Toxicity Characterisation, Life Cycle Assessment, and Management of Industrial Wastewater: A case study of a cluster of textile industries

THESIS

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By

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CERTIFICATE

This is to certify that the thesis entitled **"Toxicity Characterisation, Life Cycle Assessment, and Management of Industrial Wastewater: A case study of a cluster of textile industries"** and submitted by **Somya Agarwal,** ID No. **2015PH440040P** for the award of Ph.D. Degree of the Institute, embodies original work done by her under my supervision.

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Abstract

With an increased economic growth and purchasing power parity, there has been an increased demand of manufactured products, especially, pharmaceuticals, clothing, packaged food, infrastructure (buildings, better transportation), etc. Manufacturing industries produce vast quantities of waste, and it has become challenging for environmentalists and engineers to manage this waste. The textile industry is one such industry which consumes enormous quantities of raw materials such as fibers, chemicals, and water. It also generates a vast quantity of coloured chemical effluent which is extremely difficult to treat and requires costly treatment techniques. The effluent discharged from industrial clusters is treated in Common effluent treatment plants (CETPs). The research focuses on providing sustainable solutions for textile industry waste management and effective ways of dealing with it. **Chapter 1** of the thesis gives an introduction to the textile industry, problems associated with it, and also the objectives of the research. **Chapter 2** deals with the literature review of all the relevant past studies conducted by eminent researchers. It also describes the various available techniques to treat the effluent need for Multi-Criteria Decision-Making (MCDM) methods for selecting sustainable Textile Wastewater Treatment Technique (TWWTT). Additionally, Chapter 2 gives an overview of the advantages and disadvantages of different treatment techniques and the use of adsorption as a pretreatment method for effluent. This chapter also discusses the past literature about the pollution potential of sludge generated from CETPs, the sustainable use of sludge as building material and its environmental impacts.

Chapter 3 explains that the TWWTT plays a prominent role in reducing effluent contaminants, thus keeping the environment cleaner. To select appropriate technology, evaluating the unified performance of TWWTTs towards social, technical, economic, and environmental sustainability parameters is of utmost importance. Though there are TWWTTs available, no ready framework exists that can help decision-makers choose the appropriate technology based on their requirement. The chapter proposes a unique and systematic decision-making framework and a comprehensive mathematical model for judiciously selecting the TWWTT. It integrates fuzzy Delphi and hybrid Fuzzy Analytical Hierarchy Process (FAHP) approach of MCDM. A total of 38 sub-indicators of sustainability are identified from past studies and expert opinions. Fuzzy Delphi is applied to identify the essential sub-indicators of sustainability, and hybrid FAHP is

used to rank the sustainability dimensions, key sub-indicators, and alternatives. Twenty-eight sub-indicators are rounded down from the initial 38. The results from hybrid FAHP indicate that the technical dimension of sustainability is of paramount importance while selecting the TWWTTs, followed by the economic dimension. The key sub-indicators for the selection of TWWTTs that scored higher than the others in technical, economic, social, and environmental aspects, respectively, are as under (i) color removal efficiency, COD removal efficiency, and quantity of sludge generation; (ii) cost of construction, operation, and maintenance; (iii) awareness within textile industries, public safety; (iv) effluent suitability for reuse and space requirements. The five TWWTTs, namely, Activated Sludge Process (ASP), Membrane Biological Reactor (MBR), Electrochemical Coagulation (EC), Moving Bed Bio Reactor (MBBR), and Rotating Biological Contactors (RBC), are compared using the estimated entropy weights also called as sustainability indices. MBR has scored the highest sustainability index value, and ASP has the least value. MBR, EC and MBBR have higher sustainability indices proving them better sustainable alternatives than ASP and RBC. The MBR permeate quality is good enough to be reused in the textile industry without any further treatment. This will reduce the effluent quantity and groundwater demand leading to cleaner textile production. The study will help the decision-makers in the overall assessment of the sustainability of TWWTTs prior to selection.

To improve the efficiency of the MBR treatment process, adsorption is considered the pretreatment process for effluents. In **Chapter 4**, a novel approach has been undertaken wherein chemically modified Wheat Straw Activated Carbon (WSAC) as an adsorbent is developed, characterized, and examined for the removal of COD and colour from the cotton dyeing industry effluent. Thirty experimental runs are designed for batch reactor study using the Central Composite Method (CCM) to optimize process parameters, namely adsorbent dose, time of contact, pH, and temperature, to examine the effect on COD and colour-removing efficiency of WSAC. The experimental data have been modelled using machine learning approaches such as polynomial quadratic regression and Artificial Neural Networks (ANN). The determined optimum conditions are pH: 7.18, time of contact: 85.229 min, adsorbent dose: 2.045 g/l, and temperature: 40.885 ºC, at which the COD and colour removal efficiency is 90.92% and 94.48%, respectively. The non-linear Pseudo Second Order (PSO) kinetic model shows excellent coefficient of determination (R^2 ~1) values. The maximum adsorption capacity for COD and color by WSAC is at the pH of 7, the temperature of 40 ºC, adsorbent dose of 2 g/l is obtained at the contact time of 80 min is 434.78 mg/g and 331.55 PCU/g, respectively. COD removal and decolorization is more than 70% in the first 20 min of the experiment. The primary adsorption mechanism involves hydrogen bonding, electrostatic attraction, n-π interactions and cation exchange. Finally, the adsorbent is environmentally benign and cost-effective, costing 16.66% less than commercially available carbon. The result indicates that WSAC is a prominent solution for treating textile effluent. The study in **Chapter 4** is beneficial in reducing the pollutants from textile effluents and increasing the reuse of treated effluent in the textile industries.

Treatment processes of textile effluent at CETP produce hazardous sludge. The toxicity, Leachate Pollution Index (LPI) and risk assessment of the leachate of hazardous sludge is very rarely and scantly studied. **Chapter 5** of this thesis evaluates the leachate characteristics of the textile industry-common effluent treatment plant sludge. X-Ray Fluorescence (XRF) analysis determines the sludge's chemical composition. The Toxicity Characteristics Leaching Procedure (TCLP) is a sample extraction method to simulate the leaching through landfills. The leachate samples are tested using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) techniques for the metal ions. The thirty TCLP tests are performed as per the scheme generated by the Central Composite Design of the Experiment (CCDoE). The study provides a novel and flexible framework for developing the Textile-Leachate Pollution Index (T-LPI) using a hybrid Fuzzy Analytical Hierarchical Process (FAHP). The metal ions' weights in the leachate (Al, Cu, Cr, Fe, Mn, Ni, Pb, Zn, K, Mg, Ca) are obtained using FAHP-infused with inter-valued triangular fuzzy numbers.

The membership grade functions are derived for each metal ion, and the leachate pollution index is estimated for thirty experiments. The experimental runs are ranked based on their LPI values. Pearson's correlation coefficient indicates a poor association between the metal ions and their presence from different sources. The Human Health Risk Assessment (HHRA) of metal ions (Al, Cu, Cr, Fe, Pb, Zn, Mn, Ni) present in leachate shows the potential non-carcinogenic impact by Ni, Pb, Zn, Cu, Cr, Mn. In contrast, Fe and Al have shown no adverse non-carcinogenic effect. The carcinogenic risk by Pb and Cr metal ions in leachate lies in the high and very high-risk levels. The ranking of hazardous sludge sites can help in the immediate disposal of higher LPI value sludge to Treatment Storage and Disposal Facility (TSDF) compared to the sludge with lower LPI. The study provides insight into the human health risk associated with the consumption (oral intake and skin absorption) of leachate-polluted surface water.

As studied in **Chapter 5**, the improper disposal of this sludge causes secondary pollution due to the presence of heavy metals. Therefore, the prerequisite for the disposal of such hazardous sludge is its stabilization and solidification. The utilization of sludge as a resource for construction materials is one of the sustainable solutions. **Chapter 6** evaluates the feasibility of partially replacing cement with the Textile Common effluent treatment plant (TCETP) sludge and mineral admixture such as Sugarcane Bagasse Ash (SBA) in cement mortar mixes. The thirteen mortar mixes are prepared consisting of a control mix, four binary mixes with sludge (2.5%, 5%, 7.5% and 10%) and eight tertiary mixes with sludge (2.5%, 5%, 7.5% and 10%) and SBA (5%, 10%) replacing cement by volume. Few binary and tertiary blended cement mortar mixes have demonstrated comparable strength, permeation, durability, and leaching properties that are on par with the control mix. The modified mortar mixes 2.5T, 5T, 2.5T5S, 5T5S, and 7.5T5S have improved strength compared to 7.5T, 10T, 10T5S, 2.5T10S, 5T10S, 7.5T10S and 10T10S. Increased strength in mortar mixes is mainly attributable to the filler effect of sludge and SBA and the development of secondary CSH gel. The mortar mixes 7.5T, 10T, 10T5S, 2.5T10S, 5T10S, 7.5T10S, and 10T10S have increased sorptivity indices showing the presence of large-size pores. Durability results suggest a loss in strength due to sulfate attack. Carbonation is not observed in the mixes, and all the mixes are alkaline. However, the leaching study shows the presence of heavy metals in leachate solution above the permissible limit, mainly with mixes having 10% sludge. It is within the permissible limit for all other mixes. The SEM image and XRD fingerprint analysis revealed the formation of porous structure at higher replacement levels and a reduction in CSH gel formation at higher replacement by sludge and SBA.

Chapter 7 evaluates the environmental impact of using the sludge and SBA in mortar mixes using the Life Cycle Assessment (LCA) approach. This study considers the cradle-to-grave method consisting of raw material, transportation manufacturing and disposal as the life cycle phases. The accuracy and reliability of LCA models depend highly on the calculation of the input and output parameters. LCA models are developed for the modified mixes prepared in the study in Chapter 6 using the UMBERTO NXT tool. The environmental impacts have been evaluated at both midpoint and endpoint indicators. The results have been analyzed and compared with the different mortar mixes. The LCA analysis results show less adverse impact at the endpoint and midpoint for the modified mortar mixes than the control mix. Finally, **Chapter 8** consists of conclusions from each chapter and focuses on the contributions made by the current thesis work. The study suggests sustainable approaches for handling textile industry wastewater and the TCETP sludge. This chapter also discusses the present research limitations and potential future scope.

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Abbreviation	Description
1,4 DCB	1,4 dichlorobenzenes
AHP	Analytical Hierarchy Process
ANN	Artificial Neural Networks
ANOVA	Analysis of Variance
AO7	Acid Orange
ASP	Activated Sludge Process
BET	Bruneuer-Emmett-Teller
BET	Brunauer-Emmett-Teller
BOD	Biochemical Oxygen Demand
C_2S	Di-Calcium Silicate
C_3S	Tri-Calcium Silicate
CAGR	Compound Annual Growth Rate
CCDoE	Central Composite Design of the Experiment
CCM	Central Composite Method
CETP	Common Effluent Treatment Plant
CH	Calcium Hydroxide
CI	Consistency Index
CM	Control Mix
COD	Chemical Oxygen Demand
CPCB	Central Pollution Control Board
CR	Carcinogenic Risk
CSH	Calcium Silicate Hydrate
DALYs	Disability Adjusted Life Years
DB38	Direct Black 38
DEHP	Diethylhexyl Phthalate
E	Ettringite

EC	Electrochemical Coagulation
ECO	Economic
EDX	Energy Dispersive X-rays
En	Environmental
EPA	Environment Protection Agency
ESP	Extremely severely polluted
EU	European Union
FA	Fly Ash
FAHP	Fuzzy Analytical Hierarchy Process
FAM	Fuzzy Assessment Matrix
FBBR	Fixed Bed Bio Reactor
FDM	Fuzzy Delphi Method
FESEM	Field Emission Scanning Electron Microscopy
FIS	Fuzzy Inference System
FS	Final Score
FTIR	Fourier Transform Infrared
F-value	Fisher's Test Value
GAC	Granule Carbon Coagulants
GHGs	Green House Gases
GP	Glass Pet
HCA	Hierarchical Cluster Analysis
HHRA	Human Health Risk Assessment
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
IUPAC	International Union for pure and Applied Chemistry
IVFSs	Inter-valued Fuzzy Sets
IVFWs	Inter-valued Fuzzy Weights
IVTFN	Inter-valued Triangular Fuzzy Numbers
LCA	Life Cycle Assessment

LCI	Life Cycle Inventory
LCIA	Life Cycle Inventory Analysis
LOI	Loss on Ignition
LP	Less polluted
LPI	Leachate Pollution Index
LPIDC	Leachate Pollution Index for Developing Countries
MBBR	Mixed Bed Bio Reactor
MBR	Membrane Biological Reactor
MCDM	Multi-Criteria Decision-Making
MoEF & CC	Ministry of Environment, Forest, and Climate Change
MP	Moderately polluted
MSE	Mean Square Error
MSW	Municipal Solid Waste
NFA	Natural Fine Aggregate
NPC	National Productivity Council
NTU	Nephelometric Turbidity unit
OPC	Ordinary Portland Cement
PAC	Poly Aluminium Chloride
PAEs	Phthalic Acid Esters
PCB	Pollution Control Board
PCU	Platinum Cobalt Unit
PDF	Potentially Dispersed Fraction
PFO	Pseudo First Order
PM	Particulate matter formation
PSO	Pseudo Second Order
PZC	Point of Zero Charge
Q	Quartz
R	Correlation Coefficient

R^2	Regression coefficient
RBC	Rotating Biological Contactors
RCI	Random Consistency Index
RCRA	Resource Conservation and Recovery Act
RM	Relationship matrix
RMSE	Root Mean Square Error
RoW	Rest of the World
RR141	Reactive Red 141
RS	Response Surface
RSA	Response Surface Approach
RSM	Response Surface Methodology
S	Social
SAW	Simple Additive Weights
SBA	Sugarcane Bagasse Ash
SBR	Sequencing Batch Reactor
SP	Severely Polluted
T	Technical
TBL	Triple Bottom Line
TCETP	Textile Common effluent treatment plant
TCLP	Toxicity Characterization Leaching Procedure
TFN	Triangular Fuzzy Number
T-LPI	Textile-Leachate Pollution Index
T-LPI	Textile Leachate Pollution Index
TOC	Total Organic Carbon
Trap	Trapezoidal membership function
Tri	Triangular membership function
TSDF	Treatment Storage and Disposal Facility
TWWTT	Textile Wastewater Treatment Technique

US EPA	United States Environment Protection Agency
WSAC	Wheat Straw Activated Carbon
WTO	World Trade Organization
WWT	Wastewater Treatment
XRD	X-Ray Diffractometer
XRF	X-Ray Fluorescence
ZLD	Zero Liquid Discharge

List of notations

Notation	Description
AET	Average exposure time
BWt	Bodyweight of residents of different age group
C_o	Concentration of the COD and color before adsorption in the effluent
C_t	Concentration of the COD and color after adsorption in the effluent
C_2	Concentration of COD and color in the desorbing agent
C	It is intercept describing the boundary layer thickness
C_i^j	Concentration of ith metal ions in leachate from j^{th} experimental run
CSF_i^{ing}	Ingestion exposure carcinogenic slope factors
CSF_i^{der}	Dermal exposure carcinogenic slope factors
DK_i	Dermal permeability coefficient
E_i	Entropy value of i^{th} textile wastewater treatment technique (alternatives)
ExD	Exposure duration
ExF	Exposure frequency
ExT	Leachate Exposure Time
F	Fraction of skin in contact to lecahte
FAM	Fuzzy assessment matrix
InR	Ingestion rate
K	Number of Sub-criteria indicating sustainability of treatment techniques
k	Number of process parameters considered in the adsorption study
k_1	Rate constant for the PFO model
k_2	Equilibrium rate constant for the PSO model
k_i	Rate constant for the intra-particle diffusion model
M	Weight coefficient of each metal ion
Ms	Number of sustainability indicators
N	Number of alternatives
q_e	Mass of COD and color adsorbed at the equilibrium condition

q_d	Desorbed mass of COD and color
q_t	Adsorption capacity
RM	Relation matrix
R^2	Determination coefficient
S	Number of experiments
s	Number of numeric factors
s_c	Replicates of the center point
SSA	Skin surface area
$\mu_L^L(x)$	Lower limit of the degree of membership functions
$\mu_L^U(x)$	Upper limit of the degree of membership functions
V	Effluent volume
VCF	Volumetric conversion factor
W	Adsorbent weight
X_j	Values of the chosen independent variables
Y_i	Response variable (COD and Color (%) removal efficiency)
Z	Pairwise comparison matrix of metal ions

Chapter 1

Introduction

1.1 Introduction

Rapid urbanization and population growth have increased the demand for manufactured goods, textiles, pharmaceuticals, and infrastructure. Industries play a crucial role in the nation's economic activities and are vital for meeting the daily demands of the populace. The continual availability of raw materials and the proper disposal of waste are two necessary phenomena for the manufacturing industries (Srivastava et al., 2023). Due to the enormous amount of waste produced by these industries on a global scale, environmental preservation and industrial expansion are inevitably at odds. Industrial waste can be hazardous or non-hazardous, and mainly in solids, liquids, and gaseous forms. These wastes, on their inappropriate disposal, pollute the nearby water source, air and soil and may get mixed with municipal solid waste, thus threatening human health (Vallero, 2022). However, each country has established laws and regulations for waste treatment, disposal, and storage. For instance, in the United States, Resource Conservation and Recovery Act (RCRA) gives Environment Protection Agency (EPA) the authority to control different types of waste. The EPA has developed standard approaches and set criteria to determine if substances exhibit hazardous or non-hazardous characteristics (EPA, 1996; Jha et al., 2022). In India, the Ministry of Environment, Forest, and Climate Change (MoEF & CC) and the central and state pollution control boards are the regulatory and administrative bodies responsible for waste management (CPCB, 2017). With the expansion of industrial activity accompanied by increased waste generation, treating and managing industrial waste has become challenging for the human community (Dasgupta et al., 2015). Industrial waste management is essential for sustainable development of the country (Psomopoulos et al., 2023). This thesis is mainly focused on the waste generated by the textile industry and ways to manage it effectively.

