Experimental Studies on Cr(VI) Removal from Wastewater by Adsorption using Pig Iron Sludge and Biochar

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CERTIFICATE

This is to certify that the thesis entitled **“Experimental Studies on Cr(VI) Removal from Wastewater by Adsorption using Pig Iron Sludge and Biochar”** submitted by **SURENDRAN.G.** ID No. 2009PHFX425G for award of Ph. D. Degree of the Institute embodies original work done by him/her under my supervision.

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Dedicated to

Shri Sadhguru Jaggi Vasudev (Isha Foundation)

and

Shirdi Saibaba

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Abstract

The present study explores the use of easily available natural and industrial adsorbents for the treatment of Cr(VI) contaminated wastewater. In the initial part of the study, Cr(VI) adsorption studies have been carried out using two representative bio-sorbent viz *Sorghastrum Nutans L. Nash* and *Cocos Nucifera.* The effect of various parameters such as initial pH of adsorbate solution, initial concentration of Cr(VI), dosage, time and particle size has been studied. The adsorbent *Sorghastrum Nutans L. Nash* was characterized before and after adsorption using FTIR, SEM, EDAX, and XRD analysis. Among different functional groups present in the adsorbent, OH bending, CN stretching/bending and NH stretching plays a major role in Cr(VI) adsorption. Batch experiments shows that adsorption coupled reduction i.e. indirect reduction is the mechanism of Cr(VI) removal by the biomaterial. Adsorbent surface became highly positively charged at lower pH, adsorption rate of Cr(VI) is faster and reduction reaction also accelerates at lower pH since, the binding of negatively charged Cr(VI) ion species to the cationic groups is enhanced and protons take part in this reaction.

In case of *Sorghastrum Nutans L. Nash,* it was observed that the adsorption capacity was high at pH 1 whereas, the adsorption capacity was very low at higher pH. In case of *Cocos Nucifera*, the adsorption capacity was significantly high at higher pH as compared to *Sorghastrum Nutans L. Nash.* However, in both the cases, the effluent pH was highly acidic and hence required further neutralization steps which may not be economical. Further, these adsorbents in their present form cannot be regenerated or recycled for industrial use. In addition, the water-soluble compounds present in the bio-sorbents can leach-out to the effluent which may create further environmental problem.

To overcome the above problem, pig iron sludge is explored as an adsorbent for the treatment of Cr(VI) contaminated wastewater. From the batch adsorption experiments it was observed that, the uptake capacity of the adsorbent was low as compared to the bio-sorbent. Whereas, the effluent pH in case of using pig iron sludge was higher compared to the bio-sorbents. Further, this adsorbent in its present form can be recycled to ferrochrome manufacturing process.

Since the uptake capacity of the pig iron sludge is very less, biochar prepared from *Sorghastrum Nutans L. Nash* was used as an adsorbent. It was observed that the adsorption capacity of biochar is higher than other three adsorbents at higher solution pH. In addition, the effluent pH is also higher than the other three cases and the Cr(VI) adsorbed biochar can be recycled as a raw material to ferrochrome or steel manufacturing industry. In this study, a process flow sheet for ferrochrome industry is proposed showing the possible location of using the biochar. Adsorption kinetics, isotherms and rate limiting steps have been established for all the adsorbents used in this study. From the study, it was found that, adsorption process followed pseudo 2nd order kinetics and Langmuir adsorption isotherm and surface diffusion is the rate limiting step.

To optimize the operating conditions, a full factorial design of experiment was used within pH, adsorbent dosage, adsorbate concentration and contact time as the independent variable and percentage of adsorption as the response variable. Empirical model was developed using factorial design of experiment and use of different tools like MINITAB, MATLAB and LabVIEW to simulate or analyze the empirical model. From the normal probability, residual, contour, 3D surface, main effect and interaction plot along with t test, ANOVA and F-test, it is observed that initial solution pH has the most significant effect on the percentage removal followed by adsorbent dosage, time and adsorbate concentration. The interaction effects of independent variables are evaluated and found to be significant.

There is a requirement of easy, organized and rational methods to choose an adsorbent among the large options available by considering all possible factors and their interaction. In this study, fuzzy logic method is used for selection of a suitable adsorbent for the Cr(VI) removal. Multiple attribute decision making (MADM) is used to determine the corresponding weighting values for the selected adsorbent. The preference index is calculated by using the subjective and objective weights. The normalized value associated with each parameter has given on the basis of effect of each parameter on the Cr(VI) removal and uptake capacity of each material. The associated MADM method results and the limitations of the approaches are discussed to lay the foundation for further improvement.

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Chapter-1

Introduction and Literature Review

1.1. Introduction

Water is the most important natural resources for all life on earth. The water sources are either surface water or ground water. Water is made available by the natural hydrologic cycle. Water vaporizes as vapor from lakes, oceans, and rivers. It is then falls as rain through condensation process in the air, moves over and through the ground into water bodies where the cycle begins again. Water resources are used for various purposes including direct consumption, domestic use, irrigation, fisheries, recreation, navigation, livestock, mining, hydropower and other industries.

The quantity and quality of water played major role, not only determining where people can live, but also their quality of life. In spite of there has been abundant quantity of fresh water on earth, water has not been suitable quality for all uses. The steadiness between supply and demand for water is a delicate one. Good quality of water has its own resource but that has limits and boundaries to its availability and aptness for use.

Chromium (from the Greek word for color, chroma) is a naturally occurring element that may be found in oxidation states of - 2 to +6. It is found primarily in the trivalent and hexavalent forms (Saha et al, 2011). It was first discovered in 1797 in the form of Siberian red lead (Crocoites $PbCrO_4$) and occurs only in combination with other elements primarily as halides, oxides or sulfides. Chromium is found most abundantly in chromites ore ($FeCr_2O_4$). Elemental chromium does not naturally occur. Oxidation state of Chromium occurs in two stable states Cr(II1) and Cr(VI). Cr (V1) occurs as $HCrO_4^-$ bichromate ion, CrO_4^{2-} chromate ion, and $Cr_2O_7^{2-}$dichromate ion depending on the pH and concentration of the solution.

1.2 Redox Reaction of Chromium

Cr(III) is converted into Cr(VI) in presence of oxidizing agent such as peroxides and hypo halide at alkaline condition.

Oxidation of Cr(III)

In alkaline medium,

$$2Cr_2O_3 + 8OH^- + 3O_2 \rightarrow 4CrO_4^- + 4H_2O \qquad (1)$$

In acidic medium,

$$2Cr_2O_3 + 3O_2 + 2H_2O \rightarrow 2Cr_2O_7^{2-} + 4H^+ \qquad (2)$$

Reduction of Cr(VI)

Using reducing agent chromium can be reduced indo lower oxidation state.

$$Cr_2O_7^{\ 2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \text{ (6 e- from reducing agents)} \qquad (3)$$

1.3 Importance of Harmful Effects

At present, various ill effects of health caused by the use of polluted water appears large on the horizons of developing and developed countries. The major source of water pollution is the effluents from industries which are discharged into natural water bodies. Water pollution are the physio-chemical, or biological changes in the quality of water that has become unsafe condition to any living thing that drinks or uses or lives in it. This problem of ecosystem damage is worldwide and probably no country in the world is unaffected. Cheronobyl in Ukraine, Linfen in China and Ranipet in India are among the ten most polluted locations in the world (Blacksmith Institute Report, 2006). Water pollution makes unsuitable for the desired use. Several trace elements are found in polluted water. The most potential among them are the toxic inorganic ions like Cr(VI), Pb(II), Cd(II), As(III), F^- etc. Due to the toxic and carcinogenic properties of Cr(V1) as compared to non-toxic Cr(III), Cr(VI) was major concern (Reddy et al, 1997; and Romero-Gonzalez et al, 2005). Most important factors leading the toxicity of chromium compounds are solubility and its oxidation state. Cr(VI) compounds, generally very powerful oxidizing properties and thus leads to irritating nature and very corrosive, appear to be higher toxic than Cr(III) compounds, considering similar in quantity and solubility. Most of the cases the mechanisms of biological contact are unclear, this variation in toxicity may be related to the ease with which Cr(VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates.

1.4 Sources of Cr(VI) in Wastewater

The chromium has been used widely in metallurgy, leather tanning, electroplating and other industries and that release the chromium into the environment (Guohua et al, 2011).

Tannery industry is one of the oldest and fastest growing industries in India and there are about 2,000 tanneries excluding cottage mainly concentrated in Ranipet, Ambathur and Vanyambadi (Tamilnadu); Kanpur and Agra (Uttar Pradesh); Jalandhar (Punjab) and Delhi discharging approximately 9,420,000 m^3 waste water annually into environment (Sharma and Goyal, 2009). Their removal from effluents prior to disposal is essential from environmental health, management and economics points of view.

Because of the strong corrosion resistance and high strengthening effect made chromium as an important alloying material for steel. The high-speed tool steels contain between 3 to 5% chromium. Stainless steel, the main corrosion-proof metal alloy is formed when chromium in the form of ferro-chromium is added to iron in sufficient (usually more than 11%) concentration. The acidic chromate or dichromate solution which has got relatively good corrosion resistance and high hardness used as good surface coating material (Dennis and Such, 1993).

Aluminum anodization is another electrochemical process, in which chromic acid used as electrolyte instead of sulphuric acid to have improved oxide layers but does not lead to deposition of chromium (Sprague and Smidt, 1994). Chrome yellow (PbCrO4), chrome red ($PbCrO_4$ and PbO), chrome green and chrome oxide green (Cr(III) oxide) are the pigments used in paints (Worobec and Hogue, 1992). Cr(III) is also used in producing synthetic rubies. In order to prevent the wood like timber against attack of decay fungi, insects like termites and marine-borers chromated copper arsenate (CCA) salt has been used in timber treatment (Hingston *et al.*, 2001). In leather industry, for tanning of leather the Cr(III) salts in the form of chrome alum or Cr(III) sulphate have been used. This Cr(III) stabilizes leather by crosslinking the collagen fibres within the leather (Brown, 1997).

The high heat resistivity and high melting point makes chromite and Cr(III) oxide a material for high temperature refractory applications like blast furnaces, cement kilns, molds for firing of bricks and as foundry sands for casting of metals (Papp and Lipin,2006). Several chromium compounds are used as catalyst, for example the Phillips catalyst for the production of polyethylene is mixtures of chromium and silicon dioxide or mixtures of chromium, titanium and aluminium oxide (Weckhuysen, 1999).

Chromic acid is a powerful oxidizing agent and is a useful compound for cleaning laboratory glassware of any trace of organic compounds. Potassium dichromate is used as a mordant for dyes in fabric. The multifarious uses of chromium and its compounds have made it an indispensable part of industrial world these days. The increased usage of Chromium has led to a great growth in chromium based industries.

Another major industrial source of Cr(VI) is from production of Ferrochrome industries, which in turn, used for making stainless steel. The ferrochrome in the following categories are being used for the production of stainless steel based on the content of carbon. (Goel, 1997)

- High carbon ferrochromium :(Cr: >60%, C: 6-9%)
- Charge chrome: (Cr: 50-60%, C: 6-9%)
- Medium carbon ferrochromium: (Cr: 56-70%, C: 1-4%) and
- Low carbon ferrochromium: (Cr 56-70%, C: 0.015-1.0%)

There are two operation places where Chromium can be discharged with effluent one is that during Grinding and Filtering stage and another is flue gas during heating in Arc Furnace. Our main focus is that finding the possibilities of using natural adsorbent to remove the 100% Chromium from the any industrial effluent by normal adsorption process and feed this chromium adsorbed adsorbent along with feed material for production ferrochrome in sintering operation.

1.5 Cr(VI) contaminated wastewater Treatment Technologies

Selection of method depends on the different factors such as type of industrial effluent, concentration of Cr, form of Cr in solution i.e. Cr(III) or Cr(VI), cost of method, efficiency of method, etc. Following are some methods used for removal of chromium.

1.5.1 Chemical precipitation

It is the process for formulation of separate solid material from the solution, either by converting the metal ion into insoluble form or by changing the oxidation state metal to reduce the solubility of the compound formed. The removal of chromium from effluent can be done by precipitation method. Cr(VI) can be precipitated as Cr(III) after reduction of Cr(VI) to Cr(III) by using suitable reducing agent such as ferrous sulphate, Fe metal, sodium sulphite, hydrogen peroxide, etc. At alkaline medium Cr(III) get converted into its hydroxide form which is water insoluble. Like hydroxide, Cr(III) can be precipitated as chromium sulphide, chromium phosphate, etc. Chemical precipitation methods required addition of other chemicals, this finally generated high content of sludge. The deposits are collected and disposed of to land dumps or oceans or by incineration.

Precipitation process required low cost, and can be used at high concentration of Cr(III) in solution. The speed and completeness of the reduction of Cr(VI) to Cr(III) mainly depends on pH value. The greatest speed is observed in an acidic medium at a pH 2-2.5 and it usually requires additional acidification of the wastewater. In practice, this is carried out by Sulphuric and other mineral acids. When metallic iron is used for the acidification of chromium containing waste water, the water is filtered through a layer of iron shavings in the reactor. By using iron shavings as reducer, solid phase content in formed deposits increases four-fold as 1 part (by 16 weight) of $Cr(OH)_3$ and 3.12 parts (by weight) of $Fe(OH)_3$ (Smirnov and Genkin, 1989) will be deposited at the same time. All the chemical methods have a common disadvantage where a great deal of slime is formed.

Ferrous iron is used for reduction of chromium from higher state to lower state from aqueous solution (Scott, 1996). The stoichiometrically and kinetically reduction of hexavalent chromium from aqueous solution by hydrogen sulfide is feasible. Hexavalent chromium can be reduced by sodium sulphide in stabilization processes in pilot scale. In this process cement, lime and gypsum is used as the stabilizing agents. With the help reducing agent such as sodium meta- bisulphite and ferrous sulphate the reduction of hexavalent chromium to trivalent chromium can be takes place, and completely reduction of chromium done with the help of precipitating reagent by using base (Karale et. al., 2007). The reduction of hexavalent chromium from aqueous solution can be done by using sodium sulphide and sodium meta-bisulphite at pH 2 (Beukes et. al., 1999).

$2H_2CrO_4 + 3SO_2 \longrightarrow Cr_2(SO_4)_3 + 2H_2O$ (4)

$4H_2CrO_4 + 3Na_2S_2O_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6NaHSO_4 + 7H_2O$ (5)

$K_2Cr_2O_7 + 6FeSO_4 + 8H_2SO_4 \longrightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 3Fe(SO_4)_3 + 7H_2O$ (6)

1.5.2 Chemical Reduction

Chemical methods involve reduction reaction of Cr(VI) of wastewaters to Cr(III) by chemical or electrochemical means and there is deposition of Cr(III) as hydroxides form. Thus, the clean- up of wastewater leads to the pollution of environment for a second time. Seepage from untreated wastewaters deposited into dumps is in turn a potential source of chromium contamination of the soil and underground waters.

1.5.3 Photo catalysis

With the help of UV or Visible radiations and proper catalyst (TiO_2) reduction of Cr(VI) is possible to Cr(III) this process is known as photo-catalysis. In the photo-catalysis reaction reduction of Cr(VI) to Cr(III) can be done. Cr(III) then precipitate out at alkaline pH and finally completely removal of chromium take place. Photo-catalysis reaction is useful for reduction of different heavy metals from aqueous solution. One disadvantage of this method is this reaction required more time as compared to other methods.

1.5.4 Membrane Filtration

Membrane filtration technique has also received a significant attention. Many types of membranes such as inorganic polymeric and liquid membranes can be used for Cr(VI) removal. Pugazhenthi et al. (2005) made non-interpenetrating ultra-filtration carbon membrane by gas phase interaction using NOx and amination using hydrazine hydrate, for separation of Cr(VI) from aqueous solution. Muthukrishnan and Guha (2008) made use of different nano-filtration composite polyamide membranes and found that percent rejection of chromium was dependent upon pH of the feed solution and less on the concentration of Cr(VI) in feed solution. Again, the incomplete metal removal, high reagent and energy requirement, generation of toxic sludge, besides economic consideration, are the major hurdles in the acceptance of this technique.

1.5.5 Electro-dialysis

Removal of hexavalent chromium from aqueous solution was done with the help of iron and aluminium electrodes by electro coagulation process. By electro coagulation process completely reduction of heavy metals from industrial and synthetic wastewater can be done. The disadvantages of electro-dialysis method are it required high cost, required highly trained human resources, the fouling and scaling of membranes.

Electro-dialysis is the process in which electrical current is applied for generation of ions with the help of electrode. In this method ions are transported through ion permeable membranes under the influence of potential gradients from one solution to another solution. The electrical charge on the ion is responsible for transfer of ions through the membrane made-up from ion- exchange polymers. Selection of membrane depends on the ability to transport ions having positive or negative charges. In the electro-dialysis method, the ion permeable membranes sheets of ion-exchange resins are used, in some cases polymer is also used to increases mechanical strength and elasticity.

1.5.6 Biopolymer

Physico-chemical methods presently in use have several disadvantages such as unpredictable metal removal, high chemical requirements and formation of sludge and its disposal. Further, the installation and operational cost of the processes are very high (Deepa et al., 2006). Search for newer treatment technologies for removal of toxic metals from waste water has directed attention to bio-sorption. The review of literature, thus supports the drawbacks of the existing conventional treatment methods for Cr(VI) contaminated surface and ground waters as any one of the following:

- High energy expenditure in the process,
- Use of expensive and toxic chemical reductant,
- Inefficient removal of low Cr(VI) concentrations in wastewater,
- Economically non-viable, and generation of secondary waste needs further disposal methods (Zvinowanda et al., 2009).

Therefore, none of these techniques is entirely satisfactory, one being a temporary solution, simply immobilizing the contaminant and others being costly when applied on large scale (Adriano et al, 1995).

1.5.7 Adsorption and Bio-adsorption

Adsorption means liquid or gas phase substance can be accumulated on surface of solid phase. Chromium in the form of Cr(III) and Cr(VI) can be removed using a different adsorbent. Among all these methods, adsorption process is considered better than other methods because of convenience, easy operation and simplicity of design. Further, this process can remove/ minimize different types of pollutants and thus have wider applicability in water pollution control. A fundamentally important characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption sites (Bhatnagar, 2006). The different adsorbents that can be used are activated charcoal, Fe_2O_3, chemically treated biomasses, etc. Adsorption can occur either by chemical adsorption or physical adsorption or a combination of both. For adsorption of chromium various adsorbents are used. Activated charcoal is one of the most important and effective way to remove the chromium from industrial effluents. Activated charcoal is derived from various raw materials such as nut shell, sawdust and coconut shells. As particle size of adsorbent decreases, increases the removal efficiency of Cr(VI) (Hamadi et. al., 2001). Adsorption capacity of chromium highly depends on pH of solution (Natale et. al., 2007).

Biosorption is a process in which living or inactive, dead, microbial biomass can be used for removal of heavy metals from aqueous solutions. Bio-sorption use functional groups for bio- sorption are –COOH, $-NH_2$, -CO, -OH etc. For the removal of chromium or heavy metals the advantages of bio-sorption process is that these are technically feasible, low cost and ecological. This method has less intensity of bio-sorption and can be used at low concentration of metal ion solution. Conventional methods are ineffective in the removal of low concentrations of chromium metal ions. Different biosorbent used for the treatment of Cr(VI) contaminated wastewater is summarized in Table 1.1.

1.5.8 Mechanism of bio-sorption

The active mechanisms of bio-sorption are complex and often selective. They have not been completely elucidated, are not yet well understood and still unclear. Bio-sorption has a chemical, equilibrated and saturation mechanism (Dilek, et al 2002). Such a process includes active participation of several ligands present on the bio-sorbent like amino, phosphoryl, carboxyl, sulfhydryl and hydroxyl groups to biosorb metal ions. They differ depending on the bio-sorbent species, the origin and processing of the bio-sorbent and solution chemistry. Despite the complexity of the bio-sorption process which includes several mechanisms, adsorption isotherms have been used to characterize metal uptake and they appear to be of use for projected industrial applications (Tsezos and Volesky, 1981). A rich literature on the biosorption of heavy metals by various bio-sorbents is readily available. Bio-sorption of some heavy metals, their concentrations, bio-sorbents used and the extent of biosorption from their aqueous solutions played major role for the removal of toxic substances in solution.

1.5.9 Adsorption of Cr(VI) by using various industrial waste

Wide spread industrial activities are producing large amount of solid waste materials. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. The industrial waste material is available almost free of cost and causes major disposal problem. If the solid wastes could be used as low cost adsorbents, it will provide a two- fold advantage in reducing the pollution. Firstly, the volume of waste materials could be partly reduced and secondly the developed low-cost adsorbent can reduce the pollution of wastewaters at a reasonable cost. A number of industrial wastes have been investigated with or without treatment as adsorbents for the removal pollutants from wastewaters. Important industrial wastes with their metal uptake, pH, adsorption kinetics and isotherms for various industrial wastes were compared in the Table 1.2. But in all the cases, there is no proper explanation about reuse of adsorbent.

1.6 Conclusion

Many technologies adopted for the removal of chromium from industrial wastewaters include precipitation, membrane filtration, solvent extraction with amines; ion-exchange, activated carbon adsorption, electro-deposition, and various biological processes. Most of these methods suffer set-backs because of high capital and operational cost and lack of skilled personnel problem. Adsorption process has been extensively used for the removal of toxic metals. Recently various natural adsorbents such as agriculture wastes and activated carbon prepared from agriculture wastes, have been used for the removal of toxic metals from aquatic environment. The technologies available for the removal/recovery of chromium metal ions and the operating conditions are listed in Table 1.3. The versatility, simplicity and other technology characteristics will contribute to the overall process costs, both capital and operational.

In present study, it is intended to find the suitability of various adsorbents like bio-sorbent, sludge and carbonized Biochar used to remove the Cr(VI) from aqueous solution.

- It is proposed to study the effect of different parameters like pH, initial concentration of Chromium, dosage, time and particle size.
- Suitability of various adsorption isotherm and to establish the kinetics and rate limiting mechanism of Chromium adsorption.
- Mathematical and statistical techniques useful for developing, improving and optimizing the process condition and can be used to evaluate the relative significance of several affecting factors individually and also combined.
- Possibility of recycle and reuse of adsorbed Chromium by industrial recycle like Pig iron sludge.
- Use the Carbonized Biochar as adsorbent to remove the Cr(VI) and finding the possible location in Ferrochrome industry.

Table 1.1: Review of Literature for the adsorption of Cr(VI) by using bio-sorbents

Material	**Metal uptake, mg/g**	**pH**	**Isotherms**	**Kinetics Order**	**Reference**
Lignin	31.6	2	Freundlich	2nd	(Albadarin et al., 2011)
Oak bark char	7.51	2	Langmuir,	2nd	(Mohan et al., 2009)
Chestnut tannins	42	4	Langmuir	2nd	(Tahiri et al., 2011)
Mimosa tannins	38	4	Langmuir	2nd	(Tahiri et al., 2011)
Boiled Rice husk	8.5	2	Freundlich, DR-Model	---	(Garg et al., 2009)
Boiled Sunflower stem waste	4.9	2	Langmuir, Freundlich, DR-Model	---	(Garg et al., 2009)
Ocimum americanum L.Seed pods	83.33	1.5	Langmuir	2nd	(Levankumar et al., 2009)
Ground nut hull	30.95	2	Langmuir, Freundlich	2nd	(Qaiser et al., 2009)
Walnut hull	98.13	1	Langmuir, Freundlich	1st	(Wang et al., 2009)
Alligator weed	82.57	1	Langmuir , Freundlich, Tempkin	2nd Elovich	(Wang et al., 2009)
Rubber wood saw dust	4.87	2	--	---	(Wang et al., 2009)
Saw dust	20.70	3	Langmuir , Freundlich		(Bhattacharya et al., 2008)
Neem bark	19.60	2	Langmuir , Freundlich		(Bhattacharya et al., 2008)
Maize bran	312.52	2	Langmuir		(Hasan et al., 2008)
Treated oil palm	22.73	1.5	Langmuir,		(Isa et al., 2008)
Mangrove leaves	8.87	4.5	Langmuir, Fruendlich		(Philip et al., 2008)
Hazelnut shell	17.7	2.5	Langmuir , Freundlich		(Climino et al., 2000)

Table 1.2: Review of Literature for the adsorption of Cr(VI) by using different industrial waste

Material	**Uptake**	**pH**	**Isotherm**	**Order of Kinetics**	**References**
Dolochar from sponge industry	5.21	1	Langmuir	2^{nd}	(Das et al., 2011)
Tannery waste	177	2	Langmuir	2^{nd}	(Mandal et al., 2011)
Carbon slurry from fertilizers	15.24	2	Langmuir	2^{nd}	(Gupta et al., 2010)
Solid waste from leather industry	133	1	Langmuir	NA	(Oliveira et al., 2008)
$Mg(OH)_2$ (MF5-1) in cement industry	7.2	9.4	Langmuir	1^{st}	(Gasser et al., 2007)
Waste pomace from olive oil factory	12.15	2	Langmuir	NA	(Malkoc et al., 2006)
Activated red mud	1.6	2	Langmuir Freundlich	NA	(Pradhan et al., 1999)
Blast furnace slag	7.5	1	Langmuir Freundlich	1^{st}	(Srivastava et al., 1997)
Iron (III)/Cr(III) hydroxide	0.47	5.6	Langmuir Freundlich	NA	Namasivayam et al., 1993

Table 1.3: Comparison of Cr(VI) treatment technology

Process Technology	**pH change**	**Influence of suspended solids**	**Tolerance of organic molecules**	**Working level for appropriate metal concentration (mg/L)**
Electro chemical	Tolerant	Engineered to tolerate	Can be accommodated	>10
Ion exchange	Limited tolerance	Fouled	Can be poisoned	<100
Membrane	Limited tolerance	Fouled	Intolerant	>10
Precipitation	Limited tolerant	Tolerant	Tolerant	>10
Adsorption	Tolerant	Tolerant	Tolerant	<10

Chapter-2

Bio-sorption of Cr(VI) from wastewater using *Sorghastrum Nutans L. Nash*

2.1. Materials

The adsorbent used in this study is a natural grass known as *Sorghastrum Nutans L-Nash* which grows profusely in our campus. The grass was collected and cleaned with distilled water thrice and dried for 48 hours. In order to remove the remaining moisture after drying, the grass was kept in an oven at 60^0C for 8 hours. The dried grass was then ground into powder form and sieved (British Standard Screens) to different size fractions. The sieved powdered grass samples were then stored in an airtight container for further use. A stock solution was then prepared by dissolving known quantity of potassium dichromate in double distilled water. In order to meet the prescribed concentration for experiments, the solution was further diluted as required. The initial pH of the solution was maintained by adding the dilute HCl or NaOH (concentration of 0.1 N) made as appropriate before adsorption. The complexing agent, Di-Phenyl Carbazide (DPC) solution was ready by dissolving requisite amount of Di-phenyl Carbazide in acetone and kept in an air tight volumetric flask in a dark place until further use. 6N H_2SO_4 solution was prepared from the concentrated solution by using the appropriate amount of distilled water and kept in a standard flask for use in the spectrophotometric analysis of Cr(VI) concentration. All the chemicals used for experiments were obtained from Merck of standard analytical grade.

2.2. Methods

Adsorption experiments were conducted by using 500 ml prepared chromium known concentration solution in a beaker at constant temperature. The mixtures were well mixed using a magnetic stirrer (REMI maker) with speed controller. 5 ml of sample was collected at regular time intervals and filtered through a Whatman42 filter paper. In order to maintain the solid to liquid ratio, the samples were collected under dynamic conditions. The residual Cr(VI) concentration in the filtrate was analysed using an UV spectrometer (Hach DR5000, model 1201) at a wavelength of 540 nm after complexing with metal ion by 1,5 Di-Phenyl Carbazide under acidic conditions (Baral et al, 2009). Percentage adsorption of Cr(VI) was calculated as follows

$$\%\ \text{Adso.} = \frac{(C_o - C_t)}{C_o} \times 100 \tag{2.1}$$

where E, C_o and C_t denote percentage adsorption and Cr(VI) concentration (mg L^{-1}) at the beginning and after time t respectively. The uptake capacity (mg/g) of chromium at equilibrium was calculated from the difference of metal concentration in the solution before and after adsorption, according to the equation below:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (2.2)$$

where V is the volume (L) of the solution and C_e is equilibrium chromium concentration respectively.

2.3. Results and Discussion

2.3.1. Characterizations

In order to find out the major components and their existing phase in the adsorbent X-ray diffraction (XRD) analysis was carried out using Cu K_∞ radiation on a computer controlled Rigaku Miniflex 600 diffractometer. XRD analysis pattern were recorded with scan speed of 0.5° 2 h per minute with step size of 0.01. The XRD plot is shown in Fig. 2.1. The figure showed only one major peaks which is identified as the peak for carbon. In order to find out the morphological changes in the adsorbent, the powdered adsorbent (before and after adsorption) was analyzed using a Scanning electron microprobe images are (SEM JXO-8100) at 1000X magnification. The outcomes are presented in Fig. 2.2 and 2.3. From the micrograph image, it is clearly observed that there is a change in surface morphology before and after adsorption. Where in, the structure of adsorbent is seen to change from an irregular porous structure to smooth nature after adsorption. An EDAX analysis data further confirmed, adsorption of Cr(VI) on the surface of adsorbent. EDAX data for the adsorbent before and after adsorption are shown in Fig. 2.4 and 2.5. The results indicate an increase in mass percentage of chromium from 0.45 to 9.36% after adsorption.

FTIR Spectroscopy was conducted to identify existing functional groups in the adsorbent before and after adsorption. The samples were finely powdered with 200 mg of moisture less KBr in a mortar and placed in 10 mm diameter disks, under 10 tons of pressure for FTIR analysis. The adsorbent spectra with the array of 400 - 4000 cm^{-1} wave number were measured. The FTIR spectra of the adsorbents display a number of absorption peaks, signifying the complex nature of the adsorbent. The percentage transmittance and important peaks of the adsorbents before and after adsorption is shown in Table 2.1. As can be observed in Fig.2.6 the spectrum of grass before and after the adsorption process displays substantial drop in the intensity at an absorption bands of 3132 cm^{-1} which relates the hydroxyl stretching vibrations and hydrogen bonding of celloligo-saccharides and their degradation products (Peng et al, 2010). Broad peak of percentage transmittance difference has been observed at an absorption band of 1653 cm^{-1} which were attributed to C=N vibration mode. The peak observed at 1400 cm^{-1} corresponds to NH Stretching and bending vibration of N=O group present in the adsorbent. The adsorption bands observed at 1269.16 and 1261.45 cm^{-1} corresponds to CN stretching and CN vibration (Sahayaraj et al, 2015). The band at 1045 cm^{-1} was found to be OH group bending (Lee et al, 2015), whereas the band at 898 cm^{-1} indicates C-O-C stretching and CH deformation (Ciolacu et al, 2011). From Table 2.1 it can be observed from the adsorption peaks that, either a reduction or shift in adsorption band after adsorption signifying that all the functional groups have played major role. These band shifts specify that there is OH bending, CN stretching/bending and NH stretching particularly play an important role in chromium bio-sorption on the adsorbent. Analogous results has been observed by various researchers (Malcok et al, 2006; Baral et al, 2008).

2.3.2 Effect of Contact time on Cr(VI) adsorption

It is important to get the equilibrium contact time; the experiments were carried out up to 600 min. The other process parameters such as adsorbate concentration, temperature and pH of the solution were kept stable at 100 mg/L, 30^{o}C and 1.5 respectively during the experiment under the constant stirring speed (800 rpm). The results are depicted in Fig. 2.7. It is clearly seen from the plot linking contact time versus percentage adsorption that the rate was rapid for the first 30 min followed by slower rate. Out of total adsorption, 70% has been reached during the faster phase. The reason for faster rate at beginning is due to more free surface area. When the free surface is congested, the adsorbate molecules come into the pores which are called as intra-particle diffusion and get adsorbed inside the pores. At later stage, slower rate was shown by intra-particle diffusion (Matheickal & Yu, 1996). Equilibrium is achieved within 10 h in this process and further than that, there was not much alteration in concentration. So, the remaining studies were carried out for 10 h.

2.3.3 Effects of pH on Cr(VI) adsorption

pH plays a vital role in the adsorption process (Park et al, 2004; Karthikeyen et al, 2005). In general Chromium exhibits three oxidation states (2^+, 3^+ and 6^+) out of which Cr^{2+} is not stable and its hydrolysis is less significant in research. The hydrolysis of Cr(VI) predominantly produces only anionic species like $HCrO_4^-$, $CrO_4^-$and $Cr_2O_7^{2-}$ which are pH sensitive. CrO_4^-will generally be the dominating species when pH is more than 6.5. and while in pH range of 1 - 6, $Cr_2O_7^{2-}$ is dominates. If pH <1(high acidic conditions), it is changed to chromic acid ($H_2Cr_2O_7$). As the current studies were in the pH range 1.8–3.0, we can assume all the Chromium in the form of $Cr_2O_7^{2-}$. Sequentially to observe the consequences of pH on the removal of Cr(VI) and uptake capacity, the experiments were considered by varying pH between 1.0 and 3. The results were revealed in Fig.2.8. It is clear, that the maximum adsorption takes place at pH of 1.0 and the sorption capacity increases with decrease in the pH. The percentage of adsorption increases from 4 to 95.5 with decreasing pH of solution from 3 to 1 respectively. Further the final pH of the Cr(VI) solution increases after the adsorption.

There is considerable debate on the mechanism of Cr(VI) adsorption onto the surface of the bio-adsorbent. In literature, different adsorption mechanism such as cation or anion exchange, complexation, chemisorption, surface adsorption, adsorption with reduction and adsorption–complexation have been reported by different researchers. Views vary as to how complexation emerges among adsorbent and Chromium ions. It was reported in many bio-sorption that, a strong type of adsorption called chemisorption in which ions are not exchanged but electrons may be exchanged. (Lazaridis et al, 2003). The consequence of pH on Cr(VI) adsorption can be well elucidated by considering diverse mechanisms like electrostatic forces, cation and anion exchange, and chemical reaction. Electrostatic forces either attraction or repulsion among adsorbent and adsorbate is the most common mechanisms proposed in the literature. It is widely claimed in literature that the removal of Chromium is through a mechanism, where the negatively charged

Cr(VI) ions were combine to the cationic groups of bio-adsorbent (Park et al, 2004). The following two mechanisms are proposed for the removal of Cr(VI) by bio-adsorbent:

I. Direct reduction (Fig. 2.9) (Park et al, 2005) where Chromium ions simply reduced to Cr(III) in the aqueous phase by combining with the groups having lower reduction potential (electron donor) compare to that of Cr(VI).
II. Indirect reduction mechanisms as shown in (Fig. 2.10).

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The indirect reduction mechanism contains three steps: first binding of negatively charged Cr(VI) species to the cationic groups of the biomass, followed by reduction of Cr(VI) to Cr(III) and finally desorption of Cr(III) ions into the solution due to repulsive force from the cationic groups, or forming complication of Cr(III) with adjacent groups which are capable of binding (Park et al, 2005). Cr(III) concentration in the solution has to increase with time, in case of direct reduction mechanism. To confirm the direct reduction mechanism, difference of Concentration of Cr(III) at initial and final Cr(II) in the solution were assessed using an Atomic Absorption Spectrometer (AAS) and the results found that concentration remains same. Because of this, it is concluded that direct reduction is not the factual mechanism for the adsorption process. Further amine and electron donor groups are capable of affecting indirect reduction. At low pH a huge number of H^+ ions can easily synchronize with the hydroxyl, amino, CN etc. available on the surface of biosorbent. This is also quite evident from the fact that the final pH after adsorption is higher than the initial pH of the solution. The proposed mechanism of Cr(VI) on the prorogated amine groups of the adsorbent is shown in Fig. 2.10 (Bodu et al, 2003). Hence, biosorbent surface become more positively charged at low pH which enhances the Cr(VI) removal rate from the solution, because the binding of negatively charged Cr(VI) ions to the positively charged groups is enhanced (Park et al 2005). The reduction reaction is also faster at lower pH, because the protons also play a part in this reaction. Therefore, the solution pH is the main influential parameter in the practical use of the adsorbent in the adsorption process (Nuhoglu & Oguz, 2003). In addition, if the biosorbent or protons in the aqueous phase has got less number of electrons donor groups, bounded chromium can be in the form hexavalent state. Thus, the mechanism of adsorption highly depends on the adsorption process parameters like solution pH, dose, Chromium concentration and temperature (Park et al, 2005).

2.3.4 Effect of Adsorbent dose

Adsorption experiments were performed to find the outcome of the adsorbent dosage on the removal of Cr(VI). The consequence of the adsorbent dose on the percentage adsorption of Cr(VI) is shown in Fig. 2.11. The percentage of adsorption rise from 25 to 100 with the increase in adsorbent dose from 1.0 to 10 g/L respectively. When the adsorbent dose is increased, because of that more available sites in the adsorbent there will be increase in percentage of adsorption. On the other hand, Cr(VI) uptake of the adsorbent decreased from 25.6 to 10 mg/g with increase in adsorbent dose from 1 to 10 g/L. Further, it was seen that the percentage of adsorption increases rapidly with the increase in adsorbent dose up to 3.0 g/L, and thereafter attain an asymptotic value for larger doses of adsorbent. The sluggish nature of the percentage adsorption beyond an optimum dosage may be described to the accomplishment of equilibrium between adsorbate and adsorbent under the experimental conditions. This is due to cause of overcrowding of particles called “solid concentration effect” (Mehrotra et al, 1999).

2.3.5 Effects of Initial adsorbate concentration

Measurement of the effect of the initial adsorbate concentration on the adsorption of Cr(VI) on adsorbent was carried out by varying the initial Cr(VI) concentration and the results were shown in Fig 2.12. It was seen that when increasing adsorbate concentration, the percentage of adsorption has been decreased. This may be due to the fact for the fixed adsorbent dose, the number of available active sites for the adsorbate ions increase with higher initial concentration. So, the loading is quicker with higher concentration of adsorbate (Zhang et al, 2010). Further, at high initial adsorbate concentration (at 200 ppm) the driving force is adequate to overcome various mass transfer resistances of the metal ions from the aqueous to the solid phase ensuing in higher probability of collision between Cr(VI) ions and the active sites. Thus, the Cr(VI) uptake of the adsorbent increased for the given amount of adsorbent.

2.3.6 Effects of particle size on Cr(VI) adsorption

The particle size of the adsorbent was varied from 36 BSS to 150 BSS to evaluate the effect of particle size on percentage Cr(VI) adsorption and uptake capacity. The results are shown in Fig. 2.13. The percentage of adsorption increased from 66.13 to 92.31 when the particle size decreased from 36 BSS to 150 BSS and also the uptake increase from 13.23 to 18.46 mg/g under the same conditions. The increase in percentage adsorption as well as uptake with increase in particle size may be attributed to the increase in specific surface area of the adsorbent. Further, at 50 BSS there is a significant change percentage adsorption which is may be due to the nonlinear changes in the surface area at different particle size.

