycles < max_cycles)
                  && (vectors_in_buffer !=0))
                  || ((backp.get_training_value()==0)
                  && (total_cycles < 1))
                  || ((backp.get_training_value()==1)
                  && (startup==1))
                  )
{
startup=0;
error_last_cycle=0; // reset for each cycle
patterns_per_cycle=0;
// process all the vectors in the datafile
// going through one buffer at a time
// pattern by pattern



while ((vectors_in_buffer==MAX_VECTORS))
      {

      vectors_in_buffer=
            backp.fill_IObuffer(data_file_ptr); // fill buffer
            if (vectors_in_buffer < 0)
                  {
                  cout << "error in reading in vectors, aborting\n";
                  cout << "check that there are on extra linefeeds\n";
                  cout << "in your data file, and that the number\n";
                  cout << "of layers and size of layers match the\n";
                  cout << "the parameters provided.\n";
                  exit(1);
                  }

            // process vectors
```

```
            for (i=0; i<vectors_in_buffer; i++)
                  {
                  // get next pattern
                  backp.set_up_pattern(i);

                  total_patterns++;
                  patterns_per_cycle++;
                  // forward propagate

                  backp.forward_prop();

                  if (backp.get_training_value()==0)
                        backp.write_outputs(output_file_ptr);

                  // back_propagate, if appropriate
                  if (backp.get_training_value()==1)
                        {

                        backp.backward_prop(error_last_pattern);
                        error_last_cycle +=
                              error_last_pattern*error_last_pattern;
                        backp.update_weights(learning_parameter);
                        // backp.list_weights(); // can
                        // see change in weights by
                        // using list_weights before and
                        // after back_propagation
                        }

                  }

      error_last_pattern = 0;
      }

avgerr_per_pattern=((float)sqrt((double)error_last_cycle/patterns_per_cy
cle));
total_error += error_last_cycle;
total_cycles++;

// most character displays are 25 lines
// user will see a corner display of the cycle count
// as it changes

cout << "\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n\n";
cout << total_cycles << "\t" << avgerr_per_pattern << "\n";

fseek(data_file_ptr, 0L, SEEK_SET); // reset the file pointer
                         // to the beginning of
                         // the file
vectors_in_buffer = MAX_VECTORS; // reset

} // end main loop

cout << "\n\n\n\n\n\n\n\n\n\n\n";
cout << "---------------------------------------------------\n";
cout << "   done: results in file output.dat\n";
//cout << "      training: last vector only\n";
//cout << "      not training: full cycle\n\n";
if (backp.get_training_value()==1)
      {
      backp.write_weights(weights_file_ptr);
```

```
      backp.write_outputs(output_file_ptr);
      avg_error_per_cycle=
(float)sqrt((double)total_error/total_cycles);
      error_last_cycle=(float)sqrt((double)error_last_cycle);

cout << "         weights saved in file weights.dat\n";
cout << "\n";
cout << "---->average error per cycle = " << avg_error_per_cycle << " <-
--\n";
cout << "---->error last cycle = " << error_last_cycle << " <---\n";
cout << "->error last cycle per pattern= " << avgerr_per_pattern << " <-
--\n";

      }

cout << "------------>total cycles = " << total_cycles << " <---\n";
cout << "------------>total patterns = " << total_patterns << " <---\n";
cout << "--------------------------------------------------\n";
// close all files
fclose(data_file_ptr);
fclose(weights_file_ptr);
fclose(output_file_ptr);

}
```

Appendix-H

CODE DEVELOPED FOR HOMOGENEOUS SURFACE DIFFUSION MODEL BASED ON PURE-IMPLICIT SCHEME OF FINITE DIFFERENCE METHOD AND SIMPSON'S 1/3RD RULE