1.1.1 Textile industries and their economic significance

The textile, clothing and fashion industry is essential to everyday life. It is one of the global industries and comprised more than $1000 billion of global trade in 2022, which is expected to increase at the Compound Annual Growth Rate (CAGR) of 4% from 2022 to 2030 (Grand View

Research, 2022). The three major countries exporting the textile worldwide in 2021 are China, European Union and India (WTO, 2018). The textile industry in India is one of the largest employing sectors, contributing about 2% to the country's GDP and sharing about 5% of the global trade, thus generating a massive revenue of $103.4 billion in 2019-20 (MoT, 2020).

The constituents and framework for the textile industry vary from country-to-country depending on the availability of raw materials, chemicals, and machinery, the size of the industry, local demand and trends in the fashion industry (Neto et al., 2022). These industries use cotton, woolen, and synthetic fibers as raw materials (Holkar et al., 2016). These raw fibers go through various manufacturing processes using chemicals to produce the finished fabrics. The different textile processes are mainly divided into wet and dry processes. Dry processes produce solid waste, while wet processes produce liquid waste as their end waste. In this thesis, liquid waste generated during the processing of the raw fabric is studied. Various wet processes are sizing, de-sizing, bleaching, scouring, mercerizing, dying, printing, and finishing (Aljerf, 2018). Each process consumes a large quantity of water and various chemicals, such as caustic soda, natural and artificial dyes, hydrogen peroxide, sodium silicate, starch and waxes resulting in hazardous textile effluent (Yaseen & Scholz, 2019). Among the various chemicals used in the industry, dye is the major recalcitrant pollutant which is toxic and carcinogenic (Behera et al., 2021).

1.1.2 Textile industry waste (liquid and solid)

The textile industry generates millions of tons of waste in the form of effluent, thus making this sector one of the prominent environment polluters in the world (Ruiz et al., 2023). The textile industry is a prominent consumer of water, dyes, and chemicals during various stages of textile processing. Subsequently, this industry releases excessive pollutants into the environment, mainly chemically contaminated water, which is unsuitable for further usage (Holkar et al., 2016). It can be assessed that the textile industry, on average, uses between 230 and 270 ton of water to produce 1 ton of finished textile fabric (Keskin et al., 2021).The effluent is rich in color, complex chemicals, salt, inorganic chemical compounds and have high total dissolved solids, Chemical Oxygen Demand (COD) (Dasgupta et al., 2015). Textile industries are also a predominant emitter of micropollutants, mainly Phthalic Acid Esters (PAEs) i.e., Diethylhexyl Phthalate (DEHP) and pentachlorophenol (Yakamercan & Aygün, 2021). According to the EPA, textile industry waste is hazardous due to its high volume, toxicity characteristics, and thus it is hard-to-treat (EPA, 1996). Among the various contaminants present in the effluents, dyes are the primary and recalcitrant toxic and carcinogenic pollutants (Zhou et al., 2019). Skin irritations, dermatitis, allergic reactions, asthma are a few of the health-related issues reported in textile industry employees mainly due to close contact with the reactive dyestuffs dust (Khattab et al., 2020). Further, chronic impact of dyestuffs such as 2-napthylamine, benzidine, Basic Violet 14, Direct Blue 6 on the employees is reported. The employees with higher number of cases of tumors mainly in bladder were reported and animal testing indicates presence of carcinogenic agents in these dyes (Zhang & Zhang, 2015). Additionally, some of the azo dyes do not dissolve into aromatic amines and have poor biodegradability; 60-70% of them are mutagenic and carcinogenic for both human being and animals (Chung, 2016; Rawat et al., 2018). The discharge of raw effluent into freshwater bodies or in sewer lines adversely affects the dissolved oxygen, inhibits the biological treatment process, increases turbidity and is aesthetically unpleasant, affecting the overall water quality of the water body and the surrounding environment (Keskin et al., 2021). Fish and other aquatic organisms leached with dyes or textile industry effluent on consumption by humans can cause symptoms of cramps, fever, and hypertension (Sharma et al., 2022). The dye contaminated water also inhibits the growth of microalgae in aquatic ecosystems (Sharma et al. 2021). Textile dye effluent also has adverse impact on the soil chemistry and alters the balance of soil microbial flora. Dyes and organic pollutants have detrimental impact on seed germination, seedling heights and plant growth (Arshad et., 2020; Zou et al., 2019). Hence, it imparts toxicity to the environment's biotic and abiotic components, comprising air, soil, water, and terrestrial and aquatic life (Hussain & Wahab, 2018). However, the profit-making attitude, industrial reluctance, and difficulty in treating due to its voluminous amount, makes the textile wastewater treatment plant inefficient (Behera et al., 2021).

The textile industry poses one of the greatest dangers to the environment due to its water intensiveness resulting in the depletion of freshwater, both surface and groundwater. The increased scarcity of water resources and the decline in water quality with the increasing water demand in industries have obliged researchers to assess the appropriateness of various Textile Wastewater Treatment Techniques (TWWTTs) for proper disposal and reuse of effluent. Numerous methods exist for treating textile wastewater. These are physical, chemical, biological and hybrid processes (Tohamy et al., 2022). Most of these processes vary in terms of their fundamental working principle and are compared based on their performance, the cost involved, and the merits/demerits associated with them. For instance, the conventional biological treatment processes are insufficient for treating the chemical-rich industrial effluent.

On the contrary, physicochemical methods such as coagulation/flocculation, electrocoagulation, Fenton, and advanced oxidation generate chemical sludges as their end-product. At the same time, membrane filtrations require high initial investment and maintenance/ operation costs (E. Yakamercan & Aygün, 2021). Additionally, choosing a sustainable TWWTT is a complex undertaking with many potential issues for decision-makers and is a MCDM problem (Sawaf & Karaca, 2018).

In India, textile industries are found in different states such as Rajasthan, Tamil Nadu, Gujarat, Uttar Pradesh, and West Bengal in clusters of about 500 small, medium, and large-scale industries (Patel & Pandey, 2009). Some textile manufacturing industries deploy their treatment plant and abide by the Zero Liquids Discharge (ZLD) policy. In contrast, the remaining industries send their effluent to CETP run by the industrial associations and monitored by the state or central government Pollution Control Boards (PCB). The effluent is subjected to various physiochemical treatments and advanced filtration processes at CETP. The sludge is generated as a part of the end product of the effluent treatment process and contains heavy metals, salts, precipitated dyes after coagulation/flocculation and other chemicals. This sludge is considered hazardous as per Indian Hazardous Waste (Management, Handling and Transboundary Movement) Rules in National Productivity Council (NPC) report, 2016. Any waste is called as hazardous if its characteristics, such as physical, chemical, toxic, biological, corrosive, explosive or flammable, is likely to cause danger to health and the environment, whether alone or in contact with other substances (NPC Report, 2016).

The traditional and commonly practiced sludge disposal methods are landfilling, incineration, open dumping, and agricultural use. Open dumping and incineration are the sources of secondary pollution through leaching and air pollution (Zhan et al., 2020). However, textile sludge has been prescribed for agricultural use in European Union (EU) countries because of its high nutrient content after detoxification using integrated Ultrasound/Fenton-like processes (Zou et al., 2019). In India, CPCB has established strict and stringent regulations for sludge disposal, which is considered hazardous waste (Paul et al., 2023). Considering the hazardous nature of textile sludge, this sludge is disposed of at the Treatment Storage Disposal Facilities (TSDF). The sludge sometimes remains at the CETP premises waiting for its disposal at TSDF (Patel & Pandey, 2012). It is essential to study the leaching of heavy metals discharged from textile sludge in the surface water, as sludge can be exposed to water during the rainy season. A sustainable solution for sludge disposal is its stabilization and solidification by using it as the building material in the construction industry. Solidification is the process of mixing binding material and waste to form a solid material so that the surface area of the sludge exposed for leaching reduces and, thereby migration of contaminants. Stabilization is the process of chemical reactions between heavy metal/hazardous chemicals present in sludge and stabilizers to form a stable compound, thereby reducing their solubility in water (Ioannidis & Zouboulis, 2005). Researchers have explored using processed or stabilized textile sludge as the partial replacement for clay in bricks, natural fine aggregate and cement in mortar and concrete blocks (Anwar et al., 2018; Goyal et al., 2019; Zhan et al., 2020). The leaching study indicates the stabilization of heavy metals and minimal leaching from the solidified samples (Patel & Pandey, 2012). Along with the leaching study, it is imperative to quantify the environmental impacts of using the textile effluent treatment plant sludge as a partial replacement building material.

1.2 Research objectives

The primary objective of the study is to assess and analyze the probable impact on the surrounding environment of hazardous waste generated from the textile industries. The study also aims to devise a more sustainable framework and decision-making approach for selecting textile wastewater treatment techniques and give a workable solution for treating textile industry effluent. The study aims to quantify the environmental impact of hazardous textile effluent sludge as a building material.

The objectives of this research work are as follows:

1. Toxicity characterization of industrial effluent and TCETP sludge.
2. Development of a novel decision-making framework for judiciously selecting Textile Wastewater Treatment Techniques (TWWTTs) with their sustainability scores.
3. To explore a cost-effective and environment-friendly solution for treating textile industry effluent using agricultural waste-based adsorbent.

4. To study the toxicity effects of leaching of the sludge and develop Textile-Leachate Pollution Index (T-LPI) to assess the severity level of pollution.
5. To study the Human Health Risk Assessment (HHRA) by the leachate induced from the textile effluent treatment plant sludge.
6. To explore the feasibility of utilization of textile sludge as potential building materials (e.g., partially replacing cement in mortar mixes).
7. To assess the environmental impact of reutilizing the sludge and suggest remediation action plans using the Life Cycle Assessment (LCA).

1.3 Scope of the study

The present study initially focuses on identifying the different textile wastewater treatment techniques available in the literature and developing a suitable novel and systematic decision-making framework for appropriately judging and selecting the treatment technique. The hybrid FAHP approach of MCDM has been employed for developing the mathematical model for selecting sustainable TWWTT. This approach helps decision-makers evaluate the unified performance of any TWWTTs towards social, economic, environmental, and technical sustainability parameters.

The second part of the study consists of the physiochemical analysis of the textile industry wastewater collected from the industrial cluster of Balotra, Rajasthan, which is necessary to understand the chemical composition and the primary contaminants. Several parameters, such as Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Organic Carbon (TOC), color, heavy metals, turbidity, and pH, are determined using advanced laboratory techniques. Later, the WSAC carbon is developed, and its COD and color removal efficiency are studied. The developed adsorbent is eco-friendly and cost-effective.

The study also analyses the physiochemical characteristics of textile effluent treatment plant sludge, which is imperative for understanding the potential leaching. The leaching study on the sludge aims at quantifying the environmental impact. The impact of leachate contamination on surface water and its possible consumption through dermal or ingestion by a human being are quantified. It will assess the risk associated with human health and their possible long-term impact on the residents of the industrial clusters. The chemical and physical properties of sludge aid in finding a sustainable, feasible solution for utilizing it as a building material. The environmental impact of utilizing sludge in cement mortar mixes as a partial replacement for cement is quantified using the LCA approach.

Furthermore, the study aims to find the answers to various questions encountered whilst performing the literature survey on the textile industry waste (solid and liquid). These questions are:

1. How to find the most appropriate TWWTTs considering their sustainability?
2. How does the adsorption by activated carbon benefit in reducing color and COD from the industrial effluent?
3. How much does an improper disposal of hazardous sludge impact the environment and the leaching impact of it on surface water?
4. How the TCETP sludge can be utilized such that the strength of the component does not get affected?
5. What will be the environmental impact of using TCETP sludge as the building material and how to quantify the same?

The study provides a decision-making framework for selecting TWWTTs, innovative and cost-effective solutions for treating liquid waste, and feasible, sustainable solutions for sludge reuse in the construction industry. The study will help solve an environmental problem and will aid in resource conservation, thereby contributing to cleaner production where the waste generated from the industrial process can be treated and reused. This will help in converting the waste into a resource. The selection of an appropriate treatment technology based on the sustainability index would encourage the reuse of the treated textile wastewater industry, thus contributing to a clean environment, and reduced use of freshwater resources. The use of sludge generated from the effluent treatment plant as a partial replacement for cement will help in reducing the cement demand.

1.4 Organization of the thesis

The thesis consists of eight chapters. The details covered in each of these chapters are described as follows:

Chapter 1 introduces the broad area of the study undertaken considering the wastes discharged from the textile industry globally and Indian context. It also extends the need for various research activities, and highlights the objectives, scope, and detailed organization of work.

Chapter 2 covers the details of the previous research work and explains the need for current research work. This chapter also explains the research gaps from the past literature, followed by the concluding remarks.

Chapter 3 evaluates the performance of different textile wastewater treatment techniques using the hybrid FAHP approach. The study provides a novel decision-making framework determining the sustainability index of TWWTTs based on the experts' opinions.

Chapter 4 deals with the physiochemical testing of textile industry effluent, preparation and characterization of novel WSAC for using it as an adsorbent. This chapter also discusses the color and COD removal efficiency of WSAC for the textile industry effluent. A batch reactor study is performed using both the approaches i.e., one parameter at the time and response surface methodology. The removal efficiency data is modelled using an analytical approach, such as a polynomial quadratic regression model and artificial neural network.

Chapter 5 covers the characterization of textile sludge using XRF and a leaching study of the hazardous TCETP sludge is performed considering the TCLP method. The batch reactor experiments are designed using the response surface method. The results of the elemental analysis of the leachate fluid are summarized in this chapter. Later T-LPI was developed using the hybrid FAHP approach infused with Inter Valued Triangular Fuzzy Numbers (IVTFN). Additionally, the HHRA study results are also summarized.

Chapter 6 studies the possible and sustainable use of textile effluent treatment plant sludge by partially replacing cement in mortar mixes. The design mix of sludge and sludge with sugarcane bagasse ash is explained. The mortar samples are tested for 7, 28 and 90 days for mechanical, durability, permeation, carbonation, alkalinity, and leaching tests. The microstructure of the different mixes is studied.