2.4 Kinetic of adsorption

It is vital to understand the kinetics of adsorption process to estimate the rates at which metal ions adsorb on the adsorbent surface. The kinetics study provides an insight into the possible adsorption mechanism by which the adsorbate gathered on the surface of a solid and gets adsorbed to the surface. It is also important to find the adsorption rate for a given system in order to design the continuous column. The adsorption process generally follows four diffusive processes.

- Bulk diffusion
- Film diffusion.
- Surface diffusion
- Intra-particle diffusion

In kinetic modelling, last three steps are grouped together and it is presumed that the difference of average solid phase concentration with equilibrium concentration is the main driving force for adsorption. In addition, it is observed that the external boundary hardly had any effect under the optimum agitation speed. So, it depends mainly on the initial and final concentration at dynamic interval. Sequentially to examine the mechanism of adsorption, different kinetic models have been suggested. Various kinetic models have described the reaction order of adsorption systems based on solution concentration (Febrianto et al, 2009).

2.4.1. Lagergren' spseudo first-ordermodel

The Lagergren equation is possibly the earliest known rate law describing the rate of adsorption in the liquid-phase systems. This model describes liquid-solid phase adsorption systems and is derived based on the adsorption capacity of the adsorbent. This equation (Lagergren & Zur, 1898) has been widely used for the adsorption in liquid and solid phase particularly for sorption of a solute from a liquid solution. According to Lagergren, the overall rate of uptake capacity is directly proportional to the difference in equilibrium uptake and uptake at any time. So, the kinetic equation expressed as follows:

$$\frac{dq}{dt} = k\,(q_e - q) \tag{2.3}$$

Where $q_e$is the uptake at equilibrium, q is uptake at any time t, k is the rate constant. Equation (2.3) integrated with boundary condition resulted in the following equation:

$$\log(q_e - q) = \log q_e - \frac{k}{2.303} t \tag{2.4}$$

The values of 'k' were interpreted from the slope of the graph between $\log(q_e - q)$ and 't' for different adsorption parameters under the experiments has been studied. The correlation coefficients and rate constants are given in Table 2.2. The correlation coefficients were in acquiescence with the pseudo first-order kinetics.

2.4.2. Ritchie's second order model

Ritchie reported model for the adsorption of gases and liquid systems. Considering that the rate of adsorption depends exclusively on the fraction of sites which are empty at time t, then

$$\frac{d\theta}{dt} = k\,(1 - \theta)^n \tag{2.5}$$

Where, θ is fraction of surface occupied, k is the rate constant, n is the number of surface sites occupied and t is the time (in minutes). After integrating with Boundary condition and introducing the uptake capacity (mg of adsorbate/g of adsorbent), the equation (2.5) becomes

$$\frac{q_e}{q_e - q_t} = 1 + kt \tag{2.6}$$

Where q_e is the uptake capacity at equilibrium, q_t is the uptake capacity at any time t. The above equation was fitted to the investigational dataand model parameters were calculated along with the R^2 values. The evaluated value of the kinetic model parameters has been presented with correlation coefficient R^2 in Table 2.2.

2.4.3. First Order Reversible model

The following bio-sorption reaction mechanism assumed that, Chromium adsorption follows the first order reversible reaction, which gives as

$$A \leftrightarrow B$$

In turn, the rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_1C_A - k_2C_B = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{B0} - C_{A0}) \tag{2.7}$$

Solving the above equation with Boundary condition yields,

$$\ln(1 - U_t) = -(k_1 + k_2)t \tag{2.8}$$

Where $U_t = \frac{(C_{A0} - C_A)}{(C_{A0} - C_{Ae})}$

and C_A is concentration of the adsorbate in solution (mg/L), C_{AO} is initial concentration of the adsorbate, and C_{Ae} is concentration of the adsorbate in the solution at equilibrium condition. Model parameters and R^2 values are calculated from the graph between ln (1-U_t) vs t and shown in Table 2.2.

2.4.4. Pseudo second order model

The pseudo second order kinetics is usually associated with the situation where the rate of uptake capacity depends on the square of the driving force, that is nothing but the accessible fraction of the active sites. The rate of reaction depends on the quantity of metal ions on the surface of the adsorbent and the quantity of metal ions adsorbed at equilibrium. The rate expression for the adsorption is illustrated as (Ho, 2006):

$$\frac{dq}{dt} = k[q_e - q]^2 \tag{2.9}$$

Where q_e is the quantity of Cr(VI) ions adsorbed at equilibrium, q is the amount of Cr(VI) ions adsorbed at any time t and k is the rate constant.

Integrating the equation (2.9) with boundary condition t=0 to t=t and q=0 to q=q

$$\frac{t}{q} = \frac{1}{k_2{q_e}^2} - \frac{t}{q_e} \tag{2.10}$$

The values of model parameters along with R^2 are calculated from the plot between t/q vs t/qe and is reported in Table 2.2. From the R^2 values in the table shows and confirming that the adsorption process is pseudo second order kinetics (R^2= 0.999).

2.5. Rate controlling mechanism

On porous adsorbents, the adsorption of Cr(VI) is governed by four steps in series. The four steps are bulk diffusion in solution followed by film diffusion, surface diffusion and intra-particle diffusion. Either of the above individual steps or combinations of the steps may control the rate. In case of low stirring speed, the mixing is poor and hence external transport, i.e., bulk diffusion and film diffusion can be the rate limiting steps. In the current adsorption process, the adsorbent used is porous in nature and therefore pore diffusion is also anticipated additionally to surface diffusion. The time variation experimental data can be used to find out the rate limiting step in the sorption procedure (Baral et al, 2009). In order to minimise the resistance to external transport, batch adsorption is carried out at higher agitation speeds. At higher stirring speeds, the resistance to the external transport reduces significantly due to reduction in thickness of the film adjoining the adsorbent. Thus, at this stirring speed, it can be safely assumed that external transport isn’t the rate limiting step. Therefore, either intra-particle or surface diffusion is the rate-determining step. As they happen simultaneously, among the two transport processes, the slower one will be the rate limiting step. The intra-particle diffusion model can be interpreted (Baral et al, 2009) as follows:

$$q_t = k_{id} t^{1/2} \tag{2.11}$$

where q_t= mg of adsorbate adsorbed per gram of adsorbent (mg/g), t = time of contact (min) and k_{id} = coefficient for intra-particle diffusion (mg/g min$^{1/2}$). Linear plots are drawn between q_t versus $t^{1/2}$ and the k_{id} values are determined from the slope. Outcome of various experiments are given in Table 2.3. The R^2 values in the table specify that, intra-particle diffusion is the rate determining steps for the adsorption process. Further analysis of data shows non-linear behaviour of time versus percentage adsorption plot for different sorption parameters. Therefore, it is assumed that numerous steps may well influence the Cr(VI) sorption process. So, the entire sorption process is occurring in two different steps: the early curved portion is the surface diffusion and the latter linear portion is the intra-particle diffusion. With the assumption that adsorbent particles are spherical in geometry the following equations can be used for surface and intra-particle diffusion:

$$\frac{q_t}{q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{1/2} t^{1/2} \qquad (2.12)$$

$$ln\left(1 - \frac{q_t}{q_e}\right) = ln\left(\frac{6}{\pi^2}\right) - \left(\frac{D_2\pi^2 t}{a^2}\right) \qquad (2.13)$$

For equation 2.13, a plot between q_t/q_e and $t^{1/2}$ is drawn for the initial curved portion. The values of diffusivity for surface diffusion 'D_1' and regression coefficient R^2 at different sorption parameter are calculated from the slope of the curve and are shown in Table 2.3. In order to calculate, 'D_2' values, plots were drawn between $\ln(1-q_t/q_e)$ and 't' under diverse adsorption parameters. The values of D_2 were calculated from the slope of the curve and are given in Table 2.3, which showed D_2 is always greater than that of the D_1. Therefore, surface diffusion is the slowest steps and hence is the rate limiting steps.

2.6. Equilibrium Adsorption Isotherm

The equilibrium partition between the two phases is an important criterion to be considered for the successful representation of the dynamic adsorptive separation of the solute from solution into an adsorbent (Akkaya & Ozer, 2005). An adsorption isotherm plays a major role, which relates the surface properties and resemblance of the adsorbent to compare various pollutants uptake capacity (Dursun et al, 2005). Sequentially to find out the mechanism of Cr(VI) adsorption by the grass and determine the relationship the experimental data were applied to different isotherm equations.

2.6.1. Freundlich isotherm model

Freundlich isotherm which relates the uptake capacity with equilibrium concentration widely used isotherms for including bio-sorbents. This equation is outlined below

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (2.14)$$

where, K_F and $1/n$ are the Freundlich constants. The q_e (mg/g) is the uptake capacity and C_e (mg/L) is the adsorbate concentration in solution at equilibrium correspondingly. The values of Freundlich constants are calculated from the graph between $\log q_e$ vs. $\log C_e$

and are shown in Table 2.4. From the table values it clear that it is not following the Frendlich Isotherm model.

2.6.2. Langmuir isotherm model

The equilibrium relationship between a bulk liquid phase and coverage of molecules on a solid phase at a fixed temperature was given by Langmuir isotherm (Davis et al, 2003). There are three important assumptions on the basis of which the Langmuir adsorption was derived. The assumptions are:

- On the adsorbent surface, only monolayer is possible.
- All surface sites are same in physical nature.
- The adsorption of a molecule on a given site is not dependent on its adjacent sites occupancy.

Based on the above assumptions, the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \qquad (2.15)$$

Where, C_e and q_e are the concentration(mg/L), uptake capacity (mg/g) at equilibrium. Q_0 and K are related to uptake capacity and energy of adsorption and are the Langmuir constants. The model parameters along with the regression coefficients are calculated from the plot between C_e/q_e vs C_e and are shown in Table 2.4. From the table it is observed that experimental data follows the Langmuir isotherm model, as the R^2 values are close to 1. 0.

2.6.3. Temkin Isotherm

Temkin Isotherm is derived based on the assumption that the heat of adsorption decreases linearly. The equation for Temkin isotherm model is given by:

$$q_e = \frac{RT}{b} \, lnA + \frac{RT}{B} \ln C_e \qquad (2.16)$$

$$q_e = B \, ln \, A \, + \, B \, ln \, C_e \qquad (2.17)$$

Where, q_e is the uptake capacity in mg/g, Ce is the equilibrium adsorbate concentration in mg/L and B= RT/b. in the model equation T (K) is the absolute temperature and R is the universal gas constant. The constant b is related to the heat of Cr(VI) adsorption

(Pearse et al, 2003). From the Table 2.4 it is evident that our experiment does not fall on the Temkin isotherm because of low values of regression coefficients.

2.7. Conclusions

In the present study a novel, low cost, easily accessible and ecofriendly adsorbent i.e. *Sorghastrum NutansL. Nash* is used for the treatment of Cr(VI) contaminated wastewater. The adsorbent is characterized by using XRD, FTIR, SEM and EDAX analysis. Among different functional groups present in the adsorbent, OH bending, CN stretching/bending and NH stretching plays a foremost role in Cr(VI) adsorption on the adsorbent. The mechanism of adsorption is found to be indirect reduction. outcome of various adsorption parameters like time, pH, concentration and doses on the uptake capacity of the sorbent is premeditated. Experimental data followed the pseudo second order reaction and Langmuir isotherm and surface dispersal was found as the rate controlling step.

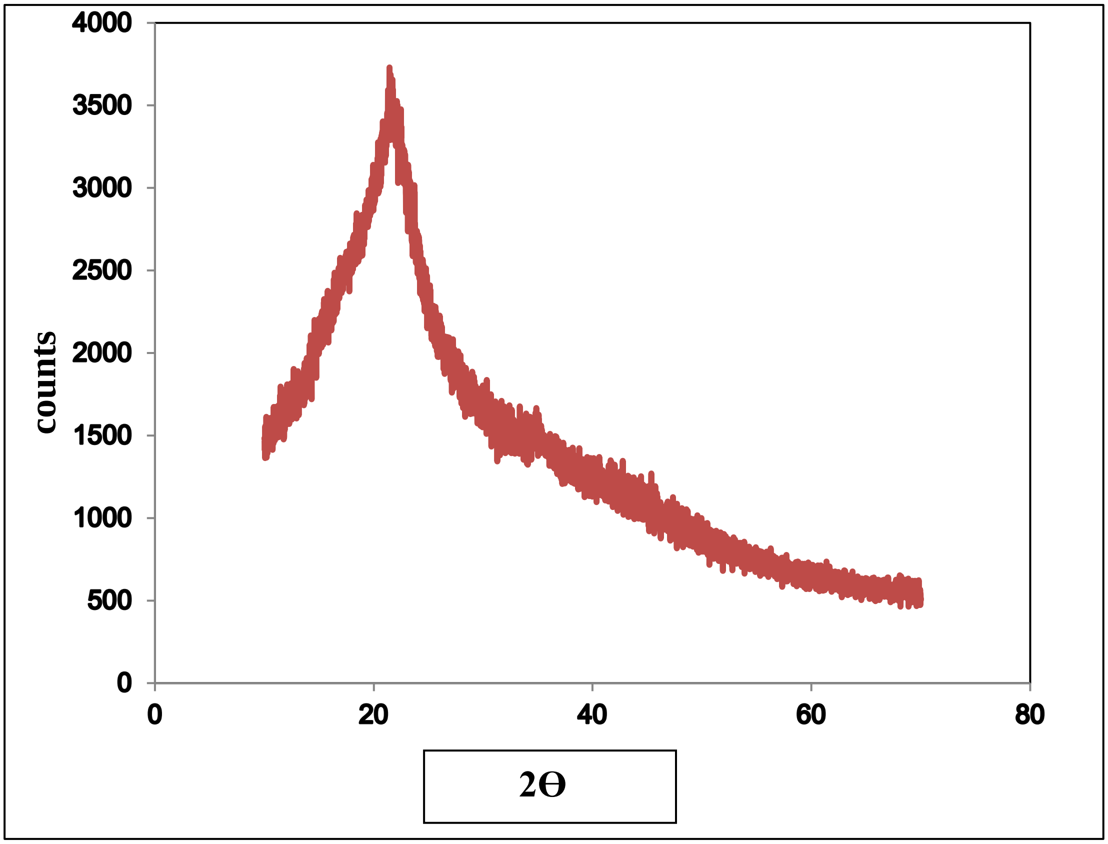


Fig. 2.1: XRD analysis of adsorbent after adsorption and before adsorption

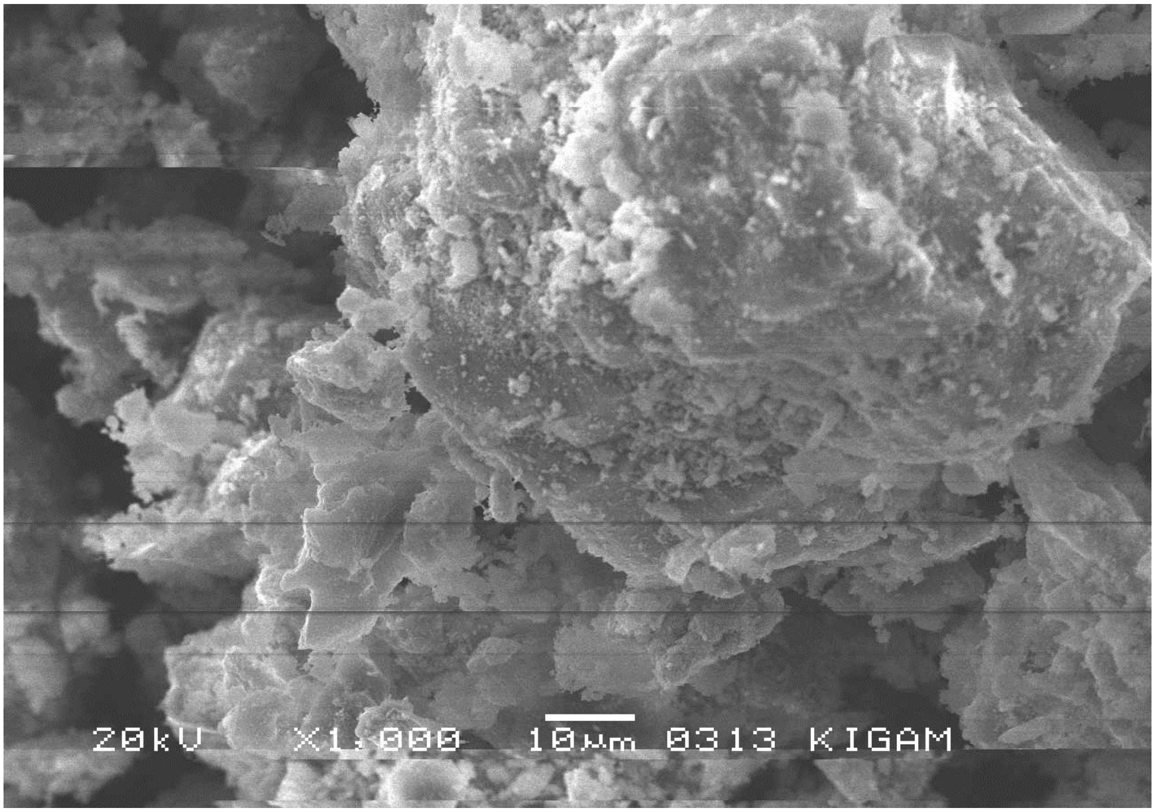


Fig. 2.2: SEM image of adsorbent before adsorption.

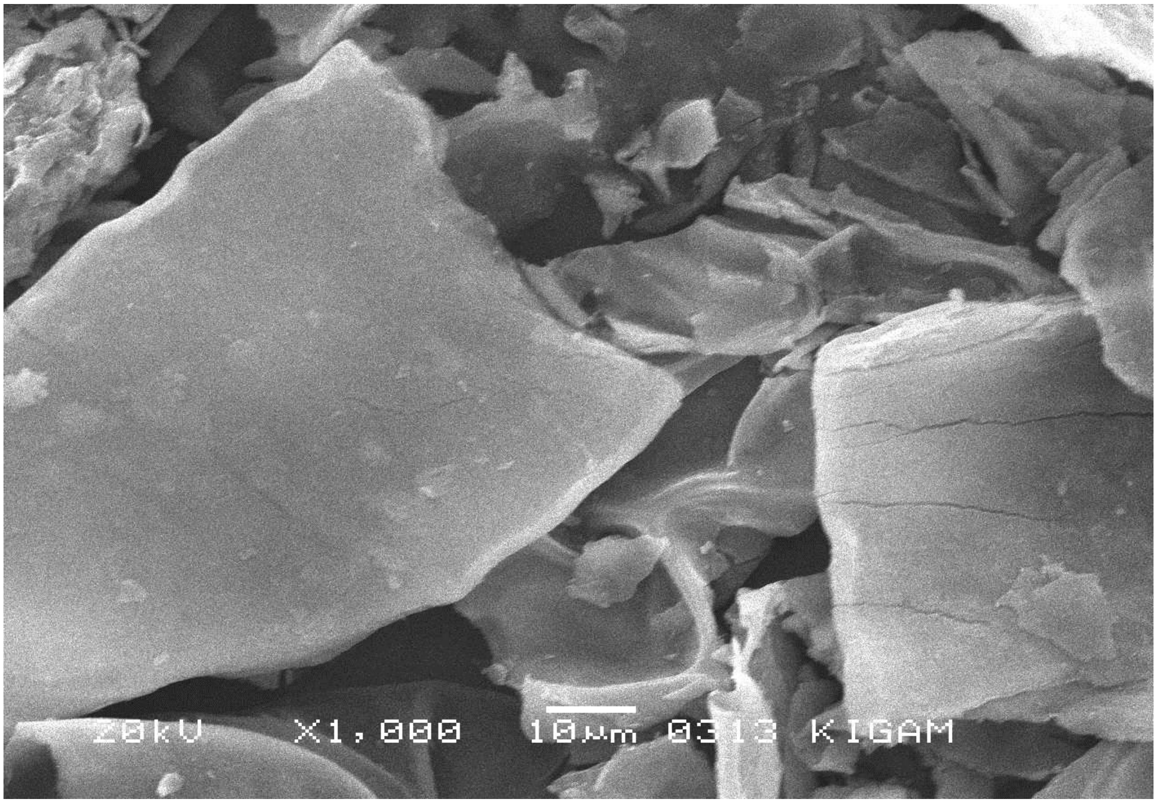


Fig. 2.3: SEM image of adsorbent after adsorption.

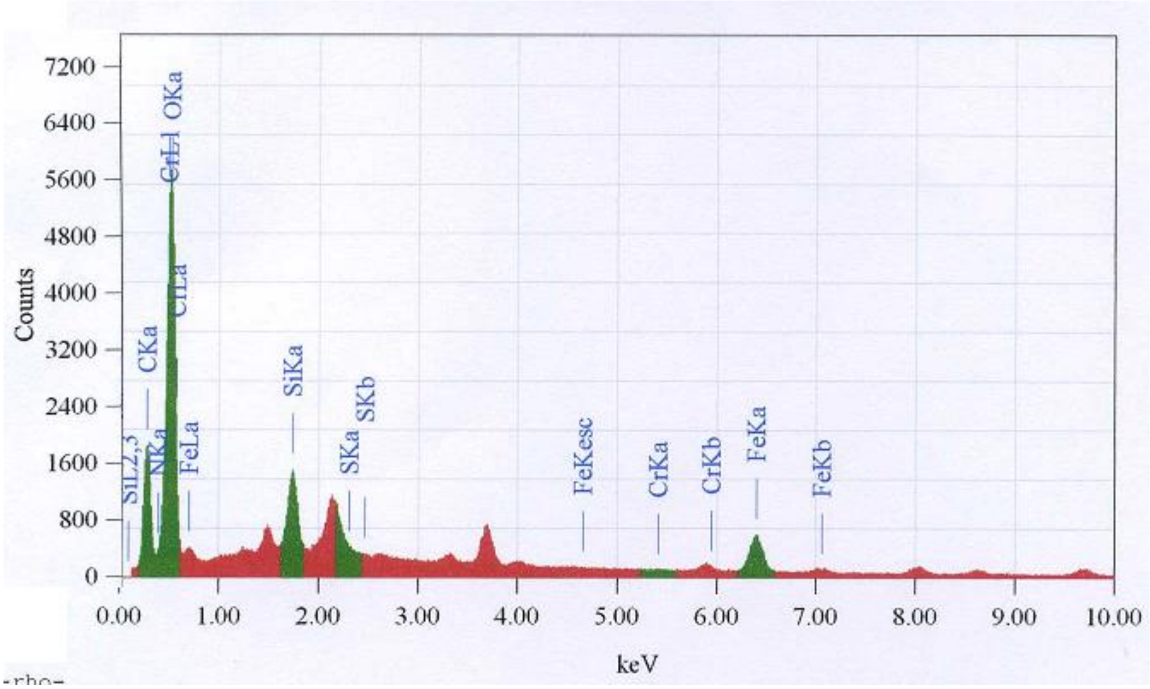
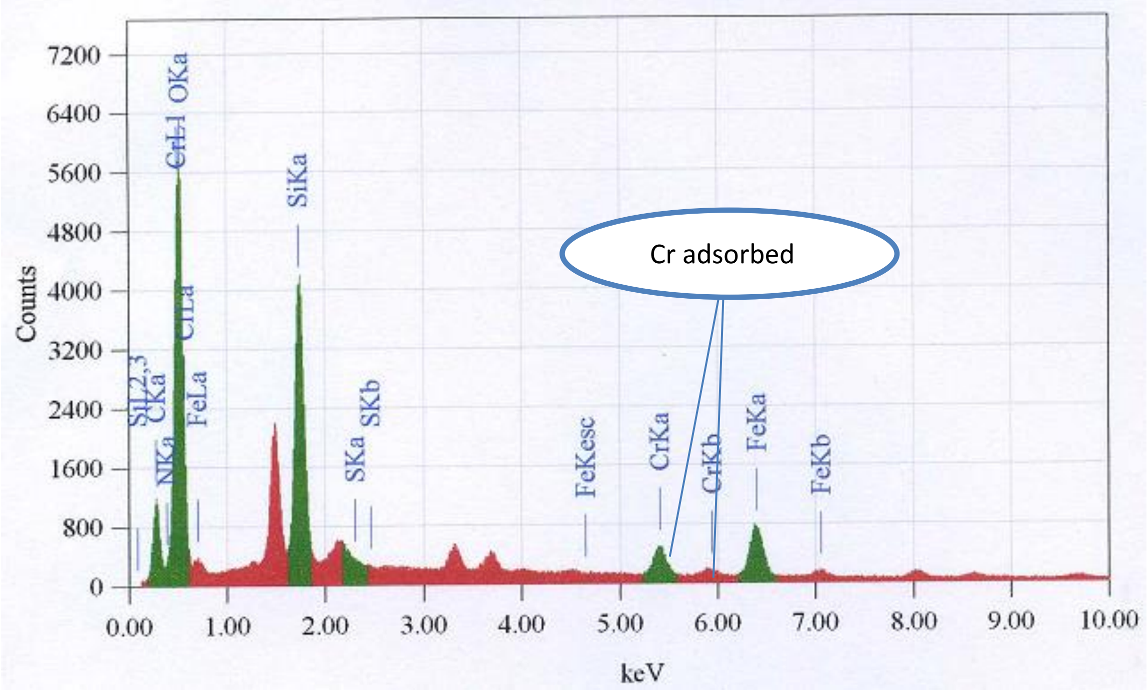


Fig. 2.4: EDAX image of adsorbent before adsorption.



Cr adsorbed

Fig. 2.5: EDAX image of adsorbent after adsorption

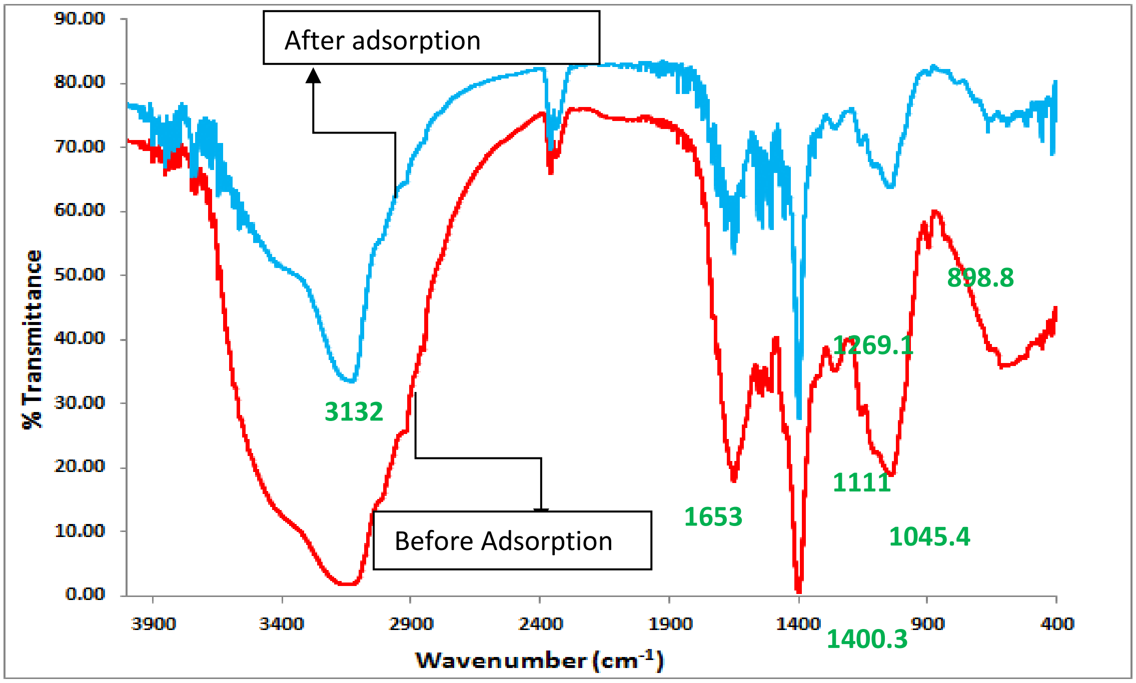


Fig. 2.6: FTIR analysis of the adsorbent before and after Cr(VI) adsorption

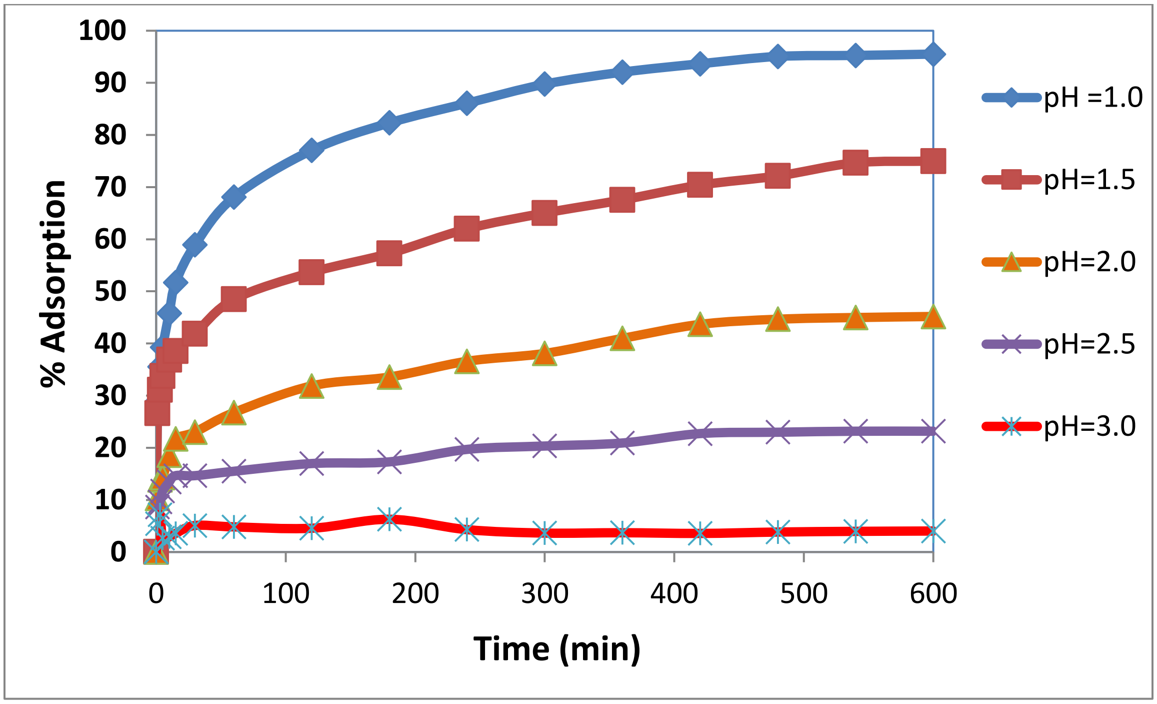


Fig. 2.7: Effect of contact time on percentage Cr(VI) adsorption. Condition: Concentration:100 ppm, dose: 5 g/L, Temp:30^{o}C

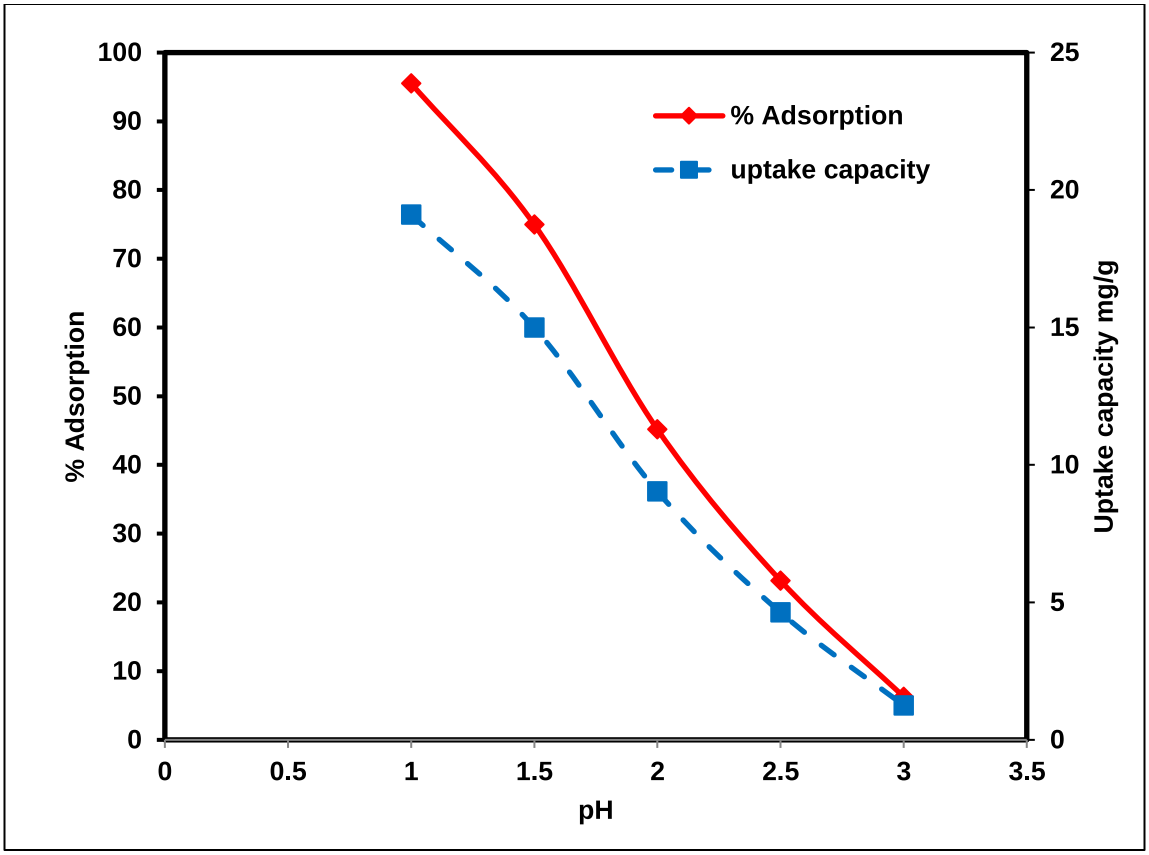


Fig. 2.8: Effects of pH on percentage Cr(VI) adsorption and uptake capacity. Condition. Concentration: 100 ppm, dose: 5g/L, Temp:30ºC

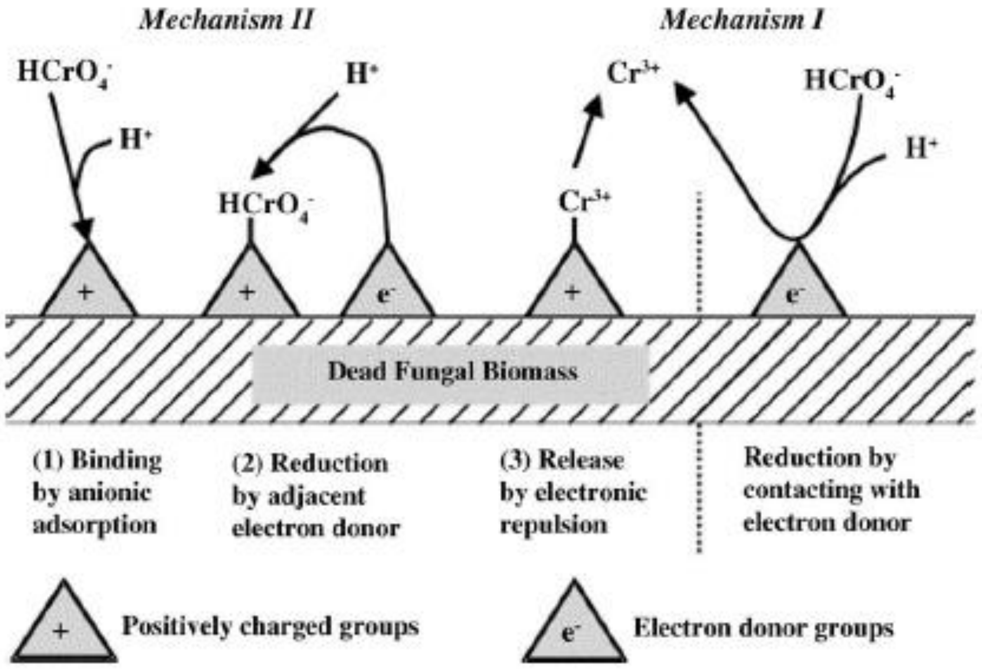


Fig. 2.9: Mechanism for Cr(VI) removal by the biomass. *Source*: Park et al. 2005

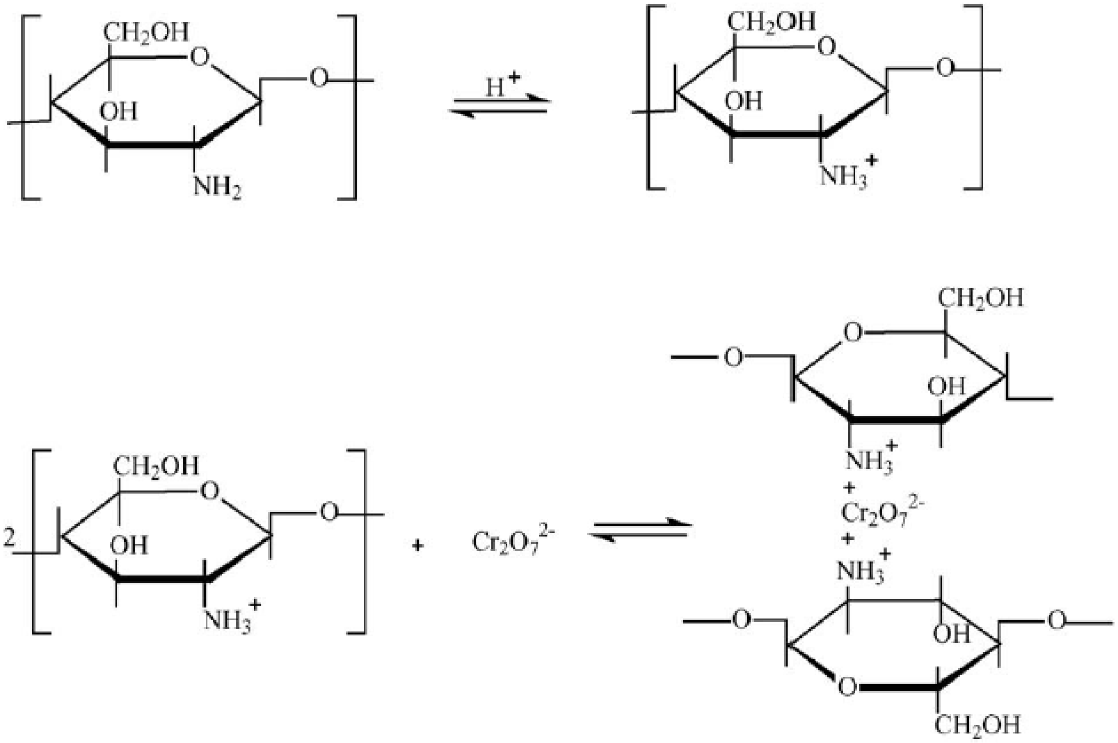


Fig. 2.10: Mechanism of Cr(VI) adsorption on grass. Source: (Boddu et al. 2003)