```
#include<stdio.h>
#include<math.h>
#define M 100      /* (M+1)=Total number of equations to be solved */

main()
{
int i;                /* i=integer used in program */
int j;                * i=integer used in program */
int eqn[M+2];
long double xx;     /*xx=used for output of dimensionless distance (-)*/
long double R;                    /* R=radius (m) */
long double Ds;                   /* Diffusion coefficient (m2/s) */
long double t;                    /* Time (s) */
long double theta;         /* theta=Dimensionless time for finite difference
                           method (-) */
long double dtheta;               /* dtheta=Dimensionless time step for finite
                                  difference method (-) */
long double kf;                   /* kf=mass transfer coefficient (m/s) */
long double row;           /* row=density of solid particle (kg/m3) */
long double Bi;                   /* Biot number */
long double c0;                   /*          */
long double Cb;    /* bulk concentration normalized to c0 (kg/m3) */
long double bb;                   /* Isothermal constant (m3/kg) */
long double qmax;          /*               */
long double q0;                   /*              */
long double Cs[M+2];       /* bulk phase concentration at the surface of the
                           adsorbent particle normalized to c0(-) */
long double Q[M+2];        /* Concentration (kg/kg) */
long double x[M+2];        /* x=Dimensionless radial distance (-) */
long double dx;            /* dx=Dimensionless radial distance step for finite
                           difference method (-) */

long double a[M+2];
long double b[M+2];        /* a-d=VARIBLE USED IN ASSIGNING VALUES */
long double c[M+2];               /* IN TRIDIAGONAL MATRIX */
long double d[M+2];
long double beta[M+2];     /* beta=used while calculating theta (-) */
long double gamma[M+2];    /* gamma=used while calculating theta (-) */
/*long double Cb[M+2];*//* Bulk concentration (kg/m3) */
long double fx[M+2];       /* Function used in Simpson's 1/3 Rule */
long double Qavg;          /* Average concentration (-) */
long double lemda;         /*     */
long double store;         /* To store the previous value of Qavg */
long double mc;            /*     */
long double V;             /*     */

int k;
long double sum_even, sum_odd, sum_total, term1, term2;

/* INPUT */
```

```
/*CONSTANTS*/

store=0.0;
R=3.72*pow(10.0, -4.0);
Ds=2.29*pow(10.0,-11.0);
theta=0.000165;
dtheta=0.000165;
kf=12.0*pow(10.0, -2.0);
row=500.0;//particle density = (row) * (1-porosity)

mc=0.0001;
V=0.0125;

c0=110.0*pow(10.0,-9.0);
bb=9.15*pow(10.0, 6.0);
qmax=123.0*pow(10.0, -6.0);

q0=(qmax*bb*c0)/(1.0+bb*c0);
Bi=(kf*R*c0)/(Ds*row*q0);

lemda=(mc*q0)/(V*c0);
dx=(1.0/M);
x[1]=(1.0/M);
eqn[0]=1;

for(i=0;i<=M;i++)
{
eqn[i+1]=eqn[i]+1;
}


/* INITIAL CONDITION */

for(i=0;i<=M;i++)
{
Cs[i]=0.0;
}

for(i=0;i<=M;i++)
{
Q[i]=0.0;
}

Cb=1.0;

/*PROGRAM OF FINITE DIFFERENCE METHOD BASED ON PURE IMPLICIT SCHEME*/

while(1)
{

t=(theta*pow(R,2.0))/(Ds);

for(i=1;i<=M-1;i++)
{
a[i]=((dtheta)/(dx*x[i]))-((dtheta)/(dx*dx));
x[i+1]=x[i]+dx;
}
a[M]=((-2.0*dtheta)/(dx*dx));

b[0]=(((6.0*dtheta)/(dx*dx))+(1.0));
for(i=1;i<=M;i++)
```

```
{
b[i]=((2.0*dtheta)/(dx*dx)+1.0);
}

c[0]=(-6.0*dtheta)/(dx*dx);
for(i=1;i<=M-1;i++)
{
c[i]=((-dtheta)/(dx*x[i]))-((dtheta)/(dx*dx));
x[i+1]=x[i]+dx;
}

for(i=0;i<=M-1;i++)
{
d[i]=Q[i];
}

d[M]=Q[M]+(1.0+(1.0/dx))*2.0*dtheta*Bi*(Cb-Cs[M]);