Chapter 7 deals with the environmental impact assessment using LCA approach for sludge and SBA incorporated mortar mixes. The study uses ReCiPe method of LCA and Umberto NXT which include both endpoint and midpoint levels of impact assessment.

Finally, **Chapter 8** of the thesis concludes the study findings and highlights the contributions of the present research. The study proposes a sustainable approach for treating and selecting textile industry effluent treatment techniques. This chapter also includes the future scope and limitations of the present research.

1.5 Bibliographical note

Parts of chapter 2, 3, 4, 5 appear in the following journal papers.

- Agarwal, S., and Singh, A.P. (2022). Performance evaluation of textile wastewater treatment techniques using sustainability index: An integrated fuzzy approach of assessment, Journal of Cleaner Production. 337. 130384.https://doi.org/10.1016/j.jclepro.2022.130384(SCIE and SCOPUS indexed) (I.F. 11.072).
- Agarwal, S., Singh, A.P. & Mathur, S. (2023). Removal of COD and color from textile industrial wastewater using wheat straw activated carbon: an application of response surface and artificial neural network modelling, Environmental Science and Pollution Research. https://doi.org/10.1007/s11356-022-25066-2 (SCIE and SCOPUS indexed) (I.F.: 5.190).
- Agarwal, S., Singh, A.P., Mathur, S. (2022). Utilizing the Potential of Textile Effluent Treatment Sludge in Construction Industry: Current Status, Opportunities, Challenges, and Solutions. In: Kanwar, V.S., Sharma, S.K., Prakasam, C. (eds) Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD – 2021). pp. 279–290, Springer, Cham. https://doi.org/10.1007/978-3-030-93936-6_22 (SCOPUS indexed).
- Agarwal, S., Singh, A.P. Assessment of Toxicity Characteristics in Leachate from the Textile Industry–Based Sludge Using Leachate Pollution Index. *Water Air Soil Pollut* 234, 774 (2023). https://doi.org/10.1007/s11270-023-06785-9 (SCI and SCOPUS indexed) (I.F.: 2.90).

1.6 Summary

This chapter of the thesis introduces the textile industries and their economic significance at international and national levels. Additionally, it also discusses the environmental issues raised by the textile industry, such as water intensiveness, massive consumption of chemicals and dyes, and subsequent production of toxic, hazardous industrial effluent. The objectives of the research work have been defined while taking into consideration the environmental issues related to these industries.

Research has been done in the subsequent chapters of the thesis to accomplish these objectives. The next chapter of the thesis is composed of a review of the relevant literature and discusses the research gaps.

Chapter 2

Literature review

2.1 Introduction

Textile industries are significant water polluters contributing about 20% of global water pollution (Periyasamy et al., 2018). During the wet processing of fabrics, a large quantity of chemicals such as hydrogen peroxide, azo dyes, metal salts, caustic soda, phenols, and silica gel are mixed with water, thus generating a considerable quantity of effluent. Sustainable planning and reusing treated effluent back in the industry has become the need of the hour. The literature shows the existence of well-established methods for the treatment of industrial effluents. These treatment processes are categorized based on their fundamental working principles: physical, chemical, biological and hybrid. The working efficiency of these treatment techniques varies based on the physio-chemical composition of the effluent to be treated. For instance, the textile industry effluent has strong, stable dyes, and their treatment by aerobic and anaerobic processes is complex (Holkar et al., 2016). Few of these processes are discussed in the context of the textile industry effluent.

2.2 Physio-chemical and biological treatment process

Physical treatment processes are employed at several steps during the design of the effluent treatment process. During the primary treatment, small granules, mud, stones, dirt particles, suspended solids, oils, and lubricants are separated from the untreated effluent. This primary treatment is followed by physio-chemical treatment of coagulation/flocculation using natural and chemical-based coagulants (Karam et al., 2021), ion exchange using zeolite/ resins (Bensalah et al., 2023), adsorption using activated carbons (Bakar et al., 2021), and membrane filtration (Ji et al., 2021).

In the coagulation process, chemical agents, mainly organic and inorganic coagulants, are added to the effluent. Inorganic coagulants include alum, poly-aluminium chloride, granular ferric hydroxide, chitosan-aided poly-aluminium chloride, poly-aluminium ferric chloride, and poly-ferrous sulfate (Dotto et al., 2019). The organic coagulants are derived from the plants and marine shells such as maize, chitosan and moringa oleifera (Patel & Vashi, 2012). Coagulation/flocculation is a promising, efficient, and cost-effective method for removing dyes

(Verma et al., 2012). The main problems associated with coagulation are the disposal of hazardous chemical sludge generated in large quantities and the ineffectiveness of coagulants towards some extremely soluble dyes. Additionally, industries produce mixed effluent due to the use of several chemical additives and dyes, which reduces the coagulant efficiency and requires higher dose, thus producing a greater quantity of sludge. Due to their high solubility, the coagulation-based removal of water-soluble and complex structured dyes is difficult. It requires continuously re-evaluation of optimum doses, pH, mixing speed, mixing and settling time (Dotto et al., 2019).

Similarly, ion exchange is inefficient and costly method for decolorizing dyes from the effluent (Behera et al., 2021). Adsorption is a feasible, efficient technique and has recently gained importance with the development of nanomaterial and magnetic adsorbents. The adsorbents derived from agricultural waste such as corn cob, pomegranate peels, banana peels, sugarcane bagasse, wheat straw, and rice husk are eco-friendly and are efficient in adsorbing cationic, anionic and reactive dyes (Tran et al., 2017; Zazycki et al., 2018). Membrane-based contaminant separation is also effective in removing rigid textile dyes from effluents. Membrane filtrations are of the following types: microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis (Dasgupta et al., 2015; Ji et al., 2021; K et al., 2021; Ye et al., 2017; Zhao et al., 2017).

The chemical treatment process includes mainly oxidation of dyes by hydrogen peroxide (H_2O_2), Fenton's reagent (Fe^{2+} / H_2O_2), ozonation, and electrochemical advanced oxidation process, electro-Fenton process and photoelectron-Fenton process (Dutta et al., 2015; Sathya et al., 2019; Titchou et al., 2022). Chemical oxidation helps in removing the rigid dyes from the effluents which are resistant to biological treatment. Effluent treatment by chemical oxidation is a lengthy and time taking process. These treatment processes are an environmental menace considering the safe disposal of chemical sludge and the treated dye effluent or its reuse (Behera et al., 2021). However, ample opportunities lie in developing new eco-friendly, cost-effective materials derived from agricultural waste.

Biological treatment primarily uses phytoplankton remediation (plants), microbial treatment (algae-based), microorganisms (aerobic or anaerobic), Activated Sludge Process (ASP), Moving Bed Bio Reactors (MBBR), Rotating Biological Contractors (RBC) and Membrane Bioreactor

(MBR) to remove the pollutants from the effluents (Asif et al., 2018; Bharathiraja et al., 2018; El-Sheekh et al., 2021; Jamee & Siddique, 2019; Kurade et al., 2012; Wickramasinghe & Jayawardana, 2018; Yang et al., 2018). Biological treatment techniques are considered potential dye removal techniques and require less operation and maintenance cost, less sludge production, and are environment-friendly (Yang et al., 2020). Further, the Table 2.1 summarizes few of the textile effluent treatment techniques and their contaminants removal efficiency.

Table 2.1 Efficiency of different treatment process in removing contaminants

Treatment process	Effluent quality	Removal efficiency	Reference
Coagulation/Flocculation $Al(OH)_3$–polyacrylamide hybrid polymer	C-T reactive dye 19 (1000 mg/l)	Dye- 92%,	Al-Ani and Li, 2012
Coagulation/Flocculation Aluminum sulphate (AS) Moringa oleifera-KCl (MO-KCl)	Apparent color (4500 Pt-Co/l) COD (5820 mg O_2/l)	AS, MO-KCL COD- 84%, 82% Color- 24%, 82.2%	Dotto et al., 2019
Coagulation/Flocculation Chemically treated Aleppo pine seeds	Congo red (50 mg/l)	Dye- 81%	Hadadi et al., 2023
Adsorption Chemically modified sugarcane bagasse	Methylene blue (500 mg/l)	Dye- 98.39%	Yadav et al., 2021
Adsorption Modified wheat straw	Acid orange (AO7) (250 mg/l)	Dye- 99%	Mohammadi et al, 2021

Treatment process	**Effluent quality**	**Removal efficiency**	**Reference**
Adsorption Lathyrus sativus husk	Methylene blue (50 mg/l)	Dye- 99%	Ghosh et al., 2021
Ion exchange Cation exchange Resin	Disperse violet 28 (500 mg/l)	Dye- 91.7	Bayramoglu et al., 2020
Ion exchange Anion exchange resin	Acid orange 10 (2262 mg/l)	Dye- 97%	Marin et al., 2019
Membrane Filtration Novel Nanofiltration membrane	Methyl blue, Congo red, Crystal violet (100 mg/l)	Dye- 99.9%-92.86	Li et al., 2018
Membrane Filtration Ultrafiltration Membrane	Direct red 23 (100 ppm)	Dye- 98.65%	Yang et al., 2020
Membrane Filtration Forward osmosis	Methylene blue (10 mg/l)	Dye- 94%	He et al., 2023
Chemical processes Photocatalytic degradation (ZnO nanoparticles)	Eriochrome Black T (1000 ppm)	Dye- 99.64%	Lanjwani et al., 2023
Chemical processes Photocatalytic degradation (nano-ZrO2/UV/Persulfate)	Direct Blue 71 (50 mg/l)	Dye- 100%	Moradi et al., 2016
Photocatalysis Oyster shell synthesized CaO	Methylene blue (50 ppm)	Dye- 98%	Eddy et al., 2023

Treatment process	Effluent quality	Removal efficiency	Reference
nanoparticles			
Advanced Oxidation UV-LED + Chlorine	Reactive Blue 19 (20 -100 mg/l)	Dye- 99.4%-34.5%	Gholizade et al., 2023
Biological process SBR Aerobic conditions	Vat Yellow 1 (40 mg/l)	Dye- 75.12%	Solomon et al., 2020
Biological process SBR anoxic-aerobic conditions	Reactive Orange 16 (250 mg/l)	Dye- 65%	Ong et al., 2020
Biological process Anaerobic sequenced batch reactor	Methyl Orange (25-500 mg/l)	Dye- 75%	Yu et al., 2015

2.3 Need for MCDM to select sustainable TWWTTs

There are an ample number of effluent treatment processes with both merits and demerits. Apart from treating the effluent, developing treatment units requires extensive infrastructure, consumes a considerable amount of energy during their operational life, harms the ecosystem's hydrology and contributes to carbon footprint (Sawaf & Karaca, 2018).The treatment of effluents reduces the contamination level and makes it safe for reuse and disposal, but it has the inherent limitation of producing hazardous sludge and its disposal is expensive. However, most textile wastewater treatment facilities in third-world nations are not even operational due to industrial resistance and a profit-making mentality. In addition, the outdated conventional treatment systems suffer from the high energy, time, infrastructure, material, land, labour, and capital requirements. This makes integrating new advancements and systems feasible even with traditional technologies (Behera et al., 2021). Consequently, the selection of a sustainable TWWTT is a multidimensional and challenging task where decision-makers face multiple conflicts. Thus, the selection of appropriate TWWTT is an MCDM problem (Sawaf & Karaca, 2018).

The sustainability concept here means the performance of TWWTTs should be balanced by the environmental, economic and societal dimensions (Muga & Mihelcic, 2008). Some studies have considered technical and management aspects of sustainability. The related articles suggest divergent use of sustainability in the studies. Padilla-Rivera et al. (2016) and Tsalidis et al. (2020) have focused only on the social aspects of the sustainability of Wastewater Treatment (WWT) alternatives. Muga & Mihelcic (2008) have evaluated the performance of WWT using the social, environmental and economic dimensions. Yang et al. (2020) have compared the technical, economic and environmental perspectives of TWWTTs. Garrido-Baserba et al. (2014)considered the environmental criteria while selecting the WWTT. Pretel et al. (2016) studied sustainability's economic and environmental aspects. The performance evaluation of the sustainability aspects can be done by incorporating the judgement of different experts in the field of wastewater treatment (Srinivas & Singh, 2018). The suggestions and opinions of experts need to be put together using a mathematical model. This will help the decision-makers inmaking a single, functional, and efficient decision. The MCDM mathematical methods have been used widely in studies. Ouyang et al. (2015) have considered the environmental, ecological, management and technical aspects to assess the performance of natural WWT facilities using a unified approach of the multidimensional scaling and fuzzy analytical process. Zheng et al. (2016) established a scenario-based framework to compare the socio-economic dimensions of sustainability of different WWT facilities using multi-criteria decision analysis. Ren & Liang (2017) have used the intuitionistic fuzzy set theory to measure WWT processes' sustainability. Lizot et al. (2021) integrated the AHP and ELECTRE II methods to prioritize the WWT system. Omran et al. (2021) evaluated the sustainability of WWT techniques for the urban regions of Iraq using the weighted sum model of multi-criteria decision analysis.

Though all these studies are focused on wastewater treatment, scant attention has been paid towards evaluating the sustainability of TWWTTs. Kumar et al. (2016) optimized the process parameters for the bio-treatment of textile wastewater using the Fuzzy Inference System (FIS). Dogdu et al. (2017) monitored the performance of vertical flow wetlands in treating the real textile effluent using fuzzy logic. Periyasamy et al. (2018) reviewed and discussed the various sustainable TWWTTs considering the primary, secondary and tertiary treatment levels. Sawaf & Karaca (2018) investigated the difference in stakeholders' opinions towards the sustainability of common WTT used for the textile industry in Turkey using the Analytical Hierarchical Process (AHP), Simple Additive Weighing (SAW) approach. Many studies have applied the AHP approach to derive the scores of different criteria or alternatives of WWT processes. The summary of related research articles is presented in Table 2.2. Limited studies have focused on the prioritization of textile effluent treatment techniques.

Table 2.2 Review of MCDM techniques for selection of WWT technology

Contribution	Sustainability dimensions				Methodology	Authors
	ECO	En	S	T		
Selection of WWT technologies	✓	✓	✓			Muga and Mihelcic, 2008
Selection of natural WWT alternatives	✓	✓		✓	AHP	Ouyang et al, 2015
Addressing the social dimension of sustainability of WWT technologies.			✓		Basic requirement scale	Rivera et al., 2016
Framework for the planning of wastewater infrastructure under uncertainty	✓	✓	✓		Stochastic multi-criteria acceptability analysis, Monte Carlo simulations	Zheng et al., 2016
Sustainability measurement of WWT processes	✓	✓	✓	✓	Intuitionistic fuzzy set theory	Ren and Liang, 2017
Selection of WWT facilities	✓	✓	✓	✓	AHP, ELECTRE II	Lizot et al., 2021
Sustainability assessment of WWT facilities for urban areas	✓	✓	✓	✓	Weighted sum model	Omran et al., 2021

Contribution	Sustainability dimensions				Methodology	Authors
	ECO	En	S	T		
of Iraq						
Bio-treatment process for real textile industry effluent- process parameter modelling and optimization				✓	Fuzzy inference system, Mamdani's method	Kumar et al., 2016
Monitored the performance of vertical flow constructed wetlands for textile industry effluent				✓	Fuzzy logic	Dogdu et al., 2017
Comparison of different stakeholder opinions towards the sustainability of TWWTTs	✓	✓	✓	✓	AHP, SAW, CP, TOPSIS	Sawaf and Karaca, 2018

***Economic = ECO, *Environmental = En, *Technical = T, *Social = S**

2.4 Advantages and disadvantages of TWWTTs

The researchers have proposed various treatment processes that are already in practice. As discussed, these processes entail physical, chemical, and biological methods. The physical treatment processes useful for reducing the contaminants from the textile effluents are gravity settling, stabilization, ion exchange, membrane filtration, and adsorption (Behera et al., 2021; Saravanan et al., 2021). Coagulation using chemicals, electrocoagulation, and oxidation are some chemical treatment processes. The biological methods include aerobic and anaerobic decomposition using Activated Sludge Process (ASP) and Rotating Biological Contractors (RBC). A combination of biological and physical processes, such as Fixed Bed Bio Reactor (FBBR), Moving Bed Biofilm Reactor (MBBR) and Membrane Bioreactors (MBR), etc. are also widely used (Behera et al., 2021). Although the chemical methods are efficient and capable of treating wastewater, they are cost-ineffective, and the byproduct (chemical sludge) is enormous and challenging to store. The biological treatment processes are complex to manage, cannot immediately adapt to pollutant concentration, occupy considerable space, and are costly. MBR is the most widely adopted technology for treating industrial effluents (Akhoundi & Nazif, 2018; Luong et al., 2016). However, the main drawback is the fouling of the membrane and the need to change it frequently, which increases the operation and maintenance cost of the treatment process. An additional pre-treatment process can reduce membrane fouling, thus resulting in low operation/maintenance costs (Iorhemen et al., 2016). The physical treatment processes such as adsorption are relatively simple, less costly, and environment benign (Holkar et al., 2016). Adsorption is an efficient, economical, unsophisticated practice for treating textile wastewater to reduce contaminants and color (Beyan et al., 2021).