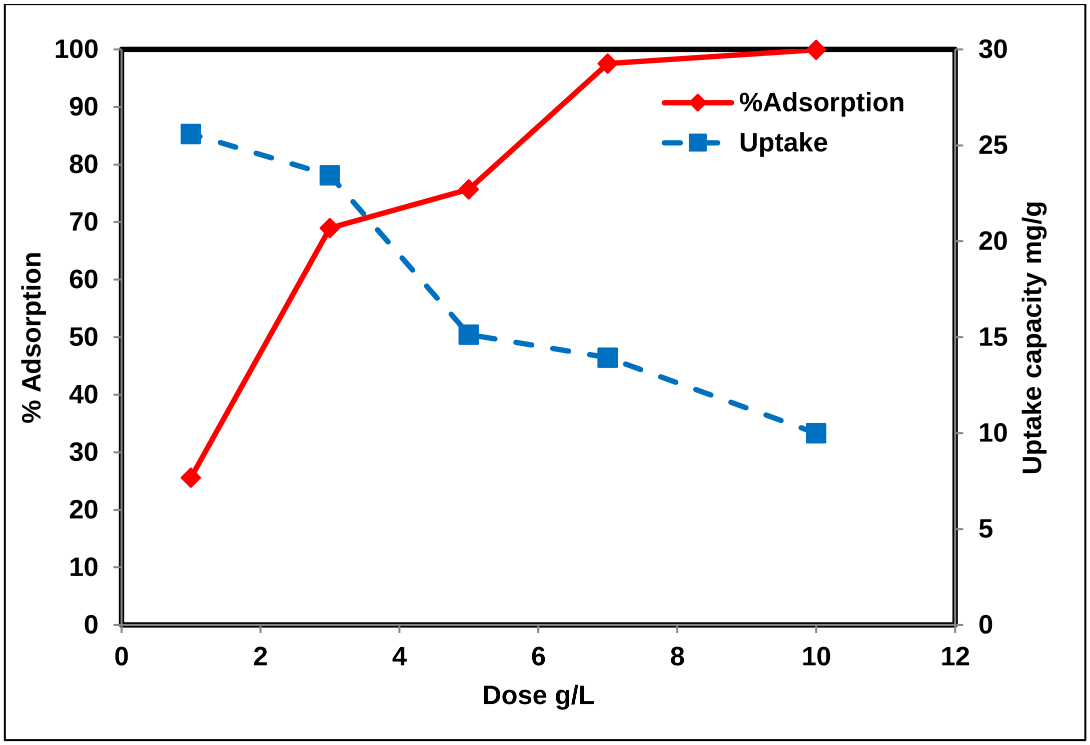


Fig. 2.11: Effect of adsorbent dose on the percentage Cr(VI) adsorption and uptake capacity. Condition: Concentration:100 ppm, pH: 1.5, Temp:30°C, Size :72 BSS

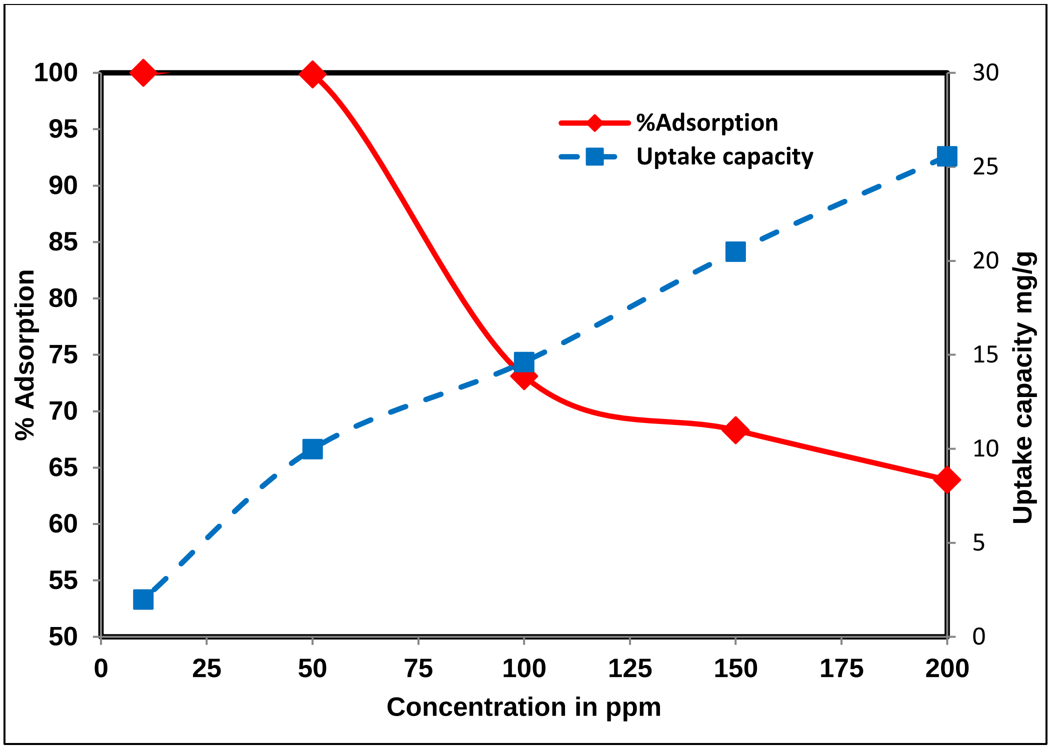


Fig. 2.12: Effect of initial adsorbate concentration on the percentage of Cr(VI) concentration and uptake capacity. pH: 1.5, Dose:5 g/L, Size: 72 BSS, Temp:30^{o}C

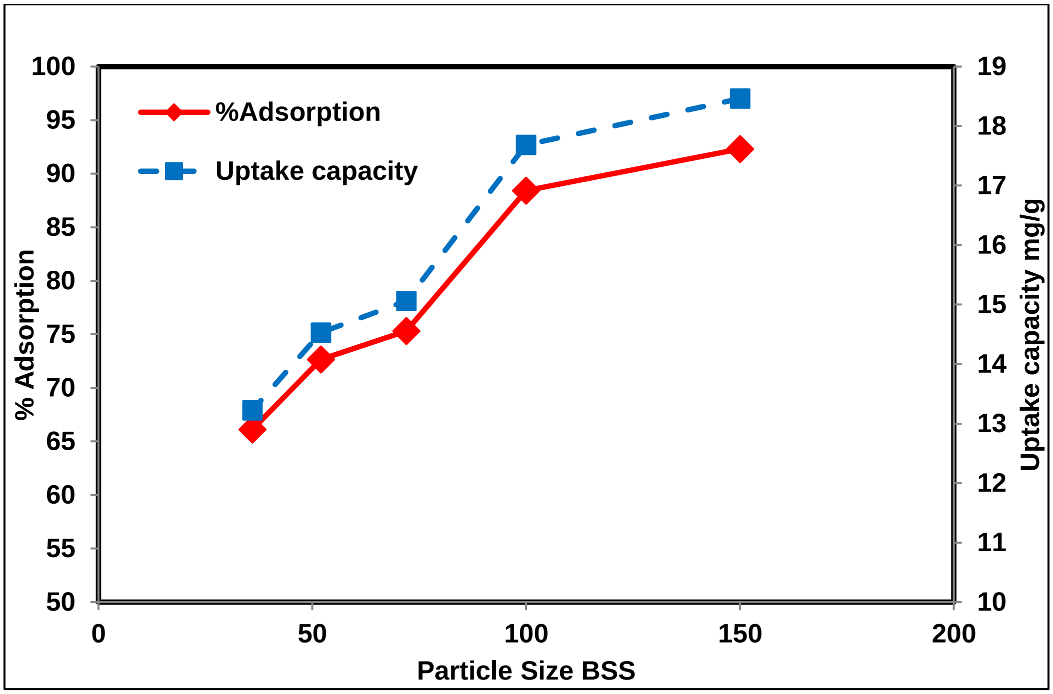


Fig. 2.13: Effect particle size on percentage Cr(VI) adsorption and uptake capacity. Condition: pH:1.5, Concentration:100 ppm, dose:5 g/L, Temp:30^{o}C

Table 2.1: FTIR Spectrum Analysis of the adsorbent before and after adsorption

IR peak number	Adsorption band			% Transmittance			Group Assigned
	Before	After	Diff.	After	Before	Diff.	
3132				33.35	1.69	31.66	Hydroxyl stretching vibrations and hydrogen bonding of celloligo-saccharides and their degradation products.
1653				53.67	17.80	35.87	C=N Vibration mode
1400	1400.32	1398.39	1.93	27.91	0.58	27.33	NH Stretching and bending vibration of N=O group
1269	1261.45	1269.16	7.71	73.05	35.07	37.98	CN stretching and CN vibration
1111	1107.14	1111	3.86	67.01	22.17	44.84	CN Stretching
1045	1041.56	1045.42	3.86	63.67	18.91	44.76	OH bending
898	896.83	898.83	2.0	81.24	54.26	26.98	C-O-C stretching and CH deformation

Table 2.2: Adsorption Kinetic models parameters

Parameter	**Values**	**Pseudo 1st order**		**Richie's 2nd order**		**Pseudo 2nd order**		**First order reversible**		
		k	**R^2**	**k**	**R^2**	**k**	**R^2**	**k1**	**k2**	**R^2**
Adsorbent dose (g/L)	1	0.221	0.723	0.078	0.365	0.0008	0.97	0.043	0.124	0.669
	3	0.306	0.904	0.137	0.562	0.0017	0.995	0.103	0.133	0.844
	5	0.226	0.91	0.056	0.647	0.0030	0.994	0.075	0.129	0.897
	7	0.336	0.811	0.542	0.321	0.0044	0.997	0.229	0.042	0.774
	10	0.410	0.865	0.408	0.65	0.0060	0.999	0.351	0.002	0.843
Particle mesh size (BSS)	36	0.237	0.84	0.076	0.475	0.0027	0.987	0.054	0.143	0.807
	52	0.274	0.86	0.122	0.533	0.0030	0.993	0.077	0.149	0.829
	72	0.246	0.831	0.101	0.444	0.0029	0.991	0.078	0.133	0.809
	100	0.306	0.895	0.195	0.633	0.0040	0.997	0.158	0.113	0.879
	150	0.292	0.896	0.193	0.605	0.0047	0.998	0.187	0.090	0.893
pH	1	0.375	0.886	0.409	0.565	0.0032	0.997	0.008	0.002	0.934
	1.5	0.267	0.781	0.182	0.358	0.0028	0.991	0.003	0.004	0.821
	2	0.318	0.813	0.221	0.497	0.0039	0.989	0.001	0.007	0.909
	2.5	0.269	0.771	0.139	0.538	0.0103	0.991	0.000	0.007	0.780
Initial Concentration (ppm)	50	0.470	0.771	0.921	0.736	0.0348	0.999	0.042	0.001	0.661
	100	0.258	0.907	0.078	0.785	0.0034	0.992	0.002	0.001	0.772
	150	0.302	0.904	0.9	0.679	0.0022	0.988	0.004	0.007	0.819
	200	0.276	0.939	0.067	0.915	0.0013	0.984	0.005	0.008	0.843

Table 2.3: Mass Transfer Model parameters

Parameter	**Values**	**q_t vs $t^{1/2}$**		**q_t/q_e vs $t^{1/2}$**		**$\ln(1-(q_t/q_e))$ vs t**	
		k_{id} mg/g $min^{(1/2)}$	**R^2**	**D_1 mm^2/time 10^{-5}**	**R^2**	**D_2 mm^2/time 10^{-3}**	**R^2**
Adsorbent dose (g/L)	1	1.481	0.973	0.544	0.869	1.61	0.946
	3	1.483	0.977	0.913	0.984	3.47	0.985
	5	0.707	0.97	0.52	0.971	3.48	0.933
	7	0.653	0.947	1.012	0.989	3.93	0.984
	10	0.368	0.903	1.046	0.992	3.48	0.953
Particle mesh size (BSS)	36	0.672	0.986	0.639	0.979	3.29	0.989
	52	0.708	0.976	0.819	0.988	4.10	0.944
	72	0.701	0.983	0.52	0.971	3.26	0.980
	100	0.708	0.954	0.496	0.982	3.89	0.975
	150	0.63	0.958	0.385	0.985	3.44	0.994

Parameter	**Values**	**q_t vs $t^{1/2}$**		**q_t/q_e vs $t^{1/2}$**		**$\ln(1-(q_t/q_e))$ vs t**	
		k_{id} mg/g min$^{(1/2)}$	**R^2**	**D_1 mm^2/time 10^{-5}**	**R^2**	**D_2 mm^2/time 10^{-3}**	**R^2**
pH	1	0.975	0.932	1.224	0.988	4.68	0.985
	1.5	0.699	0.982	0.52	0.971	3.41	0.976
	2	0.508	0.976	0.978	0.981	2.87	0.949
	2.5	0.202	0.974	0.731	0.939	2.81	0.952
Initial Concentration (ppm)	50	0.295	0.765	1.187	0.98	4.16	1.000
	100	0.681	0.975	0.544	0.971	5.29	0.918
	150	1.329	0.944	1.299	0.943	7	0.954
	200	1.825	0.967	1.843	0.996	7.23	0.925

Table 2.4: Equilibrium Adsorption Isotherm models parameters

Parameter	**Values**	**Freundlich Isotherm**			**Langmuir Isotherm**		**Temkin Isotherm**	
		Slope 1/n	**log K_f**	**R^2**	**$1/q_{max}$**	**R^2**	**RT/b**	**R^2**
Adsorbent dose (g/L)	1	0.049	0.723	0.924	0.039	1.0	-5.011	0.746
	3	0.047	0.772	0.906	0.042	1.0	-4.058	0.799
	5	0.032	0.737	0.954	0.066	1.0	-2.432	0.789
	7	0.030	0.754	0.917	0.071	1.0	-1.478	0.668
	10	0.032	0.676	0.955	0.100	1.0	-1.107	0.772
Particle mesh size (BSS)	36	0.037	0.606	0.965	0.075	1.0	0.997	0.748
	52	0.035	0.699	0.944	0.068	1.0	1.146	0.607
	72	0.032	0.735	0.967	0.066	1.0	1.17	0.510
	100	0.025	0.914	0.947	0.056	1.0	1.481	0.220
	150	0.02	0.995	0.950	0.054	1.0	1.576	0.136

Parameter	**Values**	**Freundlich Isotherm**			**Langmuir Isotherm**		**Temkin Isotherm**	
		Slope 1/n	**log K_f**	**R^2**	**$1/q_{max}$**	**R^2**	**RT/b**	**R^2**
pH	1	-0.297	1.467	0.762	0.052	1.0	-2.28	0.726
	1.5	-0.332	1.402	0.820	0.066	1.0	-2.053	0.728
	2	-0.434	0.831	0.855	0.110	1.0	-1.305	0.736
	2.5	-0.430	1.182	0.729	0.215	1.0	-0.626	0.758
Initial Concentration (ppm)	50	-0.296	1.170	0.867	0.10	1.0	-1.049	0.739
	100	-0.274	1.309	0.782	0.066	1.0	-2.071	0.794
	150	-0.427	1.616	0.665	0.048	1.0	-2.966	0.732
	200	-0.636	2.060	0.445	0.025	1.0	-3.924	0.648

Chapter-3

Removal of Cr(VI) from wastewater using *Cocos Nucifera*

3.1 Introduction

In the previous study, *Sorghastrum Nutans L. Nash* is used for the treatment of Cr(VI) contaminated wastewater. From the experiments it was observed that the percentage of Cr(VI) removal at pH 3 was only 4 %. Hence the adsorption capacity of the adsorbent was very low at higher pH. There is a significant increase in percentage adsorption as well as uptake capacity of the adsorbent with decrease in pH. Although the adsorption capacity is significant at lower pH, but adsorption at lower pH will produce acidic effluent which requires acid neutralization steps which may not be economical and environmental friendly. Further, using of inorganic acid for the initial pH adjustment can lead to increase of total solids in the effluent. Therefore, the aim of this study was to explore a new adsorbent which will have high adsorption capacity at higher pH. The present study explored the use of natural, environmental friendly and easily available coconut tree (**Cocos Nucifera**) leaves as an adsorbent to remove the Cr(VI) from wastewater. Batch adsorption experiments were carried out in-order to study the effect of different parameters on adsorption process. The influence of pH, contact time, initial chromium concentration and adsorbent dosage on the removal of Cr(VI) from the solutions has been investigated. The removal efficiency and uptake capacity have been correlated with the initial Cr(VI) concentration, adsorbent dosage as well as the contact time.

3.2 Materials

The adsorbent used in this study is a Coconut leaf which grows in most of the coastal part of India. The leaves collected from the campus was washed with water thrice to remove the adherent substance and kept for drying. In order to remove the remaining moisture after sun drying, the leaves were kept in an oven at 80^0C for 24 hours. The dried leaves then grounded to powder form and sieved to different size fractions. The sieved powdered samples were kept in airtight container for further use.

3.3 Methods

The preparation of representative samples of different Cr(VI) concentration were done as explained in chapter-2. The pH of the solution was maintained at desired value by adding weak organic acid i.e. acetic acid (instead of strong inorganic acid in the previous studies) before adsorption. All the chemicals used were of analytical reagent grade and were obtained from Merck. Adsorption experiments were conducted at a constant temperature 30^{o}C in 500 ml beaker using 250 ml of Cr(VI) solution. The mixtures were agitated by a magnetic stirrer with speed regulator. 5 ml of samples were collected (by using different tips) at dynamic condition in a regular time interval and it has been analyzed. The mixture was filtered through filter paper. The residual Cr(VI) concentration in the filtrate and uptake was analyzed same as like in the case of grass.

3.4 Results and Discussion

3.4.1 Effect of Contact time

Adsorption experiments were carried out over 600 min to find the equilibrium contact time. During the experiment, the other adsorption parameters such as stirring speed, adsorbate concentration, dose, particle size and temperature of the solution were kept constant 100 ppm, 20g/L, 52 BSS and 30 ^{0}C, respectively. The results are shown in Fig 3.1. It can be seen from the figure that the kinetics was very fast during the first 30 min followed by a slower kinetics. During the faster phase, 80% of the total adsorption was reached. The adsorption process attained equilibrium within 6 h and beyond that there was hardly any change in concentration. The initial faster rate may be due to the higher free surface available initially (Prasad, 2013). Once the available free surface is clogged, then the adsorbate molecules penetrate through the pores and get adsorbed inside the pore, which is known as intra-particle diffusion. The intra-particle diffusion accounts for the slower kinetics at the later stage

3.4.2 Effect of pH

pH is an important parameter affecting the adsorption process. Experiments were carried out by varying pH between 1.0 and 3 to find out its effect on the percentage of adsorption and Cr(VI) uptake capacity of the adsorbent (Huang, 2015; Aliabadi, 2006). The results are shown in Fig.3.2 below. It was observed that the maximum adsorption takes place at pH of 1.0. Sorption capacity also increases with decreasing the pH. The reason for increase in adsorption with increase in pH was elaborated in chapter 2. The percentage adsorption as well as Cr(VI) uptake capacity was maximum at pH 1.0 however, the effluent after adsorption is highly acidic pH of 2.2. Acidic effluent is not environmental friendly and hence required acid neutralization steps. Further, neutralization of effluent can lead to increase in total solid and the may not be cost effective process. Therefore, the rest of the experiments were carried out at pH 3.0.

3.4.3 Effect of dose

The trend of adsorption at varying doses of adsorbent is shown in Fig. 3.3. The percentage of Cr(VI) removal increased from 45 to 100 with increase in adsorbent dose from 1.0 to 10 g/L. The trend was as per expectations since more active sites of adsorbent were exposed when the adsorbent dose increased. However, the Cr(VI) uptake capacity of the adsorbent decreased from 4.4 mg/g to 1 mg/g when the adsorbent increases from 1 g/L to 10 g/L. This is mainly because of the fact that with increase in adsorbent dose the number of active site available for adsorption increases whereas limited number of adsorbate molecule present for the adsorption

3.4.4 Effect of Particle size

The effect of adsorbent particle size was studied under constant initial Cr(VI) concentration, pH, speed, dosage and temperature. Initially the crushed coconut leaves have been screened in BSS (British Standard Screen) sieves with different mesh screen. Experiments were carried out by varying the particle size between 52 BSS to 150 BSS. It was found that initial the percentage adsorption as well as uptake increases with decrease in particle size whereas afterword there is no change in percentage adsorption. This is may be due to the fact that limited number of adsorbate particle present for the large adsorbent surface. Particles size 100– 150 mesh shows in Fig 3.4, the maximum adsorption capacity. The percentage adsorption is increases from 91.9% to 100% with increase in mesh size from 52 BSS to 150 BSS and the Cr(VI) uptake increases from 1.8 mg/g to 2 mg/g.

3.4.5 Effect of Initial Cr(VI) concentration

Assessment of the effect of initial concentration on the adsorption of Cr(VI) on coconut leaves was carried out by varying the initial Cr(VI) concentration from 10 mg/L to 100 mg/L and the results is shown in Fig 3.5. It was observed that the percentage adsorption decreased with the increase of adsorbate concentration whereas uptake capacity increases with increase initial Cr(VI) concentration. The percentage adsorption decreases from 91 % to 40 % with increase in adsorbate concentration from 10 mg/L to 100 mg/L. The uptake capacity of the adsorbent increases from 1.82 mg/g to 8 mg/g with increase in adsorbate concentration from 10 mg/L to 100 mg/L. This is fact that at fixed adsorbent dose, the number of active sites to accommodate the adsorbate ions increases with higher initial concentration. So the loading is faster with higher concentration of adsorbate.

3.5 Kinetic Model

It is very important to find the rate at which adsorption takes place for a given system in order to design the continuous column. In order to investigate the mechanism of adsorption, various kinetic models have been suggested. Numerous kinetic models have described the reaction order of adsorption systems based on solution concentration (Krishna, 2012; Allen, 1995). In the present study four different popularly used adsorption kinetic models i.e. Lagergren's pseudo first-order, Ritchie's second order, First Order Reversible and Pseudo second order model were used (Veeram, 2003). All the experimental data has been applied to these kinetic model equation as described in chapter-2. The rate constant along with the R^2 values are evaluated and reported in Table 3.1. From the table it was observed that Cr(VI) adsorption by coconut leaves follows the pseudo second order kinetic model.

3.6 Equilibrium Adsorption Isotherm

The equilibrium separation between the two phases is an important criterion to be considered for the successful representation of the dynamic adsorptive separation of the solute from solution into an adsorbent (Liang, 2014). An adsorption isotherm plays a major role, which relates the surface properties and affinity of the adsorbent to compare the various pollutants uptake capacity. In order to find out the mechanism of Cr(VI) adsorption by the coconut leave and determine the maximum uptake capacity of the adsorption three popular adsorption isotherms were used to fit the experimental data. The isotherm used were Freundlich isotherm, Langmuir isotherm and Temkin Isotherm (Mutongo, 2014; Durga, 2012). Experimental data were used to find out the isotherm constant and R^2 values as discussed in chapter-2. The values of isotherm parameters along with the R^2 values are reported in Table 3.2. From the Table 3.2, it is clear that adsorption follows the Langmuir adsorption isotherm.

3.7 Rate controlling mechanism

On porous adsorbents, the adsorption of Cr(VI) is governed by four steps in series as we have discussed in previous chapter. In order to find out the rate limiting step during the adsorption process, different model have been used. As discussed in chapter-2, experimental data were used in the three model to find out the best fit. The model parameters along with the regression coefficients were calculated and are reported in Table 3.3. It is found from the Table 3.3 that surface diffusion is the slowest steps and hence is the rate limiting steps.

3.8 Conclusion

A new, readily available and environmental friendly adsorbent is used for the treatment of Cr(VI) contaminated wastewater. Experimental results show the ability to remove the Cr(VI) by using locally available coconut leaves. It has been observed that under the optimum condition (pH: 3.0, Chromium concentration 10 mg/L, adsorbent doze 5 g/L, temperature 30°C and particle size of 52 BSS) the sorption efficiency 91% and this has been increased to 100% at adsorbent dose of 10 g/L. Kinetic analysis revealed that pseudo second order kinetic model is better as compared to all other kinetic models. Experimental results show that it follows the Langmuir isotherm and surface diffusion is the rate limiting step. But the adsorption takes place at low pH of 1.5 and treated effluent water has got pH of 2.2. The uptake capacity is found to be slightly less than the grass.

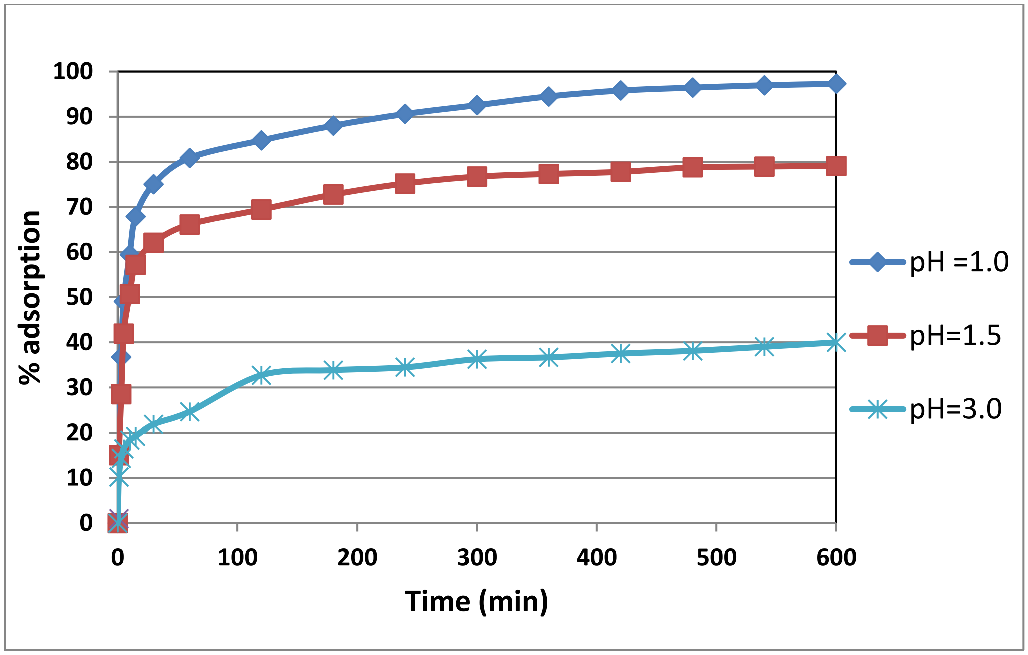


Fig. 3.1: Effect of contact time on percentage of Cr(VI) adsorption. Condition: 10 ppm, Temp :30^{o}C, dose 20g/L, Shaker speed: 180, Size:52 BSS.

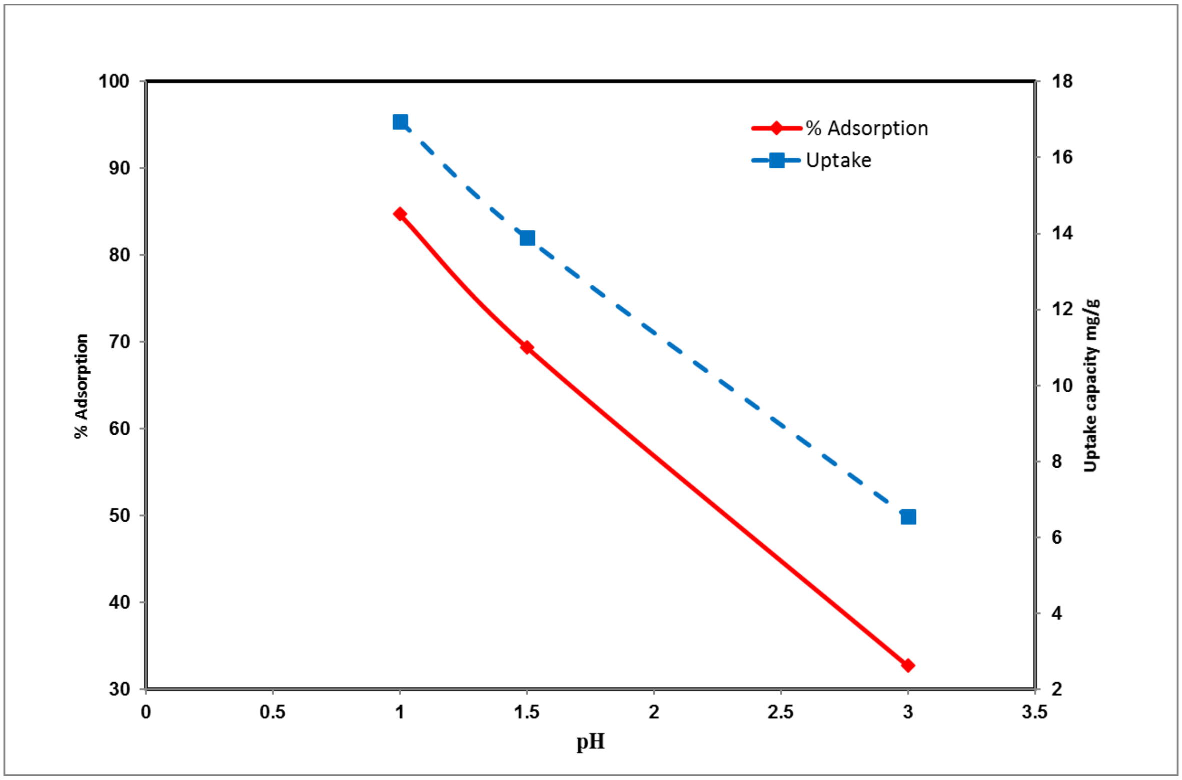


Fig 3.2: Effect of pH on percentage of Cr(VI) adsorption. Condition: 10 ppm, Temp :30^{o}C, dose 20g/L, Shaker speed: 180, Size:52 BSS.

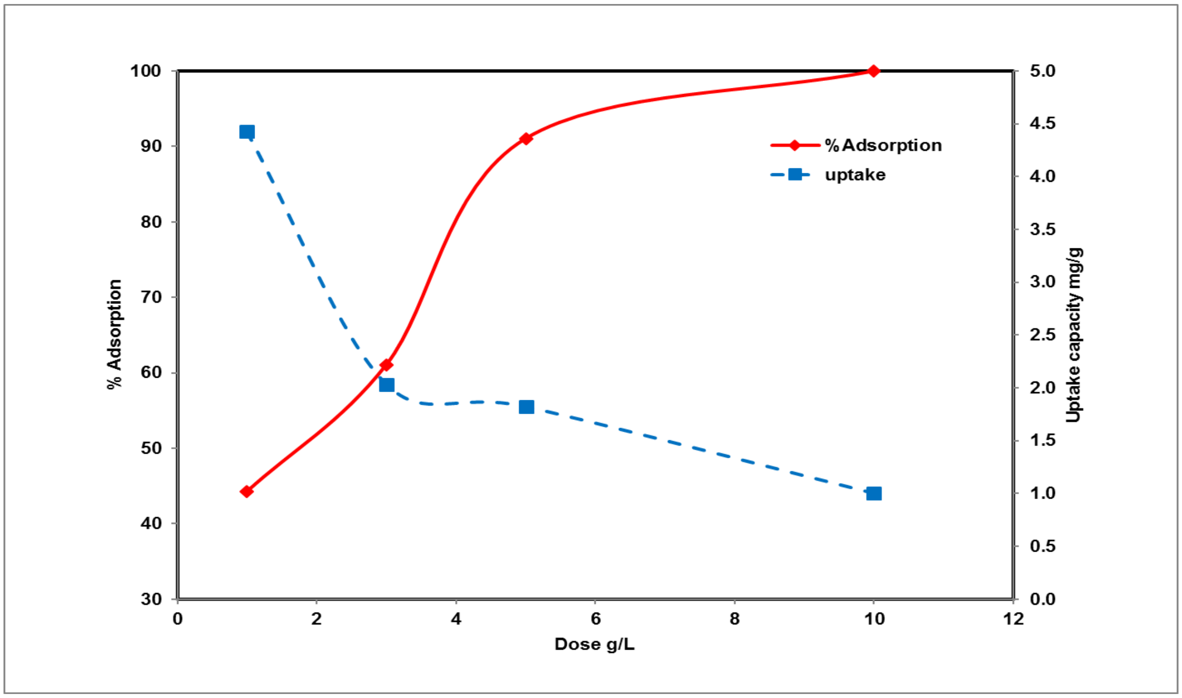


Fig. 3.3: Effect of Adsorbent Dose on percentage of Cr(VI) adsorption. Condition: 10 ppm, Temp :30^{o}C, pH: 1.5, Size:52 BSS

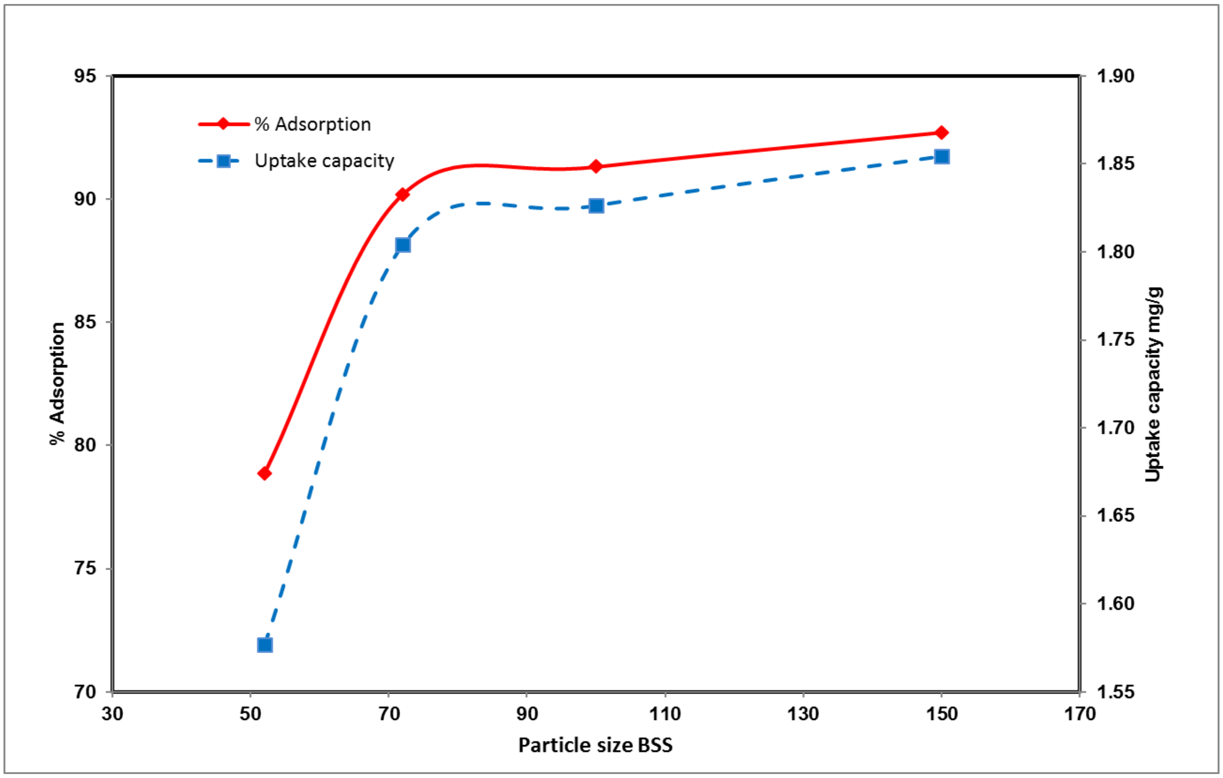


Fig. 3.4: Effect of Particle Size on percentage of Cr(VI) adsorption. Condition: 10 ppm, Temp :30^{o}C, pH: 1.5, dose:5 g/L.

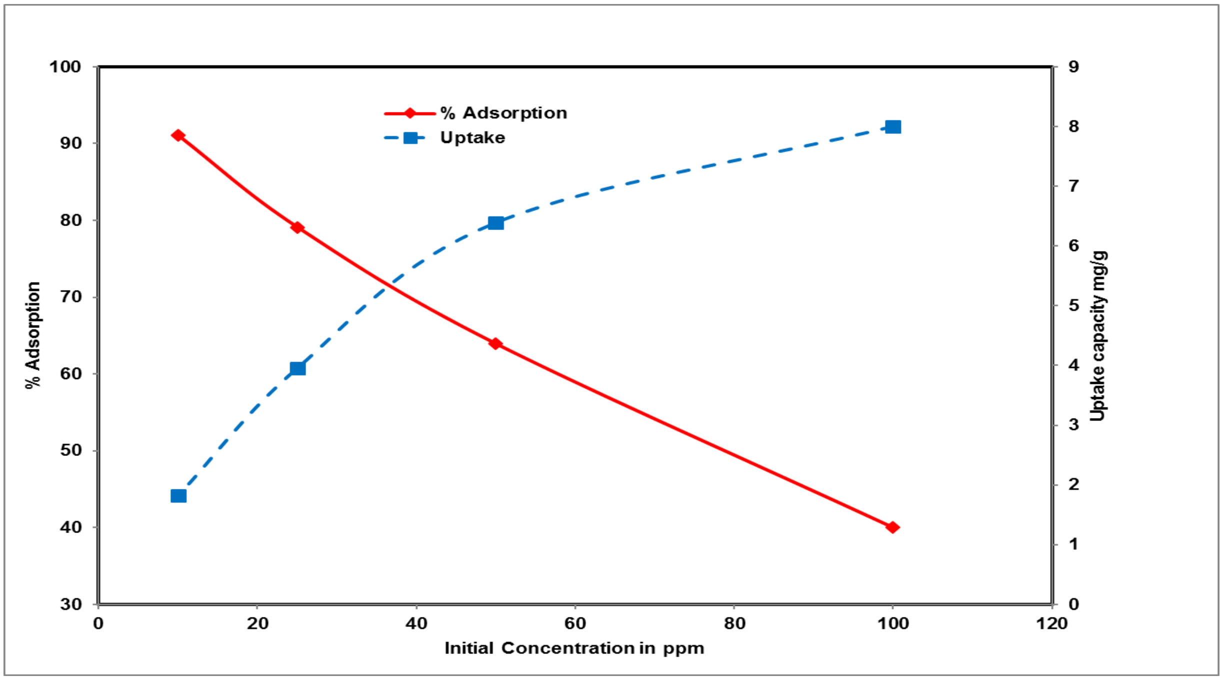


Fig. 3.5: Effect of Initial Cr(VI) Concentration on percentage of Cr(VI) adsorption. Condition: pH :1.5, dose :5 g/L, Size:52 BSS, Temp :30^{o}C.