//DETERMINING CONSTANTS USING TRIDIAGONAL MATRIX METHOD

beta[0]=b[0];
for(i=1;i<=M;i++)
{
beta[i]=b[i]-(a[i]*c[i-1])/(beta[i-1]);
}


gamma[0]=d[0]/beta[0];
for(i=1;i<=M;i++)
{
gamma[i]=(d[i]-a[i]*gamma[i-1])/(beta[i]);
}

Q[M]=gamma[M];
i=M;
for(j=1;j<=M;j++)
{
Q[M-j]=(gamma[M-j])-((c[M-j]*Q[i])/(beta[M-j]));
i=i-1;
}

for(i=0;i<=M;i++)
{
Cs[i]=(Q[i])/(1.0+bb*c0-bb*c0*Q[i]);
}

/* CALCULATIONS USING SIMPSONS RULE*/

        xx=0.0;

        for(i=0;i<=M;i++)
        {
        fx[i]=(Q[i])*xx*xx;
        xx=xx+(1.0/M); /* increment equals to 1/M*/
        }

        term1 = fx[0];
        term2 = fx[M];

        sum_even=0.0;
        sum_odd=0.0;
```

```
    sum_total = 0.0;

    for (i=1; i<=M; i++)
    {
        j = 2*i; //for even numbers
        if(j<=M-1)
        {
            sum_even = sum_even+fx[j];
        }

        k = j-1; //for odd numbers
        if(k<=M-1)
        {
            sum_odd = sum_odd+fx[k];
        }

    }

    sum_total= term1+term2+(4.0*sum_odd)+(2.0*sum_even);
    Qavg=(1.0/M)*(1.0/3.0)*(3.0)*sum_total;

Cb=Cb-lemda*(Qavg-store);
store = Qavg;
printf("\n time: %0.4Lf ; Cb: %0.6Lf\n", t, Cb);

xx=xx+(1.0/M);
getchar();

theta=theta+dtheta;
if(Cb<=0.10) /* this value is variable depending on reqt of PRE*/
break;
}
}//end of file
```

CODE DEVELOPED FOR DETERMINING ADSORPTION PARAMETERS FROM BATCH STUDIES

```
#include<stdio.h>
#include<math.h>
#include<conio.h>
#include<ctype.h>
#include<string.h>
#include<stdlib.h>

void reg(float a[25],float b[25],int c);
void lang(float a[25],float b[25],int c);
void rate(float a[25],float b[25],int c);
void fruend(float a[25],float b[25],int c);
void langiso(float a[25],float b[25],int c);
void mass(float a[25],float b[25],int c);
void calc(float a[25],float b[25],int c);
void gen(float a[25],float b[25],int c);
void diff(float a[25],float b[25],int c);
void averageq(float a[25],float b[25],int c);
void diffusion(float a[25],float b[25],int c,float d);

void main()
{
float ic[1],c[1][25],ti[1][25],k[24],m[24],u,v,g,o;
float n[11][25],t[11][25],mv,x,q,r,y,z,p,e,su,kt,as,add;
int a,i,b,j,d,w,s,f;

printf("enter the initial concentration in mg/l \n");/*input*/
scanf("%f",&g);/*initial concentration*/
      ic[0]=g*pow(10,-3);
      printf("enter the number of values \n");
      scanf("%d",&b);
      for(j=0;j<b;j++)
            {
                  fflush(stdin);
                  printf("enter the ratios \n");/*ratios*/
                  scanf("%f",&c[0][j]);
            }
            for(j=0;j<b;j++)
            {
            printf("enter the time in minutes \n");
                  scanf("%f",&ti[0][j]);
                  ti[0][j]=(60*ti[0][j]);
            }

       printf("enter the adsorbent dose in kg/cubic meter \n");
       scanf("%f",&mv);/*adsorbent dosage*/
       fflush(stdin);
```