2.5 Adsorption and adsorbent selection and its need

Adsorption is the transfer of pollutants such as heavy metals, dye pigments, emerging contaminants-drugs and personal care products, and chemicals from the liquid phase to the surface of the solid phase called adsorbents. Activated carbons are the most commonly used adsorbent materials produced by heating agricultural wastes at high temperatures in the presence or absence of air (Cossu et al., 2018). Numerous bio-sorbents such as sugarcane bagasse, date palm waste, maize straw, pepper straw, cotton straw, wheat straw, rice husk, corn cobs, peanut shells, orange peel and banana peel have been investigated for the removal of dyes, organic matter, ions and heavy metals (Bakar et al., 2021; Georgin et al., 2016; Liu et al., 2012; Ratan et al., 2018; Tokay & Akpınar, 2021).

Cueva-Orjuela et al. (2017) mentioned that the 95% removal of basic red dye is possible using sugarcane bagasse-based activated carbon. Yadav et al. (2021) have used sugarcane bagasse for biosorption of methylene blue dye about 98.3% and have carried out kinetic, isotherm and thermodynamic modelling. Tran et al. (2017d) have studied golden shower pod, coconut shell and orange peel for adsorption of cationic dye methylene green 5 and achieved 87-93% removal efficiency. Tran et al. (2017b) have prepared the golden shower activated carbon using the three-step process and achieved 50-73% removal of methylene green 5 dye within a minute. Georgin et al. (2016) have prepared peanut shell adsorbent using pyrolysis and studied the removal of Reactive Red 141 (RR141) and Direct Black 38 (DB38). Nayl et al. (2017) have used the date palm seed adsorbent to remove BOD and COD from treated sewage and have achieved 92.8%

and 95.4 % removal efficiency, respectively. Beyan et al. (2021) have studied the adsorption of BOD (95%) and COD (92%) from the textile effluent using the activated carbon of sugarcane bagasse. Adewoye et al. (2021) studied the adsorption of TOC using functionalized multiwalled carbon nanotubes and found 93.6% removal of TOC. Assila et al. (2020) have used the naturally available minerals for adsorption studies for the removal of COD (88-79%) and heavy metals (Cr -39% and Cu-28%) from textile effluents. Ghosh et al. (2021) have achieved 99% removal efficiency of methylene blue using the Lathyrus sativus husk as an adsorbent. Mohammadi et al. (2021) have studied removing 2-Naphthol and Acid Orange (AO7) dye from the aqueous solutions using wheat bran as an adsorbent and achieved maximum removal efficiency of 99%. Ata et al. (2012) used wheat bran for Coomassie brilliant blue dye adsorption and observed 95.70% removal efficiency. Zhang et al. (2019) have prepared activated carbon using wheat bran for the adsorption of methylene blue, and 89% removal efficiency is observed. Wheat straw remains after cultivation and is locally available, cheap, and non-hazardous. The polymeric structure of the wheat straw has cellulose (45%), hemicellulose (28%) and lignin (20%) (Kapoor et al., 2016). Wheat straw contains hydroxyl, carbonyl, and carboxylic groups with a potential of adsorbing dyes through ion exchange, making it an attractive, inexpensive, and effective adsorbent (Dai et al., 2018; Rangabhashiyam et al., 2013). The use of local agricultural waste (wheat straw) as raw material for adsorbent is suggested in the study. The studies on removal of dyes using the controlled dye solution are available in literature, but detailed studies on using the textile effluent is limited.

2.6 Development of Textile-Leachate Pollution Index (T-LPI)

Textile effluent is a mix of dyes, chemicals and requires a combination of treatment processes. In India, the effluent from the industrial cluster is treated CETP through a series of physio-chemical and biological processes. Treated effluent and hazardous sludge are generated as end products from these CETPs. This hazardous sludge contains organic and inorganic salts, heavy metals and other chemicals used in the textile industry and during treatment of effluent in CETP (Paul et al., 2023). The two traditional methods used for sludge disposal are landfilling and incineration. However, the low calorific value of the TCETP sludge makes it unsuitable for incineration in cement manufacturing industry kilns (Goyal et al., 2022). Landfilling and open dumping is not recommended for hazardous wastes by the Central Pollution Control Board (CPCB) of India, and the sludge is disposed of in the Treatment, Storage and Disposal Facilities (TSDFs) (Patel & Pandey, 2012). However, during the field survey, it was observed that a large quantity of sludge lies in CETP, waiting for its disposal by TSDFs. Further, this sludge is also being used for landfilling and agricultural purposes in European countries due to its high nutritional value (Zou et al., 2019).

Landfilling and open sludge disposal before its transfer to the TSDF site have the potential to pollute the surrounding air, surface, and groundwater. The landfills containing hazardous sludge produce odour and leachate. This highly toxic leachate contains inorganic and organic compounds and heavy metals (Ma et al., 2022). Due to the severe polluting potential of leachate, it is imperative to quantify it and estimate the possible human health risk (Rajoo et al., 2020). A tool is required to enumerate the true pollution potential of industrial sludge leachate. The Textile-Leachate Pollution Index (T-LPI) will aid in sludge management and ranking of the sites for immediate waste disposal at the TSDF site.

The landfill LPI was first formulated in 2005 for Municipal Solid Waste (MSW) (Kumar & Alappat, 2005). The LPI was developed based on the feedback of 80 experts, and 18 parameters were included. Rajoo et al. (2020) have developed the Leachate Pollution Index for Developing Countries (LPIDC) based on the concept that the waste composition of MSW landfills from developed and developing countries varies. Chaudhary et al. (2021) have studied the temporal variation in LPI of four MSW dumping sites in Delhi, India. The LPI was revised, and a different optimal aggregation function was selected (Bisht et al., 2022). The LPI index highly depends on the waste type and composition.

In contrast, industrial sludge, such as TCETP sludge, consists of chemicals used for the treatment process and those present in effluents before treatment. The chemical composition and the concentration of heavy metals in the leachate discharged from industrial sludges would be very high and different from the MSW. Hence, using the same index to determine the pollution impact of leachate from the MSW and industrial effluent treatment plant sludge would yield an inaccurate pollution potential of the leachate. Therefore, the existing LPI cannot be used to evaluate the pollution potential of leachate from industrial waste accurately. Developing a flexible and precise pollution index concerning TCETP sludge is essential.

2.7 Sustainable utilization of TCETP sludge

With an increasing interest in converting waste to resources and recycling, reusing of waste, there is a need to research the best practices for using industrial waste as construction material. The TCETP sludge has chromium (Cr), zinc (Zn), lead (Pb), ammonium and other potentially harmful chemicals. The primary aim of using TCETP sludge as building material is to stabilize it such that dissolution of heavy metal on contact with water reduces and additionally converting sludge into valuable materials. Over the years, researchers have investigated the reuse potential of TCETP sludge as a partial replacement material for building materials such as cement, clay, and Natural Fine Aggregate (NFA) in different binder systems.

2.7.1 Physical and chemical properties TCETP sludge

The detailed study on the physical and chemical properties of the TCETP sludge will help in identifying the possible variation in the properties of concrete, mortar, and bricks. These properties of the different TCETPs sludge from the past literature are given in Table 2.3 and Table 2.4. The properties of TCETP sludge are governed by the type of chemicals used, textile processing, and effluent treatment process (Holkar et al., 2016). It is evident from Table 2.3 that the specific gravity of TCETP sludge is less than that of Ordinary Portland Cement (OPC) and almost like that of clay. The lower specific gravity increases the sludge volume for the same weight as the material. For instance, on replacing the cement on a weight basis, the weight of the sludge used to replace the cement will be the same, but the volume of sludge will be more. The increased volume of binder requires more water however, at constant water content, the flowability of cement-sludge paste decreases (Zhan & Poon, 2015). The low specific gravity and the higher fineness of sludge than the cement increases the water/cement ratio for adequate consistency. The excess of water creates air voids on evaporation resulting in reduced strength.

The chemical composition of the substituting material helps determine and analyse its possible reactivity in different binder systems. The percentage composition of TCETP sludge consists of CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_4 and MgO and is presented in Table 2.3. The presence of low SiO_2 and Al_2O_3 and high CaO compared to cement indicates that it may contribute to any pozzolanic activity. Along with this, the Zn and Pb form a calcium hydroxyl zincate membrane which surround the cement particles, thereby hindering hydration and reducing the strength (Patel

&Pandey, 2012; Zhan et al., 2020). High value of Loss on Ignition (LOI) indicates the presence of significant amount of organic matter.

Table 2.3 Physical properties of TCETP sludge

Authors	Water content (%)	Specific gravity	pH	Blaine fineness	Total volatile solids (%)
Balasubramanian et al., 2006	28.72	2.4	9.13	-	31.85
Baskar et al., 2006	-	2.32	10.5	-	-
Patel and Pandey, 2012	10.50	0.94	8.70	-	36.60
Zhan and Poon, 2015	75.24	1.14	-	-	-
Rahman et al., 2017	35-75.64	2.3	4.5-5	-	35.95
Chen and Wu, 2018	35.98	-	6.04	-	-
Anwar et al., 2018	80	-	-	-	70
Goyal et al., 2019	-	2.32	-	426	-

Table 2.4 Chemical constituents of TCETP sludge

Authors	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	LOI
Balasubramanian et al., 2006	108.22	-	-	180.5	0.0012	154.30	-
Baskar et al., 2006	28.4	7.1	0.698	9.1	-	-	-
Zhan & Poon, 2015	0.87	3.40	6.20	60.45	24.95	-	11.81
Rahman et al., 2017	2.5	12.15	53.14	15.65	3.0	-	-
Goyal et al., 2019	33.5	3.8	0.3	18.9	-	-	40.6

Authors	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	LOI
Zhan et al., 2020	0.94	2.5	4.56	44.51	-	-	26.3
Goyal et al., 2022	33.2	22	5.93	2.5	2.12	2.86	29

2.7.2 Utilization of TCETP sludge in different types of binder systems

2.7.2.1 Use of TCETP sludge in cement and mortar

The researchers have used the TCETP sludge as supplementary cementitious materials (Chen & Wu, 2018; Goyal et al., 2022). The presence of lime and silica in sludge indicates that it may impart pozzolanic activity. Standard consistency, initial setting time and final setting time of cement-sludge paste are the few tests performed to study the workability of the mixes. The increase in the mix's setting time (initial and final) is reported with the increase in sludge content. It is due to the high fineness of sludge and the low specific gravity (Begum et al., 2013).

The TCETP sludge is used as a partial replacement of cement in concrete and mortar. The modified mortar and concrete mixes are tested for mechanical properties such as compressive, split tensile strength and the leaching of heavy metals. The compressive strength of blended mortar with cement and sludge as binder material at the 28 days of moist curing is shown in Fig. 2.1.

Adding TCETP sludge in concrete/mortar does not negatively impact the compressive strength up to the optimum replacement level; beyond it, the strength decreases drastically. The compressive strength at 5% replacement is almost similar to that of the control mix; however, a considerable loss in strength was observed at 20% cement replacement by sludge (Balasubramanian et al., 2006). The cement-sludge blocks with 30-70% partial replacement of PPC cement by sludge show a variation in unconfined compressive strength from 3.62-33.3 MPa (Patel & Pandey, 2012). The sludge is used in the 0-50% ratio by weight for the partial cement replacement in mortar. A reduction in compressive strength from 27- 5 MPa is observed (Rahman et al., 2017). The TCETP sludge is used to substitutes the cement up to 0-20% by weight, and the minimal decrease in compressive strength is observed for 5% replacement (Goyal et al., 2019). Balasubramanian et al. (2006) have observed 0- 20% of cement can be replaced by TCETP sludge to produce hollow load-bearing blocks and up to 30% for producing non-load-bearing concrete blocks. Goyal et al. (2022) have stabilized the textile sludge using MgO and reported that 10% replacement of cement with sludge has no negative impact on the compressive strength of the mortar. The heterogeneity in sludge physical and chemical properties is responsible for different strength reductions at the same replacement level.

The impact of substituting cement with sludge on the split tensile strength in cement/mortar shows a similar pattern as compressive strength (Rahman et al., 2017). The researchers have studied permeation properties such as water absorption and sorptivity. The improvement in the properties for 5% replacement of cement by sludge indicates the dominance of the filler effect of sludge in voids. However, as the sludge content increases, the hydration of cement reduces, and hence large voids develop (Zhan et al., 2020).

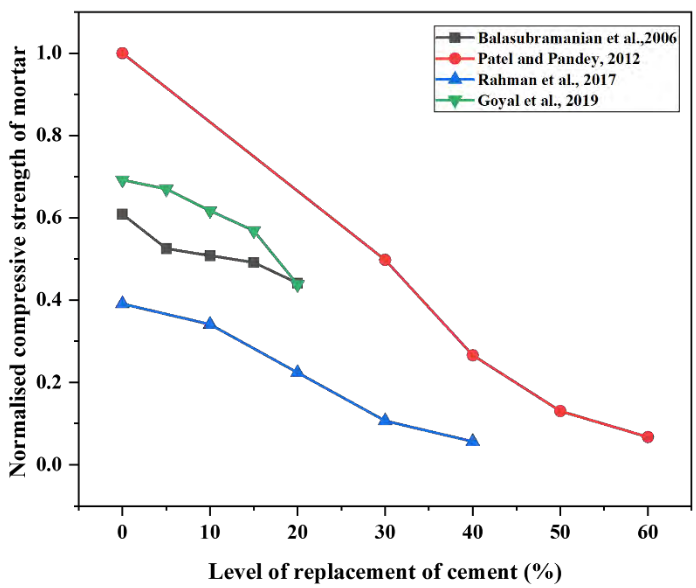


Fig. 2.1 Normalised compressive strength of TCETP sludge blended mortar

2.7.2.2 Use of TCETP sludge as fine aggregate

Along with partial replacement for cement, the TCETP sludge is also used as the partial substitute for NFA in concrete and mortar. Generally, concrete and mortar consist of 30% of fine aggregate. A large quantity of fine natural aggregate is required, and its demand has increased drastically over the past few decades. The river sand is obtained from the mining of the riverbed. River sand mining is accountable for the riverbed deterioration and change in the direction of river flow hence increasing the number of floods. Owing to these problems associated with river sand mining, several states have banned it in India, such as Uttar Pradesh, Tamil Nadu, Maharashtra, Rajasthan, and Bihar. As the procurement of river sand has become difficult, the need for an alternate solution to meet the growing demand has increased (Santhosh et al., 2021). Therefore, applying TCETP sludge as a fine aggregate will reduce the pressure on river sand mining and could be used as an alternate material for river sand. However, hazardous materials in sludge make it challenging to replace NFA in a higher percentage for the concerned design strength.