Table 3.1: Adsorption Kinetic models parameters

Parameter	**Values**	**Pseudo 1st order**		**Richie's 2nd order**		**Pseudo 2nd order**		**First order reversible**		
		k	**R^2**	**k**	**R^2**	**k**	**R^2**	**k_1**	**k_2**	**R^2**
Adsorbent dose (g/L)	1	0.25	0.93	0.04	0.74	0.003	0.965	4.42	0.006	0.986
	3	0.34	0.91	0.156	0.554	0.090	0.997	2.00	0.009	0.984
	5	0.30	0.95	0.142	0.644	0.050	0.999	1.30	0.010	0.803
	10	0.31	0.93	0.17	0.603	0.100	0.999	71.4	0.010	0.690
pH	1	0.34	0.96	0.312	0.564	0.005	0.999	32.0	0.010	0.837
	1.5	0.4	0.94	0.59	0.517	0.007	0.999	34.5	0.011	0.867
	3	0.24	0.95	0.05	0.8	0.019	0.997	22.0	0.007	0.870
Size	52	0.32	0.90	0.22	0.53	0.042	0.996	1.33	0.010	0.830
	72	0.35	0.95	0.22	0.63	0.058	0.999	1.57	0.011	0.750
	100	0.33	0.97	0.13	0.86	0.060	0.999	1.66	0.012	0.634
	150	0.35	0.97	0.14	0.93	0.072	0.999	1.90	0.013	0.540
Initial Concentration (ppm)	10	0.30	0.954	0.142	0.644	0.046	0.999	1.30	0.010	0.804
	25	0.40	0.91	0.6	0.517	0.029	0.999	4.10	0.011	0.853
	50	0.32	0.94	0.191	0.522	0.009	0.997	6.42	0.090	0.920
	100	0.24	0.96	0.050	0.80	0.007	0.997	1.28	0.090	0.920

Table 3.2: Adsorption isotherm models parameters

Parameter	**Values**	**Freundlich Isotherm**			**Langmuir Isotherm**		**Temkin Isotherm**	
		Slope 1/n	**log K_f**	**R^2**	**$1/q_{max}$**	**R^2**	**RT/b**	**R^2**
Adsorbent dose (g/L)	1	0.980	0.52	0.52	0.23	1.0	1.29	0.86
	3	0.600	0.50	0.50	0.50	1.0	0.42	0.78
	5	0.220	0.73	0.73	0.55	1.0	0.27	0.80
	10	0.172	0.75	0.75	1.00	1.0	0.13	0.80
pH	1	0.22	1.35	0.51	0.13	1.0	2.50	0.68
	1.5	0.18	1.20	0.50	0.06	1.0	1.74	0.65
	3	0.35	1.02	0.79	0.05	1.0	1.73	0.88
Size (BSS)	52	0.261	0.16	0.75	0.54	1.0	0.32	0.82
	72	0.2	0.17	0.73	0.50	1.0	0.28	0.79
	100	0.231	0.19	0.80	0.50	1.0	0.32	0.86
	150	0.240	0.19	0.82	0.50	1.0	0.33	0.88
Initial Concentration(ppm)	10	0.18	0.49	0.50	0.55	1.0	0.27	0.80
	25	0.24	0.78	0.63	0.25	1.0	0.44	0.65
	50	0.22	0.13	0.73	0.16	1.0	0.96	0.75
	100	0.35	1.02	0.79	0.13	1.0	1.73	0.88

Table 3.3: Rate controlling mechanism

		q_t vs $t^{1/2}$		**q_t/q_e vs $t^{1/2}$**			**$\ln(1-(q_t/q_a))$ vs t**		
Parameter	**Values**	**k_{id} mg/g min$^{(1/2)}$**	**R^2**	**$6(D_1/\Pi a^2)^{1/2}$**	**D_1 mm^2/time 10^{-6}**	**R^2**	**$D_2 \Pi/a^2$**	**D_2 mm^2/time 10^{-3}**	**R^2**
Adsorbent dose (g/L)	1	0.04	0.91	0.06	1.69	0.97	0.33	0.58	0.97
	3	0.09	0.91	0.07	2.42	0.95	0.27	0.47	0.91
	5	0.16	0.94	0.09	3.66	0.95	0.53	0.93	0.97
	10	0.34	0.96	0.07	2.58	0.96	0.33	0.57	0.99
pH	1	0.93	0.81	0.09	3.72	0.93	0.45	0.79	0.98
	1.5	0.74	0.80	0.11	5.41	0.95	0.50	0.87	0.94
	3	0.41	0.93	0.06	1.44	0.97	0.23	0.40	0.98
Size(BSS)	52	0.09	0.90	0.07	2.50	0.95	0.37	0.65	0.84
	72	0.09	0.85	0.08	3.31	0.94	0.45	0.79	0.93
	100	0.09	0.84	0.08	3.17	0.93	0.38	0.66	0.96
	150	0.08	0.82	0.09	3.47	0.96	0.38	0.66	0.99
Initial Concentration (ppm)	10	0.09	0.91	0.07	2.42	0.95	0.18	0.31	1.00
	25	0.19	0.80	0.11	5.41	0.95	0.58	1.00	0.94
	50	0.34	0.94	0.08	2.99	0.99	0.52	0.90	0.95
	100	0.41	0.93	0.05	1.44	0.97	0.27	0.47	0.95

Chapter-4

Removal of Cr(VI) from wastewater using pig iron sludge

4.1 Introduction

From the extensive literature survey, it is observed that naturally available, low cost bio-sorbents have a potential for the treatment of Cr(VI) contaminated wastewater. But from our previous studies, it was observed that the adsorption capacity of the bio-sorbents is high at lower pH. Adsorptive removal of Cr(VI) at lower pH is not environmental friendly and requires further neutralization steps which may not be environmental friendly in terms of TDS increase. Further, the tannin and lignin presents in the biomaterials may leach out and create environmental pollution and hence requires suitable pre-treatment which may not be economical and environmental friendly. In addition, the economics of an adsorption process is dependent on the number of adsorption-desorption cycle of each adsorbent. The amine and electron donor groups presence in the biomaterials leads indirect reduction and increases the chemisorption. As the pH of the aqueous phase is lowered, a large number of hydrogen ions can easily coordinate with the amino, hydroxyl, CN and react with the $Cr_2O_7^{2-}$ which is irreversible. Therefore, regeneration of the adsorbents is not possible and hence the use of such adsorbents may not be economically feasible and thus can lead to disposal problems. Therefore, the present study aimed at finding a pig iron sludge as an adsorbent which can be recycled along with the adsorbed Cr(VI).

The present study explored the use of pig iron sludge as adsorbent to remove the Cr(VI) from wastewater. Batch adsorption process was carried out in-order to study the effect of different parameters on adsorption process. The study of different parameters like pH, contact time, initial Cr(VI) concentration and adsorbent dose, on the removal of Cr (VI) from the solutions has been investigated. The removal efficiency has been correlated with all the parameters.

Generally Iron ore in the form of hematite (Fe_2O_3) or magnetite (Fe_3O_4). Natural Ores contain high quantity of hematite or magnetite (greater than 60% Fe) implying that they can be used directly in blast furnaces for iron making. Pig Iron which is produced from this Iron ore is the main resources for the production of steel. Approximately 98% of this mined iron ore is used to produce steel. Also, most Indian ores are low in Phosphorous content and hence are ideally suited for smelting in iron and steel. (Indian Minerials Year Book, 2012, part III).

Goa is the fourth largest producer of iron ore in India. Goa produces about 18 per cent of the total iron ore of the country. The iron ore of north Goa is of superior quality. The main deposits and mining centers are at Pirna-Adolpale-Asnora, Sanquelim Onda, Kundem-Surla, and Sirigao-Bicholim-Dalda in north Goa. The nearby Marmagao seaport is a big advantage to these mines for the export of iron ore. The iron ore is exported mainly to Japan and Iran. The mining area in Goa covers 700 sq. km approximately.

Capacity of this plant is 2,50,000 tons as per 2014 data and there will be a expansion in 2017. The following is the overall reaction involved in the production of Pig Iron manufacturing unit.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

Fig. 4.1 represents the sequence of operation involved in the ore mining and pig iron manufacturing plant.

Iron bearing minerals namely biotite, hematite, pyrite, magnetite etc., have also demonstrated their effectiveness in Cr(VI) removal (Eary & Rai, 1989; Ilton & Veblen, 1994; Bidoglio et al, 1993; Peterson et al, 1996; Peterson et al, 1997). During the production of Pig iron in open cast furnace, a large quantity of fine particles used to come out as an overhead product. This fine particle of ore is wet-scrubbed and the sludge is recycling back to the initial stage i.e. filtering stage. We have used sludge as an adsorbent to remove the Cr(VI) and recycle this adsorbent along with the adsorbed Cr(VI) into the pig iron processing unit. This paper discusses the process of recycling these dumped sludge (containing moisture with high iron content) in the plant. This sludge is dehydrated and combined with the raw material in the processing stage of filtering. The proposed flow diagram (Fig. 4.2) shows that how to use the sludge as a raw material to remove the Cr(VI) present in the industrial effluent and recycle back to the filtering stage.

4.2 Materials

The adsorbent used in this study was collected from the pig iron manufacture industry of Sesa Goa, Vedanta limited. Vedanta has large iron ore mines in Goa and Karnataka and a pig iron plant in Goa, and consists of exploration, mining and processing of iron ore, pig iron and metallurgical coke and power generation. The Sesa Goa is located at Amona, Goa which 40 km from BITS Pilani K. K. Birla Goa Campus. In order to remove the moisture, the adsorbent is dried at 100^0C in an oven for 24 hours. The composition of the sludge is shown in Table 4.1. The dried sludge which was in the powdered form was sieved (BSS standard screens) to different size fraction and were kept in airtight container for further use. A stock Cr(VI) solution and complexing agent solution was prepared as discussed in chapter 2. In order to meet the desired and maintain the value pH of the solution done by adding diluted organic acid (concentration of 0.1 N) solution before adsorption. All the chemicals used were of Merck analytical reagent grade.

4.3 Methods

Adsorption experiments were conducted at a constant temperature in 250 ml beaker using 200 ml of Cr(VI) solution. In order to make uniform concentration along the beaker, the mixtures were stirred with speed regulator. 5 ml of samples were collected (by using different tips) under dynamic condition in a regular time interval and it has been analyzed. Whatman 42 filter paper has been used to collect the filtered solution. The residual filtrate Cr(VI) concentration has been analyzed spectrophotometrically after complexation of Cr(VI) ion with 1,5 Di-Phenyl Carbazide in acidic condition. UV/Visible Spectrophotometer (Hach DR 5000, model: 1201) was used to find the Absorbance and it is recorded at 540 nm.

4.4 Results and Discussion

4.4.1 Characterization of Adsorbent

In order to find out the morphological changes in the adsorbent, the powdered adsorbent both before and after adsorption was investigated by the Scanning electron microprobe images are (SEM JXO-8100) at 1000X magnification. These results were presented in Fig. 4.3 and 4.4. From the micrograph image, it is clearly observed that there is a change in surface morphology before and after adsorption. From the figure, the structure of adsorbent was in irregular structure and it becomes smooth in nature after adsorption. The elemental analysis by EDAX method further confirmed that the adsorption of Cr(VI) on the surface of adsorbent. EDAX pictures for the adsorbent before and after adsorption are shown in Fig. 4.5 and 4.6. From the EDAX images, there is an increase in mass percentage of Cr(VI)

4.4.2 Effect of Contact time and pH

The pH of the aqueous solution is clearly a vital parameter that controls the process of adsorption (Karthikeyen et al 2005). The experiments were conducted under the constant temperature (30^0C), shaker speed of 150 rpm, initial Cr(VI) concentration (10 mg/L) and adsorbent dose of (16 gm/L). The pH of solution was varied between 2 to 5 and the percentage removal of Cr(VI) has been inspected. The experimental results are shown in Fig. 4.7 and Fig 4.8. As it is shown, the percentage of Cr(VI) adsorption increases with decrease in pH from 5 to 3 and thereafter there is hardly any change in percentage adsorption. In the aqueous solution, Cr(VI) present in the form of $Cr_2O_7^{2-}$. As the pH of the aqueous phase is decreased, a large number of hydrogen ions can simply coordinate with adsorbent surface, which becomes positively charged, so that it can easily absorb the negatively charged Cr ions. No change in percentage adsorption below pH 3.0 may be due to the fact that at pH 3.0, all the active surface in the adsorbent becomes positively charged and hence there is not much change in surface charge by further lowering down the pH to 2.0 which in turns not affect the percentage adsorption. (Pragathiswaran et al, 2013). As pH is increased beyond 3.5, there is no much adsorption takes place. The reason for this is due to the not having strong attraction between the oppositely charged adsorbate and adsorbent that eventually lead to the decrease in adsorption capacity (Baral et al, 2006).

After the adsorption process, the effluent leaves as a waste water to treatment process. Most of the researchers have done the adsorption process in the lower in pH to increase the percentage removal of Cr(VI), but the effluent will have high pH. It is necessary to neutralize the effluent in the effluent treatment plant. We have studied the effect of pH before and after the adsorption during the study of effect of pH on adsorption. All the further experiments were carried out in the pH range of 3.0 to have the effluent pH close to 5.0 after the adsorption process. Change of pH before and after the adsorption for varying all parameters have shown in table 4.2.

4.4.3 Effect of Adsorbent Dose

Keeping all other parameters constant, the adsorbent dose was varied from 5 to 20 gm/L. the results are shown in Fig. 4.9. From the figure, it is observed that, with increase in adsorbent dose the percentage adsorption increases from 44% to 100%. It was expected trend as because, the exposed active sites of adsorbent were more when the adsorbent dose increased (Thamilarasu &Karunakaran, 2013; Gayathri et al, 2013). However, the uptake capacity of the adsorbent decreases with increase in adsorbent which may be due to the availability of unsaturated surface. It is also observed from the figure that an adsorbent dose of 20 gm/L is sufficient to remove the all Cr(VI) present in the effluent

4.4.4 Effect of Initial Concentration

In order to study the effect of initial concentration on the percentage of Cr(VI) adsorption by sludge, experiments were carried by varying the initial Cr(VI) concentration from 10 to 200 mg/L and the results were shown in Fig. 4.10. It was observed that the percentage adsorption diminished with the increase of Cr(VI) concentration (Mukhopadhyay et al 2011; Elangovan et al 2008). But at the same time the uptake capacity increases with increasing the initial concentration. This is obvious that at fixed adsorbent dose, the number of active sites to put up the adsorbate ions increases with higher initial concentration. So the binding of Cr(VI) is quicker with higher concentration of adsorbate (Zhang et al, 2010; Prasad et al 2011). All other experiments were carried out with 20 g/L.

4.4.5 Kinetics of Adsorption

Four kinetics models i.e. Pseudo 1st order, Richie's 2nd order, Pseudo 2nd order and First order reversible models were used to find out the adsorption kinetics. Experimental data were fitted to the above said models and kinetics parameters along regression coefficients were calculated for each model. The kinetics parameters along with the regression coefficients for each model at different adsorption parameters shown in Table 4.3. From the table, it can be observed that the regression coefficients are either 1 or very close to 1 in case of pseudo 2^{nd} order kinetics. Hence experimental data follows pseudo 2^{nd} order kinetics.

4.4.6 Rate Controlling Mechanism

The adsorbent used in the study is porous in nature. Therefore, pore diffusion is also plays a major role on the adsorption process in additionally to surface diffusion. It is important to find the rate limiting steps. The time variation experimental data is used to find out the rate limiting step in the present study. The experimental data were fitted to equation 2.11, 2.12 and 2.13. The rate constant along with the regression coefficients were calculated and shown in Table 4.4. From the it is observed that D_2 is always greater than D_1 and hence intra-particle diffusion is faster as compare to the surface diffusion. Therefore, surface diffusion is the rate limiting steps as it is the slowest step.

4.4.7 Equilibrium Adsorption Isotherm

As discussed in chapter 2, the adsorption equilibrium between the two phases is an important criterion to be considered for the successful representation of the dynamic adsorptive separation of the solute from solution into an adsorbent. In order to find out the adsorption capacity of the adsorbent, three Freundlich isotherm, Langmuir isotherm and Temkin isotherm were used. Experimental data were fitted to equation 2.14, 2.15 and 2.17 and isotherm parameters along with regression coefficients are calculated. The values of isotherm parameters along with regression coefficients are reported in Table 4.5. From the R^2 values in the table it can be conclude that adsorption follows Langmuir isotherm

4.5 Conclusion

A detailed literature review indicates that, a large number of adsorbents were investigated and found to be suitable for the treatment of Cr(VI) contaminated wastewater. Among different adsorbents, bio-adsorbent are found to be having high adsorption capacity, However, the disadvantage with bio-adsorbents is that their adsorption capacity is high at lower solution pH and also required pretreatment for eliminating the possibility of leaching out of water soluble component such as tannin and ligand. Further, bio-sorption is an adsorption cum reduction process and hence desorption is not possible. Considering the above fact in mind, present work deals with the finding a new low cost adsorbent which can be recycle to the industry. To manufacture the Pig iron in SESA industries Ltd, Goa, Iron ore has been used as the raw material, which is in turn used to make steel. During the production of Pig iron in open cast furnace, a huge amount of fine particles use to come out as an overhead product. This fine particle of ore is wet-scrubbed and the sludge is recycling back to the initial stage i.e. filtering stage. We have proposed a possible flowchart by using this sludge as adsorbent to remove the Cr(VI) from any industrial effluent and then this sludge goes back for drying followed by filtration. The adsorbed Cr(VI) will be useful for making steel in the blast furnace. In the present study, the sludge which is a byproduct from the pig iron manufacturing industries is used as an adsorbent for the treatment of Cr(VI) contaminated wastewater. The sludge is low cost and environmental friendly adsorbent which can be recycle to the pig iron industry. The adsorption capacity of the adsorbent was established through batch adsorption process. The effect of different adsorption parameters on the uptake capacity of the adsorbent was studied. The percentage adsorption increases with decrease in pH up to 3 and hardly any change with further decrease in pH. As usual the equilibrium uptake of the adsorbate decreases with increase in adsorbent dose whereas, the percentage adsorption increases with increase in adsorbent dose. Increase in initial adsorbate concentration has a synergetic effect on the uptake capacity whereas, antagonism effect on the percentage adsorption. The adsorption kinetics, isotherm and rate controlling mechanics also established. From the study, it was observed that adsorption kinetics followed Pseudo 2nd order kinetics. The experimental data followed Langmuir adsorption isotherm. It was also observed from the experiments that D_2 (discussed in Chapter-2) is always greater than that of the D_1. Therefore, surface diffusion is the slowest steps and hence is the rate limiting steps. Finally, we have proposed a new flow sheet for the recycling of the sludge to the pig iron industry after using as an adsorbent.

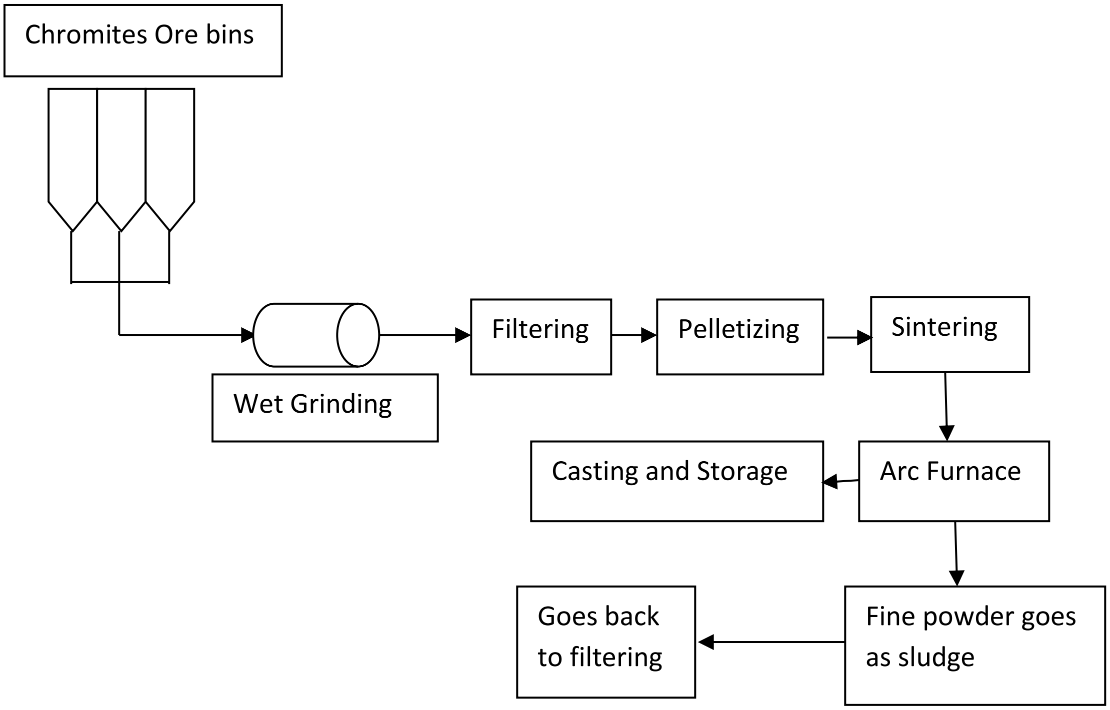


Fig. 4.1: Flowchart of existing Pig iron manufacturing unit

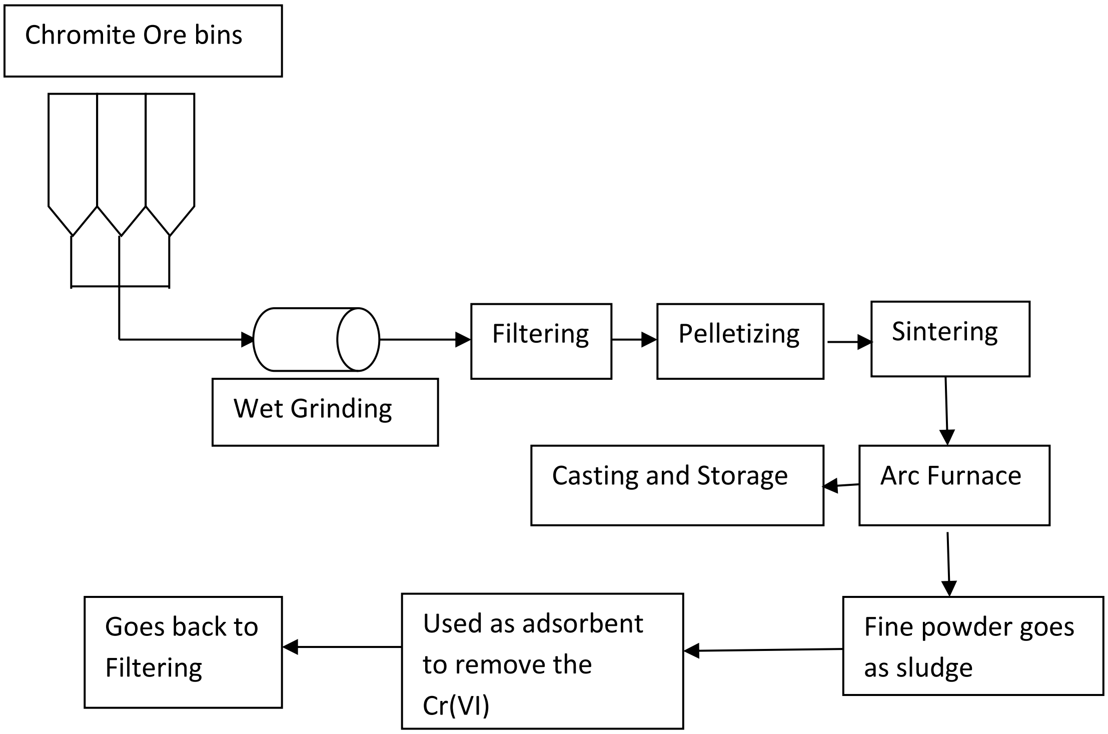


Fig. 4.2: Proposed flowchart for Pig Iron Manufacturing Unit

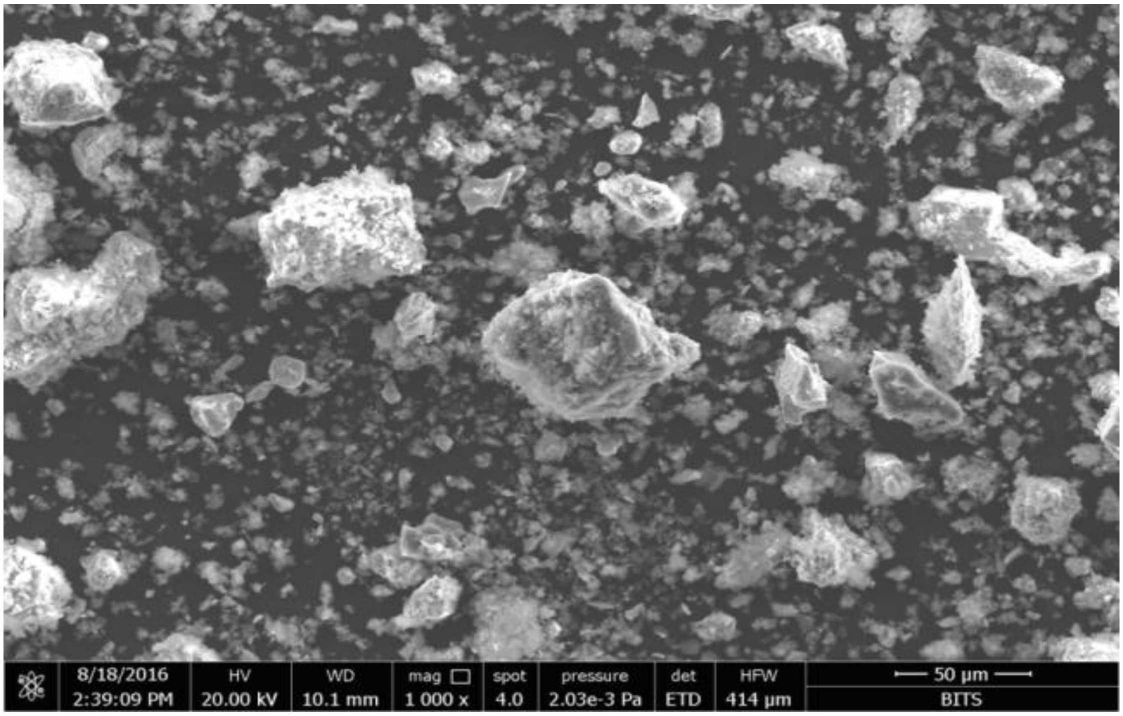


Fig. 4.3: SEM image before adsorption

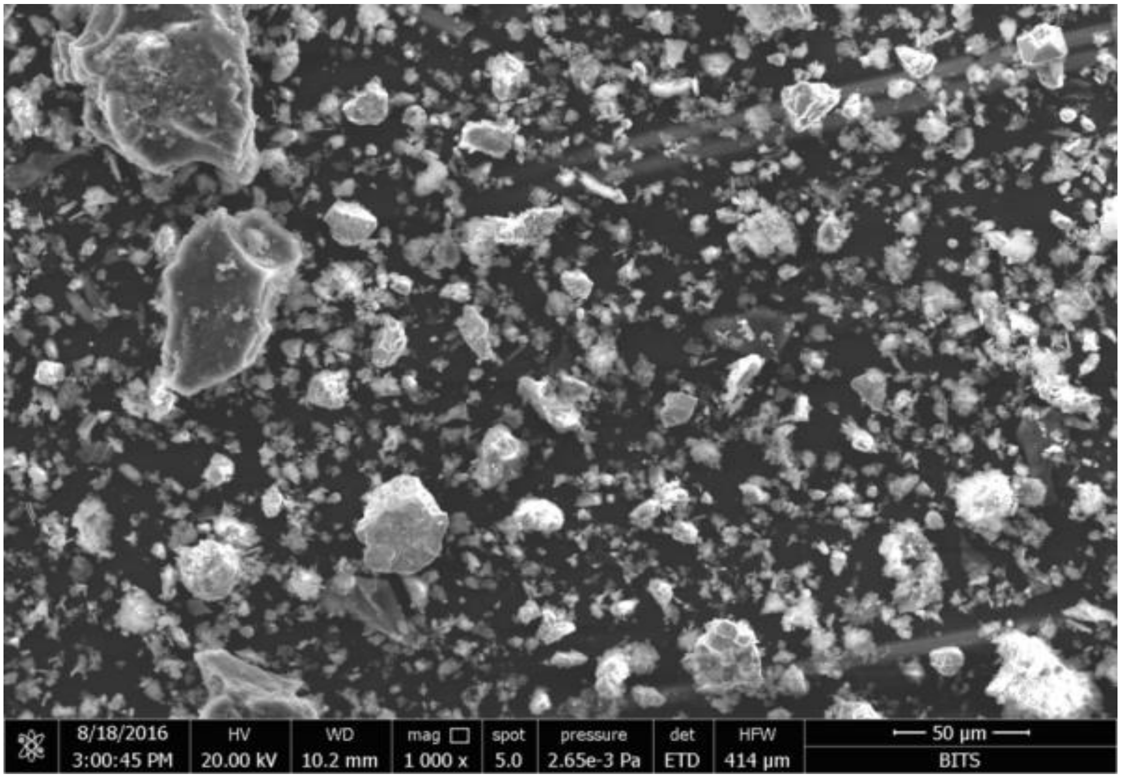


Fig. 4.4: SEM image after Adsorption

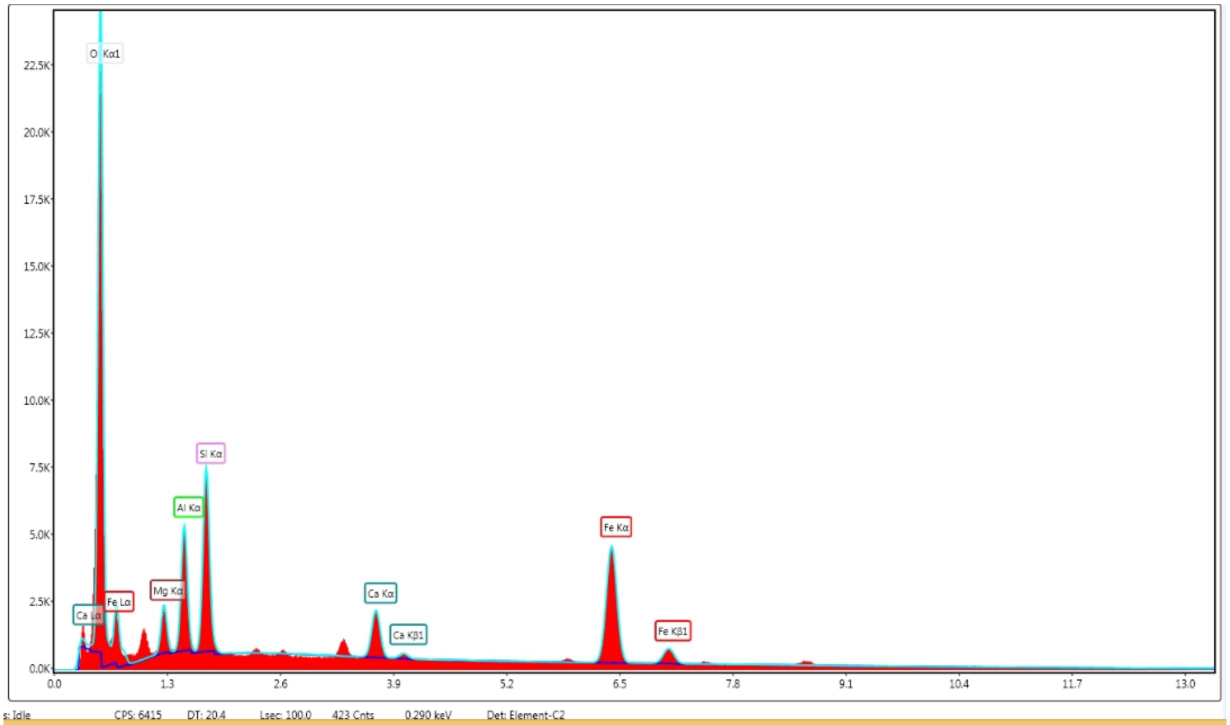


Fig. 4.5: EDAX image before Adsorption

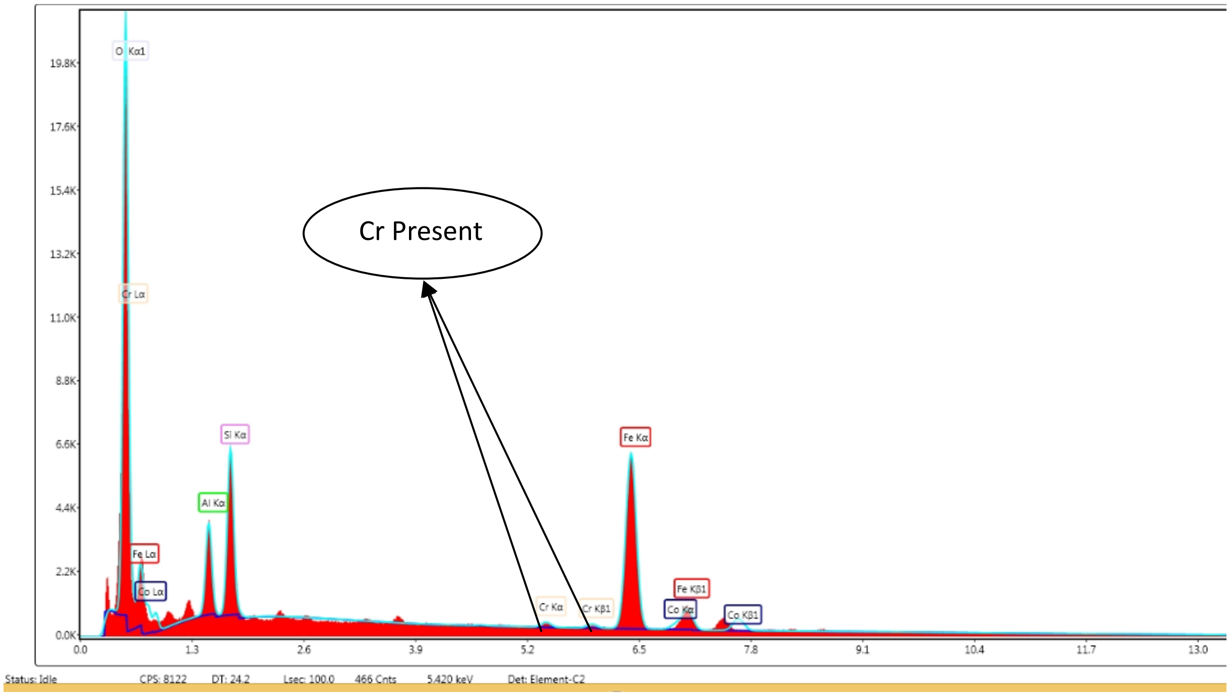


Fig. 4.6: EDAX image after adsorption

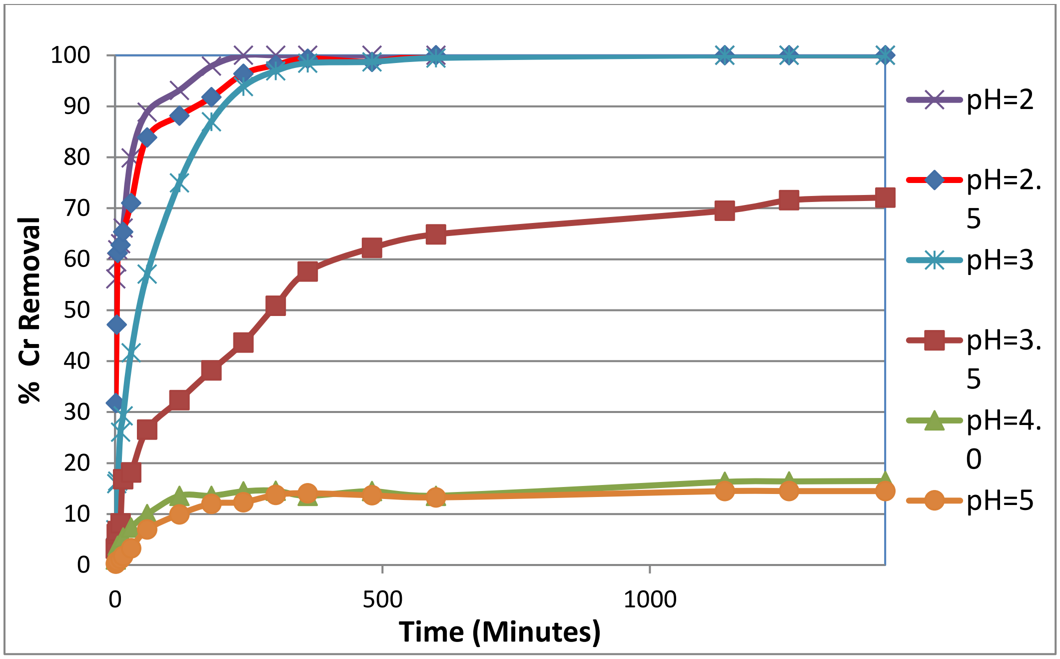


Fig. 4.7: Effect of contact time on percentage of Cr(VI) adsorption. Condition: 10ppm, dose:20g/L, Temp :30^{o}C, Shaker Speed :180.