```
for(s=0;s>=0;s++)
{
printf("MAIN MENU \n \n");
printf("1.Empirical model to predict PRE at any time \n \n");
printf("2.Empirical model to predict amount adsorbed at any time \n
\n");
printf("3.Fruendlich isotherm \n \n");
printf("4.Langmuir isotherm \n \n");
printf("5.Estimation of effective diffusion coefficient using uptake
approach \n \n");
printf("6.Estimation of external diffusion coefficient using alternate
LDF approach \n \n");
printf("7.McKay and Allen model to calculate external mass transfer
coefficient  \n \n");
printf("8.Thermodynamic constants using Langmuir constant\n \n");
printf("9.Thermodyanmic constants using rate constant\n \n");
printf("10.Estimation of external mass transfer coefficient using LDF
approach \n \n");
printf("11.Exit the program \n \n");

printf("Enter u r option \n \n");
scanf("%d",&f);


if(f==1){
/*generation of data for each model*/

printf("1. Estimation of adsorbent removal as a function of time \n");
for(j=0;j<b;j++)
{
        t[0][j]=log(ti[0][j]);
        y=(1-c[0][j])*100;
        n[0][j]=log(y);
}
      reg(t[0],n[0],b);

        }


if(f==2){
printf("Estimation of adsorbate removal taking (1/q) and (1/t) \n");

for(j=0;j<b;j++)
{
        t[1][j]=((1/ti[0][j]));
        x=(ic[0]*c[0][j]);
        n[1][j]=((mv/(ic[0]-x)));
}
        gen(t[1],n[1],b);
        }

if(f==8){
printf("Thermodynamic constants using Langmuir constants \n");
printf("enter the number of values \n");/*input*/
scanf("%d",&a);
for(i=0;i<a;i++)
        {
```

```
      printf("enter the values of temp in degree centigrade \n");
      scanf("%f",&t[7][i]);
      printf("enter the value of b \n");
      scanf("%f",&n[7][i]);
      t[7][i]=(1/(t[7][i]+273));
      n[7][i]=log(n[7][i]);
      }
      lang(t[7],n[7],a);
      }

if(f==9){
printf("Thermodynamic constants using rate constant \n");
printf("enter the number of values \n");
scanf("%d",&a);
for(i=0;i<a;i++)
{
      printf("enter the values of temp in degree centigrade \n");
      scanf("%f",&t[8][i]);
      printf("enter the value of kc \n");
      scanf("%f",&n[8][i]);
      t[8][i]=(1/(t[8][i]+273));
      n[8][i]=log(n[8][i]);
}
      rate(t[8],n[8],a);
      fflush(stdin);
       }


if(f==3){
printf("Fruendlich isotherm \n");
printf("enter the number of values \n");
scanf("%d",&d);
printf("enter the adsorbent dose in kg/cu m \n");
scanf("%f",&add);
for(i=0;i<d;i++)
{
        printf("enter the initial concentration in mg/l \n");
        scanf("%f",&u);
        u=u*pow(10,-3);
        printf("enter the ratio \n");
        scanf("%f",&v);
        o=(v*u);
        t[2][i]=log(o);
        z=((u-(u*v))/add);
        n[2][i]=log(z);
}
        fruend(t[2],n[2],d);
      }


if(f==4){
printf("Langmuir isotherm \n");
printf("enter the number of values \n");
scanf("%d",&a);
printf("enter the adsorbent dose in kg/cu m\n");
scanf("%f",&add);
for(i=0;i<a;i++)
```

```
{
        printf("enter the initial concentration in mg/l \n");
        scanf("%f",&u);
        u=u*pow(10,-3);
        printf("enter the ratio \n");
        scanf("%f",&v);
        t[3][i]=(1/(u*v));
        n[3][i]=1/((u-(u*v))/add);