Zhan and Poon (2015) have pretreated TCETP sludge with lime. The pre-treatment has reduced the excess ammonia present in the sludge and has positively impacted the mechanical properties of concrete. The pre-treated sludge is used for replacing the fine aggregate by 0-30% by weight in concrete and 10% replacement has resulted in 43.3 MPa strength. Rahman et al. (2017) have used TCETP sludge for replacing the NFA by 0-80% by weight in the mortar. The reduction in compressive strength in mortar specimens from 27-9 MPa is observed.

2.7.2.3 Use of TCETP sludge as clay in bricks

TCETP sludge has frequently been utilized by researchers to partially replace clay in bricks. The use of sludge has the advantage of replacing natural clay and serving as an immobilizing agent to stabilize heavy metals in the sludge. The high organic matter and decent calorific value make the TCETP sludge-incorporated bricks more environment friendly by reducing the clay content and decreasing the energy required for brick firing (Anwar et al., 2018). Baskar et al. (2006) have used TCETP sludge as 3-30% partial replacement for Clay. It was observed that the firing time, temperature of firing, and sludge content are the critical parameters determining the brick's quality. The bricks produced by adding TCETP sludge up to 9% at the firing temperature of 800^{o}C and for the time of 8 h has satisfied the requirements for IS1077 (1992) of minimum strength of burnt clay bricks is 3.5 MPa. Balasubramanian et al. (2006) have substituted of clay from 10-30% by TCETP sludge and the results shows bricks containing 10% sludge can be used for load-bearing structures while the bricks having 30% sludge can be used for non-load-bearing structures. Begum et al. (2013) have incorporated 0-50% of TCETP sludge in bricks and the results indicated that the 15% and 30% substitution can produce first-class and second-class bricks, respectively, according to Indian Standards. Anwar et al. (2018) have used TCETP sludge in bricks with different proportion of 0.5-5.25% and was evaluated for compressive strength. About 77% increase in compressive strength of TCETP sludge incorporated clay fired bricks than conventional bricks are observed. The use of sludge in bricks can solve the environmental problem of disposal of it and will reduce the consumption of clayey soil.

2.7.2.4 Leaching and toxicity study of TCETP sludge

The TCETP sludge samples are analyzed for measuring the composition of inorganic elements, i.e., heavy metals. The heavy metal composition of TCETP sludge varies depending on the type of textile processing, chemicals used in industry, the dosage of chemicals and the process/steps followed for the treatment of textile effluent (Anwar et al., 2018). The presence of heavy metals indicates that the sludge cannot be discarded into the environment directly without treatment/stabilization due to its possibility of leaching into the soil and contaminating the surface and groundwater. The heavy metals present in TCETP sludge and reported by the researchers are given in Table 2.5.

Table 2.5 Heavy metals concentration in (mg/kg) in raw TCETP sludge

References	Cd	Cu	Cr	Zn	Ni	Pb	Co
Balasubramanian et al., 2006	3.96	57.48	2.98	91.60	0.64	12.1	-
Patel and Pandey, 2012	5.17	225.48	231.45	186.47	89.67	44.75	11.20
Zhan and Poon, 2015	18.39	455.1	110.0	291.40	63.38	304.0	-
Rahman et al., 2017	0.664	-	2.98	-	-	-	-
Anwar et al., 2018	5.6	58	10	131	32	12	-

The existence of heavy metals in the TCETP sludge necessitates the study of the leaching of metals ions before and after its utilization in the construction industry. The brick, mortar, and concrete sample are studied for the leaching of heavy metals using TCLP test as per EPA method 1311 (Goyal et al., 2022; US EPA 1311, 1992; Zhan et al., 2020). Patel and Pandey (2012) have replaced 70% cement with TCETP sludge in solid blocks and tested for leaching of heavy metals such as Pb, Cd, Cr, Cu, Ni, Co, and Zn. The results were found to be within the stipulated limit. Zhan and Poon (2015) have tested for heavy metal leaching from the concrete blocks (up to 10% partial replacement of fine aggregates by TCETP sludge) and found to be within the prescribed limits. Rahman et al. (2017) have tested sludge incorporated mortar and concrete specimens for the leaching of heavy metals and other parameters such as BOD/COD/SO_4^{2-} /Cl^- and are found to be within the limit prescribed by the Department of Environment in Bangladesh. Therefore, it can be said that using hazardous textile sludge in building components could be one way of stabilizing the contaminants into stable products and reducing the uncontrolled exploitation of natural resources.

The literature has reported that the lower amount of silica in textile sludges results in poor pozzolanic activity on addition in the cement mixes (Goyal et al., 2019). However, the mineral admixture from the agricultural waste rich in silica, i.e., Sugarcane Bagasse Ash (SBA), can be added to improve the pozzolanic activity by providing silica needed for converting CH into secondary CSH in the later stages of mortar mixes. SBA is responsible for developing secondary CSH gel and improving the cement mixes' strength, permeation and durability properties (Minnu et al., 2021).

2.9 Previous studies on sugarcane bagasse ash as a partial substitute for cement

The sugarcane bagasse is the waste generated by the sugar industry and is used in cogeneration boilers for electricity production. Sugarcane Bagasse Ash (SBA) is produced as waste in boilers and is disposed at the landfills (Xu et al., 2018). The uncontrolled disposal of SBA leads to environmental issues such as air pollution, and the particulate matter present in SBA is hazardous to human health. The SBA has flaky, tubular, irregular-shaped, lightweight porous particles rich in silica and alumina (Bahurudeen et al., 2015; Batool et al., 2020; Gupta et al., 2022). Gupta et al. (2022) observed the maximum compressive strength for the 5% substitution of cement with SBA. Batool et al. (2020) have partially substituted the cement with SBA in concrete, and 10% is the optimal replacement for higher compressive strength. Chi (2012) has also indicated 10% as the optimal replacement of binder material with SBA for mortar. Mohan et al. (2021) have suggested 15% optimal cement replacement in mortar mixes using the high temperature (750-800 °C) cogeneration plant bagasse. Nassar et al. (2022) reported that 10% is the optimal cement replacement by SBA. Quedou et al. (2021) have inferred that the concrete mixes with 10% binder material replaced with SBA have shown positive performance. Therefore, considering the above-reported studies, 5% and 10% substitution are considered in this study, along with the TCETP sludge.

2.10 Life Cycle Assessment (LCA)of utilizing TCETP sludge in mortar mixes.

The CETP treating textile industrial effluents generates hazardous sludges. Hazardous sludges are stored in Treatment, Storage, and Disposal Facilities (TSDFs). The sustainable solution for the stabilization and solidification of sludge is its use as a partial replacement for building material, mainly cement (Anwar et al., 2018). Environmental benefits of sludge re-utilization are reduced waste and, at the same time, reduced need for cement, thus reducing requirements for the natural resources for cement manufacturing (Farinha et al., 2019).

The growing infrastructure requirement has increased the need for concrete/ mortar due to its versatility, cost, and availability, thus increasing the need for cement. The construction industry is one of the major consumers of non-renewable raw materials such as limestone, fine natural aggregate, natural coarse aggregate, and fossil fuels. It is reported that the construction industry contributes about 23% of the total CO_2 released globally by different economic activities. Cement production plants consume limestone and fossil fuels to produce cement clinkers. Thus, fossil fuel combustion and limestone de-carbonation are the two main processes of cement production responsible for CO_2 emission (Charitha et al., 2021). It has been reported that for every ton of cement production, 0.95 tons of CO_2 is emitted (Fayomi et al., 2019). In 2017, cement production in India was about 330 million tons (Bajpai et al., 2020), and worldwide production was 4.1 billion tons in 2017 (U.S. Geological Survey, 2018). The higher demand for the infrastructure increases cement demand to develop it, thus increasing the Green House Gases (GHGs), mainly CO_2 emissions. Attempts have been made to use supplementary cementitious materials such as sludges, slags, sugarcane bagasse ash, and rice husk ash to reduce the cement requirement, reducing CO_2 gas emission. Other than CO_2 gas emissions, other environmental factors arise during the whole life cycle of mortar. A systematic scientific approach is required to quantify the environmental impact of using the TCETP sludge and SBA to replace cement in mortar mixes.

The LCA method is often used to compare the potential environmental impacts of various alternatives of processes and products (Nakic, 2018). This study uses the LCA approach to evaluate the environmental consequence of using sludge-bagasse incorporated mortar. The purpose of conducting an LCA study is to justify the adoption of sludge-incorporated cement mortar as an environmentally friendly alternative to cement mortar. Using LCA, environmental impacts generated during any product's life cycle phases, such as raw material, transportation, manufacturing, and disposal after its utilization, can be estimated using the cradle-to-grave approach (Dandautiya & Singh, 2019). LCA is a diverse method, and its accuracy depends on the correctness of the Life Cycle Inventory (LCI), mainly volume, distance, mass, and energy of the input and output data. In this way, the environmental differences of the mortar can be quantitatively examined, and thus, the decision can be made when choosing the mortar (Jiménez et al., 2015).

Past literature on the environmental impact of the LCA approach of using partially substituting cement with alternate materials is summarized here. Moraesa et al. (2010) studied the environmental impact of incorporating rice husk ash in the mortar and found better technical and environmental performance. Irshidat et al. (2021) have recycled Waste Carbon Black (WCB) in cement mortar mixes and have studied the LCA of it. The results indicate that WCB can replace 10% of cement, and a significant reduction in emissions to the environment is observed in LCA analysis. Demirel et al. (2019) have performed LCA for the Self-Compacting Mortars (SCMs) incorporating Fly Ash (FA) and waste Glass PET (GP), and the use of FA and GP has adversely affected the mechanical and microstructural properties but has a positive impact on environmental performance. Bumaniset al. (2022) used phosphor gypsum-Portland cement-metakaolin as the binder material for mortar mixes, and results indicated 57% reduced CO_2 emission. Pavlík et al. (2019) have used sewage sludge to replace cement in mortar mixes and have observed a 10% decrease in energy consumption for each 10% of sludge used. Almeida et al. (2021) studied the LCA of mortar mixes prepared by partially replacing cement with mining residues. The results demonstrated that modified mortar mixes have decreased global warming potential. Navaratnam et al. (2023) have compared the environmental impact of partially substituting (15% by weight) cement with industrial wastes such as fly ash, blast furnace slag, bottom ash, recycled glass, ferronickel slag, expanded polystyrene and wood ash. Mortar having fly ash showed lower environmental impacts compared to other materials. Tosti et al. (2020) reused biomass fly ash to replace cement in mortar mixes and observed an 11% -26% reduction in CO_2-Eq compared to landfill disposal of biomass ash. Li et al. (2020) have developed eco-friendly mortar using high-volume diatomite and fly ash as a partial substitute for cement. LCA of the mixes showed the environmental benefits of using it. LCA study is imperative to quantify the environmental impact of using textile sludge as a partial replacement in mortar mixes.

2.11 Research gaps

A thorough examination of the literature reveals numerous research studies on treating industrial wastewater from the textile sector and sustainable recycling and reuse of CETP sludge. Numerous research works are available and being conducted to develop TWWTTs that are more effective and economical. However, no mathematical model is available to select the appropriate TWWTTs considering sustainability's technical, social, environmental, and economic aspects. The research gaps identified based on the literature review are: (1) Most articles have investigated the sustainability of WWT techniques, and the same results cannot be applied to textile wastewater treatment processes. The discarded textile effluent contains dyes, salts, and other pollutants, and hence the efficiency of the treatment process changes, influencing their sustainability; (2) No study has comprehensively identified the sub-criteria for the sustainability dimensions of TWWTTs; (3) There is a need for developing a decision-making framework and a mathematical model for a unified performance assessment of the sustainability of different TWWTTs. The model should incorporate the fuzziness associated with stakeholders from various backgrounds.

The literature review indicates the need for more effective and efficient adsorbents using different agricultural wastes, for treating effluent. However, limited studies have focused on using WSAC for textile effluent treatment and determining the detailed effect of adsorbent on the treated textile effluent quality. The research gaps ascertained based on the summary of relevant literature are (1) The studies on using wheat straw as an adsorbent are minimal; (2) Most studies have focused mainly on dye removal using artificial dye solutions. The studies using real textile effluent for experimental work are limited; (3) The impact of the addition of WSAC on the COD and colour of the effluent has not been studied. No study has comprehensively examined the effect of adsorbents on industrial textile effluents.

Treatment of effluent at CETPs produces hazardous sludge and treated water. This textile CETPs sludge has chemicals used for the treatment process and the chemicals present in effluent before treatment. The sludge remains at CETP premises before being disposed of at TSDFs. The potential leaching from the textile sludge and the method to quantify the toxicity behaviour of TCETP sludge has been scarcely available in the literature. The chemical composition and the concentration of heavy metals in the leachate from industrial sludges would be very high and different from the MSW. Hence using the same index to determine the pollution impact of leachate from the MSW and industrial effluent treatment plant sludge would yield an inaccurate pollution potential of the leachate. Therefore, the existing LPI cannot be used to evaluate the pollution potential of leachate from industrial waste accurately. Developing a flexible and precise leachate pollution index concerning TCETP sludge is essential. The present study proposes a novel framework for developing the T-LPI using the hybrid fuzzy model. Further, the human health risk assessment study for leachate-contaminated surface water consumption through ingestion and the dermal route is unavailable.

The solidification and stabilization of TCETP sludge into complex matrices are essential to reduce the dissolution of heavy metals when the sludge encounters water. One way of solidification/stabilization of sludges is their use as a building material in replacing various ingredients of mortar and concrete. Researchers have used TCETP sludge to partially substitute clay, natural fine aggregate, and cement in bricks, concrete, and mortar. Studies on the tertiary mixes of mortar containing TCETP sludge and mineral admixture are limited and need further exploration. Further, most of the past research has been on the weight replacement of building materials with TCETP sludge and SBA despite the difference in the specific gravity of cement and TCETP sludge and SBA. The literature shows that several researchers in recent years have attempted to use sludge as a partial replacement for cement. Limited studies exist on the durability assessment of textile sludge based-cement mortar mixes.

The researchers have yet to investigate the environmental impact assessment by the LCA approach of using TCETP sludge and SBA in mortar mixes as a partial replacement for cement. This study would be one of its kind in quantifying the environmental impact of utilizing cement, TCETP sludge, and SBA as binders in tertiary mortar mixes.

2.12 Summary

This chapter discusses the various TWWTTs available and possible approaches to enhance sustainability in the textile industry and encourage cleaner production practices. This chapter also discusses the use of the MCDM technique for selecting appropriate TWWTTs. The shortcoming of the selected treatment technique can be overcome by providing a physio-chemical pre-treatment by adsorption of contaminants from the effluent. Literature on using various adsorbents for dye removal for the textile industries is being reviewed. The effluent treatment at CETPs generates chemical sludges, and disposal and reuse are challenging. The studies on the leaching of heavy metals from TCETP sludge and its suitability as the building material are reviewed. Furthermore, literature on the environmental impact of using various admixtures as a building material is briefed. The extensive literature review helped identify, formulate, and thoroughly discuss the research gap. This literature review analysis shows that the research must be accelerated to develop sustainable solutions for handling waste produced by the treatment of waste produced by textile industries. Rigorous attempts have been made in the present thesis to provide suitable scientific and engineered solutions for the identified shortcomings. This thesis contributes towards waste management and cleaner production. The subsequent Chapter 3 discusses the novel framework for selecting TWWTTs.