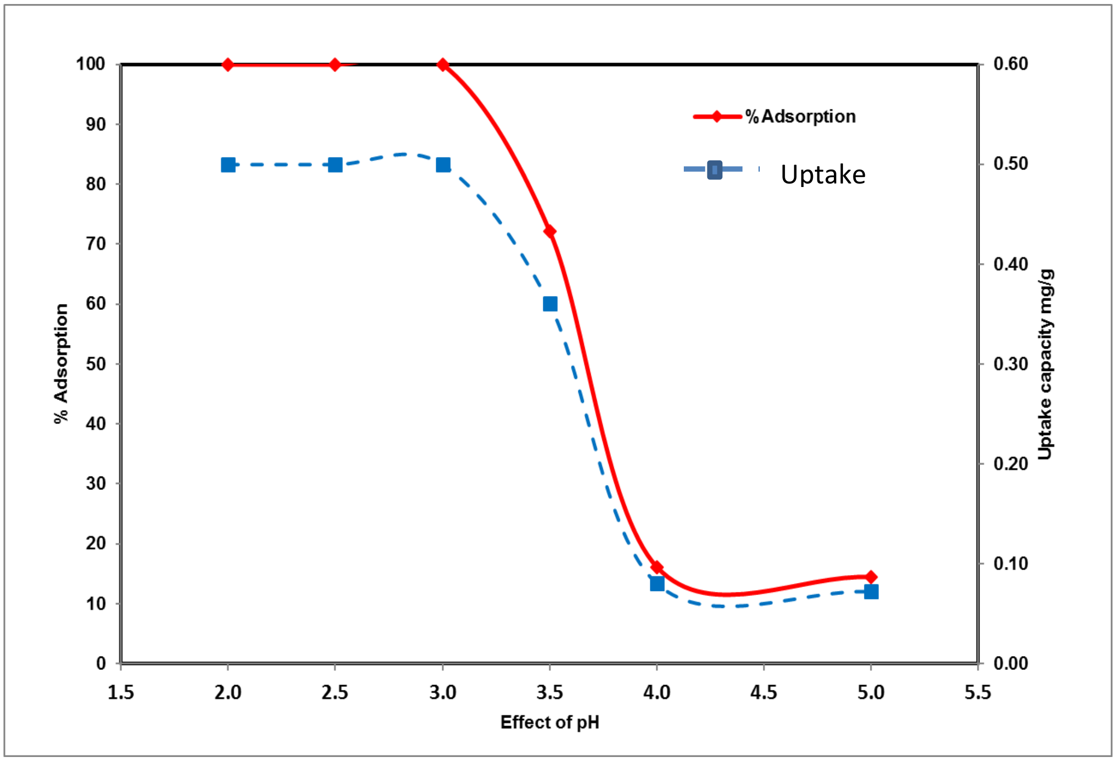


Fig. 4.8: Effect of pH on percentage of Cr(VI) adsorption. Condition: 10ppm, dose:20g/L, Temp :30^{o}C, Shaker Speed :180.

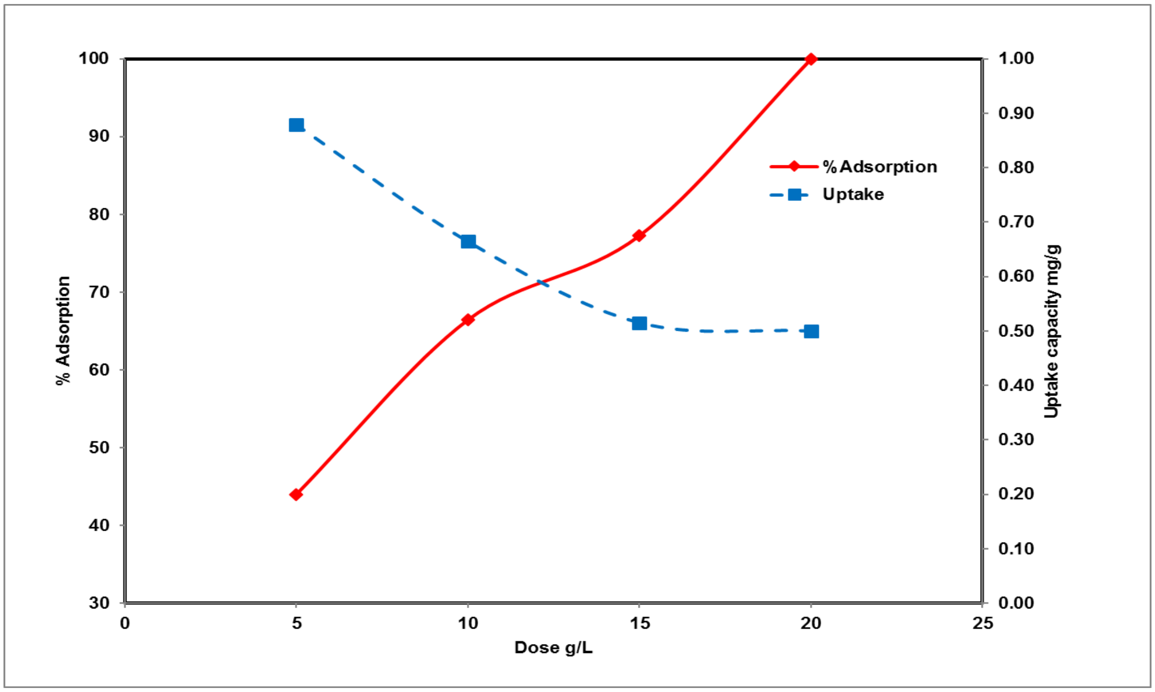


Fig. 4.9: Effect of Adsorbent Dose on percentage of Cr(VI) adsorption. Condition: 10ppm, pH :3.0, Temp :30^{o}C, Shaker Speed :180.

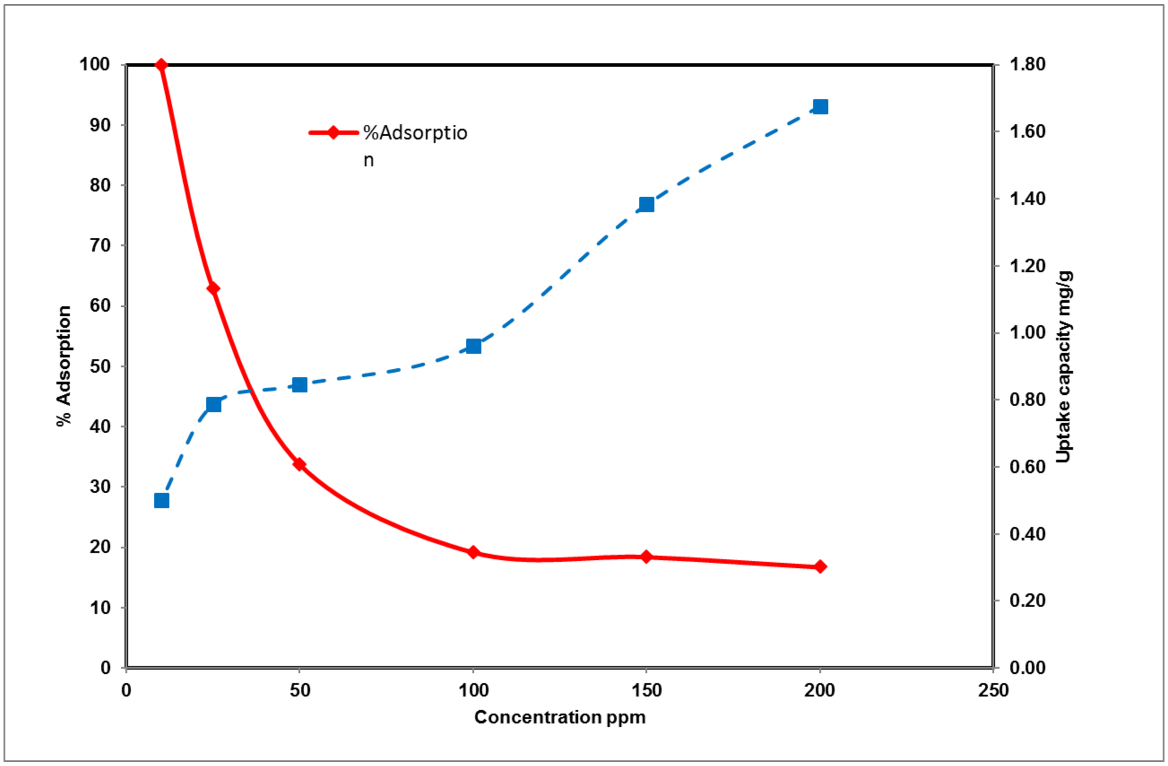


Fig. 4.10: Effect of Initial Cr(VI) Concentration on percentage of Cr(VI) adsorption. Condition: pH :3.0, dose:20g/L, Temp: 30^{o}C, Shaker Speed :180.

Table: 4.1: Composition of Sludge

Sr.No	Component	Wt %	Component	Wt%
1	Fe	37.23	MgO	4.15
2	SiO_2	15.56	C	13.88
3	Al_2O_3	4.4	Moisture	16.5
4	Mn	1.46	Ti, ,Na_2O, K_2O,S,P	1.25
5	CaO	5.57		

Table 4.2: Change of pH before and after adsorption process

Sr. No	Parameters varied	Dose (g/Lit)	Original pH Solution	pH After Adsorption
1	10 ppm	4	2.5	3.41
2	10 ppm	4	3	4.98
3	10 ppm	4	3.5	7.7
4	10 ppm	4	4	8.47
5	10 ppm	4	5	8.55
6	25 ppm	4	3	4.75
7	50 ppm	4	3	4.62
8	100 ppm	4	3	4.75
9	1 g	1	3	4.1
10	2 g	2	3	4.4
11	3 g	3	3	4.51
12	4 g	4	3	4.75

Table 4.3: Adsorption Kinetic models parameters

Parameter	**Values**	**Pseudo 1st order**		**Richie's 2nd order**		**Pseudo 2nd order**		**First order reversible**		
		k	**R^2**	**k**	**R^2**	**k**	**R^2**	**k_1**	**k_2**	**R^2**
Adsorbent dose (g/L)	5	0.206	0.864	0.022	0.837	0.0240	0.993	0.000	0.003	0.894
	10	0.328	0.714	0.304	0.74	0.0260	0.997	0.000	0.005	0.982
	15	0.300	0.835	0.113	0.78	0.0410	0.998	0.000	0.004	0.945
	20	0.420	0.905	0.245	0.795	0.0700	0.999	0.001	0.001	0.956
pH	2	0.342	0.809	0.215	0.869	0.4700	1	0.004	0.019	0.451
	2.5	0.412	0.912	0.376	0.8	0.2423	1.0	0.006	0.006	0.830
	3	0.416	0.905	0.245	0.795	0.0730	1.0	0.005	0.005	0.960
	3.5	0.255	0.785	0.067	0.6	0.0325	0.994	0.000	0.008	0.953
	4	0.249	0.947	0.045	0.686	0.4213	0.999	0.000	0.004	0.953
	5	0.182	0.956	0.041	0.882	0.1870	0.998	0.000	0.008	0.953
Initial Concentration (ppm)	10	0.417	0.906	0.245	0.795	0.0730	0.999	0.001	0.001	0.960
	25	0.117	0.847	0.07	0.76	0.0320	0.997	0.000	0.004	0.912
	50	0.108	0.784	0.052	0.731	0.0096	0.99	0.000	0.004	0.970
	100	0.069	0.9242	0.014	0.933	0.0220	0.9934	0.000	0.004	0.838
	150	0.095	0.826	0.031	0.772	0.0120	0.993	0.000	0.003	0.920
	200	0.076	0.664	0.022	0.71	0.0070	0.941	0.000	0.003	0.970

Table 4.4: Rate controlling mechanism

		q_t vs $t^{1/2}$		**q_t/q_e vs $t^{1/2}$**			**ln(1-(q_t/q_a)) vs t**		
Parameter	**Values**	**k_{id} mg/g min$^{(1/2)}$**	**R^2**	**$6(D_1/\Pi\ a^2)^{1/2}$**	**D_1 mm^2/time 10^{-6}**	**R^2**	**D_2 Π/a^2**	**D_2 mm^2/time 10^{-3}**	**R^2**
Adsorbent dose (g/L)	5	0.055	0.967	0.054	1.39	0.958	0.632	1.103	0.990
	10	0.043	0.961	0.066	2.08	0.857	0.472	0.823	0.762
	15	0.032	0.944	0.066	2.08	0.866	0.246	0.429	0.970
	20	0.034	0.8811	0.077	2.83	0.936	0.280	0.488	0.925
pH	2	0.016	0.8101	0.0564	1.52	0.932	1.170	2.040	1.000
	2.5	0.0196	0.8379	0.0664	2.11	0.96	0.691	1.206	0.983
	3	0.135	0.8811	0.0999	4.77	0.965	0.632	1.102	0.990
	3.5	0.0997	0.9775	0.0751	2.69	0.974	0.460	0.802	0.840
	4	0.0198	0.8748	0.099	4.68	0.955	0.252	0.439	0.730
	5	0.022	0.8929	0.106	5.37	0.89	0.332	0.579	0.952
Initial Concentration (ppm)	10	0.034	0.8811	0.077	2.83	0.934	0.703	1.226	1.000
	25	0.049	0.9862	0.080	3.03	0.934	0.321	0.560	0.982
	50	0.097	0.99	0.056	1.50	0.945	0.377	0.657	0.873
	100	0.056	0.984	0.0597	1.70	0.934	0.210	0.366	0.950
	150	0.087	0.96	0.0341	0.56	0.67	0.222	0.387	0.932
	200	0.1024	0.96	0.040	0.77	0.995	0.271	0.473	0.770

Table 4.5: Adsorption isotherm models parameters

Parameter	**Values**	**Freundlich Isotherm**			**Langmuir Isotherm**		**Temkin Isotherm**	
		Slope 1/n	**log K_f**	**R^2**	**$1/q_{max}$**	**R^2**	**RT/b**	**R^2**
Adsorbent dose (g/L)	5	0.655	0.34	0.656	1.138	1.0	0.242	0.840
	10	0.300	0.487	0.453	1.506	1.0	0.094	0.627
	15	0.522	0.5274	0.625	2.078	1.0	0.089	0.720
	20	0.242	1.095	0.8253	2	1.0	0.089	0.818
pH	2	0.189	0.389	0.856	2	1.0	0.073	0.890
	2.5	0.162	0.435	0.625	2	1.0	0.056	0.746
	3	0.379	0.565	0.635	2.0	1.0	0.09	0.818
	3.5	0.538	0.713	0.5253	2.8	1.0	0.078	0.743
	4	0.503	1.63	0.66	12.4	1.0	0.019	0.829
	5	0.940	2.06	0.703	13.8	1.0	0.023	0.900
Initial Concentration (ppm)	10	0.379	0.565	0.635	2.00	1.0	0.09	0.820
	25	0.441	0.192	0.454	1.27	1.0	0.152	0.750
	50	0.493	0.222	0.547	0.682	1.0	0.318	0.780
	100	0.773	0.3173	0.706	1.04	1.0	0.34	0.920
	150	0.53	0.2644	0.608	0.723	1.0	0.34	0.810
	200	0.621	0.020	0.528	0.596	1.0	0.437	0.830

Chapter-5

Removal of Cr(VI) from wastewater using Carbonized Grass

5.1 Introduction

From the literature, it is evident that bio-sorbents have high Cr(VI) uptake capacity as compare to other adsorbents. However, the disadvantages with the bio-sorbent is that, the adsorption capacity is higher at lower pH, treatment at lower pH requires neutralization steps which are not economic and environmental friendly and regeneration is not possible because of adsorption cum reduction mechanism. Therefore, a new industrial waste was used in the chapter four with an aim to reuse the adsorbent along with the adsorbed Cr(VI) in the production of ferrochrome. From the experimental results, it is observed that the adsorption capacity of the adsorbent was very low at higher pH. Therefore, the present study aimed at finding an alternative adsorbent i.e. Biochar to remove the Cr(VI) from the wastewater and use this chromium adsorbed Biochar in Ferrochrome industry. Ferrochrome is a major intermediate raw material for the production of stainless steel. Worldwide more than 80% of the ferrochrome production is used in steel industry (Goel, 1997; Montiano et al, 2014). During the process of manufacture of steel generate large amount of CO_2 due to their use of fossil fuels either as a reductant or as a fuel (Wiklund et al, 2012; Norgate et al, 2009; Norgate et al, 2012). The potential of Biochar has been assessed in terms of its CO_2 abatement potential and economic viewpoint. The results indicate the potential for 18-40% mitigation of CO_2 (Bruzual, 2014; Ariyama, 2005). Apart from the CO_2 reduction, the experience of charcoal based iron making reveals following benefits to the process (Bruzual, 2014).

1. Lower impurity content – Biochar contains less sulphur and phosphor content than coke.
2. Ash content – ash in Biochar can be lower than in coke.
3. High reactivity – Biochar is highly porous, with a large specific area, this improves combustion rates.

Finding from the economic point of view Biochar cannot compete with fossil coal on price, but the amount of Biochar addition is very small percentage so the effect of cost will be negligible. In order to study the effect of different parameters on adsorption of Biochar, batch adsorption process was carried out. The study of effect of different parameter like pH, contact time, initial Cr(VI) concentration and adsorbent dose, on the removal of Cr(VI) from the solutions has been investigated by using this Biochar. The removal efficiency has been correlated with all the parameters.

5.2 Manufacturing Process of Ferrochrome

The Fig. 5.1 explains the process flow for Ferrochrome production. The Composition of Raw Material for Ferrochrome production is shown in Table 5.1. The chromite ore input in the form of Friable and Lumpy ore is processed through Grinding, Filtering, Palletizing and Sintering (GFPS) to make pellets. Initially the chrome ore was grounded in the grinding mill after adding the water and the slurry is filtered in a drum filter unit then pellets are formed in the palletizing disc, the pellets are then sintered in the shaft furnace called sintering operation. This pellets along with chrome lumps, coke as a reductant, and quartzite as flux are added to submerged arc furnace-8. The smelting is done in the Submerged Arc furnace (Samaradivakera and Sahu, 2013). It is a closed type furnace. After smelting, the molten metal and slag are tapped from the furnace. The molten metal is casted in the casting bed. The present study is exploring the possibility of using biochar as an adsorbent for the treatment of Cr(VI) contaminated wastewater. The advantages of using Biochar as an adsorbent is that, the used Biochar can be reused in a ferrochrome industry as a source of carbon i.e. fuel. Further, the adsorbed Cr(VI) can be used as a raw material for the ferrochrome production.

5.3 Materials and Methods

In order to make Biochar from *Sorghastrum Nutans* (L) Nash (grass) which is having higher uptake capacity as compared to other bio-sorbent we have used, were heated in a Muffle furnace at 700^0C. Experimental set-up is shown in Fig 5.2 which consist of cylindrical pipe made of cast iron (length of 60 cm and diameter of 7.6 cm ID) with one end closed and other side i.e. front side is flange threaded to main frame which is packed with glass wool as heat resistance medium. Through the outer flange, a small copper tube (6 mm ID) inserted with length of 50 cm through which N_2 gas was supplied. The N_2 gas used as inert medium. The dried powder form of adsorbent was carbonized at a temperature of 700^0C in inert atmosphere (N_2 gas and this gas exit as a flue gas). The flow rate of N_2 adjusted from N_2 gas cylinder with purity of 99.9 % by using proper flow control valve.

This entire setup is kept inside (up to mainframe) the muffle furnace and heated to desired temperature. Heating is adjusted by using temperature controller in the furnace system. Once the Temperature reaches to desired value and it was maintained for 3 hours at same temperature to burn the entire mass in inert medium. The carbonized adsorbent is kept in an air tight bottle for further use. The batch adsorption experiments were carried out as discussed in chapter-2. The pH adjustment, analysis of Cr(VI), variation of parameters and chemical used are similar to that explained in chapter-3.

5.4 Result and Discussion

5.4.1 Effect of contact time

It is important to get the equilibrium contact time; the experiments were carried out up to 600 min. The other process parameters such as adsorbate concentration, temperature and dose of the solution were kept stable at 100 mg/L, 30^{o}C and 5 g/L respectively during the experiment under the constant stirring speed for different pH. The results are depicted in Fig. 5.3 It is clearly seen from the plot linking contact time versus percentage adsorption that the kinetics was rapid for the first 30 min followed by slower kinetics. Out of total adsorption, 80% has been reached during the faster phase. The reason for faster rate at beginning is due to more free surface area. When the free surface is congested, the adsorbate molecules come into the pores which are called as intra-particle diffusion and get adsorbed inside the pores. At later stage, slower kinetics was shown by intra-particle diffusion. Equilibrium is achieved within 10 h in this process and further than that, there was not much alteration in concentration. So, the remaining studies were carried out for 10 hrs.

5.4.2 Effect of Initial pH of Solution

The initial pH is a most influential parameter affecting the adsorption process (Matheikal et al, 1996). Experiments were carried out by varying pH between 2.0 and 4.0 to find out its effect on the percentage of adsorption and Cr(VI) uptake capacity of the adsorbent. The results are shown in Fig. 5.4 below. From the experiments, it was observed that the percentage adsorption as well as the uptake capacity of the adsorbent increases with decrease in pH. The increase in adsorption capacity with decrease in pH may be due to the fact that at lower pH, the adsorbent surface becomes more positively charge because of presence of large number of H^+ ion. Further the low pH favors the chemisorption as explained in chapter-2. It was observed that the maximum adsorption (100 %) takes place when initial pH of 2.0 and 2.5. The uptake capacity increased from 10.7 mg/g at pH of 4.0 to 20 mg/g at pH of 2.0. Although the maximum adsorption capacity observed to be at pH 2.0, but the effluent from the process will be highly acidic and hence required acid neutralization steps which may not be economical and environmental friendly. Further, the used adsorbent may not be suitable for recycle to the ferrochrome industry, if the treatment carried out at a such lower pH. Therefore, the remaining adsorption studies were carried out pH of 3. The final pH of the effluent of the process increased to more than 5.

5.4.2 Effect of Adsorbent Dose

Adsorption experiments were carried out over 600 minutes to find the equilibrium contact time. The concentration of initial Cr(VI) solution was 10 ppm for all further studies. During the experiment, the other adsorption parameters such as adsorbate concentration, pH and temperature of the solution were kept constant 10 ppm, 3.0 and 30^{o}C, respectively under constant stirring speed. The results are shown in Fig 5.5. It can be seen from the figure that the kinetics was very fast during the first 30 min followed by a slower kinetics. During the faster phase, 80% of the total adsorption was reached. The adsorption process attained equilibrium within 6 h and beyond that there was hardly any change in concentration. The theory of effect of contact and dose with the percentage of Cr(VI) removal has been well explained in chapter 2. The percentage of removal was increased from 59 % to 100 % with increase in adsorbent dose from 1.0 to 10 g/L. The trend was as per expectations since more active sites of adsorbent were exposed when the adsorbent dose increased (El-Sikaily et al, 2007). However, the Cr(VI) uptake capacity of the adsorbent has decreased from 5.9 to 1.4 mg/g when the adsorbent dose increases from 1 g/L to 10 g/L.

5.4.3 Effect of Initial Cr(VI) Concentration

The effect of initial concentration of Cr(VI) by Biochar adsorption studied by varying the initial Cr(VI) concentration and the results were shown in Fig 5.6. It was observed that the percentage adsorption decreased with the increase of adsorbate concentration (Jadav et al, 2015). This is fact that at fixed adsorbent dose, the number of active sites to accommodate the adsorbate ions increases with higher initial concentration. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake (Malkoc, and Nuhoglu, 2007). So, the loading is faster with higher concentration of adsorbate. The maximum removal was 100% at 10 ppm has decreased to 94% at 100 ppm of initial Cr(VI) concentration. The uptake capacity has been increased from 2 mg/g at 10 ppm to 18.9 mg/g at 100 ppm.

5.5 Kinetic Model

It is very important to find the rate at which adsorption takes place for a given system in order to design the continuous column. In order to investigate the mechanism of adsorption, various kinetic models have been suggested. Numerous kinetic models have described the reaction order of adsorption systems based on solution concentration (Rane and Sapkal, 2014). All the data has been applied to different kinetic model equation as described in previous chapter and it was found that Cr(VI) adsorption by Biochar follows the pseudo second order kinetic model. All the value of kinetic parameter and R^2 has been tabulated in Table 5.2.

5.6 Equilibrium Adsorption Isotherm

The equilibrium separation between the two phases is an important criterion to be considered for the successful representation of the dynamic adsorptive separation of the solute from solution into an adsorbent. An adsorption isotherm plays a major role, which relates the surface properties and affinity of the adsorbent to compare the various pollutants uptake capacity. In order to find out the mechanism of Cr(VI) adsorption by the Biochar and determine the relationship the experimental data were applied to different isotherm equations. From the Table 5.3, it is clear that it follows the Langmuir adsorption isotherm.

5.7 Rate Controlling Mechanism

On porous adsorbents, the adsorption of Cr(VI) us governed by four steps i.e. are bulk diffusion in solution followed by film diffusion, surface diffusion and intra-particle diffusion in series as we have discussed in previous chapter. In order to find out the rate limiting step during the adsorption process, different model has been used as discussed in chapter 2. Experimental data were used to find the rate constants along with the regression coefficients. From the R^2 values it can be observed that experimental fitted well to all the three models. The model parameters along with the regression coefficients are shown in Table 5.4. From the values of the diffusivity in the table it can be concluded that surface diffusion is the slowest steps and hence is the rate limiting steps.

5.8 **Comparison among adsorbents**

The Cr(VI) uptake capacities of different sorbents are presented in Table 5.5. It is tough to directly relate Cr(VI) uptake capacities of various adsorbents due to a dearth of uniformity in the information from the literature. The uptake capacity was estimated at dissimilar pH, temperatures, Cr(VI) concentrations, adsorbent doses and at various temperatures. Further, the adsorbents were used for treating wastewater from various sources such as drinking water, ground water, artificial and real wastewater. So, the kinds and amount of inquisitive metal ions are dissimilar and not acknowledged in detail. Large number of the adsorption experiments were conducted in batch modes and few experiments in uninterrupted column modes which definitely cannot be readily compared. In addition, most research has been restricted to laboratory scale calculations of Cr(VI) uptake capacity and the mechanism od adsorption. In batch adsorption experiments, the uptake capacities are calculated from different isotherms or experimentally which makes comparisons more complex to pursue. The cost of adsorbents from different wastes is not reported in the literature. Further, the adsorbents cost depends on source, accessibility, pretreatment methods, longevity and recyclability. Numerous adsorbents have been used for chromium adsorption after chemical modifications. However, the cost involved in the chemical alteration of adsorbents is never reported in the literature. Further, cost evaluation for Pilot scale studies remains to be explored. Therefore, rigorous, accurate and direct comparisons among the reported adsorbents is highly dreadful. With above caveats in observance, few adsorbents were chosen from the literature and compared in Table 5.5. From the table, it can be concluded that, present adsorbent is comparable with various adsorbent reported in the literature.

5.9 Conclusion

As seen from chapter 2, 3 and 4, the adsorption capacity of the adsorbent is low at higher pH. Further the bio-sorbent neither can be regenerated nor can be used directly in any industrial process. Therefore, in the present study biochar is used as an adsorbent for the treatment of Cr(VI) contaminated wastewater. The advantages of using Biochar as an adsorbent is that the used Biochar can be reused in a ferrochrome industry as a source of carbon i.e. fuel. Further, the adsorbed Cr(VI) can be used as a raw material for the ferrochrome production. Therefore, no regeneration or disposal of the adsorbent is required which may create environmental problem and hence can be treated as clean treatment technology. The adsorption experiments were carried by varying different adsorption parameters such as time, pH, adsorbent dose and adsorbate concentrations to find out their effects on the percentage adsorption as well as uptake capacity of the adsorbent. As usual the adsorption capacity and percentage adsorption increases with decrease in pH. The percentage adsorption increases with increase in adsorbent dose whereas, the uptake capacity decrease with increase in adsorbent dose. In case of increase in adsorbate concentration, the percentage adsorption decreases whereas the uptake capacity increases. The adsorption process followed pseudo 2nd order kinetic model and Langmuir adsorption isotherm. The surface diffusion is found to be the rate limiting steps for the adsorption process.

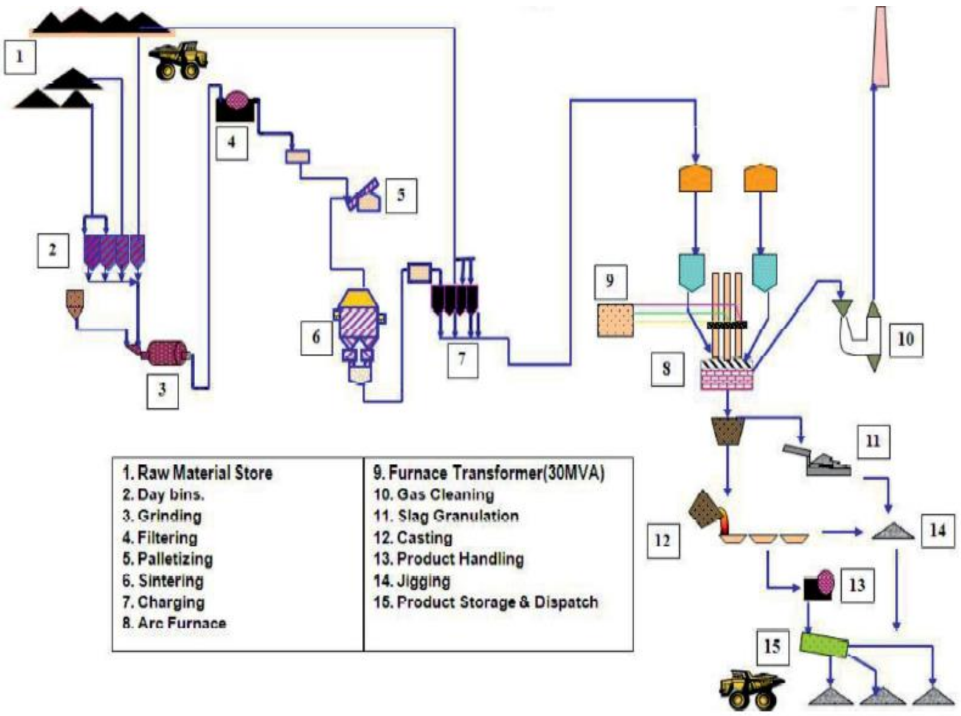


Fig. 5.1: Production of Ferrochrome

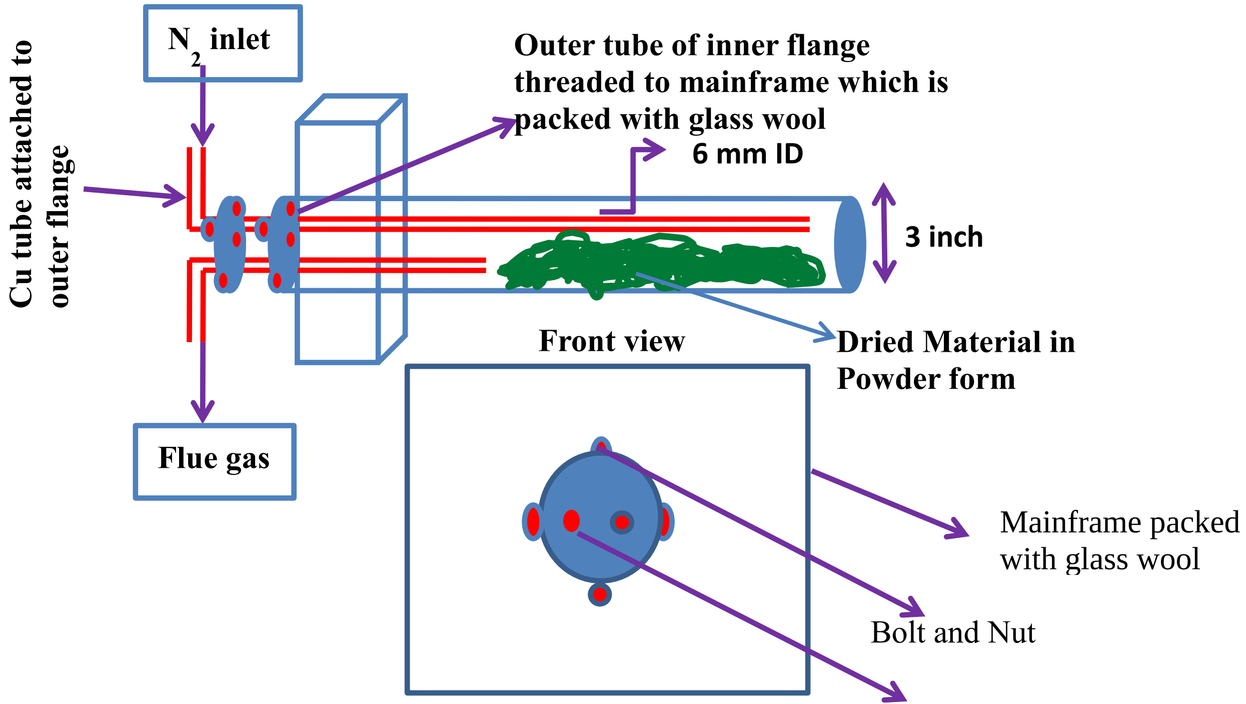


Fig. 5.2: Experimental Setup for Carbonization of Grass

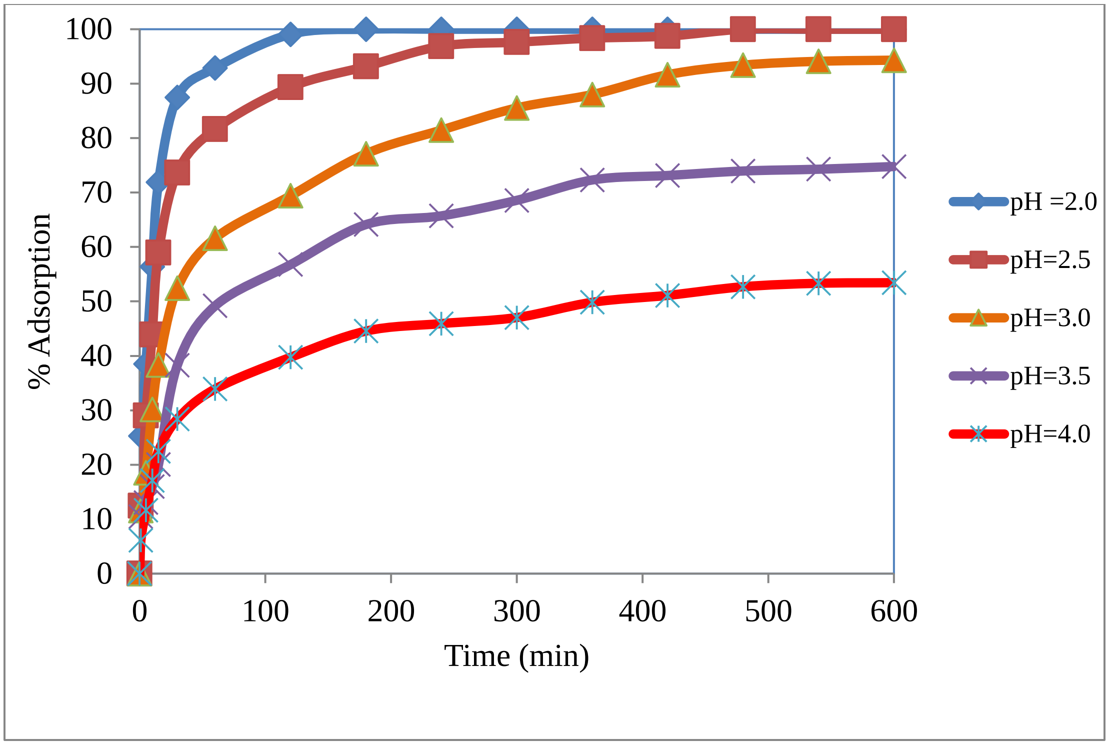


Fig. 5.3: Effect of contact time on percentage of Cr(VI) adsorption. Condition: Concentration:100 ppm, Dose: 5 g/L, Temp:30^{o}C.

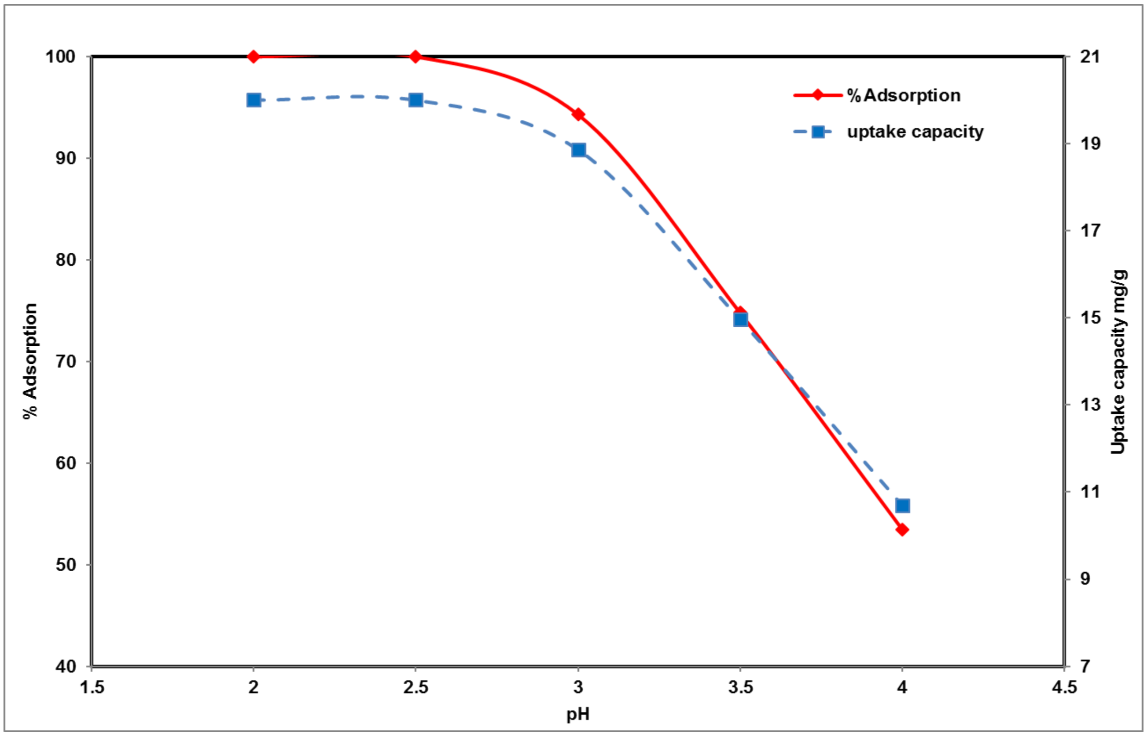


Fig. 5.4: Effect of pH on percentage of Cr(VI) adsorption. Condition: Concentration: 10 ppm, Dose: 5 g/L, Temp: 30^{o}C.