}
        langiso(t[3],n[3],a);
       }

       fflush(stdin);


if(f==5){
printf("7.Mass transfer coefficient \n");
for(i=0;i<(b-1);i++)
{
       t[4][i]=ti[0][i];
       x=(1-c[0][i]);
       q=(1-c[0][b-1]);
       r=(x/q);
       p=(1-r);
       n[4][i]=log(p);
}
       mass(t[4],n[4],(b-1));
       }


if(f==6){
printf("8.Calculation of kf \n");
for(i=0;i<b;i++)
{
        k[i]=((ic[0]*(1-c[0][i]))/mv);
        if(i==0){
        m[i]=0;
        continue;
              }
 else
        {
        w=(i-1);
        m[i]=((k[i]+k[w])/2);
        t[5][w]=(ic[0]*c[0][i]);
        n[5][w]=(m[w]-m[i])/(ti[0][w]-ti[0][i]);
        }
}

 calc(t[5],n[5],(b-1));
        }


if(f==10){
printf("9.Calculation of diffusion coefficient using average value of q
\n");
for(i=0;i<b;i++)
```

```
{
        k[i]=(((ic[0]*(1-c[0][i]))/mv)*pow(10,4));
        if(i==0){
              m[i]=0;
              continue;
              }
              else
              {
              w=(i-1);
              m[i]=((k[i]+k[w])/2);
              t[9][w]=((k[i]+k[w])/2);
              n[9][w]=(m[w]-m[i])/(ti[0][w]-ti[0][i]);
              }
        }
        averageq(t[9],n[9],(b-1));
}


if(f==7){
printf("Enter the value of k \n");
scanf("%f",&kt);
as=(1/(1+(mv*kt)));
for(i=0;i<b;i++)
{
       n[10][i]=log(c[0][i]-as);
       t[10][i]=ti[0][i];
}
       diffusion(t[10],n[10],b,kt);
       }


if(f==11)
       exit(0);

}

}
void reg(float a[25],float b[25],int c)
{
int i;
float p,q, sum_x=0, sum_y=0;
float product_xy=0,square_x=0,sum_square=0,slope,inter;

for(i=0;i<c;i++)
{
       sum_x=(sum_x+ a[i]);
       sum_y=(sum_y+b[i]);
       product_xy=(product_xy+(a[i]*b[i]));
       square_x=(square_x+(a[i]*a[i]));
}
sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
p=slope;
q=pow(2.718,inter);
printf("the slope and the intercept %f %f \n",slope,inter);
```

```
printf("the value of m and k %f %f \n",p,q);
}

void gen(float a[25],float b[25],int c)
{
int i;
float p, q, sum_x=0; sum_y=0;
float product_xy=0,square_x=0,sum_square=0,slope,inter;

for(i=0;i<c;i++)
{
        sum_x=(sum_x+ a[i]);
        sum_y=(sum_y+b[i]);
        product_xy=(product_xy+(a[i]*b[i]));
        square_x=(square_x+(a[i]*a[i]));
}
sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
p=(1/inter);
q=(inter/slope);
printf("the slope and the intercept %f %f \n",slope,inter);
printf("the value of qe and B %f %f \n",p,q);
}

void lang(float a[25],float b[25],int c)
{
int i;
float sum_x=0,sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float h;

for(i=0;i<c;i++)
{
        sum_x=(sum_x+ a[i]);
        sum_y=(sum_y+b[i]);
        product_xy=(product_xy+(a[i]*b[i]));
        square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
h=(-8.314*slope);
printf("the enthalpy is %f \n",h);
}


void rate(float a[25],float b[25],int c)
{
int i;
float sum_x=0,sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float h,s;

for(i=0;i<c;i++)
```

```
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
h=(-8.314*slope);
s=(8.314*inter);
printf("the enthalpy and entropy are %f %f \n",h,s);
}


void fruend(float a[25],float b[25],int c)
{
int i;
float
p,q,r,sum_x=0,sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float n,kf,add;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
n=(1/slope);
printf("%f \n",inter);
kf=pow(2.718,inter);
printf("the value of n and kf %f %f \n",n,kf);
printf("verification \n");
printf("enter the initial concentration\n");
scanf("%f",&p);
p=(p*pow(10,-3));
printf("enter the ratio \n");
scanf("%f",&q);
r=p*q;
add=((p-r)/(kf*pow(r,slope)));
printf("the value of the adsorbent dose %f kg/cubic meter \n",add);
}

void langiso(float a[25],float b[25],int c)
{
int i;
float sum_x=0,sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
```