Chapter 3

Development of a framework for the selection of textile wastewater treatment techniques based on the sustainability index

3.1 Introduction

Unquestionably, the textile sector helps meet fundamental human necessities and is also the prominent environment polluter (Yaseen & Scholz, 2019). Textile industry generates a significant amount of chemically contaminated water, which is unsuitable for further usage (Holkar et al., 2016). These industries pose danger to the environment due to its water intensiveness resulting in depletion of freshwater as well as groundwater. The increased scarcity of water resources and the decline in water quality with the increasing water demand in industries has obliged the researchers to assess the suitability of various TWWTTs for proper disposal and reuse of the effluent. Numerous methods exist for treating textile wastewater as discussed in chapter 2. These are categorized as physical, chemical, biological and hybrid processes (Behera et al., 2021). Most of these processes have different core operating principles, but they are contrasted depending on their performance, cost, and other advantages or disadvantages. The treatment of effluents reduces the contamination level and makes it safe for reuse and disposal, but also has the inherent limitation of producing hazardous sludge and requiring expensive disposal. Consequently, the selection of a sustainable TWWTT is a multidimensional and challenging task where decision-makers must resolve numerous conflicts. It can be concluded that the selection of appropriate TWWTT is an MCDM problem.

In accordance with the identified research gaps as mentioned in chapter 2, the main contributions of chapter 3 are: (1) developing a hierarchal evaluation system for this decision-making problem; (2) identification of sub-criteria in the context of TWWTTs which may positively or negatively impact the sustainability dimensions; (3) developing a novel decision framework using the hybrid MCDM method established on fuzzy set theory for aiding the decision-makers in prioritizing the textile effluent treatment techniques. To achieve these objectives, a fuzzy Delphi and hybrid FAHP approach are used in this study. The Fuzzy Delphi Method (FDM) is used to select the critical sub-criteria for maximizing the sustainability of TWWTTs. Hybrid FAHP is used to rank the different TWWTTs and to determine the sustainability indices. Fig. 3.1 represents the overall structure of the study presented in this chapter.

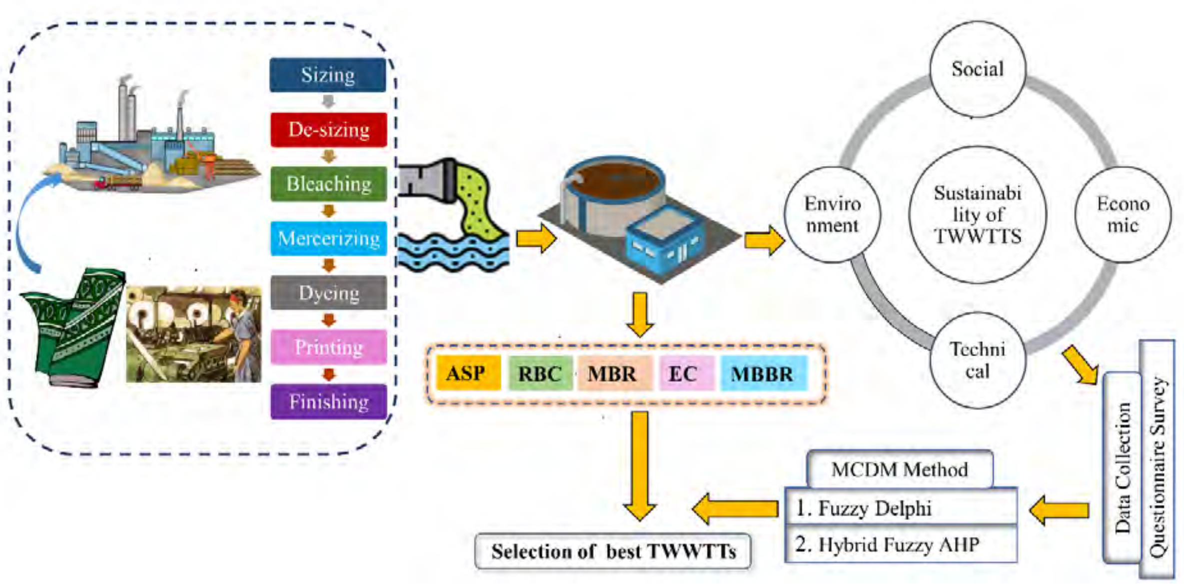


Fig. 3.1 Graphical structure of the study

The chapter is structured as follows: Section 3.1 explains introduces the need for MCDM approach and section 3.2 reviews the related literature to identify the criteria and sub-criteria. The research methodology for explaining the FDM and hybrid FAHP methods is presented in section 3.3, followed by a case study in Section 3.4. The results and discussion are presented in section 3.5, and the summary is provided in section 3.6.

3.2 Selection of sustainability criteria and sub-criteria

The sustainability criteria and sub-criteria are gleaned through the literature review in this section. The three main aspects of sustainability viz. economy, environment and society are used in the Triple Bottom Line (TBL) approach (Nozari et al., 2021). Apart from these, the sub-criteria in the technical and managerial aspects considerably influence the overall sustainability of the technology considered (Ouyang et al., 2015). The four aspects of sustainability, viz. economic, social, environmental, and technical, are considered in this chapter, whereas some of the managerial sub-criteria are included in the economic and technical aspects. Sawaf and Karaca (2018) have comprehensively listed the set of sub-criteria for the textile industries. Table 3.1 summarizes the sustainable sub-indicators and 38 sub-criteria based on past literature.

Table 3.1 Sustainability indicators, sub-criteria classification

Sustainable indicators	Sub-criteria	Source
Technical	Energy consumption, Maintenance frequency, Hydraulic retention time, BOD removal efficiency, COD removal efficiency, TSS removal efficiency, Color removal efficiency, Turbidity removal efficiency, NH_3 removal efficiency, Odor removal, Sludge generation, Durability, Flexibility, Reliability, Complexity, Construction ease, Upgradability ease, Accessibility ease.	Lizot et al., 2021; Omran et al., 2021; Sawaf and Karaca, 2018; Ouyang et al., 2015; Dogdu et al., 2017;
Economic	Technology cost, Construction cost, Operation and maintenance cost, Capacity up-gradation cost, Use of locally available material.	Lizot et al., 2021; Omran et al., 2021; Ouyang et al., 2015; Ren and Liang, 2017; Sawaf and Karaca, 2018
Environmental	Space requirement, Soil contamination, Effect on the surrounding environment, Odor problem, Poor aesthetics, Footprint requirement, Implications on flora and fauna, Effluent suitability for reuse.	Lizot et al., 2021; Omran et al., 2021; Ouyang et al., 2015; Ren and Liang, 2017; Sawaf and Karaca, 2018
Social	Public safety, Employee health, Community participation, Awareness within industries, Acoustic/visual comfort, Hiring local services.	Omran et al., 2021; Padilla-Rivera et al., 2016; Sawaf and Karaca, 2018; Lizot et al., 2021;

3.3 Methodology

An extensive literature review helped identify the gaps in the existing studies and decide upon the sustainability indicators and sub-criteria. The prominent sub-indicators had to be selected from this list, and fuzzy Delphi approach of MCDM is used. Further, the ranking of selected criteria and sub-criteria for a TWWTT is carried out using a hybrid fuzzy AHP approach, and these TWWTTs are ranked based on their sustainability indices. The expert opinions required for the analysis are collected through a questionnaire survey as given Appendix A. Fig. 3.2. depicts the overall framework of the proposed research.

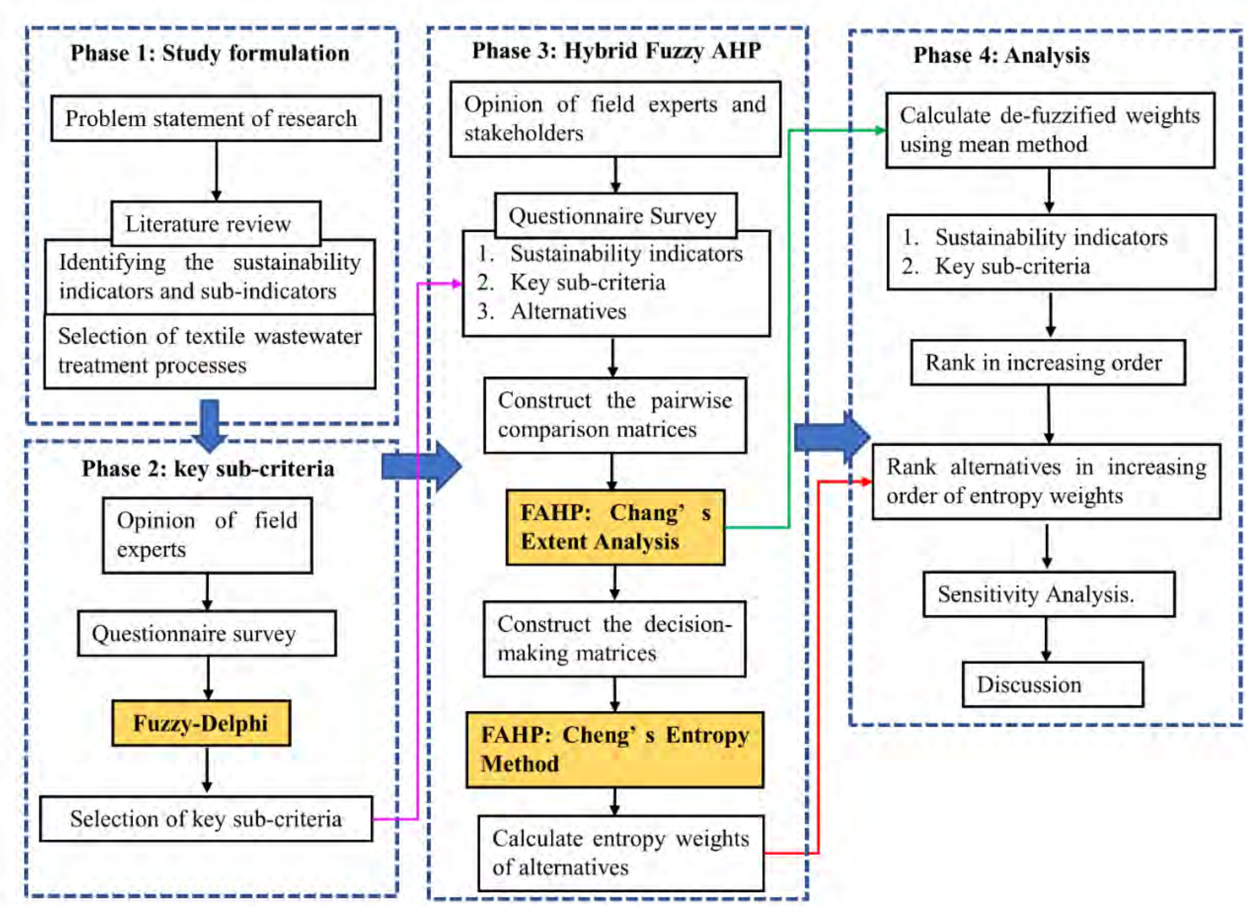


Fig. 3.2 A framework of the proposed methodology

3.3.1 Fuzzy-Delphi Method (FDM)

The concept of FDM was established by Ishikawa (1993) and it integrates the concept of the conventional Delphi method with fuzzy set theory. The traditional Delphi method is an expensive and time-consuming exercise as the experts are required to give their feedback until the desired consistency in opinion is achieved. It is also challenging to get the unanimous opinion of the experts. In the Delphi method, the expert opinion is collected in crisp numbers. These numbers do not incorporate the vagueness of human judgement. The FDM overcomes these demerits as experts are made to share their opinions in the form of a three-point membership function using Triangular Fuzzy Number (TFN) and are not required to review their judgements (Nozari et al., 2021; Zhao et al., 2019).

Due to these advantages, researchers have used the FDM in different studies to select the key variables from the available variables (Chen et al., 2018; Tsai et al., 2020; Zhao et al., 2019). In this chapter, the FDM has been used to select the crucial sub-indicators. Based on the FDM proposed by Hsu and Yang (2000), the procedure is discretized into three main steps, viz. (i) data collection, (ii) conversion of expert opinion into TFN using Table 3.2, and (iii) calculation of fuzzified weights followed by the defuzzification of the fuzzy scores. The detailed procedure of the FDM is given in Appendix B. After calculating the de-fuzzified score, the threshold value for selecting critical sub-criteria is set. The key sub-criteria are finalized for the upcoming section of the chapter.

Table 3.2 The fuzzy conversion scale for FDM

Score	Fuzzy triangular number
1	(0, 0, 0.1)
2	(0, 0.1, 0.3)
3	(0.1, 0.3, 0.5)
4	(0.3, 0.5, 0.7)
5	(0.5, 0.7, 0.9)
6	(0.7, 0.9, 1.0)
7	(0.9, 1.0, 1.0)

3.3.2 Hybrid Fuzzy Analytical Hierarchy Process (FAHP)

Analytical Hierarchy Process (AHP) is the MCDM approach introduced by Thomas L. Saaty in 1980. The technique can use both qualitative and quantitative variables and determine the relative significance of each alternative over the other for the given set of criteria (Thomas & Doherty, 1980). In the AHP, the pairwise comparison matrices of alternatives and criteria are prepared using the crisp values called as Saaty scale (Saaty, 2004). The crisp scale may not correspond to the real world due to the ambiguity, imprecision and vagueness of human judgement (Mangla et al., 2015). To overcome these drawbacks of uncertainty, the proposed methodology incorporates the objective-based approach of Fuzzy Analytical Hierarchical Process (FAHP). In FAHP, the crisp values of Saaty's scale are converted into fuzzy numbers using the chosen membership function (Anqi & Mohammed, 2021; Vyas et al., 2019). The FAHP organizes and analyses the complex decision problem in an elementary form and comes up with the best possible solution (Mangla et al., 2017). The FAHP approach developed by Chang (1996) is used for the estimation of decision matrices, and the Entropy-based FAHP by Cheng (1997) is applied for the final ranking of alternatives. The steps involved in the study for ranking the alternatives are given below.

Step A: Data collection and construction of pairwise comparison matrices

I. Based on the hierarchical structure of the study, expert opinion is gathered using the questionnaire in three steps for developing the pairwise judgement matrices as: (1) for criteria; (2) for each criterion comparing key sub-criteria; (3) for each sub-criterion comparing the alternatives.

II. The response collected from the experts is in the form of crisp numbers. These crisp numbers are converted into symmetric TFN before the aggregation of responses using the scale given in Table 3.3. The responses are combined into single pairwise assessment matrices using the mean method.

Table 3.3 The fuzzy conversion scale used for FAHP

Crisp values	TFN
1	(1, 1, 2)
2	(1, 2, 3)
3	(2, 3, 4)
4	(3, 4, 5)
5	(4, 5, 6)
6	(5, 6, 7)
7	(6, 7, 8)
8	(7, 8, 9)
9	(8, 9, 9)

Step B: **Computation of weights**

In this chapter, we utilize the FAHP synthetic extent analysis method proposed by Chang (1996) for estimating the weights of sustainable indicators, and sub-indicators and for developing the decision matrices of the alternatives. For a better understanding, the mathematical background of Chang's extent analysis is presented below.

Let, A = $\{a_1, a_2, a_3, \ldots a_n\}$ be the set of objects; and U = $\{u_1, u_2, u_3, \ldots u_m\}$ be the set of goals. According to the synthetic extent analysis of Chang, the extent of an object concerning each goal can be quantified, resulting in m extent analysis values for each object (Chang, 1996; Srdjevic & Medeiros, 2008). All $u_i^j\,(i = 1 \ldots\ldots\ldots n, j = 1 \ldots\ldots\ldots m)$ are the TFN representing the performance of the object a_i for each goal u_j. The fuzzy extent value of an object can be computed using Eq. (3.1)

$$S_i = \sum_{j=1}^{m} u_i^j \otimes \left[\sum_{i=1}^{n}\sum_{j=1}^{m} u_i^j\right]^{-1} \tag{3.1}$$

where,

$$\sum_{j=1}^{m} u_i^j = \left(\sum_{j=1}^{m} p_i, \sum_{j=1}^{m} q_i, \sum_{j=1}^{m} r_i\right), \quad \text{and} \left[\sum_{i=1}^{n}\sum_{j=1}^{m} u_i^j\right]^{-1} = \left[\frac{1}{\sum_{i=1}^{n} r_i}, \frac{1}{\sum_{i=1}^{n} q_i}, \frac{1}{\sum_{i=1}^{n} p_i}\right]$$

where, S_i is the normalized fuzzy number, and the medium values are considered unity and i = 1…n (n = the number of criteria).