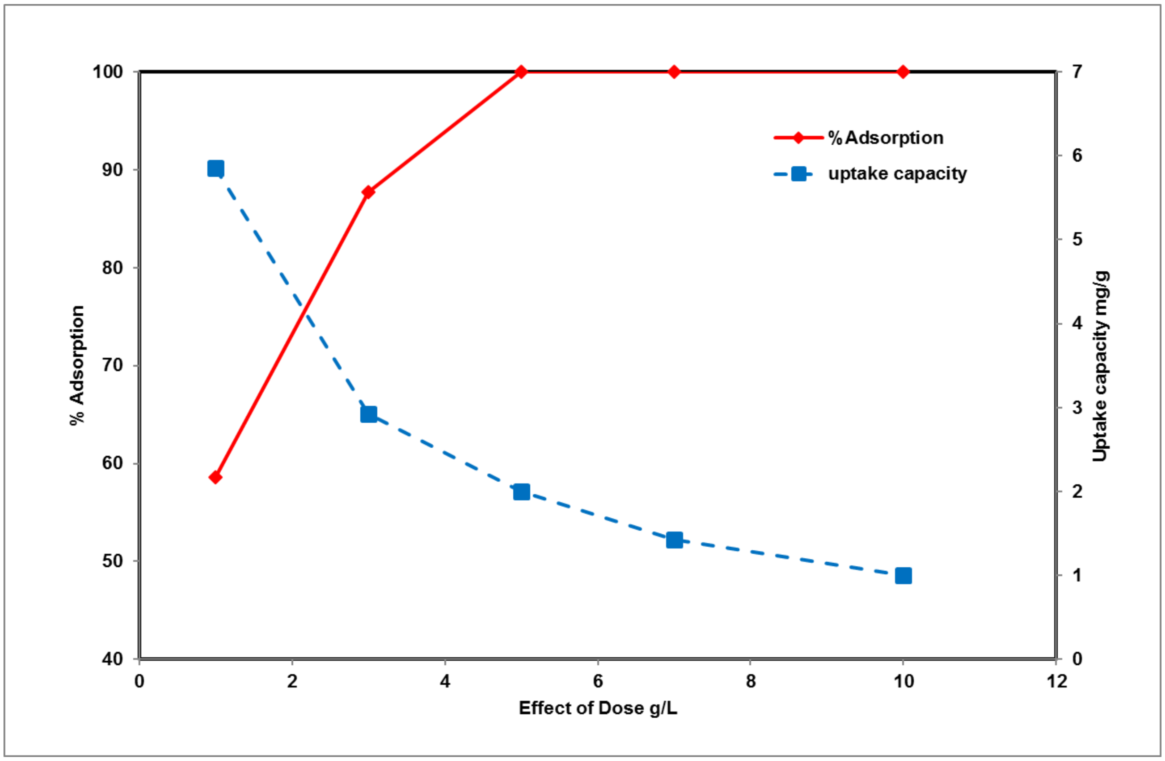


Fig. 5.5: Effect of Adsorbent Dose on percentage of Cr(VI) adsorption. Condition: pH 3.0, Concentration: 100 ppm, Temp: 30°C.

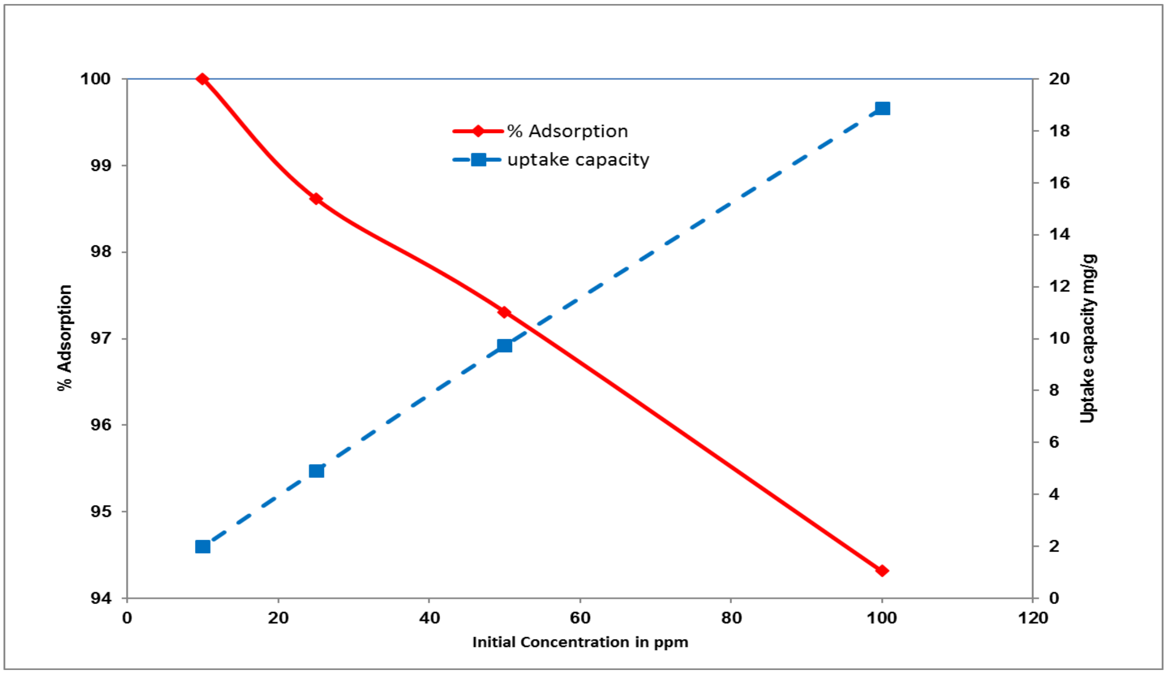
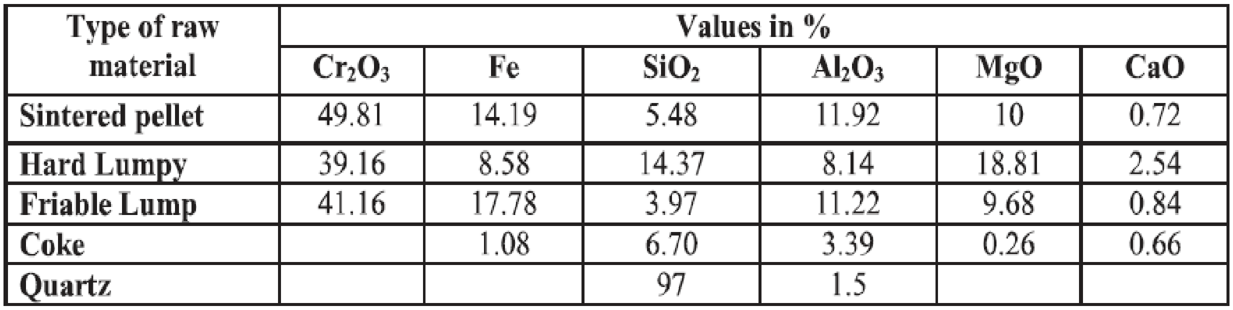


Fig. 5.6: Effect of Initial Cr(VI) Concentration on percentage of Cr(VI) adsorption. Condition: pH 3.0, Dose: 5 g/L, Temp: 30°C.

Table 5.1: Composition of Raw Material for Ferrochrome production



Type of raw material	Values in %					
	Cr_2O_3	Fe	SiO_2	Al_2O_3	MgO	CaO
Sintered pellet	49.81	14.19	5.48	11.92	10	0.72
Hard Lumpy	39.16	8.58	14.37	8.14	18.81	2.54
Friable Lump	41.16	17.78	3.97	11.22	9.68	0.84
Coke		1.08	6.70	3.39	0.26	0.66
Quartz			97	1.5		

Table 5.2: Adsorption Kinetic models parameters

Parameter	Values	Pseudo 1st order		Richie's 2nd order		Pseudo 2nd order		First order reversible		
		k	R^2	k	R^2	k	R^2	k_1	k_2	R^2
Adsorbent dose (g/L)	1	0.316	0.87	0.08	0.61	0.0400	0.973	0.026	0.180	0.740
	3	0.360	0.904	0.16	0.53	0.1300	0.995	0.047	0.200	0.790
	5	0.640	0.97	1.1	0.74	0.2530	1	0.470	0.050	0.921
	7	0.511	0.833	0.45	0.91	0.5000	1	0.070	0.360	0.860
	10	0.640	0.91	0.952	0.81	1.0200	1	0.050	0.304	0.910
pH	2	0.67	0.88	0.853	0.87	0.0030	1	0.040	0.002	0.890
	2.5	0.42	0.99	0.17	0.94	0.0020	1	0.012	0.001	0.826
	3	0.4	0.88	0.4	0.42	0.0030	0.997	0.010	0.002	0.932
	3.5	0.39	0.95	0.19	0.697	0.0050	0.998	0.004	0.006	0.977
	4	0.38	0.85	0.413	0.36	0.0090	0.996	0.010	0.007	0.903
Initial Concentration(ppm)	10	0.661	0.97	1.1	0.74	0.2530	1	0.020	0.002	0.810
	25	0.4	0.98	1.3	0.33	0.0420	1	0.010	0.002	0.840
	50	0.4	0.923	0.3	0.64	0.0100	0.997	0.008	0.002	0.960
	100	0.4	0.88	0.400	0.42	0.0030	0.997	0.008	0.002	0.930

Table 5.3: Adsorption isotherm models parameters

Parameter	Values	Freundlich Isotherm			Langmuir Isotherm		Temkin Isotherm	
		Slope 1/n	log K_f	R^2	$1/q_{max}$	R^2	RT/b	R^2
Adsorbent dose (g/L)	1	0.116	0.64	0.84	0.17	1.0	1.39	0.799
	3	0.094	0.65	0.78	0.342	1.0	0.590	0.756
	5	0.027	0.002	0.614	0.5	1.0	0.216	0.734
	7	0.023	0.1	0.565	0.7	1.0	0.344	0.900
	10	0.020	0.17	0.632	1.000	1.0	0.181	0.945
pH	2	0.264	1.414	0.638	0.05	1.0	3.19	0.760
	2.5	0.33	1.46	0.620	0.05	1.0	3.52	0.800
	3	0.266	1.34	0.510	0.053	1.0	2.67	0.680
	3.5	0.35	1.27	0.645	0.067	1.0	2.63	0.770
	4	0.270	1.03	0.490	0.094	1.0	1.51	0.660
Initial Concentration(ppm)	10	0.161	0.144	0.635	0.50	1.0	0.216	0.730
	25	0.211	0.64	0.68	0.203	1.0	0.685	0.780
	50	0.21	0.97	0.602	0.103	1.0	1.27	0.740
	100	0.197	0.970	0.491	0.05	1.0	2.28	0.623

Table 5.4: Rate controlling mechanism

		q_t vs $t^{1/2}$		q_t/q_e vs $t^{1/2}$			$\ln(1-(q_t/q_a))$ vs t		
Parameter	Values	k_{id} mg/g min$^{(1/2)}$	R^2	$6(D_1/\Pi a^2)^{1/2}$	D_1 mm^2/time 10^{-6}	R^2	$D_2 \Pi/a^2$	D_2 mm^2/time 10^{-3}	R^2
Adsorbent dose (g/L)	1	1.480	0.974	0.044	0.92	0.87	0.160	0.279	0.950
	3	1.484	0.98	0.057	1.55	0.984	0.340	0.593	0.990
	5	0.710	0.97	0.043	0.88	0.972	0.340	0.593	0.934
	7	0.650	0.95	0.06	1.72	0.99	0.380	0.663	0.980
	10	0.370	0.9	0.06	1.72	0.993	0.340	0.593	0.954
pH	2	0.91	0.66	0.13	8.07	0.97	1.300	2.267	0.900
	2.5	1.13	0.78	0.11	5.78	0.95	0.400	0.698	0.950
	3	1.23	0.912	0.11	5.78	0.995	0.564	0.984	0.930
	3.5	1.05	0.883	0.11	5.78	0.92	0.550	0.959	0.980
	4	0.69	0.915	0.1	4.78	0.99	0.980	1.709	0.910
Initial Concentration(ppm)	10	0.084	0.69	0.100	4.78	0.94	0.900	1.570	0.980
	25	0.23	0.79	0.103	5.07	0.98	0.390	0.680	0.995
	50	0.55	0.91	0.083	3.29	0.983	0.690	1.203	0.994
	100	1.235	0.91	0.107	5.47	0.99	0.564	0.984	0.930

Table 5.5: Comparison of the present adsorbent with various adsorbents reported in literature

S.No	Name of the Adsorbent	Time (min)	pH	Adsorbate conc. (mg/L)	Dose (g/L)	Temp. ^{0}C	% Ads.	Uptake capacity (mg/g)	Reference Number
1	Bael fruit shell	240	2	50	10	30	92	17.27	Anandkumar & Mandal, 2009
2	Basillus Biomass	480	2	100	1	30	15	14.9	Sivaprakash et al, 2009
3	Plant Biomass-L. Hexandra	40	2	10	4	25	95	2.5	Li et al, 2009
4	Magnetite nanoparticle	60	2.5	50	5	25	99.8	15.3	Yuan et al, 2009
5	Cetyl trimethyl ammonium bromide micellar compounds	60	2	30	2	30	100	17.89	Sadaoui et al, 2009
6	Marine biomass posidonia oceania fibre	180	2	50	10	30	50	2.4	Ncibi et al, 2009
7	Husk of Pomegranate	180	1	150	3	25	52	35.2	Nemr, 2009
8	Sulfonated Lignite	60	2	50	2.8	25	80	27.87	Zhang et al, 2010
9	Rice Straw	180	2	25	10	25	95	12.17	Singha, 2011
10	Rice Husk	360	1.5	25	10	25	90	11.39	Supriya et al, 2013
11	Neem bark	240	3	50	10	25	95	19.6	Supriya et al, 2013
12	Neem leaves	240	2	25	10	25	75	15.95	Supriya et al, 2013
13	Coconut shell	240	2	25	10	25	95	18.69	Supriya et al, 2013
14	Magnifera Indica bark	480	7	5	1	30	78	19.64	Supriya et al, 2013
15	**Biochar**	**600**	**3**	**100**	**5**	**30**	**94**	**18.9**	**Present study**

Chapter-6

Optimizing adsorption parameters using statistical design of experiments

6.1 Factorial Design of Experiments

In order to plan an adsorption process, a number of influencing parameters such as contact time, pH, adsorbate concentration, adsorbent dose, stirring speed, particle size and temperature are need to be studied. But the process of studying each and every variance separately is quite tedious as well as time consuming. Further, conventional and classical methods of studying the effect of different factors involved in the adsorption process at an unspecified constant level dose not depict the combined effect of all the factors involved (Ravikumar et al, 2005). This method requires a large number of experiments to determine the optimal levels, which are unreliable. Thus, the optimization of all the affecting parameters collectively by using different mathematical models can minimize the above difficulties (Elibol, 2002; Gun et al, 2002). Objectives of the present study is basically to

- ❑ determine those variables which are the most influential on the response
- ❑ developing empirical models based on the independent variable so that the response is almost always near the desired maximal/minimal value
- ❑ minimize the effect of uncontrollable variable inputs
- ❑ find out the optimal process parameters

Experimental design method is an important tool in the engineering science for achieving better results with minimal effort. It has also been applied extensively in the development of new processes. Application of this method in the process development can result in improved yield, reduced variability and firm confirmation to nominal or target requirements, reduced development time and reduced overall cost (Montgomary, 1991). Further, pre-design of experiments determines which factors have important bearings on an expected response as well as how the effect of one factor varies with the level of other factors (Arenas et al, 2006; Statistical home page, 2006; Montgomary, 2001; Box et al, 1978). A factorial experiment is the important source to quantitatively assess the individual independent terms including interaction effects of different coefficients and factors.

Engineering design plays a major role in optimizing the process parameters, where new products are developed and existing ones are improved. Some applications of engineering design are;

- ➢ Evaluation and comparison of basic design configuration

- Evaluation of material alteration
- Selection of designing parameters so that the product will work well under a wide variety of field conditions
- Determination of key product design parameters which have impact on the product performance

Application of statistical approach in designing and analyzing an experiment requires that everyone involved with the experiment should have a clear idea about the parameters to be studied, collection of data and at least a qualitative understanding of how the data are to be analyzed. An outline of the recommended procedure is stated in brief (Montgomery, D. C., 1991)

- *Recognition and state of the problem*: Clear statements of the problem often contribute substantially to a better understanding of the phenomena and the final solution of the problem.
- *Choice of factors and levels:* At the beginning of a study, choice should be made about the factors to be varied in the experiments, the ranges over which this factors will be varied, and a specific level at which runs will be made. Consideration must also be given to how these factors are to be controlled at the desired values and how these are to be measured.
- *Selection of the response variable*: In selecting the response variables, it must be ascertained that this variable really provides useful information about the process.
- *Choice of experimental design*: If the first three steps are performed correctly this step becomes relatively easy. Choice of design involves consideration of sample size (number of replicates) and selection of a suitable number of trials. In selecting the design, it is important to keep experimental objectives in mind.
- *Performing the experiment:* While running the experiments, it is essential to monitor the process carefully to ensure that everything is being done as per plan. Errors in experimental procedure at this stage will usually destroy experimental validity.
- *Data analysis*: Statistical method should be used to analyze the data so that the results and conclusions are objectives rather than conclusive in nature. If the

experiments have been designed correctly and if it has been performed according to the design, then the statistical methods required are not elaborate.

- *Conclusion and recommendation*: Once the data have been analyzed, practical conclusions about the results are drawn and a course of action is recommended.

In the present study, full factorial designed is used to optimize the adsorption parameters for the treatment of Cr(VI) contaminated wastewater. This chapter is broadly divided in to two parts. In the 1st part of the study, a full factorial design is used to find the effect of different adsorption parameters on the Cr(VI) adsorption capacity using ***Sorghastrum Nutans L. Nash.*** Experiments were designed using statistical design of experiments and carried out in the laboratory at the desired level of adsorption parameters. MINITAB software is used to develop the empirical model. The model is analyze using various statistical techniques such as the normal probability, residual, contour, 3D surface, main effect and interaction plot, t-test, ANOVA and F-test. In the 2nd part of the study, data were collected from the literature and analyzed using designed of experiment. Matrix method is used to develop the empirical equation relating the dependent variable and independent variables. MATLAB and LabVIEW is used to simulate the empirical model. Finally, a comparison is made among MATLAB and LabVIEW.

6.2 Design of Experiment for the Treatment of Cr(VI) Contaminated Water using *Sorghastrum Nutans L. Nash*

Full factorial design of 2^4 type was employed for the optimization of adsorption parameters and also to find out the most significant factor among the parameters. Where four parameters and two levels for each parameter is used to optimized the process. The four factors pH, adsorbent dose, initial concentration and time were selected as independent variables and % Cr(VI) sorption is chosen as the response variables. The independent variables are varied at two levels as shown in Table 6.1 to investigate their effects on the Cr(VI) removal. The effect of an independent factor on the response variable is known as the main effect. In some cases, it is found that the variation in the response between level of one factor is not the same at all levels of the other factors, which is known as an interaction effect between independent variables (Wu & Hamada, 2009). A full factorial design of n^k type can estimate all major effects and higher-order interactions. In the contemporary study, experiments were carried out by varying four parameters with two levels. There are 2^4=16 experiments carried out in the two levels and four experiments at base level to study the main effect and also the interaction effects. The experimental designed of trial runs in coded form is shown in Table 6.2. A common regression model (Meski et al, 2011) for studying main effects and interactions is.

$$Y_e = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 + b_{134}x_1x_3x_4 + b_{234}x_2x_3x_4 + b_{1234}x_1x_2x_3x_4 \quad (6.1)$$

Where

b_0 is the average value of the results obtained for the adsorbed chromium amount from all 20 experiments and b_1, b_2, b_3 and b_4 are the coefficients of the main effects and b_{12}, b_{13}…..b_{1234} are interaction coefficients of the corresponding variables. x_1, x_2, x_3 and x_4 are the dimensionless coded factors upsetting the process where x_1=time, x_2= pH, x_3= adsorbate concentration and x_4= adsorbent dosage. The main and interaction coefficients have been calculated by following relations (Singh et al, 2002).

$$b_0 = \Sigma(Y_e/N) \quad (6.2)$$

The coefficients of the main as well as interaction terms are calculated from the following equation.

$$b_j = \frac{(\Sigma x_{ij}Y_j)}{N} \quad (6.3)$$

where j =1,2,3,4…. n and i is the rows number and j the columns number.

The experimental data are used to calculate the coefficient and the resulting regression equation becomes:

$$Y_e = 62.97 + 1.43x_1 - 8.22x_2 - 1.244x_3 + 2.48x_4 + 0.644x_1x_2 + 0.32x_1x_3 + 0.269x_1x_4 + 0.32x_2x_3 + 0.343x_2x_4 - 2.81x_3x_4 + 0.606x_1x_2x_3 + 0.381x_1x_2x_4 - 0.594x_1x_3x_4 - 0.694x_2x_3x_4 - 0.7313x_1x_2x_3x_4 \quad (6.4)$$

From the resulting equation, the main effect and interactional effects were estimated. According to the equation, pH if the most significant factor and has the most influential effect on the percentage of adsorption and its co-efficient is negative indicating that, the percentage of adsorption increases as when pH of solution is decreased (Baral et al., 2009). At lower pH, the adsorbent surface becomes more positively charged due to the existence of large number of H^+ ions. The higher H^+ ion on the surface attract more anionic chromium ions. Therefore, the hexavalent chromium removal is higher at low pH values. CrO_4^-, $Cr_2O_7^{2-}$ form of Cr(VI) is dominant at higher pH and the OH^- ions are also increased. The second most influential parameter is the adsorbent dose which has a positive coefficient indicating that, adsorbent dose has a synergetic effect on percentage adsorption. As we can see from Table 6.3, the adsorbate concentration has the least influence on the percentage of Cr(VI) removal. The main effect and interaction are calculated by using multiple regression model equation.

6.2.1 Students't' Test for Signifying the Coefficient and Fisher's Adequacy Test

The implication of individual coefficient of a regression equation can be tested using student 't' test. Significance of the coefficient of each main and interaction terms was assessed in the present study using the T values from student 't' test (Devy & Bai, 2004). The result of each factor was considered to be significant for $P< 0.05$ (Abdel-Ghani et al, 2009). The unimportant terms are neglected from the equation using the above criteria. The significant interaction between the independent variable are x_1x_2, x_3x_4, $x_1x_2x_3$, $x_1x_3x_4$, $x_2x_3x_4$ and $x_1x_2x_3x_4$. The other coefficient interaction terms do not have significant effect on the basis of lower T values. The resulting equation after neglecting the insignificant interaction coefficient becomes:

$$Y_e = 62.97 + 1.43x_1 - 8.22x_2 - 1.244x_3 + 2.48x_4 + 0.644x_1x_2 - 2.81x_3x_4 + 0.606x_1x_2x_3 - 0.594x_1x_3x_4 - 0.694x_2x_3x_4 - 0.7313x_1x_2x_3x_4 \qquad (6.5)$$

All this Co-efficient data has been included in Table 6.3. We can see from the table 6.4 that the observed and predicted value of percentage of removal of Cr(VI) are very close.

6.2.2 Regression Analysis

The analysis of variance (ANOVA) test was performed for the developed mathematical model. The values of R^2, (94.33%) a measurement of the fitness of the regression equation was found satisfactory. ANOVA is performed to find out the outcome of interacting term on the percentage of chromium removal. The significance of each factor in the procedure depends on the sum of the squares of those individual factors and the importance of the corresponding factor increases with increase in the sum of square values. The main and interaction terms with P values <0.05 were assume to be potentially significant (Adinarayana et al, 2003). From Table 6.3, it is seen that, P value is almost negligible for pH, and therefore, it has the most significant effect on percentage of adsorption.

6.2.3 Normal Probability Plot of Residuals

Normality of the experimental data is very important in statistical design methods. The data points are considered to be normally distributed, if response points are fall fairly close to straight line (Kundu & Gupta, 2006; Antony, 2003; Montgomery, 2001). Consequently, to find out the normality of data, normal probability curve of the residuals was generated and shown in Fig. 6.1. It can be seen from the diagram above that most of the data points are quite closer to the straight line and it depicts that the experiments come from a normally scattered population. Thus, our assumption of normality is valid (Ucar et al, 2011).

6.2.4 Residual Graph

The residual is the differentiation among the experimental and the calculated value from the empirical equation and is shown in Table 6.4. The residual plot for the data (normal probability plot) is shown in Fig. 6.1. From the figure, it is observed that the data points are mostly aligned with the fitted model. The results are also interpreted from the histogram shown in Fig.6.2. The figure shows the allocation of the residuals for all observations. The plot between residuals and predicted response is shown in Fig. 6.3. From the Fig. 6.2 and Fig. 6.3, it can be observed that the residuals are scattered randomly about zero and hence the error have constant variance. It is also evident from these figures that the experimental values are fairly aligned and hence followed normal distribution. The consistency of the empirical equation is also verified from residuals vs Frequency plot as shown in Fig. 6.3. It indicates that the error terms against the predicted response and the number of increasing or decreasing points are significant. Further, the patterns of increasing residuals and predicted response are found to be similar. It is also observed that the positive and negative residuals are well scattered in the same range (Baskar & Shabudeen, 2015).

6.2.5 Main and Interaction Effects

The key and interaction effects of various parameters on Cr(VI) uptake have been studied. In order to establish the combined effects of the physical variables on the response, experiments are conducted at the specified level of these variables using factorial design of experiments. Fig. 6.4 shows the major effect of all the physical parameters on the response variable. The figures for main effect are used to plot data means when more independent variables are participated in the process sand also to relate the degrees of marginal means (Geyikci & Buyukgungor, 2013). From Fig. 6.4 it is evident that the grand mean of the response is at around maximum Cr(VI) removal. The magnitude of the main effect will be small, if the slope is close to zero. The main plot in Fig. 6.4 shows that the interaction of pH plays a major role as this slope is very steep. The effect of concentration and time has minor effect on the response. The interaction effects of all the physical parameters on the response are presented in Fig. 6.5. From the plot, the spread points on the graph between pH versus concentration, time versus concentration, and pH versus Dose is larger than the all three plots. Therefore, at a very low pH and high concentration the percentage of adsorption will increase.

6.2.6 Contour Plot and 3D Surface Plot

Contour plots for the significant interactions between different parameters is been shown in Fig. 6.6. Contour plot and surface plots are suitable for finding out the optima values of response variables and locating the optimal zones of the independent variables. From the contour plot, it is observed that interaction effect of adsorbent dose and pH of the solution act as key role and these two factors dominant influence on the percentage of removal (Gottipati & Mishra, 2010). The significance of the interaction among the independent variables is shown by the surface plot in Fig.6.7 which provides a 3D view, and provide an indistinct image of the response surface (Nkuzinna et al, 2014). From the surface plots in Fig. 6.7, the variation of the response variable i.e. the percentage of adsorption, with changes in independent variables. Different graphs drawn include concentration vs pH, concentration vs time, concentration vs dose, pH vs dose, time vs dose and time vs pH. From this plot, it is clear that the pH has more impact on percentage adsorption.

6.3 Modeling and Simulation for the Adsorptive Removal of Cr(VI)

In this part of the study experimental data collected from literature (Baral et al, 2008) and used for the optimization of adsorption parameters. The basic objective is to develop different alternatives techniques for modeling and simulation of Cr(VI) adsorption process. A full factorial design of the type n^k has been used for the literature data, where n is the number of levels and k is the number of factors under verification. Here time, pH and temperature were chosen as three independent factors/variables (k=3 and n=2) and the percentage of adsorption as the dependent out-put response variable. A 2^3 full-factorial experimental design (Montgomary, 2001) with number of 3 triplicates at the center point and thus a total of 11 experiments were employed in this study. For statistical calculation, the base level, which is the average of two level were calculated using the following relation

$$x_i = \frac{X_i - X_0}{\delta X} \tag{6.6}$$

The behavior of the system was explained by the following

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{23} x_2 x_3 + b_{31} x_3 x_1 + b_{123} x_1 x_2 x_3 \tag{6.7}$$

where b_0, b_1… b_{123} are the regression interaction coefficients of the concerned variables and x_1, x_2 and x_3 are the dimensionless coded factor affecting the process. Here x_1=time, x_2=pH and x_3=temperature. The factorial levels and variation interval of the coded factor are shown in Table 6.5. The parameters varied were time (5-15min), pH (1.6-1.8) and temperature (30-40°C). The variable parameters in two levels, their coded values and the condition for the base level experiments are given in Table 6.6. The +, - and 0 designations were given to the higher, lower and base levels respectively.

6.3.1 Development of Mathematical Model

Equation 6.8 is a representation of Table 6.6. X is obtained by interpolating columns 2-8 of Table 6.6 into matrix form excluding the base values. Thus, X is an 8×8 matrix obtained for all the possible combinations of x_1, x_2 and x_3, as shown in equation 6.10. Further the regression coefficients are represented by an 8×1 matrix B as shown in equation 6.11. Thus, the product of X and B is the matrix Y with values corresponding to 9th column of Table 6.6.

$$[Y]=[X]\times[B] \qquad (6.8)$$

where

$$[Y]=\begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ Y_5 \\ Y_6 \\ Y_7 \\ Y_8 \end{bmatrix} \qquad (6.9)$$

$$[X]=\begin{bmatrix}
1 & +x_1 & +x_2 & +x_3 & (+x_1)\times(+x_2) & (+x_2)\times(+x_3) & (+x_3)\times(+x_1) & (+x_1)\times(+x_2)\times(+x_3) \\
1 & -x_1 & +x_2 & +x_3 & (-x_1)\times(+x_2) & (+x_2)\times(+x_3) & (+x_3)\times(-x_1) & (-x_1)\times(+x_2)\times(+x_3) \\
1 & +x_1 & -x_2 & +x_3 & (+x_1)\times(-x_2) & (-x_2)\times(+x_3) & (+x_3)\times(+x_1) & (+x_1)\times(-x_2)\times(+x_3) \\
1 & -x_1 & -x_2 & +x_3 & (-x_1)\times(-x_2) & (-x_2)\times(+x_3) & (+x_3)\times(-x_1) & (-x_1)\times(-x_2)\times(+x_3) \\
1 & +x_1 & +x_2 & -x_3 & (+x_1)\times(+x_2) & (+x_2)\times(-x_3) & (-x_3)\times(+x_1) & (+x_1)\times(+x_2)\times(-x_3) \\
1 & -x_1 & +x_2 & -x_3 & (-x_1)\times(+x_2) & (+x_2)\times(-x_3) & (-x_3)\times(-x_1) & (-x_1)\times(+x_2)\times(-x_3) \\
1 & +x_1 & -x_2 & -x_3 & (+x_1)\times(-x_2) & (-x_2)\times(-x_3) & (-x_3)\times(+x_1) & (+x_1)\times(-x_2)\times(-x_3) \\
1 & -x_1 & -x_2 & -x_3 & (-x_1)\times(-x_2) & (-x_2)\times(-x_3) & (-x_3)\times(-x_1) & (-x_1)\times(-x_2)\times(-x_3)
\end{bmatrix}$$

(6.10)

$$[B]=\begin{bmatrix} b_0 \\ b_1 \\ b_2 \\ b_3 \\ b_{12} \\ b_{23} \\ b_{31} \\ b_{123} \end{bmatrix} \qquad (6.11)$$

6.3.2. Simulation Using MATLAB:

The MATLAB is a user-friendly tool for solving equations of various kinds by writing a proper code for the requirement Regarded as the language for technical computing, MATLAB has also been widely used by researchers in industrial and applied mathematics, as well as engineers, scientists and economists because of its efficiency in dealing with matrices and matrix algebra (Ang, 2008). In addition, the availability of special purpose toolboxes (such as Signal Processing, Optimization and Financial Toolboxes) has made it easier for researchers to use MATLAB in their work. It can be used to finish our task of solving equations easily provided the code is correct. Besides using it as a mathematical tool for solving equations MATLAB can be used as a language to write algorithms for various software like LabVIEW simulation software. Also, programming languages like C can also be coded using MATLAB. In the present study, we have used matrix method to develop a mathematical model for the adsorption process. We have written a code using MATLAB to simulate the developed mathematical model.

Simulation of adsorption process would best be implemented with a tool that can perform matrix computations efficiently, carry out numerical analysis conveniently and produce a desired output accurately. MATLAB is one such tool that can do all these computations concomitantly. In the succeeding section the development of code using MATLAB for solving equation 6.8 is outlined.

Matrices developed in section 6.3 were solved to obtain the regression interaction coefficients b_0, b_1… b_{123} of equation 6.12. Equation 6.8 was solved using MATLAB and the corresponding code is given in Table 6.7. The variation levels of parameters obtained from Table 6.5 were defined as x_p, x_o and x_n where p, n and 0 represents +, - and base values. Equation 6.10 as discussed earlier is defined for all the possible combinations of the adsorption parameters obtained from Table 6.6. By executing the code as given in Table 6.7, we obtain the values of regression interaction coefficients b_0, b_1… b_{123}. Thus, equation 6.7 can be represented as:

$$Y = 38.89 + 2.8x_1 - 4.593x_2 + 4.073x_3 + 0.0087\, x_1x_2 - 0.9812\, x_2x_3 - 0.7837\, x_3x_1 - 0.5787\, x_1x_2x_3 \tag{6.12}$$

6.3.3 Simulation Using LabVIEW

LabVIEW is an integrated data acquisition, analysis and presentation package for the graphical programming of scientific and engineering applications in the areas of measurement, simulation and control using the computer. User-written LabVIEW programs are called ‘‘virtual instruments’’(VIs). VIs has three main parts: the front panel, block diagram, and icon=connector. The front panel provides the user an interface for data inputs and outputs. The user operates the front panel by using the computer’s keyboard and mouse. Behind the front panel is the block diagram that is responsible for the actual data flow between the inputs and outputs. The icon=connector defines data flow between subroutines. LabVIEW includes device driver functions for serial and parallel interfaces and a wide range of mathematical, logic, timing and digital signal generation, processing and analysis functions. LabVIEW has been used in areas such as simulation, automated testing, data acquisition and analysis, and process control.

It is possible for amateur programmers to design programs of high quality by using LabVIEW, and it suits the thinking methods of scientists and engineers so that it can be honored with the name of engineering language (Wang et al, 2007). LabVIEW has wide application in the fields of aerospace, communications, automobile engineering, biomedicine, and so forth. However, to our knowledge, it has not yet been reported on frequently in the field of Chemical Engineering (Li et al, 2005). LabVIEW graphical programming relieves the user of writing and debugging code in conventional programming languages and replaces this with the simple and intuitive task of interconnecting functional blocks and control structures. The iconic presentation of blocks and structures and the familiar block diagram layout make the application almost self-explanatory with little need for additional documentation. The hierarchical nature of the VI concept allows complex systems to be divided into a set of more manageable sub-systems in a structured.

The block diagram was developed with an assumption that the adsorption parameters are variables. Considering the matrix approach as discussed earlier in section 6.2, the equations were solved using block diagram approach. Generally, LabVIEW accepts variables in array format only. To obtain a constant or a variable in an array format, a function for formatting these constants and variables into arrays was needed. For this, LabVIEW has a built-in application that is used for array formation. A window called “FUNCTIONS” panel which appears in the block diagram has several mathematical applications and tools required for developing a block diagram. A tool called “ARRAY” from the functions panel was used for formatting these variables and constants into arrays. Later by using matrix-templates obtained from the same panel, these arrays were arranged into their corresponding matrix forms. Thus, a block diagram as shown in Fig. 6.8 was developed.

The front panel of the virtual instrument is an interface between user and computer. Besides friendly interface and easy control, the corresponding test function can be started up by a simple manipulation. It should also be able to finish user’s task successfully. Software is a key section of the virtual instrument. Fig. 6.9 shows the front panel window where provision for the three-adsorption parameter x_1, x_2 and x_3 is provided. The values of ($+x_1$, $+x_2$, $+x_3$) & ($+x_{12}$, $+x_{22}$, $+x_{32}$) correspond to the variation values as given in Table 6.5. The real matrix and the inverse matrix obtained are shown in Fig 6.9. Result icon in the front panel window of Fig.6.9 is the desired output Y. The block diagram of the process between the inputs and output is delineated in Fig.6.8.

For further verification of the model developed, we defined three different variables x_1, x_2 and x_3, and their respective experimental Y value known in preempt. The new matrix X and the matrix B obtained from earlier calculations were used in equation 6.8 to evaluate the corresponding theoretical value of Y. Next the values of all the adsorption parameters were inputted in the front panel window and by execution we obtained the theoretical value of Y.

6.3.4 Comparison Between MATLAB and LabVIEW

In the MATLAB method of solution, our main aim was to obtain the values of regression interaction coefficients. There were a few disadvantages with MATLAB approach of solving the mathematical model. If there is a need to change the parameters which are considered as the basis for this mathematical model, the coded matrix has to be changed followed by the complete change in values of Table 6.6. This indeed requires a complete change of the code given in Table 6.7. To avoid this tedious approach of solving equation 6.7, a much user friendly method was developed using LabVIEW. In this model the values of parameters were inputted in the front panel window. The results were immediately obtained without any manual calculation in the same front panel window.

6.4 Error Analysis

In order to verify the goodness of fit of the developed mathematical models to the experimental values, it is necessary to examine the data using error analysis. A number of error analysis methods such as the sum of the square of the error (SSE), the sum of the absolute error (SAE), average relative error (ARE) and the average relative standard error (ARS) were used in the present study to verify which mathematical model is best fit to the experimental observations. The expressions for the above said error functions are as follows (Lazaridis et al, 2003; Leyva et al, 2005; Aksu and Isoglu, 2005; Kundu and Gupta, 2006):

- **The sum of the square of the error (SSE)**

$$SSE = \sum_{i=1}^{n} (Y_c - Y_e)_i^2 \tag{6.13}$$

- **The sum of the absolute error (SAE)**

$$SAE = \sum_{i=1}^{n} \left| Y_c - Y_e \right|_i \tag{6.14}$$

- **The average relative error (ARE)**

$$ARE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Y_c - Y_e}{Y_e} \right| \tag{6.15}$$

- **The average relative standard error (ARS)**

$$ARS = \sqrt{\frac{\sum_{i=1}^{n} [(Y_c - Y_e)/Y_e]^2}{n-1}} \tag{6.16}$$

where ‘n’ is the number of experimental data points, ‘y_c’ is the predicted (calculated) data, ‘y_e’ is the experimental data and ‘y’ represents the percentage of adsorption. The above statistical error expressions were applied to the mathematical model developed for different values of adsorption parameters. The above statistical criteria are applied to the equation

6.5 and 6.12. The value of the errors along with the predicted values are shown here in Table 6.4 and 6.8. It is quite evident from the values of the statistical parameters that trial data fit well to the mathematical model. It can be concluded from the values of the statistical parameters that the experimental data fit well to the mathematical model.