```
float k,x,y,r,add,p,q,s;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
x=(1/inter);
y=(inter/slope);
k=(1/slope);
printf("the values of a and b are %f %f \n",x,y);
printf("the value of k is %f \n",k);

printf("verification \n");
printf("enter the initial conc in mg/l \n");
scanf("%f",&p);
p=p*pow(10,-3);
printf("enter the ratio \n");
scanf("%f",&q);
s=p*q;
add=((p-s)*(1+(y*s)))/(x*y*s);
printf("the value of adsorbent dose %f kg/cubic meter \n",add);
r=(1/(1+(y*p)));
printf("the separation factor %f \n",r);
}

void mass(float a[25],float b[25],int c)
{
int i;
float rp, sum_x=0, sum_y=0;
float product_xy=0,square_x=0,sum_square=0,slope,inter;
float df,k,km;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
k=((-slope*15)/(3.14*3.14));
printf("the value of k is %f per second \n",k);
```

```
printf("enter the radius of the particle in microns \n");
scanf("%f",&rp);
rp=(rp*pow(10,-6));
df=((-slope*rp*rp)/(3.14*3.14));
df=(df*pow(10,11));
km=((5*df)/rp);
printf("the value of diffusion coefficient is %f *10^-11 \n",df);
printf("the value of kf in m/sec is %f *10^-11 \n",km);
}

void calc(float a[25],float b[25],int c)
{
int i;
float den, rp, sum_x=0;
float sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float kf,df;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f %f \n",slope,inter);
printf("enter the radius of the particle in microns \n");
scanf("%f",&rp);
rp=(rp*pow(10,-6));
printf("enter the value of density in kg/cubic meter\n");
scanf("%f",&den);
printf("%f\n",rp);
kf=((den*rp*slope)/3);
kf=kf*pow(10,11);
printf("the value of kf %f *10^-11 \n",kf);
df=((kf*rp)/5);
printf("the value of diffusion coefficient is:  %f *10^-11 \n",df);
}

void averageq(float a[25],float b[25],int c)
{
int i;
float rp, sum_x=0;
float sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float df,k,kf;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}
```

```
sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f  %f \n",slope,inter);
printf("enter the radius of the particle in microns \n");
scanf("%f",&rp);
rp=(rp*pow(10,-6));
df=((-slope*rp*rp)/15);
df=(df*pow(10,11));
kf=((df*5)/rp);
printf("the value of df %f *10^-11 sq.m/sec \n",df);
printf("the value of k in per second is %f \n",(-1*slope));
printf("the value of kf is %f *10^-11 m/sec \n",kf);
}

void diffusion(float a[25],float b[25],int c,float d)
{
int i;
float rp, sum_x=0;
float sum_y=0,product_xy=0,square_x=0,sum_square=0,slope,inter;
float ss,df,kf,mv,dp,den,su,k;

for(i=0;i<c;i++)
{
      sum_x=(sum_x+ a[i]);
      sum_y=(sum_y+b[i]);
      product_xy=(product_xy+(a[i]*b[i]));
      square_x=(square_x+(a[i]*a[i]));
}

sum_square=(sum_x*sum_x);
slope=(((c*product_xy)-(sum_x*sum_y))/((c*square_x)-(sum_square)));
inter=(((sum_y*square_x)-(product_xy*sum_x))/((c*square_x)-
sum_square));
printf("the slope and the intercept %f  %f \n",slope,inter);
printf("enter the adsorbent dose in kg/cubic meter \n");
scanf("%f",&mv);
printf("enter the diameter of the particle in microns \n");
scanf("%f",&dp);
dp=dp*pow(10,-6);
printf("enter the density of the particle in kg/cubic meter \n");
scanf("%f",&den);
su=((1+(mv*d))/(mv*d));
ss=((6*mv)/(dp*den));
printf("%f\n",ss);
kf=(-slope/(su*ss));
kf=(kf*pow(10,11));
printf("the value of kf is %f *10^-11 \n",kf);
df=((dp*kf)/10);
printf("the value of diffusion coefficient is %f * 10^-11 \n",df);
}
```