The fuzzy pairwise comparison matrices for the Ms number of sustainability indicators are constructed, and the weights w_j are estimated using Eq. (3.1). Similarly, for the given sustainability Ms_j, which has k_j sub-criteria, weights are calculated. The final weights for the sub-criterion are estimated by multiplying the weights with the respective sustainability indicator's weight. The total aggregated weights X are given in Eq. (3.2).

$$X = \left(\tilde{X}_1, \tilde{X}_2, \ldots\ldots\ldots\ldots \tilde{X}_K\right) \tag{3.2}$$

The de-fuzzified score for sustainable indicator and each sub-criterion is calculated using the mean method. The decision matrix for the N alternatives compared for each K sub-criteria is estimated using Eq. (3.1).

Step C: Final assessment

For the final assessment and ranking of alternatives, several methods such as the dominance method, total integral value, the α-cut with interval synthesis and the entropy method have been used by the researchers (Cheng, 1997; Hsu et al., 2010; Mahpour, 2018; Srdjevic & Medeiros, 2008). In this study, Cheng's entropy method of FAHP is used to rank the alternatives. The α-cut performance matrix, $\tilde{Z}_\alpha$ is determined with the assistance of Eq. (3.3). Here, α defines the confidence level, and the λ is an index of the optimism of the decision experts (Vyas et al., 2019).

$$\tilde{Z}_\alpha = \begin{bmatrix} [z_{11p}^\alpha, z_{11q}^\alpha] & \cdots & [z_{1np}^\alpha, z_{1nq}^\alpha] \\ \vdots & \ddots & \vdots \\ [z_{n1p}^\alpha, t_{n1q}^\alpha] & \cdots & [z_{nnp}^\alpha, z_{nnq}^\alpha] \end{bmatrix} \tag{3.3}$$

where, $z_{ijp}^\alpha = X_i^\alpha y_{ijp}^\alpha$, $z_{ijq}^\alpha = X_i^\alpha y_{ijq}^\alpha$, for 0<α<1 and for all i, j. The precise judgment matrix $\hat{Z}$ is estimated as shown in Eq. (3.4).

$$\hat{Z} = \begin{bmatrix} \hat{z}_{11}^{\alpha} & \hat{z}_{12}^{\alpha} & \cdots & \hat{z}_{1n}^{\alpha} \\ \hat{z}_{21}^{\alpha} & \hat{z}_{22}^{\alpha} & \cdots & \hat{z}_{2n}^{\alpha} \\ \vdots & \vdots & \ddots & \vdots \\ \hat{z}_{n1}^{\alpha} & \hat{z}_{n2}^{\alpha} & \cdots & \hat{z}_{nn}^{\alpha} \end{bmatrix} \quad \text{where} \quad \hat{z}_{ij}^{\alpha} = (1-\lambda) z_{ijp}^{\alpha} + \lambda z_{ijq}^{\alpha} \ \forall \lambda \in [0,1] \tag{3.4}$$

The relative frequency matrix Eq. (3.5) of the precise judgment matrix, is calculated and the entropy values are estimated using Eq. (3.6). This is followed by the calculation of entropy weights using Eq. (3.7), where E_i is the i^{th} entropy value. It is worth mentioning here that the estimated entropy weights are also called sustainability scores or the sustainability indices in the study.

$$\begin{bmatrix} \frac{z_{11}}{p_1} & \frac{z_{12}}{p_1} & \cdots & \frac{z_{1n}}{p_1} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{z_{n1}}{p_n} & \frac{z_{n2}}{p_n} & \cdots & \frac{z_{nn}}{p_n} \end{bmatrix} = \begin{bmatrix} r_{11} & r_{12} & \cdots & r_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ r_{n1} & r_{n2} & \cdots & r_{nn} \end{bmatrix} \tag{3.5}$$

where, $p_k = \sum_{j=1}^{n} z_{kj}$

$$E_n = -\sum_{j=1}^{n} (r_{nj}) \log_2 (r_{nj}) \tag{3.6}$$

$$E_i = \frac{E_j}{\sum_{j=1}^{n} E_j} \tag{3.7}$$

3.4 Case study

The study focuses on the textile industry cluster in the Balotra region of the Barmer district of Rajasthan state, India. About 500 textile industries in the cluster have an allocated discharge capacity of effluent at 15.33 MLD. These industrial units are textile processing dealing with dyeing, mercerizing, printing, and finishing. The textile effluent from these industrial clusters is collected in the CETP, and the Activated Sludge Process (ASP) is used for treatment. Due to the presence of excessive chemicals in industrial effluents such as caustic soda, dyes and other metallic salts, the ASP is insufficient to remove all these impurities and make it suitable for its reuse in industry. There is a need for an up-gradation of the treatment process. Concerning these issues, the alternatives for the study are the following five TWWTTs, Activated Sludge Process (ASP), Rotating Biological Contactor (RBC), Membrane Bioreactor (MBR), Electrochemical

Coagulation (EC) and Moving Bed Biofilm Reactor (MBBR). The ASP and RBC are conventional, while MBR, MBBR and EC are advanced treatment techniques.

3.4.1 Screening of essential sustainability sub-criteria by FDM

In this study, the FDM is used to identify the essential sub-criteria useful for evaluating the performance of TWWTTs. Initially, 38 sub-criteria in four sustainability dimensions were identified, as shown in Table 3.1. In the next step, a questionnaire survey was designed to collect the opinion of experts. The expert's selection was based on their knowledge, professional skills, background, and practical experience. For this study, five experts with different backgrounds, two academicians, an engineer working in CETP, a resident and an expert member of the prestigious National Green Tribunal (NGT) India, had been selected. Ocampo et al. (2018) have stated in their research work that there is no relation between the quality of decision and the number of experts.

The data collected was in the form of crisp numbers having their linguistic definitions further converted to fuzzy scale using Table 3.2. Once the response of the experts was gathered, the fuzzy scores were calculated as given in Appendix B**.** The typical threshold value of 0.6 for selecting the critical sub-indicator was set as per consultation with experts and from the literature (Shen et al., 2010). The sub-indicators with a score equivalent to the threshold value or above were chosen for the study's next phase. The estimated fuzzy weights and the de-fuzzified score are presented in Table 3.4. The de-fuzzified score was shared among the experts and allowed to include any additional sub-criteria. No additions were suggested by the experts. The twenty-eight sub-indicators (colored as grey) were chosen for the next phase of the analysis.

Table 3.4 Fuzzy Delphi analysis to finalize the sustainable sub-indicators.

Sustainable indicators	**Sustainable sub-indicators**	**Fuzzy weight**	**De-fuzzified Score**
Technical	Energy consumption	(0.5, 0.89, 1)	0.798
	Maintenance frequency	(0.3, 0.73, 1)	0.676
	Hydraulic Retention time	(0.1, 0.37, 0.7)	0.389

Sustainable indicators	Sustainable sub-indicators	Fuzzy weight	De-fuzzified Score
	BOD removal efficiency	(0.5, 0.77, 1)	0.758
	COD removal efficiency	(0.5, 0.89, 1)	0.798
	TSS removal efficiency	(0.5, 0.86, 1)	0.785
	Color removal efficiency	(0.5, 0.87, 1)	0.791
	Turbidity removal efficiency	(0.3, 0.65, 0.9)	0.618
	NH_3	(0.1, 0.52, 0.9)	0.505
	Odor removal	(0.1, 0.49, 1)	0.53
	Sludge generation	(0.5, 0.86, 1)	0.785
	Durability	(0.5, 0.7, 0.9)	0.7
	Reliability	(0.3, 0.57, 0.9)	0.591
	Flexibility	(0.3, 0.69, 1)	0.663
	Complexity	(0.5, 0.81, 1)	0.769
	Construction ease	(0.1, 0.48, 0.9)	0.494
	Upgradability ease	(0.3, 0.69, 1)	0.663
	Accessibility ease	(0.1, 0.41, 0.7)	0.403
Social	Public safety	(0.3, 0.69, 1)	0.663
	Employee health	(0.5, 0.81, 1)	0.771
	Community participation	(0.1, 0.58, 1)	0.560
	Awareness to industries	(0.3, 0.66, 1)	0.652
	Acoustic/visual to workers	(0.3, 0.69, 1)	0.662
	Hiring local services	(0.3, 0.69, 1)	0.663

Sustainable indicators	Sustainable sub-indicators	Fuzzy weight	De-fuzzified Score
Economic	Use of locally available material.	(0.1, 0.48, 0.9)	0.494
	Construction costs	(0.5, 0.75, 1)	0.751
	Operation /maintenance costs	(0.3, 0.78, 1)	0.692
	Capacity up-gradation	(0.5, 0.89, 1)	0.798
	Technology cost	(0.3, 0.78, 1)	0.692
Environmental	Space requirement	(0.3, 0.74, 1)	0.68
	Soil contamination	(0.1, 0.52, 0.9)	0.505
	Surface water contamination	(0.5, 0.83, 1)	0.777
	Effect on surrounding environment	(0.5, 0.81, 1)	0.771
	Footprint requirements	(0.3, 0.69, 1)	0.663
	Implications on flora and fauna	(0.1, 0.58, 1)	0.56
	Poor aesthetics	(0.5, 0.81, 1)	0.771
	Odor problems	(0.3, 0.69, 1)	0.663
	Effluent suitability for reuse	(0.3, 0.74, 1)	0.68

3.4.2 Hybrid FAHP for ranking of alternatives

To begin with, a hierarchical model is developed by including only 28 key sub-criteria, finalized after FDM as shown in Fig. 3.3. The four levels of the established hierarchical diagram are as follows: (1) the goal of the study, (2) sustainability indicators, (3) sustainability sub-criteria and (4) the TWWTTs. After developing the hierarchy model, the pairwise assessment matrices are developed with the assistance of a group of 3 experts. The expert response was collected using a questionnaire survey in the form of crisp numbers. The crisp numbers are converted into TFN using Table 3.2. With the help of Eq. (3.1), the fuzzy extent values are estimated for the sustainability indicators, sub-criteria, and alternatives. The fuzzy synthetic extent values calculations for sustainability dimension environment (En) are given below.

En = (4.656, 6.0865, 8.65) ⊗ (0.0215, 0.0274, 0.0332)

= (0.10047, 0.16730, 0.28742)

The complete result for all the sustainability aspects is shown in Table 3.5.

Table 3.5 The fuzzy evaluation matrix of sustainability indicators

Sustainability indicators	En	S	ECO	T	**Weights**
En	(1,1,2)	(3, 4, 5)	(0.225, 0.306 0.51)	(0.43, 0.78, 1.138)	0.185
S	(0.205, 0.261, 0.361)	(1, 1, 2)	(0.189, 0.23, 0.306)	(0.12, 0.129, 0.15)	0.057
ECO	(3,4,5)	(3.33 4.33 5.33)	(1,1,2)	(0.148, 0.17, 0.21)	0.28
T	(3.44, 4.16, 5)	(7, 8, 8.33)	(5,6,7)	(1,1,2)	0.541

Similarly, the fuzzified pairwise comparison matrix of the sub-criteria falling under each sustainable indicator is constructed with expert opinions. The fuzzy synthetic extent analysis values are calculated for each sub-criterion. The complete result and ranking of sustainability indicators, and sub-criteria are given in Table 3.6.

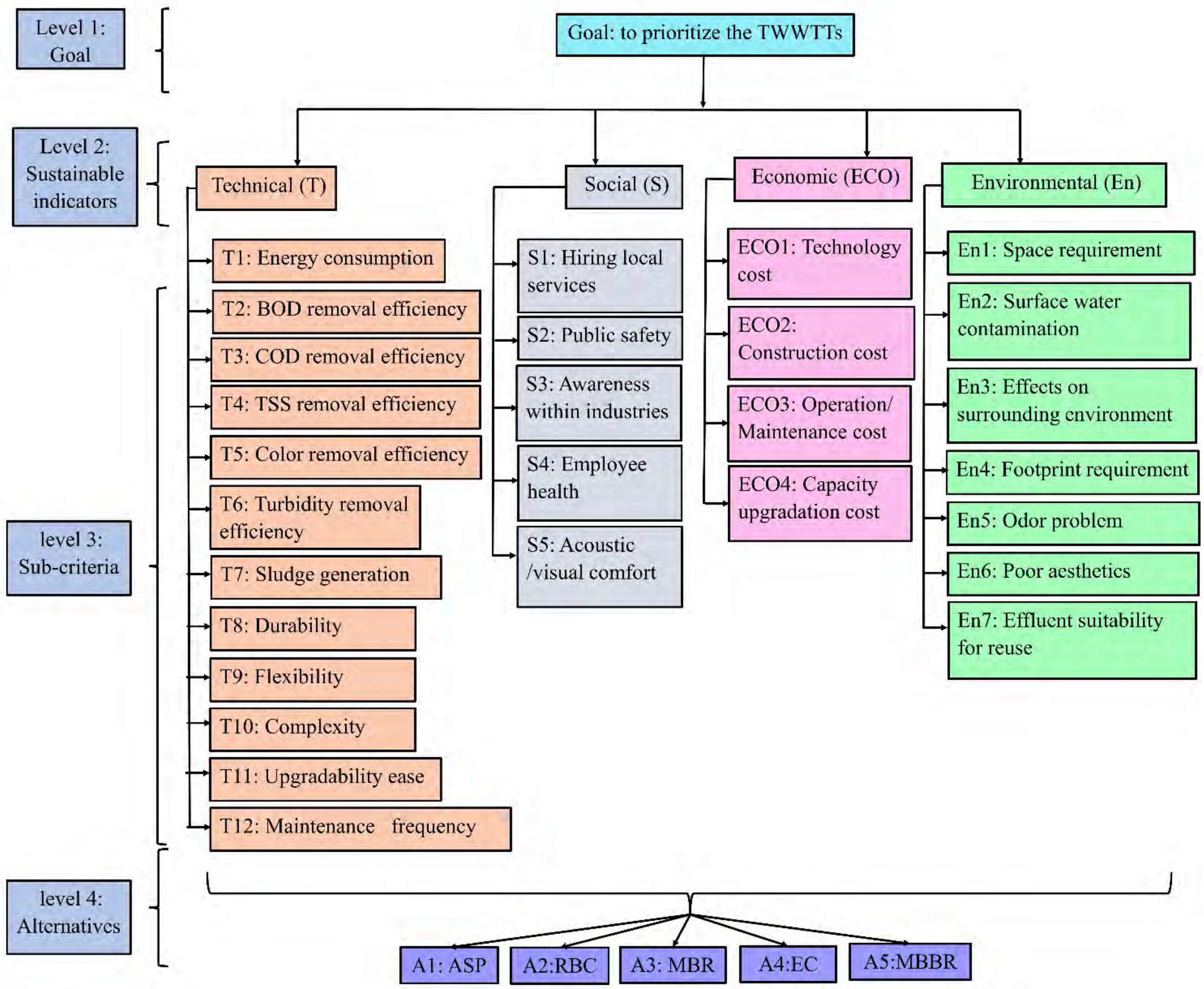


Fig. 3.3 The hierarchical structure of the study

Table 3.6 Weights of the sustainability indicators and key sub-criteria of TWWTTs

Sustainability	Weights	Rank	Sub-criteria	Weights	Rank
T	0.541	1	T1	0.0189	7
			T2	0.0214	6
			T3	0.0431	2
			T4	0.0319	4
			T5	0.0453	1
			T6	0.0249	5
			T7	0.0388	3
			T8	0.0159	9
			T9	0.0174	8
			T10	0.0059	12
			T11	0.0092	10
			T12	0.0073	11
S	0.057	4	S1	0.0192	3
			S2	0.0194	2
			S3	0.0196	1
			S4	0.0079	4
			S5	0.0022	5
ECO	0.28	2	ECO1	0.0322	3
			ECO2	0.0943	2
			ECO3	0.1791	1

Sustainability	Weights	Rank	Sub-criteria	Weights	Rank
			ECO4	0.0175	4
En	0.185	3	En1	0.0431	2
			En2	0.026	5
			En3	0.0323	3
			En4	0.0299	4
			En5	0.0081	6
			En6	0.0069	7
			En7	0.0734	1

With the help of expert opinions, the pairwise comparison matrix of alternatives for each sub-criterion is constructed. The fuzzy extent values for constructing the decision matrices of the alternatives are estimated using Eq. (3.1). To estimate the final ranking of the alternatives, the entropy weights are calculated as given in the research methodology section. Firstly, the lower and upper bounds $[z_l^{\alpha}, z_u^{\alpha}]$ are estimated from the fuzzy triplets of the alternative and sub-criterion decision matrix. All the elements of the total fuzzy judgment matrix $\tilde{Z}_{\alpha = 0.8}$ are determined, followed by the calculation of the precise judgement matrix $\hat{Z}$ as shown in Appendix C. Lastly, the entropy weights are estimated using Eq. (3.7). The obtained entropy weights are also called the sustainability score or sustainability indices of alternatives and serve as a good estimator for prioritizing the TWWTT. The alternative with a higher sustainability score should be given a higher priority and will be ranked accordingly.