6.5 Conclusion

The objective of the present chapter was to develop empirical model using factorial design of experiment and use different tools MINITAB, MATLAB and LabVIEW to simulate or analyze the empirical model. In the 1st part of study, full factorial design of experiment is used for the optimization of Cr(VI) adsorption using *Sorghastrum Nutans L. Nash*. Factorial design of 2^4 type is employed with contact time, initial pH of the solution, adsorbent doge and initial Cr(VI) concentration as independent parameters and % of Cr(VI) adsorption as the response variable. Different statistical analysis such as probability, residual, contour, 3D surface, main effect and interaction plot along with t-test, ANOVA and F-test were used to optimize the operating parameters of the process. From the statistical analysis, it was found that the pH has a negative effect and is the most influential parameter, as pH decreases, the percentage of adsorption increases significantly. The second most important parameter is doses which has a positive effect as the percentage of adsorption increases with dosage. The maximum removal was obtained at pH of 1.3, concentration 100 mg/L and adsorbent dose of 7 g/L. The present adsorbent is compared with different low cost adsorbents reported in the literature and was found to be comparable. In the second part of the optimization process, Data is collected from the literature and a 2^3 type factorial design is used to design the experiment. Empirical mathematical model was developed using matrix method. In the mathematical model, percentage adsorption of Cr(VI) was represented as a function of process variables like contact time, initial pH of the solution and temperature. The significance of different adsorption parameters along with their combined effect on the process was studied. Error analysis using statistical method indicated that the experimental values were well fitted to the mathematical model. Later the empirical model was simulated using MATLAB and LabVIEW. Among the two simulating tool the latter one was found to be much user friendly. From the analysis, it was concluded that pH had the most influential effect on the adsorption process followed by contact time. Temperature had the least influential effect on the adsorption process. Among all possible combined effects, the effect of pH and contact time was the most influential one.

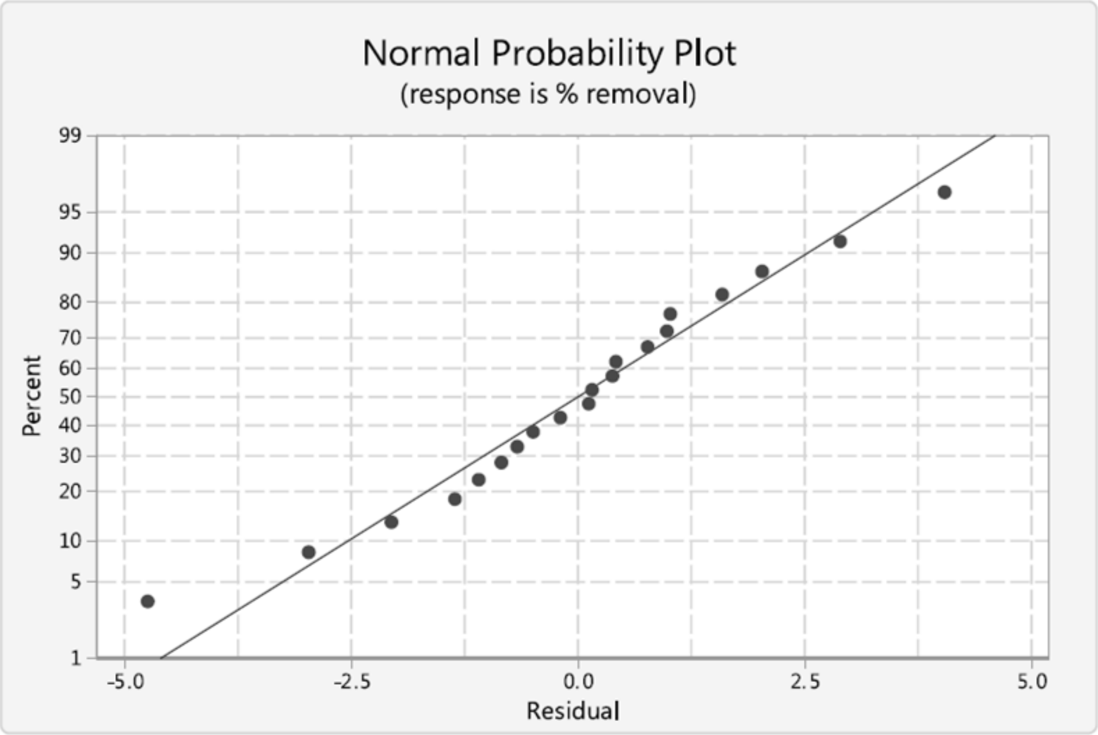


Fig. 6.1: Normal Probability chart for Cr(VI) adsorption

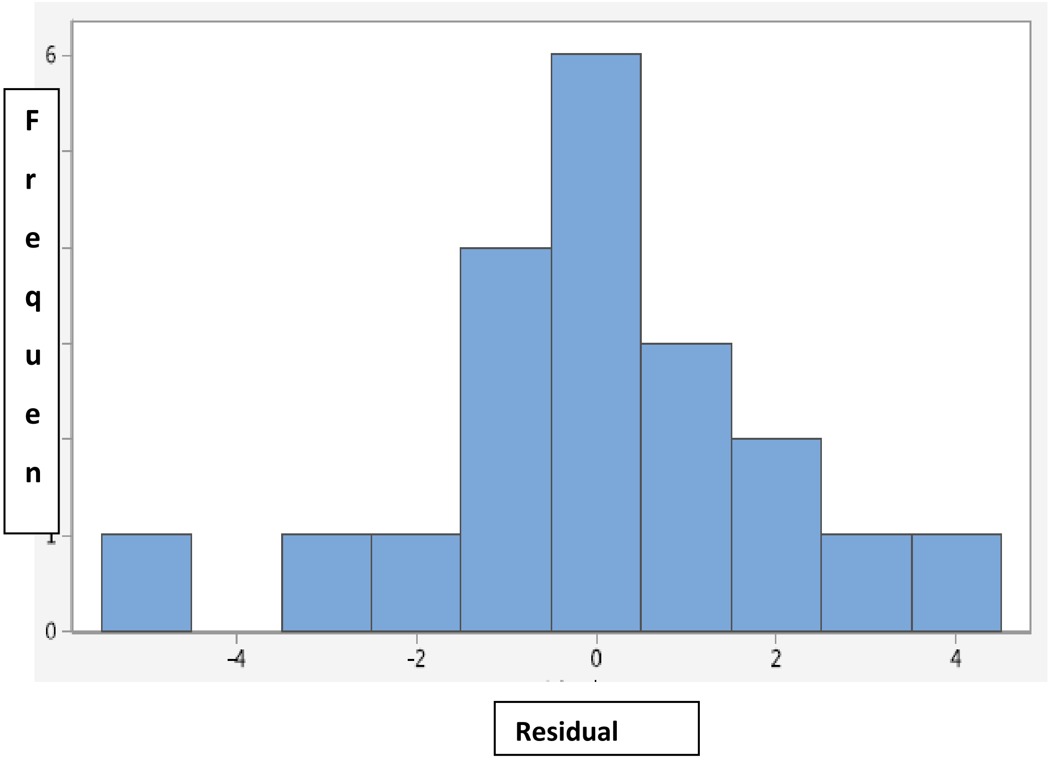


Fig. 6.2: Histogram for the factorial design of experiments

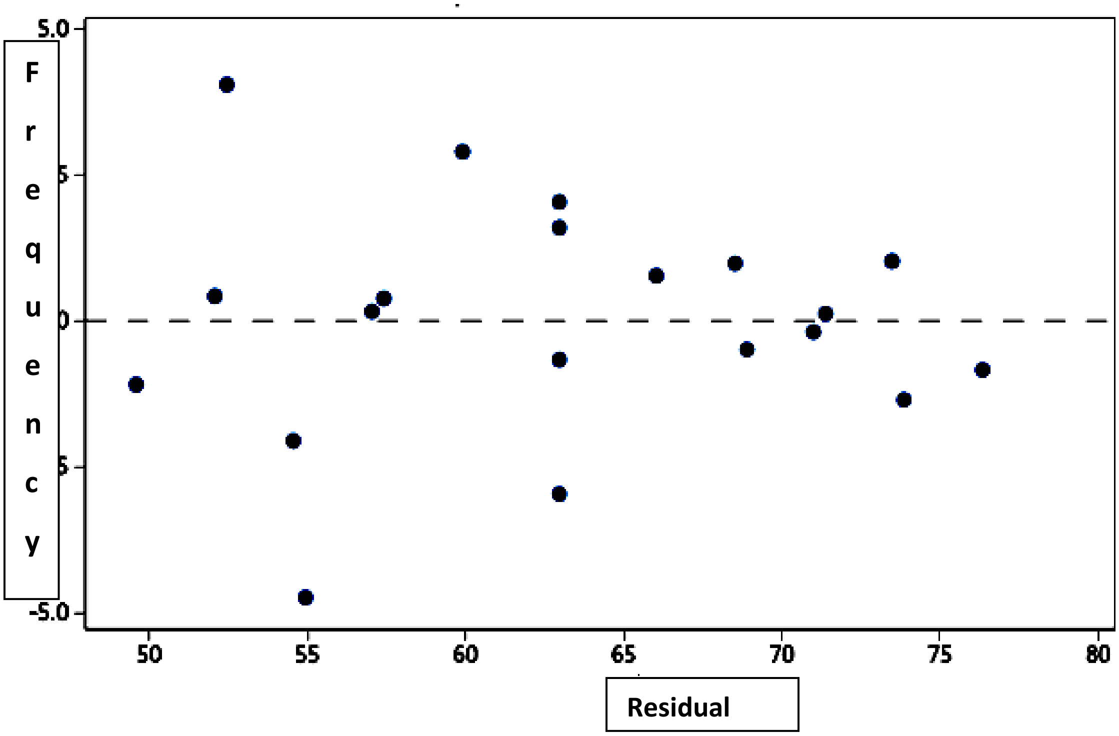


Fig. 6.3: Residual graph for percentage Cr(VI) adsorption

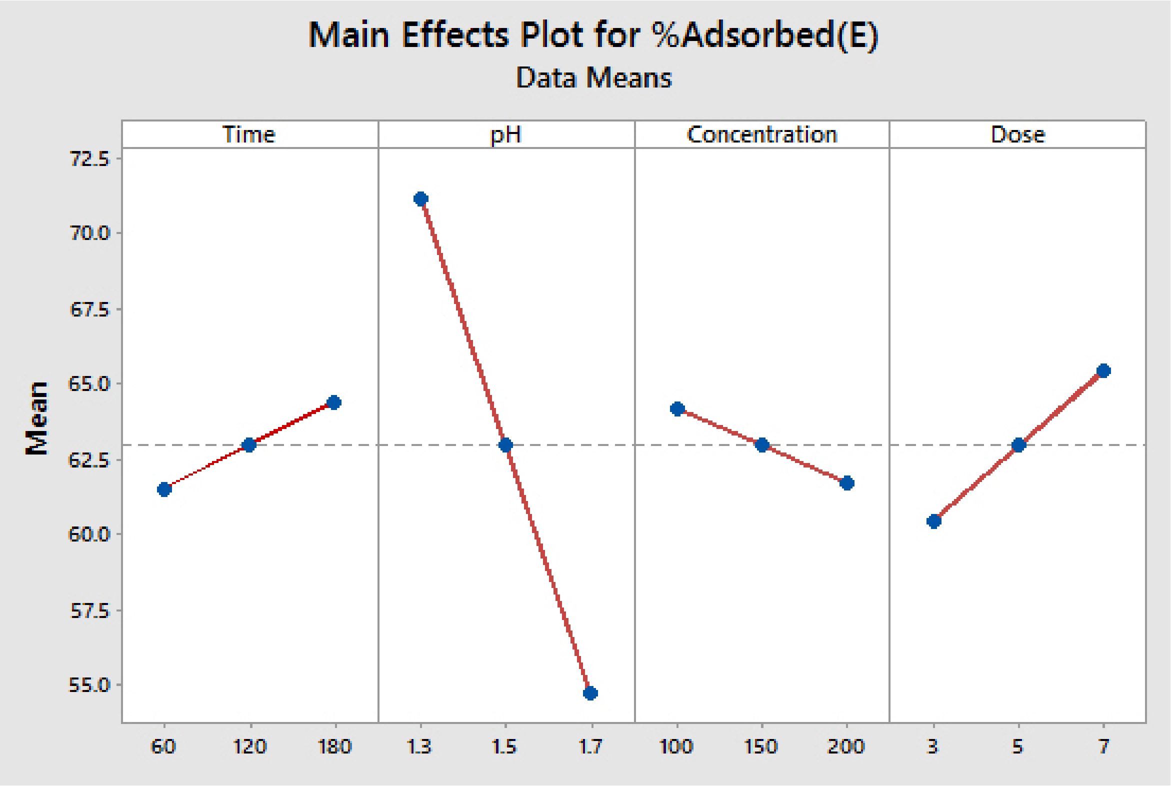


Fig. 6.4: Main effects between the independent variables and percentage Cr(VI) removal

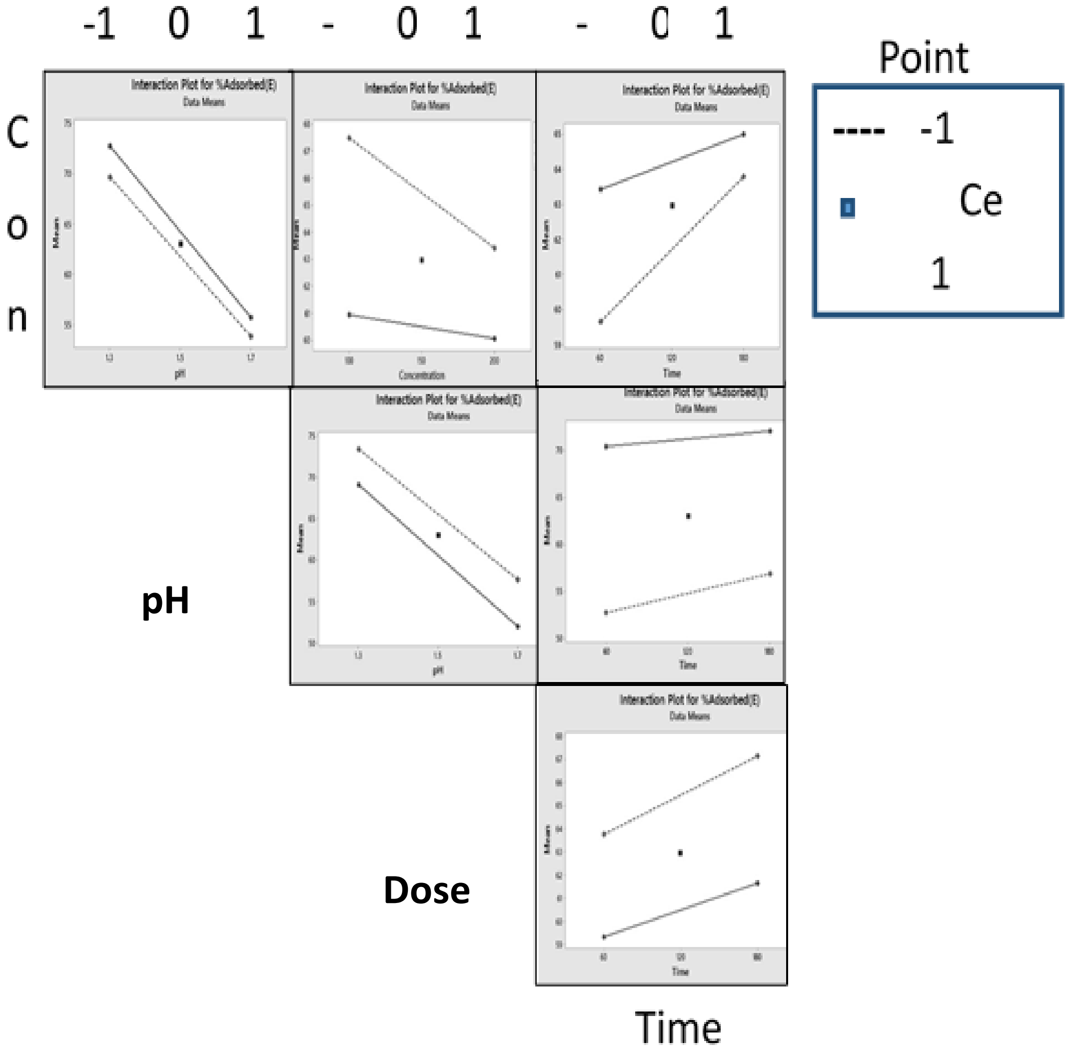
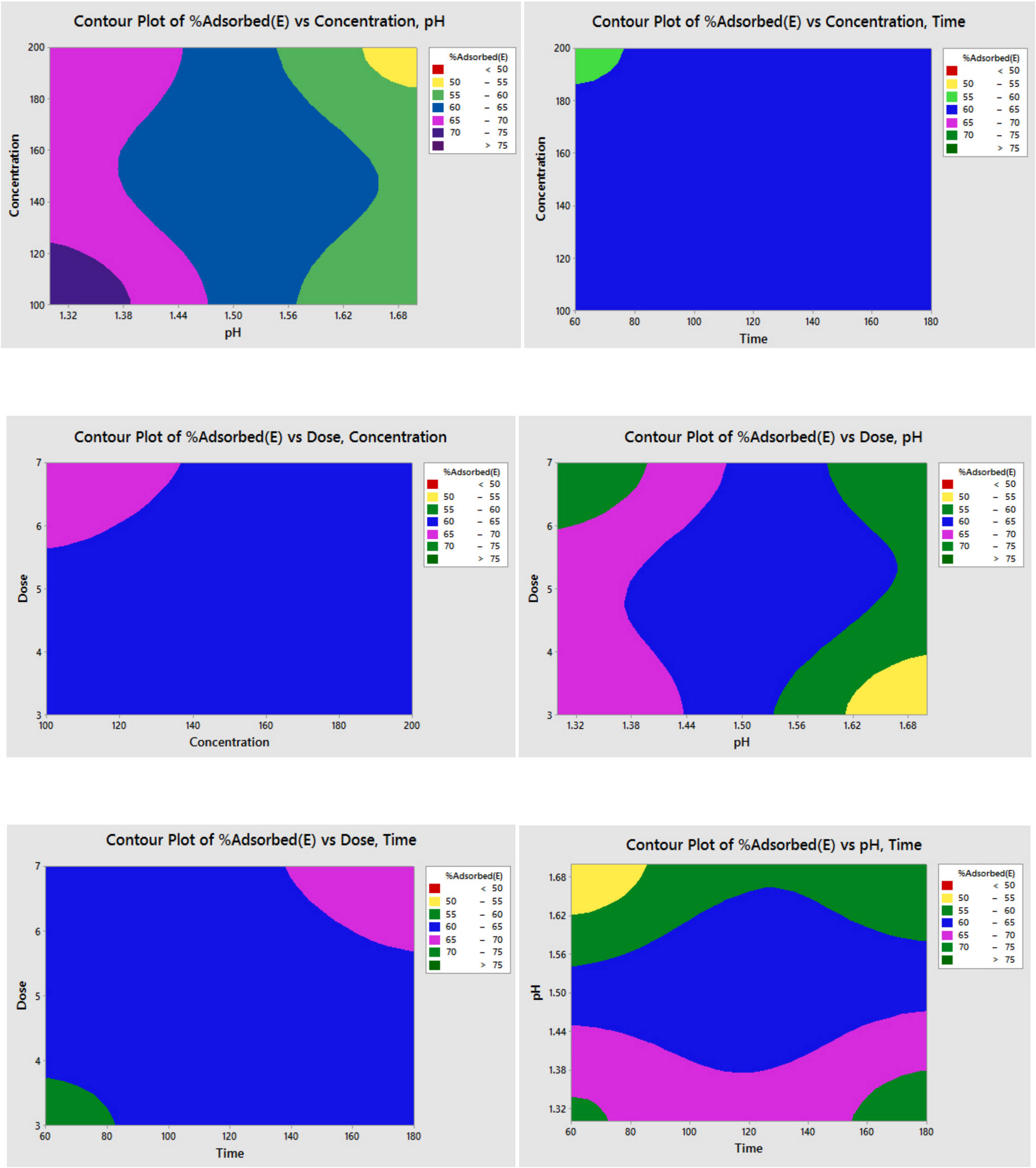


Fig. 6.5: Interaction effects between the independent variables and percentage Cr(VI) adsorption.


Contour Plot of %Adsorbed(E) vs Concentration, pH

Contour Plot of %Adsorbed(E) vs Concentration, Time

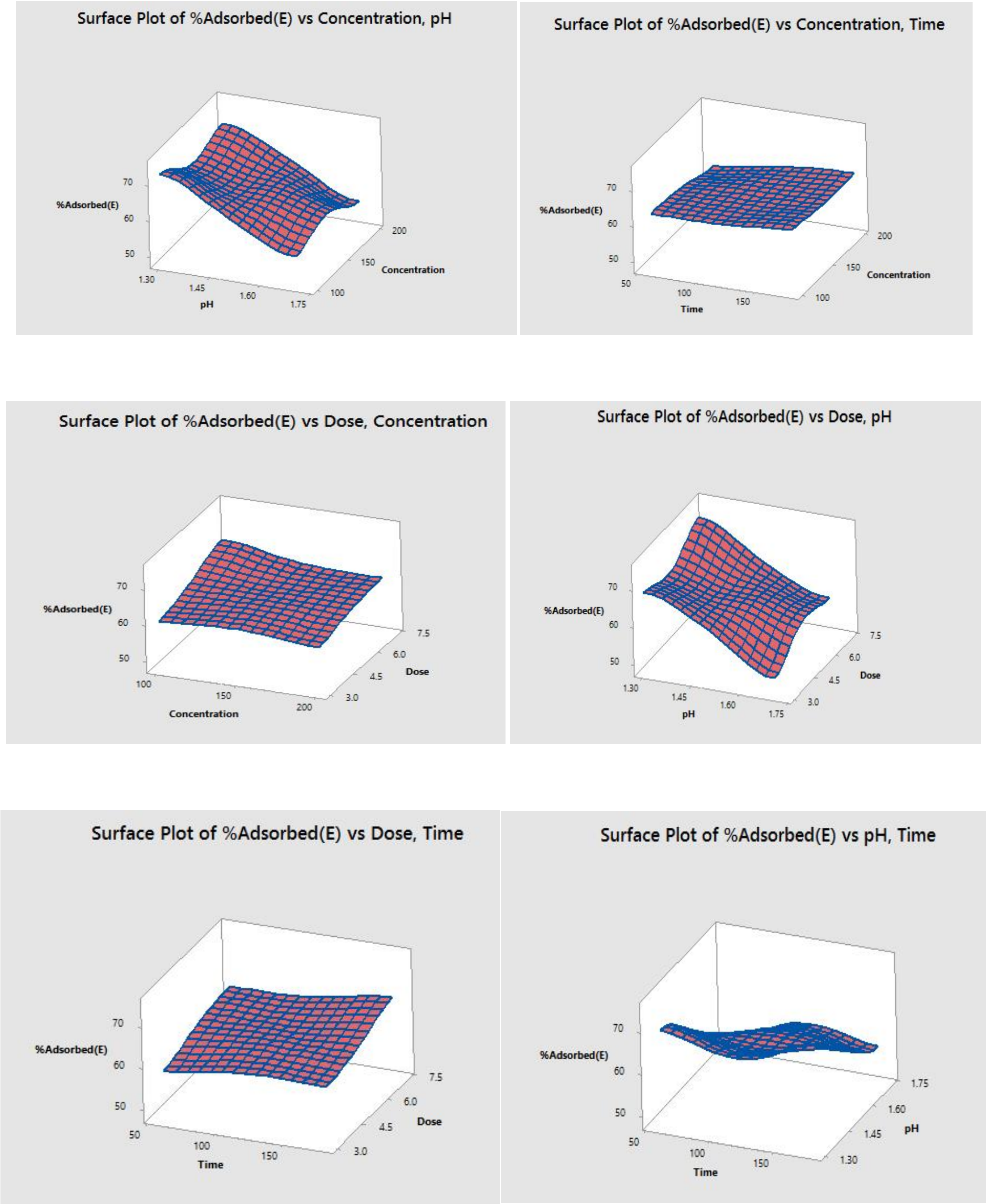
Contour Plot of %Adsorbed(E) vs Dose, Concentration

Contour Plot of %Adsorbed(E) vs Dose, pH

Contour Plot of %Adsorbed(E) vs Dose, Time

Contour Plot of %Adsorbed(E) vs pH, Time

Fig. 6.6: Contour Plot for the percentage Cr(VI) adsorption vs independent variables



Surface Plot of %Adsorbed(E) vs Concentration, pH

Surface Plot of %Adsorbed(E) vs Concentration, Time

Surface Plot of %Adsorbed(E) vs Dose, Concentration

Surface Plot of %Adsorbed(E) vs Dose, pH

Surface Plot of %Adsorbed(E) vs Dose, Time

Surface Plot of %Adsorbed(E) vs pH, Time

Fig. 6.7: 3-Dimensional Surface Plot for the response vs independent variables

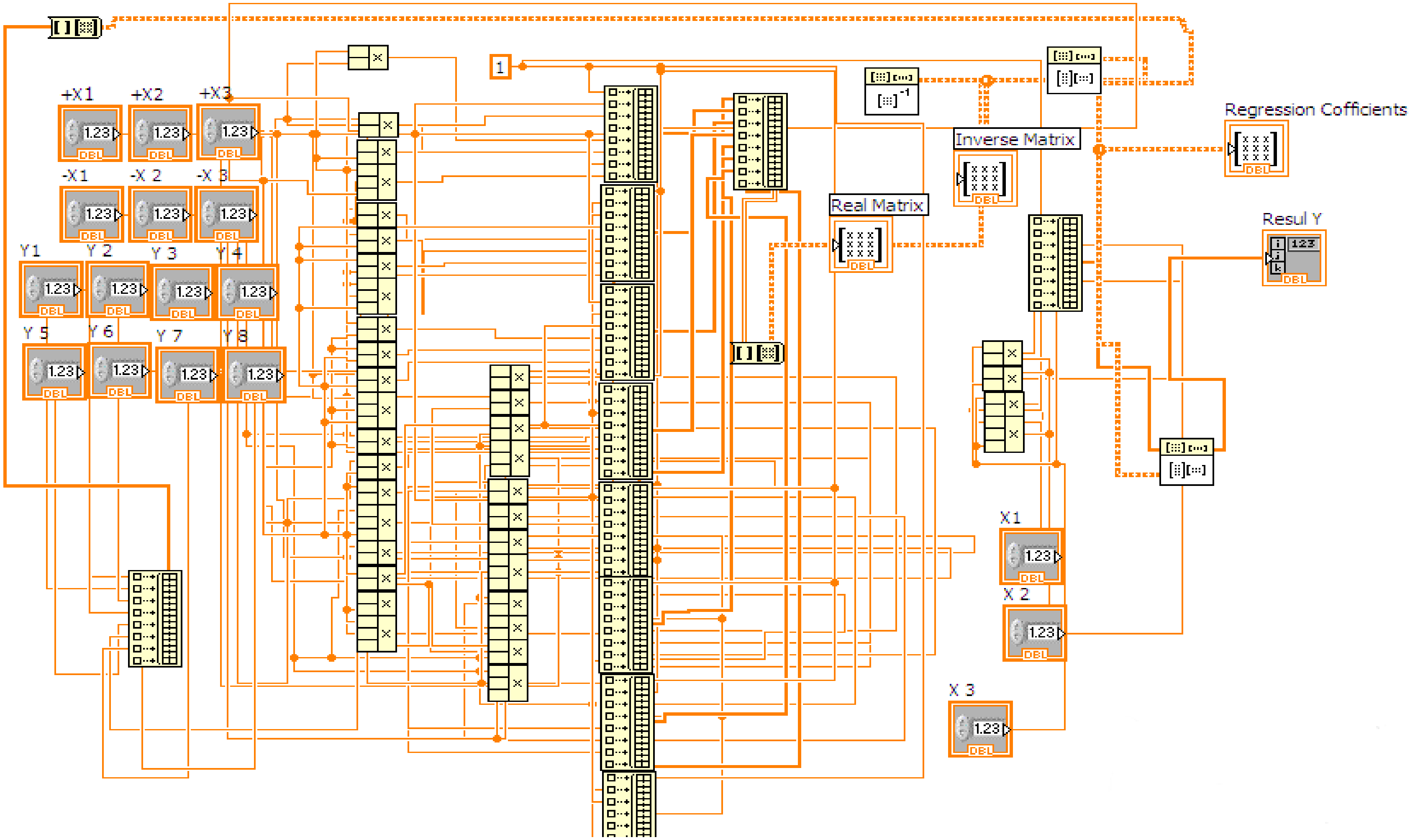
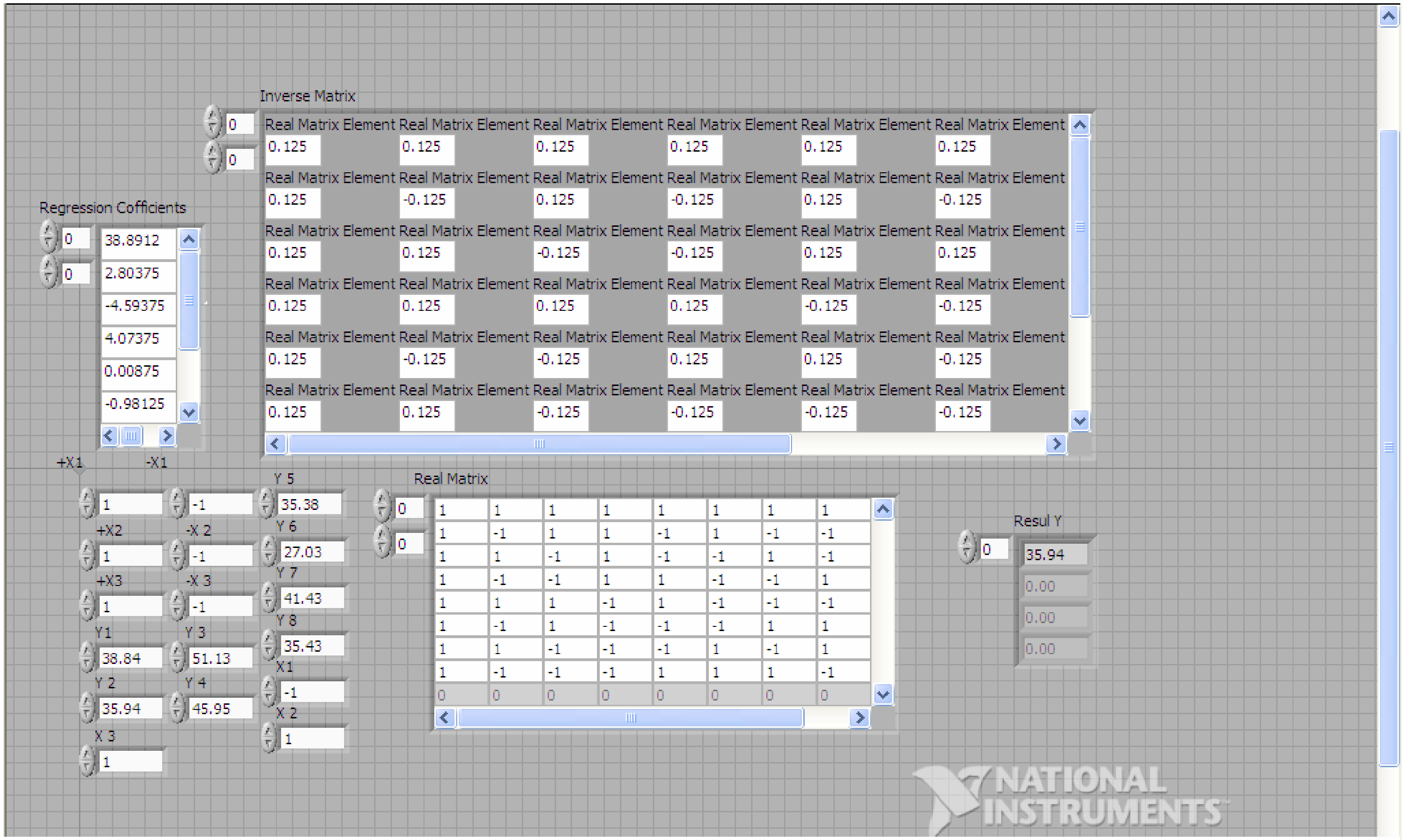


Fig. 6.8: The configuration of the VI system



Inverse Matrix

0. 125	0. 125	0. 125	0. 125	0. 125	0. 125
0. 125	-0. 125	0. 125	-0. 125	0. 125	-0. 125
0. 125	0. 125	-0. 125	-0. 125	0. 125	0. 125
0. 125	0. 125	0. 125	0. 125	-0. 125	-0. 125
0. 125	-0. 125	-0. 125	0. 125	0. 125	-0. 125
0. 125	0. 125	-0. 125	-0. 125	-0. 125	-0. 125

Regression Cofficients

38.8912
2.80375
-4.59375
4.07375
0.00875
-0.98125

+X1	1
-X1	-1
+X2	1
-X 2	-1
+X3	1
-X 3	-1
Y1	38.84
Y 3	51.13
Y 2	35.94
Y 4	45.95
X 3	1
Y 5	35.38
Y 6	27.03
Y 7	41.43
Y 8	35.43
X1	-1
X 2	1

Real Matrix

1	1	1	1	1	1	1	1
1	-1	1	1	-1	1	-1	-1
1	1	-1	1	-1	-1	1	-1
1	-1	-1	1	1	-1	-1	1
1	1	1	-1	1	-1	-1	-1
1	-1	1	-1	-1	-1	1	1
1	1	-1	-1	-1	1	-1	1
1	-1	-1	-1	1	1	1	-1
0	0	0	0	0	0	0	0

Resul Y

35.94
0.00
0.00
0.00

Fig. 6.9: The configuration of front panel window input/output

Table 6.1: Factorial levels and variation intervals.

Factors	Low level (-1)	High level (+1)	Zero level
Time (minutes) x_1	60	180	120
pH x_2	1.3	1.7	1.5
Cr(VI) Concentration ppm x_3	100	200	150
Adsorbent dosage (g/ L) x_4	3	7	5

Table 6.2: Experimental design of trial runs in coded form for adsorption of Cr(VI)

Trial	x_1	x_2	x_3	x_4	x_1x_2	x_1x_3	x_1x_4	x_2x_3	x_2x_4	x_3x_4	$x_1x_2x_3$	$x_1x_2x_4$	$x_1x_3x_4$	$x_2x_3x_4$	$x_1x_2x_3x_4$	Y
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	57.
2	+	+	+	-	+	+	-	+	-	+	+	-	-	-	-	56.
3	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-	62.
4	+	-	+	+	-	-	+	-	-	-	-	-	+	-	-	72.
5	-	+	+	+	-	+	-	+	+	+	-	-	-	+	-	52.
6	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+	50.
7	+	-	+	-	-	-	-	-	+	-	-	+	-	+	+	68.
8	+	-	-	+	-	+	+	+	-	-	+	-	-	+	+	75.
9	-	+	+	-	-	+	+	+	-	-	-	+	+	-	+	48.
10	-	+	-	+	-	-	-	-	+	-	+	-	+	-	+	57.
11	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+	70.
12	+	-	-	-	-	+	-	+	+	+	+	+	+	-	-	71.
13	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-	74.
14	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-	66.
15	-	+	-	-	-	-	+	-	-	+	+	+	-	+	-	52.
16	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+	69.
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	62.
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	65
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	64.
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	60

Table 6.3: Analysis of Variance(ANOVA)

Source	DF	Co-efficient	Adj SS	F-Value	P-Value
Model	15	119.27	81337	181.0	0.000
Dose	1	1.241	98.51	19.87	0.000
Concentration	1	-0.0249	24.75	4.99	0.041
pH	1	-41.09	1080.77	218.03	0.000
Time	1	0.02385	32.78	6.61	0.021
Dose*Concentration	1	0.1388	781.1	13.81	0.005
Dose*pH	1	7.57	1221.8	21.59	0.001
Dose*Time	1	0.1505	330.7	5.84	0.039
Concentration*pH	1	0.2079	1097.33	19.39	0.002
Concentration*Time	1	0.00476	392.44	6.94	0.027
pH*Time	1	0.2147	420.13	7.43	0.023
Dose*Concentration*pH	1	-0.1323	1284.93	22.71	0.001
Dose*Concentration*Time	1	-0.001811	590.78	10.44	0.010
Dose*pH*Time	1	-0.135	517.19	9.14	0.014
Concentration*pH*Time	1	-0.00430	599.92	10.60	0.010
Dose*Concentration*pH*Time	1	0.00141	742.85	13.13	0.006
Error	9				

Table 6.4: Experimental and theoretically predicted percentage adsorption of Cr(VI) from Factorial Design value

Sr.No	Time (min)	pH	Conc. (ppm)	Dose (g/L)	% removal observed	% removal predicted	Residual	SSE	SAE	ARE	ARS
1	180	1.7	200	14	57.80	55.5	2.3	99.12	0.04	0.00109	0.038
2	180	1.7	200	6	56.50	52.6	3.9				
3	180	1.7	100	14	62.80	65.1	-2.3				
4	180	1.3	200	14	72.50	75.2	-2.7				
5	60	1.7	200	14	52.50	51.5	1.0				
6	180	1.7	100	6	50.20	48.5	1.7				
7	180	1.3	200	6	68.40	69.4	-1.0				
8	180	1.3	100	14	75.50	78.5	-3.0				
9	60	1.7	200	6	48.50	51.5	3.0				
10	60	1.7	100	14	57.20	58.2	-1.0				
11	60	1.3	200	14	70.80	69.1	1.7				
12	180	1.3	100	6	71.50	70.5	1.0				
13	60	1.3	100	14	74.50	76.2	-1.7				
14	60	1.3	200	6	66.80	69.1	-2.3				
15	60	1.7	100	6	52.50	49.5	3.0				
16	60	1.3	100	6	69.50	67.2	2.3				
17	120	1.5	150	10	62.30	63.0	0.7				
18	120	1.5	150	10	65.00	63.0	2.0				
19	120	1.5	150	10	64.56	63.0	1.56				
20	120	1.5	150	10	60.00	63.0	3.0				

Table 6.5: Factorial levels and variation intervals

x_1=Time in min, x_2=pH, x_3=Temperature in ^{0}C				
Factors	-1	0	1	Variation interval
x_1	5	10	15	5
x_2	1.6	1.7	1.8	0.1
x_3	30	35	40	5

Table 6.6: Design of trial runs (in coded form) for adsorption of Cr(VI)

Trial No	x_1	x_2	x_3	x_1x_2	x_2x_3	x_3x_1	$x_1x_2x_3$	Y
1	+	+	+	+	+	+	+	38.84
2	-	+	+	-	+	-	-	35.94
3	+	-	+	-	-	+	-	51.13
4	-	-	+	+	-	-	+	45.95
5	+	+	-	+	-	-	-	35.38
6	-	+	-	-	-	+	+	27.03
7	+	-	-	-	+	-	+	41.43
8	-	-	-	+	+	+	-	35.43
9	0	0	0	0	0	0	0	27.14
10	0	0	0	0	0	0	0	27.1
11	0	0	0	0	0	0	0	27.15

Table 6.7: MATLAB code

$>> x_{1o} = 0;$

$>> x_{1p} = 1;$

$>> x_{1n} = -1;$

$>> x_{2o} = 0;$

$>> x_{2p} = 1;$

$>> x_{2n} = -1;$

$>> x_{3o} = 0;$

$>> x_{3p} = 1;$

$>> x_{3n} = -1;$

$>> a = [1\, x_{1p}\ \ x_{2p}\ \ x_{3p}\ (x_{1p} \times x_{2p})\,(x_{2p} \times x_{3p})(x_{3p} \times x_{1p})(x_{1p} \times x_{2p} \times x_{3p})];$

$>> b = [1\, x_{1n}\ \ x_{2p}\ \ x_{3p}\ (x_{1n} \times x_{2p})(x_{2p} \times x_{3p})(x_{3p} \times x_{1n})(x_{1n} \times x_{2p} \times x_{3p})];$

$>> c = [1\, x_{1p}\ \ x_{2n}\ x_{3p}\ (x_{1p} \times x_{2n})(x_{2n} \times x_{3p})(x_{3p} \times x_{1p})(x_{1p} \times x_{2n} \times x_{3p})];$

$>> d = [1\, x_{1n}\ \ x_{2n}\ \ x_{3p}\ (x_{1n} \times x_{2n})(x_{2n} \times x_{3p})(x_{3p} \times x_{1n})(x_{1n} \times x_{2n} \times x_{3p})];$

$>> e = [1\, x_{1p}\ \ x_{2p}\ \ x_{3n}\ (x_{1p} \times x_{2p})(x_{2p} \times x_{3n})(x_{3n} \times x_{1p})(x_{1p} \times x_{2p} \times x_{3n})];$

$>> f = [1\, x_{1n}\ \ x_{2p}\ \ x_{3n}\ (x_{1n} \times x_{2p})(x_{2p} \times x_{3n})(x_{3n} \times x_{1n})(x_{1n} \times x_{2p} \times x_{3n})];$

$>> g = [1\, x_{1p}\ \ x_{2n}\ \ x_{3n}\ (x_{1p} \times x_{2n})(x_{2n} \times x_{3n})(x_{3n} \times x_{1p})(x_{1p} \times_{x2n} \times_{x3n})];$

$>> h = [1\, x_{1n}\ \ x_{2n}\ \ x_{3n}\ (x_{1n} \times x_{2n})(x_{2n} \times x_{3n})(x_{3n} \times x_{1n})(x_{1n} \times x_{2n} \times x_{3n})];$

$>> x = [a;b;c;d;e;f;g;h];$

$>>$

$>> y = [38.84;3594;51.13;45.95;35.38;27.03;41.43;35.43];$

$>> B = x^{-1} \times y$

Table 6.8: Validation of the mathematical model by error analysis

Time (min)	pH	Temp. (^{0}C)	Ye	Yc	SSE	SAE	ARE	ARS
1	1.7	30	31.73	28.36	326.86	45.33	0.11	0.20
3	1.7	30	34.30	29.79				
5	1.8	40	35.94	35.94				
5	1.6	40	45.94	45.95				
5	1.8	30	27.03	27.03				
5	1.6	30	35.43	35.43				
10	1.7	30	38.94	34.82				
10	2	30	32.34	23.98				
10	2.5	30	14.50	5.92				
10	1.7	50	40.21	51.11				
15	1.8	40	38.83	38.84				
15	1.6	40	51.12	51.13				
15	1.8	30	35.37	37.38				
15	1.6	30	41.42	41.43				
30	1.7	30	45.73	49.17				

Chapter-7

Selection of suitable adsorbent for the removal of Cr(VI) by using Objective Based Multiple Attribute Decision Making method

7.1 Introduction

In the last few decades, adsorption has emerged as popular process in the context of its application to wastewater treatment. The commercial success of the adsorption process in wastewater treatment has resulted in extensive research that has led to the discovery of a broad range of adsorbent materials. There are wide varieties of absorbent materials available in the market for the treatment of Cr(VI) contaminated wastewater (discussed in Chapter 1) which ensure that there is a task-specific material for the application. These adsorbents are typically micro-porous materials such as activated carbon, adsorbent from agricultural product, industrial waste, domestic waste etc., They are used either in their original form or as modified by techniques such as ion exchange. During process development, several adsorbents may be identified as suitable materials for Cr(VI) removal from aqueous solution. The preliminary viability can be judged by comparing the isotherms, kinetics or/and the uptake rates of Cr(VI) from simulated solution. However, a cursory visual inspection can be misleading and does not quantify the merit of the efficiency of the adsorbent for the separation under consideration. Further, sometimes too much choice can make it more difficult to choose and help is needed to select the right absorbent. There are a large number of criteria available which has to be considered for the selection of a suitable adsorbent.

A critical literature review indicates that the literature related to the selection of adsorbent is rather scanty. In this paper, it is attempted to critically review the attributes of adsorbent for the treatment of Cr(VI) contaminated wastewater. Further, attribute based multi attribute decision making approach is used to evaluate and select the best adsorbent for the Cr(VI) adsorption process. A three-stage procedure including the elimination search is proposed to evaluate the available alternatives with the help of attributes.

From the extensive literature survey, it is observed that naturally available, low cost bio-adsorbents has very high adsorption capacity. However, the tannin and lignin presents in the biomaterials may leach out and create environmental pollution and hence required suitable pre-treatment which may not be economical and environmental friendly. Further, economy of an adsorption process dependent on the number of adsorption-desorption cycle of each adsorbent. The amine and electron donor groups presence in the biomaterials leads indirect reduction and increases the chemisorption. As the pH of the aqueous phase is lowered, a large number of hydrogen ions can easily coordinate with the amino, hydroxyl, CN and react with the $Cr_2O_7^{2-}$ which is irreversible. Therefore, regeneration of the adsorbents is not possible and hence the adsorbents may not be economical and also can create disposal problem. The adsorption capacity of some of the adsorbent is high but at lower pH and other adsorbents has very low adsorption capacity. From the above discussion, it is evident that some of the attributes in the adsorption may be of conflicting in nature i.e., for certain attributes larger values are preferred and for other attributes smaller values are preferred. Then trade-off between the attributes is required, because properties/nature of attributes is changing from case to case. Hence an expert system which will eliminate the human error and is capable of handling this type of problem is needed. Multiple Attribute Decision Making (MADM) system is a well-established expert decision system when there exist conflicting criteria to evaluate a product/system among the available options. MADM is a tool generally used to conciliate multiple evaluation criteria, taking into account the preferences of a decision-maker. In MADM method, the attribute information is processed in order to arrive at a choice.

In selecting an absorbent, a number of factors should be considered out of which few are outline bellow:

- The absorbent should encapsulate the Cr(VI) - adsorb into the particle itself and not just adhere to the outside surface of adsorbent.
- The absorbent should absorb most of the Cr(VI) in the waste water.
- The absorbent should be low cost where possible.
- The absorbent should meet all environmental requirements.
- The absorbent should have high adsorption capacity.
- The absorbent should also be safe to use on the designated fluid and not react to cause a hazard for the user and environment.

All the factors above must be used in conjunction with other important properties to select an appropriate adsorbent.

The design engineers have to consider numerous factors, like pH, initial concentration of Cr(VI), dosage, Temperature, duration and agitation speed etc. while choosing the best suitable adsorbent for adsorption process, which makes the choosing the process little bit complex than the (Ljungberg & Edwards, 2003; Ashby et al, 2004; Edwards, 2005). For the selection, proper material, where several available choices and with many influencing norms, a more appropriate mathematical methodology is needed. For the above said situation, multi-criteria decision making (MCDM) or multiple attribute decision making (MADM) methodology is useful for choosing the particular adsorbent on a numerous set of parameters/attributes. This approach/methodology (MADM) has been used in many different areas like plant layout selection (Yang & Hung, 2007), selection of electroplating system (Abhishek & Agrawal, 2009), selection of supplier (Li et al, 2007) and selection mechatronic systems (Kiran et al). This approach initially implemented by Zhang et al. (2011) which integrating both subjective and also objective information and also explained with the illustrative example by the author.

Maniya and Bhatt (2011) has proposed this method (MCDM), which was very effective and systematic and also by Jain and Raj (2013) proposed method for the selection, on the basis of preference selection index (PSI). This method MCDM technique based on Technique for Order of Preference by Similarity to Ideal Solutions (TOPSIS) which was projected by Senthil Kumar and Thirumalai (2013). TOPSIS method can be used to explore the suitable adsorption parameter and their inter relation between the parameter by fitting a polynomial equation to this experimental data in a multiple regression analysis. Chatterjee and Chakrabort (2013) have explored MCDM method based on organization. This method has been applied in Mechanical engineering in many areas like advanced manufacturing system (AMS) like in a Robot industies, Flexible manufacturing system, Rapid prototyping process, Suitable machine for flexible manufacturing cell and Non-traditional machining process.

In this paper, a MADM method is used to deal with proper adsorbent selection, considering quantitative attributes is applied in evaluating and optimizing the selection adsorbent for the Cr(VI) removal. A fuzzy conversion scale has been used to convert the qualitative attributes like pH, cost, and concentration to a judgement rank value. The projected method gives an idea for the selection of adsorbent based importance of the objective weight of attributes. In order to explain the methodology a demonstrative example is given. The step by step procedure of this method has been explained which is used friendly and easily understandable.

7.2 Multiple attributes decision-making methodology

In order to solve the problems of choosing from a fixed number of alternatives, the simple and systematic steps was proposed by Rao and Patel (2010) has been applied. Different adsorbent such as Marine Strains Yeast (Ncibi et al, 2009), Aspergillus Niger (Khambhaty, 2009), *Hydrilla Verticillate* seed (Baral et al, 2009), *Salvinia Cucutta* (Baral et al, 2008), Fungal biomaterial Coriolus versicolor (Sanghi et al, 2009) and Pomegranate husk (Nemr, 2009) from material database and along with that our research work with Pig iron sludge have been selected for the selection of better choice of adsorbent for adsorption as per MADM method. The six properties such as pH, adsorbent dose in g/L, adsorbate concentration in ppm, Speed in RPM, temperature in ^{0}C and duration in minutes has been taken in the present research work. The methodology is given below.

7.3 Decision making table

Identify the relevant measured parameters for the considered adsorbent problem and choose the adsorbent based on the easily identifiable attributes (parameters) satisfying the necessities. The attributes are divided into two types, one is beneficial where the greater values are most desired one and non-beneficial where lesser values are most desired. The accepted limiting values either in terms of qualitative or quantitative has been assigned to each parameter for the considered problem. Here we more concerned about removal of Cr(VI). After choosing the alternative adsorbent parameter and find the values associated with the parameters (Z_{ij}), a decision table, analogues one which is given in Table 7.1 containing the values of all parameters for the considered adsorbent, can be prepared.

The actual decision table for different kind of adsorbent that we have selected has been shown in Table 7.2. To change the elements in decision table into measurable and unit less quantity, then it is important to normalize their values. These values are linked with each parameters (Z_{ij}) might be in dissimilar units like Concentration in mg/L, pH, Speed in RPM, Cost etc. The normalized value of each element in decision table is obtained by the following expression r_{ij} as

$$r_{ij} = \frac{z_{ij}}{\sum_{i=1}^{n} z_{ij}} \tag{7.1}$$

Where, r_{ij} is the normalized value of Z_{ij} and $\sum_{i=1}^{n} Z_{ij}$ is the total value of jth parameter for n different adsorbents or in general different alternatives.

Equation 7.1 will deal the quantitative measurement of different attributes, but for qualitative measurement of attributes there must be a method to converts this into quantitative value as in our illustrative example like pH. We have used Crisp score assigned for each fuzzy number conversion scale to change qualitative parameter in to equal quantitative value. This approach was introduced by Chen and Hwang (1992). An 11-point scale is recommended for better understanding. Table 7.3 signifies the selected parameter in a qualitative scale can be converted to quantitative by using fuzzy number.

Based on the value of fuzzy numbers associated with each attribute, we have obtained the Table 7.4 and 7.5 which are indicating the crisp score value for each parameter of different adsorbent. After obtaining the fuzzy conversion table, our aim is to calculate the normalized data table to find the objective weight of attributes. These values have been shown in Table 7.6.

7.4 Objective weight of importance of attributes

The importance of objective weight of each parameter is found by using statistical variance. The following equation is used to estimate the importance of each parameter weightage.

$$V_J = \left(\frac{1}{n}\right) \sum_{i=1}^{n} (r_{ij} - (r_{ijmean}))^2 \tag{7.2}$$

where, V_j is the statistical variance of the data matching to the jth parameter $(r_{ij})_{mean}$ is the is the mean value of r_{ij}. V_J measures the distribution of each data points nearby their mean value. The objective weight of the jth attribute Qj^0 can be calculated by the statistical variance of each parameter divided by the total statistical variances of all the number of parameter. The given below equation has been used to calculate the importance of each attribute in objective weights. This is shown in Table 7.7.

$$Q_j^0 = \frac{V_J}{\sum_{i=1}^{m} V_J} \tag{7.3}$$

7.5 Preference index determination

Each alternative is judged with related to its weights associated to every parameter. The Preference Index (PI) is weighted sum of the overall performance score of an alternative. The PI gives rank of particular adsorbent with compared to all other adsorbent. The PI is calculated by adding all the values of Xi^0 for different alternative. Xi^0 is the multiplication result of objective weight of importance (Qj^0) and r_{ij}^{**} for different parameters. The following equations are used to estimate the preference index.

$$X_i^0 = Q_j^0 * r_{ij}^{**} \tag{7.4}$$

$$P_i^0 = \sum_{j=1}^{m} X_I^0 \tag{7.5}$$

where, $r_{ij}^{**} = [r_{ij}^{b} = (r_{ij}^{b})max]$ for beneficial parameter.

$[(r_{ij}^{nb})min = (r_{ij}^{nb})]$ for non-beneficial parameter.

where, r_{ij}^{b} indicates the normalized value of beneficial parameter and r_{ij}^{nb} indicated normalized value of non-beneficial parameter respectively. $(r_{ij}^{b})_{max}$ signifies the maximum value of j^th^ beneficial parameter and $(r_{ij}^{nb})min$ signifies the minimum value of jth non-beneficial parameter. The calculation of Preference index for each adsorbent was shown in Table 7.8. All the adsorbent alternatives have been arranged with respect to descending order of P_i^0 to obtain the preference order of alternatives. After calculating the Pi^0, the highest value of P_i^0 is the most suitable adsorbent for considered decision-making problem. This calculation has been shown in Table 7.9.

7.6 Result and Discussion

This paper presents a selection of suitable adsorbent which is the major task during the initial stage of adsorption, to remove the Cr(VI) presents in the industrial effluents. As the selection of particular adsorbent is very complex in nature due to the adsorption depends upon on many factors. So, there is a requirement of easy, organized and rational methods to direct the decision makers in considering all possible number of factors and their interaction in making correct decision. In this paper, fuzzy logic method is used for selection of suitable adsorbent for the Cr(VI) removal. Multiple attribute decision making (MADM) is used to determine the corresponding weighting values for the selected adsorbent. Selection of an optimum adsorbent for the removal of Cr(VI) can be done on the basis of their preference index prepared in the previous section. The preference index is calculated by using the subjective and objective weights. A final decision can be taken keeping in view of all practical consideration during the experimentation. This calculation has been done purely on the basis of literature survey on the Cr(VI) removal by varying different parameter of different adsorbent. The normalized value associated with each parameter has given on the basis of effect of each parameter on the Cr(VI) removal and uptake capacity of each material. However, the limitations of this computational approach still remain. Only limited number of adsorbent was chosen for comparison and this can be extended for very large data with numerous parameters to prove with respect to cover all the sustainability dimensions like the environment, economic and social dimensions. The associated MADM method results and the limitations of the approaches are discussed to lay the foundation for further improvement.

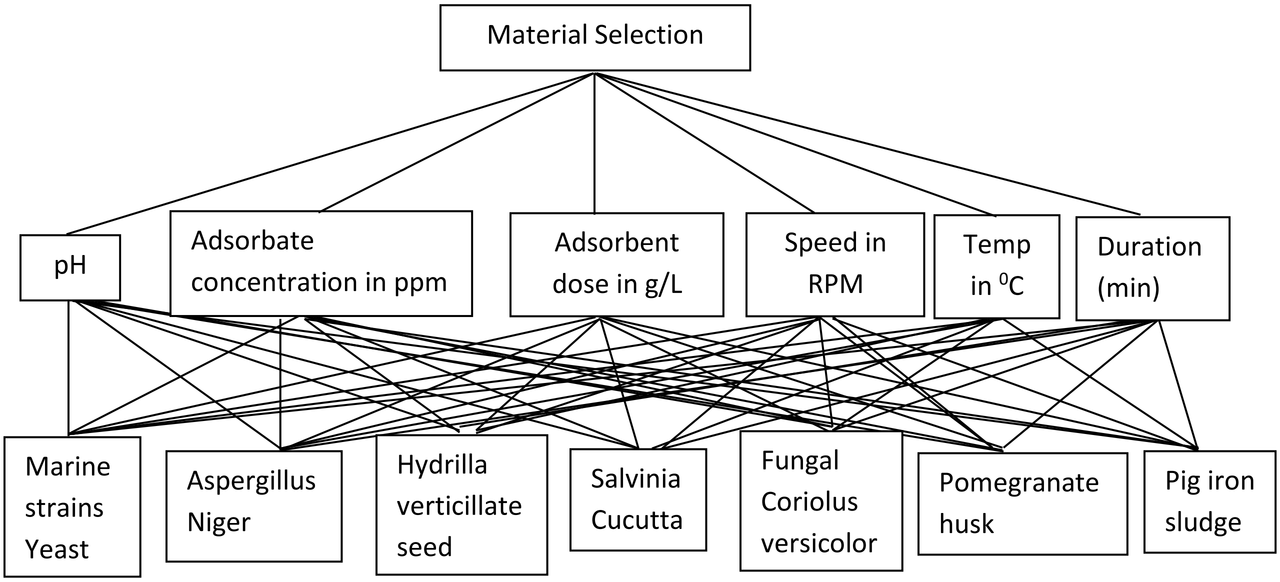


Fig. 7.1. Materials and their properties selection

Table 7.1: Decision table

Alternative	Attributes						
	B_1	B_2	B_3	B_4	-	-	B_m
A_1	Z_{11}	Z_{12}	Z_{13}	Z_{14}	-	-	Z_{1m}
A_2	Z_{21}	Z_{22}	Z_{23}	Z_{24}	-	-	Z_{2m}
A_3	Z_{31}	Z_{32}	Z_{33}	Z_{34}	-	-	Z_{3m}
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
A_n	Z_{n1}	Z_{n2}	Z_{n3}	Z_{n4}	-	-	Z_{nm}

Table 7.2: Different adsorbent used to remove the Cr(VI) and its parameters

S.No	Name of the Adsorbent	pH range	Adsorbate concentration in ppm	Adsorbent dose in g/L	Speed in RPM	Temp in ©	Duration in min	Reference
1	Marine Strains Yeast	1	200	9.3	130	35	120	[20]
2	Biosorption Aspergillus Niger	2	100	0.8	180	50	2880	[21]
3	Hydrilla Berticillate Seed weed	3	100	0.8	600	27	360	[22]
4	Salvinia cucutta weed	1.7	500	0.8	600	30	600	[23]
5	Fungal bioremedal white rot	2	50	5	160	25	180	[24]
6	Husk of Pomegranate	1	75	3	200	25	180	[25]
7	Pig iron sludge	3	10	4	170	30	360	Present Study

Table 7.3: Fuzzy scores for qualitative measure

Qualitative measurement of selection attribute	Fuzzy number	Assigned score in crisp value (3 decimal point)
Exceptionally low (EXL)	F1	0.046
Extremely low (EL)	F2	0.136
Very Low (VL)	F3	0.227
Low(L)	F4	0.318
Below Average (BA)	F5	0.409
Average (A)	F6	0.5
Above Average(AA)	F7	0.591
High (H)	F8	0.682
Very High (VH)	F9	0.773
Extremely High (EH)	F10	0.864
Exceptionally High (EXH)	F11	0.955

Table 7.4: Properties of Different adsorbent and its attributes

S.No	**Name of the Adsorbent**	**pH range**	**adsorbate concentration in ppm**	**adsorbent dose in g/L**	**Speed in RPM**	**Temp in ©**	**Duration in min**
1	Marine Strains Yeast	EXL	VH	VH	L	L	L
2	Biosorption Aspergillus Niger	VL	BA	EL	A	H	EH
3	Hydrilla Berticillate Seed weed	EXH	BA	EL	H	L	A
4	Salvinia cucutta weed	A	EXH	EL	H	L	AA
5	Fungal bioremedal white rot	VL	VL	AA	BA	VL	BA
6	Husk of Pomegranate	EXL	L	A	A	VL	BA
7	Pig iron sludge	EXH	EXL	A	A	L	A

Table 7.5: Quantitative value using fuzzy conversion scale

S.No	**Name of the Adsorbent**	**pH range**	**adsorbate concentration**	**adsorbent dose**	**Speed**	**Temperature**	**Duration**
1	Marine Strains Yeast	0.0455	0.7727	0.7727	0.3182	0.3182	0.3182
2	Biosorption Aspergillus Niger	0.2273	0.5	0.1364	0.5	0.6818	0.8636
3	Hydrilla Berticillate Seed weed	0.9545	0.5	0.1364	0.6818	0.3182	0.5
4	Salvinia cucutta weed	0.5	0.9545	0.1364	0.6818	0.3182	0.5909
5	Fungal bioremedal white rot	0.2273	0.2273	0.5909	0.4091	0.2273	0.4091
6	Husk of Pomegranate	0.0455	0.3182	0.4091	0.5	0.2273	0.4091
7	Pig iron sludge	0.9545	0.0455	0.5	0.4091	0.3182	0.5

Table 7.6: Normalized data for calculating the objective weights of parameters

S.No	Name of the Adsorbent	pH range	adsorbate concentration	adsorbent dose	Speed	Temperature	Duration
1	Marine Strains Yeast	0.015	0.233	0.288	0.091	0.132	0.089
2	Biosorption Aspergillus Niger	0.077	0.151	0.051	0.143	0.283	0.240
3	Hydrilla Berticillate Seed weed	0.323	0.151	0.051	0.195	0.132	0.139
4	Salvinia cucutta weed	0.169	0.288	0.051	0.195	0.132	0.165
5	Fungal bioremedal white rot	0.077	0.069	0.220	0.117	0.094	0.114
6	Husk of Pomegranate	0.015	0.096	0.153	0.143	0.094	0.114
7	Pig iron sludge	0.323	0.014	0.186	0.117	0.132	0.139

Table 7.7: Statistical variance and Objective weight of importance of the attributes

S.No	rj mean	0.143	0.143	0.143	0.143	0.143	0.143
1	Sum square (rj-rjmean)	0.107	0.054	0.054	0.009	0.025	0.015
2	Statistical variance Vj	0.0153	0.0077	0.0078	0.0013	0.0035	0.0021
3	Objective weight of importance Qj	0.405	0.203	0.207	0.036	0.094	0.056

Table 7.8: Preference Index (Xi values for preference index)

S.No	Name of the Adsorbent	XpH	Xconc	Xdose	Xspeed	Xtemp	Xduration
1	Marine Strains Yeast	0.0193	0.1645	0.0365	0.0358	0.0672	0.0555
2	Biosorption Aspergillus Niger	0.0964	0.1064	0.2065	0.0228	0.0314	0.0205
3	Hydrilla Berticillate Seed weed	0.4049	0.1064	0.2065	0.0167	0.0672	0.0353
4	Salvinia cucutta weed	0.2121	0.2032	0.2065	0.0167	0.0672	0.0299
5	Fungal bioremedal white rot	0.0964	0.0484	0.0477	0.0278	0.0940	0.0432
6	Husk of Pomegranate	0.0193	0.0677	0.0689	0.0228	0.0940	0.0432
7	Pig iron sludge	0.4049	0.0097	0.0563	0.0278	0.0672	0.0353

Table 7.9: Ranking of alternative adsorbent for the removal of Cr(VI) process

S.No	Name of the Adsorbent	Values of objective based Fuzzy logic (Pi)	Rank based on (Pi)
1	Marine Strains Yeast	0.38	5
2	Biosorption Aspergillus Niger	0.48	4
3	Hydrilla Verticillate Seed weed	0.84	1
4	Salvinia cucutta weed	0.74	2
5	Fungal bioremedal Coriolus versicolor	0.36	6
6	Husk of Pomegranate	0.32	7
7	Pig iron sludge	0.60	3

Chapter-8
Conclusion

8.1 Conclusion

An in-depth literature survey shows that, though incredible efforts have been taken worldwide to discover new adsorbents, finding inexpensive adsorbents with high uptake capacity is remains an area of research and development. The increased adsorption capacity of different adsorption in majority cases are not well explained. Again, the pre-treatment of adsorbents to obtain high adsorption capacity in some cases may not be economically feasible. Further, very few papers reported the optimization of adsorption parameters using full factorial design of experiments. There is no research reported on the methodology for selection of adsorbent among the large numbers of options available. The present study aims to explore the use of low cost, environmental friendly and easily available materials as adsorbent to remove the Cr(VI) from wastewater. The adsorption parameters are optimized using a full factorial design of experiments. Fuzzy logic which is one of the multi-attribute decision making method is used for the selection of adsorbents among various options available.

Sorghastrum Nutans L. Nash (grass) and Cocos Nucifera (coconut leave) were used as low cost adsorbent for the treatment of Cr(VI) contaminated wastewater. The XRD analysis of the adsorbent shows single pick which is identified as carbon. FTIR analysis of the adsorbent before and after adsorption shows the presence of various functional groups. Among different functional groups present in the adsorbent, OH bending, CN stretching/bending and NH stretching plays an important role in Cr(VI) adsorption. Various mechanisms of adsorption were considered for the process and it has been found that indirect reduction is the primary adsorption mechanism. Effects of different adsorption parameters such as time, pH, adsorbate concentration, adsorbent dose and particle size on the percentage of Cr(VI) adsorption has been studied. It is observed that with decrease in pH from 3.0 to 1.0, adsorption percentage increased from 4% to 95.5% and uptake capacity increased from 0.97 mg/g to 19.1 mg/g. The size of the particle is varied between 36 to 150 BSS and it is found that percentage of Cr(VI) increases 66 % to 92.3% and uptake capacity of the adsorbent increases from 13.2 mg/g to 18.46. The percentage of Cr(VI) adsorption decreases from 100% to 63.9% and uptake capacity increases from 2 mg/g to 23.2 mg/g when the adsorbate concentration increases from 10 ppm to 100 ppm. The percentage of

Cr(VI) adsorption increases from 74% to 100% and uptake capacity decreases from 25.6 mg/g to 10 mg/g with increase in adsorbent dose from 1 g/L to 10 g/L.

The disadvantage with the previous adsorbents used were that the adsorption capacity was very less at higher pH. Although the adsorption capacity increases with decrease in pH, but adsorption at lower pH produces acidic effluent and hence acid neutralization step is required which may not be economical and environmental friendly. Therefore, the aim of this study was to explore a new adsorbent which will have high adsorption capacity at higher pH. In this part of the study, Coconut leaves is used as an adsorbent for the treatment of Cr(VI) contaminated wastewater. Percentage of Cr(VI) adsorption increases 40% to 97.3% and uptake capacity increases from 8 mg/g to 19.5 mg/g with decrease in pH from 3 to1. The percentage adsorption increases from 44% to 100% with increase in adsorbent dose from 1 g/L to 10 g/L whereas, uptake capacity decreases from 4.4 mg/g to 1 mg/g. Particle size has the antagonism effect on both percentage Cr(VI) adsorption and uptake capacity.

Among different adsorbents, bio-adsorbents are found to be having high adsorption capacity. However, the disadvantage with bio-adsorbents is that their adsorption capacity is high at lower solution pH and also required pretreatment for eliminating the possibility of leaching out of water soluble component such as tannin and ligand. Further, bio-sorption is an adsorption cum reduction process and hence desorption is not possible. Considering the above fact in mind, a new adsorbent pig iron sludge which can be recycle to the industry was used for treatment of Cr(VI) contaminated waste water. The adsorbed Cr(VI) will be useful for making steel in the blast furnace. The adsorption capacity of the adsorbent was established through batch adsorption process. The effect of different adsorption parameters on the uptake capacity of the adsorbent was studied. The percentage adsorption increases with decrease in pH up to 3 and hardly any change with further decrease in pH. As usual the equilibrium uptake of the adsorbate decreases with increase in adsorbent dose whereas, the percentage adsorption increases with increase in adsorbent dose. Increase in initial adsorbate concentration has a synergetic effect on the uptake capacity whereas, antagonism effect on the percentage adsorption.

From our previous experimental results, it is observed that the adsorption capacity of the pig iron industry sludge was very low at higher pH. Hence, the adsorption process may not be economical. Therefore, the present study aimed at finding an alternative adsorbent i.e. Biochar (carbonised grass) is to remove the Cr(VI) from the wastewater and use this chromium adsorbed Biochar in Ferrochrome industry. The advantage of using biochar is that the biochar along with the adsorbed Cr(VI) can be used in either ferrochrome or steel making process. The Cr(VI) will be used as a raw material whereas, biochar will be used as a source of energy and reducing agent to ferrous/ferric oxide. Therefore, no regeneration or disposal of the adsorbent is required which may create environmental problem and hence it can be treated as clean treatment technology. Biochar is prepared from the grass which was used in chapter 4. It was observed that the maximum adsorption (100 %) takes place when initial pH of 2.0 and 2.5. The uptake capacity increased from 10.7 mg/g at pH of 4.0 to 20 mg/g at pH of 2.0. The percentage of removal was increased from 59 % to 100 % with increase in adsorbent dose from 1.0 to 10 g/L. However, the Cr(VI) uptake capacity of the adsorbent has decreased from 5.9 to 1.4 mg/g when the adsorbent dose increased from 1 g/L to 10 g/L. The maximum removal was 100% at 10 ppm has decreased to 94% at 100 ppm of initial Cr(VI) concentration. The uptake capacity has been increased from 2 mg/g at 10 ppm to 18.9 mg/g at 100 ppm. From the experimental results, it was observed that the adsorption capacity of biochar is higher than other three (grass, coconut leave and pig iron sludge) adsorbents. Further use of biochar can eliminate the disadvantages of using the other three adsorbent as this can be reused in ferrochrome or steel making processes.

In order to find out the rate kinetics four different kinetic models such as Lagergren's pseudo first-order model, Ritchie's second order model, First order reversible model, Pseudo second order model were used. The plots were drawn for each kinetic model and the values of model parameters along with R^2 are calculated. From the R^2 values it was observed that for all the four adsorbents, adsorption process followed pseudo second order kinetics. The time variation experimental data was used to find out the rate limiting step in the sorption procedure. It was observed that in all cases the values of diffusivity for surface diffusion 'D_1' is always smaller than the diffusivity for intra-particle diffusion 'D_2'.

Therefore, it was concluded that surface diffusion is the slowest steps and hence is the rate limiting steps. In order to find out the maximum uptake capacity of all the adsorbents three adsorption isotherms were used to fit into the experimental data. The isotherms used were Freundlich isotherm, Langmuir isotherm and Temkin Isotherm. Experimental data were used to plot the different isotherm model and the isotherm constant along with R^2 values were calculated. From the values of R^2 values it was clear that adsorption follows the Langmuir adsorption isotherm in all the four cases.

A n^K type of factorial design method is used to develop empirical model and different tools such as MINITAB, MATLAB and LabVIEW are used to simulate and analyze the empirical model. In the 1st part of study, full factorial design of experiment is used for the optimization of Cr(VI) adsorption using *Sorghastrum Nutans L. Nash***.** Factorial design of 2^4 type is employed with contact time, initial pH of the solution, adsorbent dose and initial Cr(VI) concentration as independent parameters and % of Cr(VI) adsorption as the response variable. Different statistical analysis such as probability, residual, contour, 3D surface, main effect and interaction plot along with t-test, ANOVA and F-test were used to optimize the operating parameters of the process. From the statistical analysis, it was found that the pH has a negative effect and is the most influential parameter, as pH decreases, the percentage of adsorption increases significantly. The second most important parameter is doses which has a positive effect as the percentage of adsorption increases with dosage. The maximum removal was obtained at pH of 1.3, concentration 100 mg/L and adsorbent dose of 7 g/L. In the second part of the optimization process, Data is collected from the literature and a 2^3 type factorial design is used to design the experiment. Empirical mathematical model was developed using matrix method. The empirical model was simulated using MATLAB and LabVIEW. Among the two simulating tools the latter one was found to be much user friendly. From the analysis, it was concluded that pH had the most influential effect on the adsorption process followed by contact time. Among all possible combined effects, the effect of pH and contact time was the most influential one.

As the selection of particular adsorbent is very complex in nature as because the adsorption depends upon on many factors. So there is a requirement of easy, organized and rational methods to direct the decision makers in considering all possible number of factors and their interaction in making correct decision. In this study, fuzzy logic method is used for selection of suitable adsorbent for the Cr(VI) removal. Multiple attribute decision making (MADM) is used to determine the corresponding weighting values for the selected adsorbents. Selection of an optimum adsorbent for the removal of Cr(VI) can be done on the basis of their preference index prepared in the previous section. The preference index is calculated by using the subjective and objective weights. A final decision can be taken keeping in view of all practical consideration during the experimentation. This calculation has been done purely on the basis of literature survey on the Cr(VI) removal by varying different parameter of different adsorbents. The normalized value associated with each parameter has given on the basis of effect of each parameter on the Cr(VI) removal and uptake capacity of each material. However, the limitations of this computational approach still remain. Only limited number of adsorbents was chosen for comparison and this can be extended for very large data with numerous parameters to prove with respect to cover all the sustainability dimensions like the environment, economic and social dimensions. The associated MADM method results and the limitations of the approaches are discussed to lay the foundation for further improvement.

8.2 Scope for Further Study

As discussed before, the adsorptive removal of Cr(VI) would be environmental friendly and economical only if the adsorbed Cr(VI) along with the adsorbent can be reused. Therefore, we have proposed a possible potential option of using the adsorbent along with adsorbed Cr(VI) as a raw material for the production of steel or ferrochrome. But the techno-economic of the process suggested in the thesis needs to be analysed in details. The objective needs of proposed study would be carried out for the scale up and implication in the industry are:

- To develop a detailed flow sheet using different simulation software.
- To conduct economic evaluation of the flow sheet through the process simulation.
- Characterizing the Biochar and comparing it with the coke for possible use in the blast furnace.
- Studying the carbothermic reduction capacity of the Cr(VI) adsorbed biochar.

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Publication and Conference Details

1. **G. Surendran**, B. V. Sasank, S. S. Baral, Modeling and simulation for the adsorptive removal of Cr(VI) from aqueous solution, **Desalination and Water Treatment**, Volume 52, 5652-5662/2014 **(IF 0.752)**
2. S. S. Baral,**G. Surendran,** N. Das, P.V. Rao, Statistical design of experiments for the Cr(VI) adsorption on weed *Salvinia cucullata*, **Environmental Engineering and Management Journal,** Volume 12, No: 3/2013. **(IF 1.435)**
3. **G.Surendran** and Saroj S.Baral, " Selection of Suitable adsorbent for the removal of Chromium(VI) by using Objective based Multiple Attribute Decision Making (MADM) method," International Journal of Chemical Engineering and application, Accepted.
4. **Surendran Ganesan**, Saroj Sundar Baral, "Kinetics, Isotherm and Mechanism study of Treatment of Cr(VI) contaminated waste water by using Sorghastrum Nutans(L)Nash-Natural grass," 11th Conference on Sustainable Development of Energy, Water and Environment Systems - SDEWES2016, Portugal, 2016. **Won the Best poster award**
5. **G. Surendran** and Dr.S.S.Baral , " Treatment of Cr(VI) contaminated waste water by natural grass" Paper code : ICEM 328, International Conference on Green Technology for Environmental Pollution Prevention and Control (ICGTEPC) 2014,National Institute of Technology,Tiruchirapalli on 27th-29th September, 2014
6. **G.Surendran** and Saroj Sundar Baral, "Kinetics, Isotherm and Mechanism study of Treatment of Cr(VI) contaminated waste water by using coconut leave," Accepted as Poster presentation in **CHEMCON-2016, IIT-Chennai in 27th -30th, December 2016.**
7. **G.Surendran** and Saroj Sundar Baral, "Optimization of Cr(VI) adsorption process using statistical design of experiments," Accepted as Oral presentation in **CHEMCON-2016, IIT-Chennai in 27th -30th, December 2016.**
8. **G.Surendran** and Saroj Sundar Baral, "Process technology for removal of chromium by using sludge from pig iron industry", Accepted as Oral presentation in **CHEMCON-2016, IIT-Chennai in 27th -30th, December 2016.**
9. .**G.Surendran** and Saroj S. Baral, "Bio-sorption of Chromium (VI) from waste water using Sorghastrum Nutan (L)Nash," Journal Hazardous Material, **Submitted**

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Dr. Saroj Sundar Baral is the Associate professor in Chemical Engineering group at Birla Institute of Technology and Science (BITS), Pilani- K. K. Birla Goa Campus. He received a Ph.D. in Chemical Engineering jointly from National Institute of Technology, Rourkela and Institute of Minerals and Materials Technology (CSIR), Bhubaneswar in 2008. He completed his B.E. Chemical Engineering from Indira Gandhi Institute of Technology, Sarang in 2001. He joins as assistant professor in chemical engineering group of BITS in 2008. He was working as an assistant professor in chemical engineering department of Maharashtra Academy of Engineering for one year. He was also working in Institute of Minerals and Materials Technology (CSIR), Bhubaneswar for five years.

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His research interest includes waste water treatment, separation processes, atmospheric precipitation, emission of greenhouse gases and renewable energy. Much of his research in waste water treatment has emphasized the development of new low cost adsorbents for the treatment of Cr(VI) contaminated waste water. Apart from waste water treatment, he is also attached to various environment related programs like chemical composition of aerosol, rainwater, emission of greenhouse gases from agricultural activities and anaerobic digestion of sewage sludge for biogas production.

Dr. Baral has published a number of research papers in different international journal of repute. He also presented a number of papers in different national and international conference. He has also published two books and one book chapter under different international publisher like Willey and VDM. At present, he is guiding Two students for their Ph.D and one student completed his Ph.D. under his guidance. He has guided several M.E. thesis at BITS Pilani. He is also got two project from Department of Biotechnology, Government of India.