3.5 Results and discussion

3.5.1 Sustainability indicators ranking using the FAHP approach.

The ranking of sustainability indicators is as follows: T > ECO> En> S and is shown in Fig. 3.4. It can be concluded that the 'technical sustainability indicator (T)' got the maximum score in the priority ranking, thus indicating the greater influence of the technical aspect over other aspects while selecting the treatment technique. The technical dimension consists of the operational and performance sub-criteria of the treatment technique. The technical functionality of TWWTTs is emphasized as the vital sustainability dimension due to the following reasons: (1) the physical and chemical properties of different textile industrial effluent vary, and hence, the efficiency of the treatment processes differs (2) the contaminant removal efficiency of the treatment process decides its reusability for different purposes such as irrigation or industrial usage, and (3) some of the treatment techniques are being imported and required skilled labor for its regular maintenance or during sudden breakdown resulting in relatively long recovery time. The increasing shift towards reusing treated effluent instead of disposing it back into the environment is also one of the major concerns of the stakeholders when selecting any treatment process (Akhoundi & Nazif, 2018).

The second-highest ranked indicator is economical, as the selected treatment technique should benefit the industrial sector and society and be profitable for the government. In India, most of the small-scale textile industries do not have a separate treatment plant due to the high cost of industrial effluent treatment technologies and rely on CETP run by the industrials associations, monitored by State Pollution Control Boards (SPCB). The uneconomical treatment facility would also burden the industrial association and may require repetitive funds. The increasing number of industries with time also demands an increase in the treatment facility's capacity; hence, the treatment plant may need capacity up-gradation (Behera et al., 2021).

Environmental criterion is ranked the third most important indicator. Developing any industrial effluent treatment technique harms the surrounding environment and disturbs the ecosystem. The treatment sites also serve as breeding grounds for many insects and mosquitoes. The treatment plants have environmental benefits as they mitigate effluent contaminants and produce sludge used as fertilizer by composting or as a building material (Holkar et al., 2016). However, this sludge is chemically hazardous and requires it to be disposed of safely without contaminating the environment. Adherence to the environmental standards and regulations prescribed by the CPCB of India for selecting the treatment technique is essential.

The social indicator is the lowest scorer among all the sustainability aspects. The social impact assessment of TWWTTs means considering all the issues related to TWWTTs that impact the different groups of people associated with them. The three groups are mainly concerned are the employees, community, society, and industrial administration. The variables associated with the community are employment generation and public safety. The treatment unit should have acoustic and visual comfort. There should be no or less risk of occupational disease to the employees (Rivera et al., 2016). These are the few variables of social aspects of the TWWTTs.

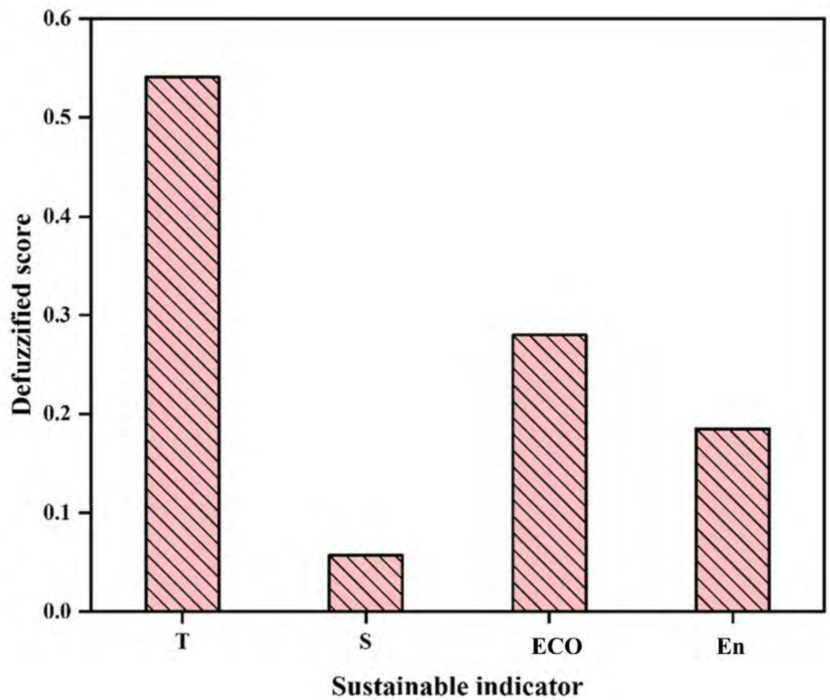


Fig. 3.4 Comparison of the score for sustainability indicators

3.5.2 Sub-criteria and the alternative ranking using FAHP

3.5.2.1 Technical sustainability indicator

The technical criterion is relevant to the operational and performance aspects of TWWTTs. This sustainability dimension has the first position in the priority ranking. The treatment techniques have the benefits of treating textile wastewater, but their operation and performance vary based on their working principles and the type of effluent to be treated. The 12 sub-criteria have been considered and are ranked accordingly. The ranking of these sub-criteria is as follow: T5 > T3 > T7 > T4 > T6 > T2 > T1 > T9 > T8 > T11 > T12 > T10. The color and COD removal efficiency, followed by the amount of sludge generated, are the three important governing attributes for the selection of the TWWTTs, and the same can be observed in Fig. 3.5 (a). Color and COD removal efficiencies are the primary focus for most textile industry effluent treatment processes (Ayed et al., 2021; Donkadokula et al., 2020). The storage of chemically active sludge from the TWWT plants is difficult and can easily be carried away by the wind and water during storms or rains; hence, it has been ranked as the third most significant sub-criterion. The operational variables such as durability (T8), flexibility (T9), complexity (T10), upgradability (T11) and maintenance frequency (T12) secured lower ranks.

The scores of TWWTTs for the technical indicator are given in Fig. 3.5 (b). The ranking of TWWTTs for the technical dimension are as follows: MBR > RBC > MBBR > EC > ASP. The MBR treatment technique is noticeably identified as the best scorer, followed by RBC and MBBR. The MBR process reduces 80-99% of COD and 83.7-98.5% of color at 525 nm (Jegatheesan et al., 2016). The color removal efficiency of ASP is 37-55% (Nawaz & Ahsan, 2014), RBC is 85% (Sawaf & Karaca, 2018), EC is 92-100% (Zazou et al., 2019), and MBBR is 61%. The COD removal efficiency of ASP is 45% (Nawaz & Ahsan, 2014), 86% for MBBR (Siddique et al., 2017), RBC is 95.5%, and EC is 90% (Sawaf & Karaca, 2018). The low score of ASP is due to poor COD, color and TSS removal efficiency. The MBR technology produces less sludge and can adapt to more pollution concentration than EC and other biological treatment processes (Keskin et al., 2021). The MBR efficiently removes the azo dyes and aromatic amines (Sahinkaya et al., 2017). The overall performance of MBR in relevance to the technical aspect is better than the other treatment techniques.

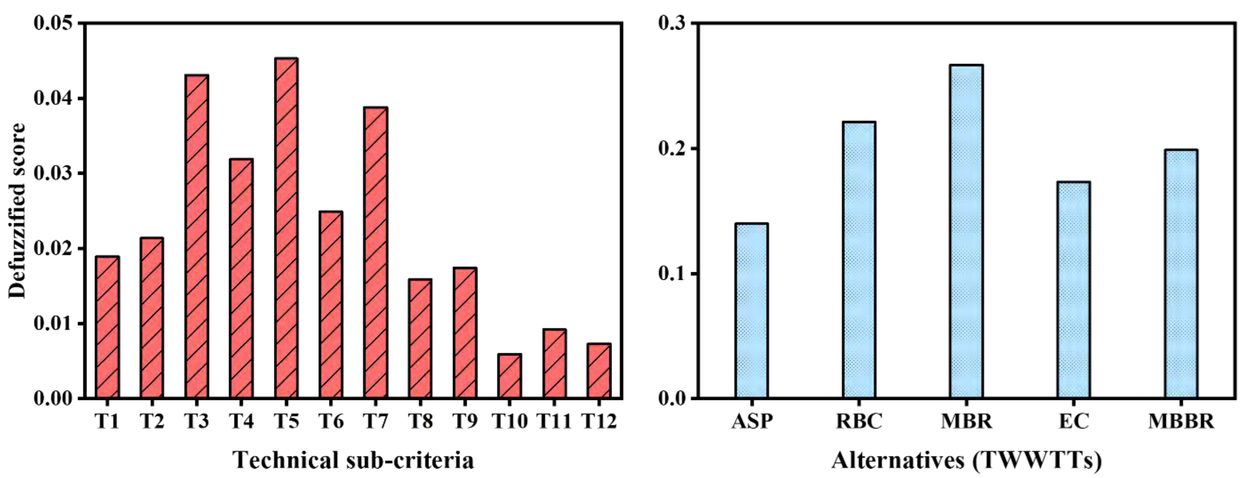


Fig. 3.5 The de-fuzzified scores of (a) sub-indicator, (b) alternatives for the technical indicator

3.5.2.2 Economic sustainability indicator

The economic dimension holds the second-highest score. This dimension is associated with all types of costs that may help in analyzing the cost-effectiveness of the TWWTTs. The technology cost (ECO1), construction cost (ECO2), operation and maintenance cost (ECO3) and capacity up-gradation cost (ECO4) are the sub-criteria of the economic dimension. The ranking of economic sub-criteria is as follows: ECO3 > ECO2 > ECO1 > ECO4, as shown in Fig. 3.6 (a). The high construction, operation and maintenance costs will exert extra economic pressure on the system (Jafarinejad, 2017). The operation and maintenance of some imported treatment technologies require skilled operators, thus increasing their costs. High construction costs for any treatment technology will not be preferred as it requires substantial initial investment (Sawaf & Karaca, 2018).

The treatment techniques' scores for the economic criterion are summarized in Fig. 3.6 (b). The ranking of TWWTTs is as follows: MBBR > EC > RBC > MBR > ASP. Kamble et al., (2019) have compared the different costs of ASP, MBBR and MBR treatment techniques for municipal wastewater. The total capital cost required for MBBR and ASP is 6.8 million Rs/MLD while for MBR is 24.7 million Rs/MLD. The land requirement for ASP is higher than MBBR. Total operation and maintenance cost per year 1.0 million Rs/MLD for MBBR, 0.83 million Rs/MLD for ASP and 1.9 million Rs/MLD. The cost of land required for ASP is highest while the technology cost for MBR is highest. The fact that MBBR uses the biofilm attached to thousands of tiny plastic media to decompose the waste present in the effluent makes it more economically viable than the other treatment techniques. The cost of plastic media used in MBBR is low, and the backwashing or cleaning of membranes is not required, reducing operational and maintenance costs. The construction cost for MBBR is also low as only one tank is required, which uses relatively lesser space (Francis & Sosamony, 2016). The operational cost of EC is relatively high due to the requirement of chemicals and high energy consumption. This increases the overall treatment cost, and the quantity of unconsumed waste products increases secondary pollutant sludge (Dasgupta et al., 2015). The RBC has operational problems with mechanical shaft failures, media support structure and bearings. This increases the operation and maintenance costs (Cortez et al., 2008). The main limitation of MBR is the high maintenance cost due to the fouling of the membrane, which requires chemical cleaning, eventually decreasing the membrane life span. This results in a frequent change of membrane resulting in high operational costs. The ASP has high construction costs and medium operation and maintenance costs (Behera et al., 2021).

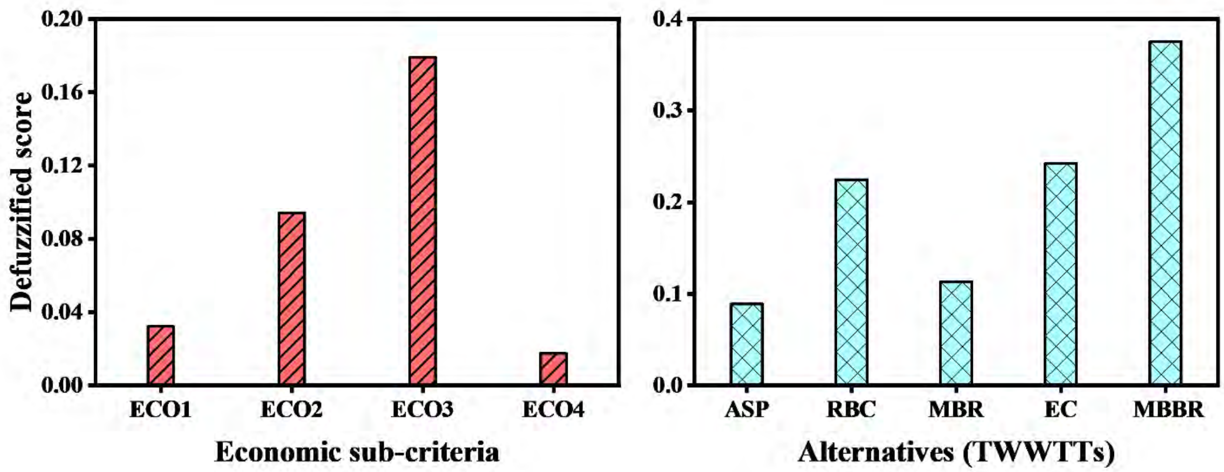


Fig. 3.6 The de-fuzzified score of (a) sub-indicators, (b) alternatives for an economic indicator

3.5.2.3 Environmental sustainability indicator

The environmental dimension has obtained the third position in ranking sustainability indicators, as shown in Fig. 3.4. The experts' perspectives towards the environmental sub-criteria are summarized in Fig. 3.7 (a). The ranking of sub-criteria is as follows: En7 > En1 > En3 > En4 > En2 > En5 > En6. The effluent suitability for reuse (En7) has the highest score. The selection of a TWWTT whose effluent is highly suitable for reuse is preferred as it will reduce the freshwater demand of the industries, saving natural resources (Sawaf & Karaca, 2018). The space required (En1) by the TWWTTs and its effect on the surrounding environment (En3) holds the second and third rank. The larger space requirement for the infrastructure will affect the nearby ecosystem and will have a nested impact on the economic aspect of sustainability.

The experts' opinions regarding the environmental dimension of TWWTTs are shown in Fig. 3.7 (b). The ranking of the textile effluent treatment techniques from the environmental aspect of sustainability is as follows: MBR > MBBR > RBC > EC > ASP. The MBR, followed by MBBR, is identified as the most environment-friendly technique by decision-makers. The effluent suitability for reuse is the best in MBR, and the space requirement is moderate as compared to

MBBR (Jegatheesan et al., 2016; Yang et al., 2020). The treated water from MBR can be reused directly in dyeing, finishing and sizing units of the textile industry without significantly decreasing the fabric quality (Cinperi et al., 2019). The effluent from the other treatment techniques requires further treatment prior to its reuse (Keskin et al., 2021). The RBC, EC and ASP are least preferred due to their poor effluent suitability for reuse and higher space requirements (Behera et al., 2021).

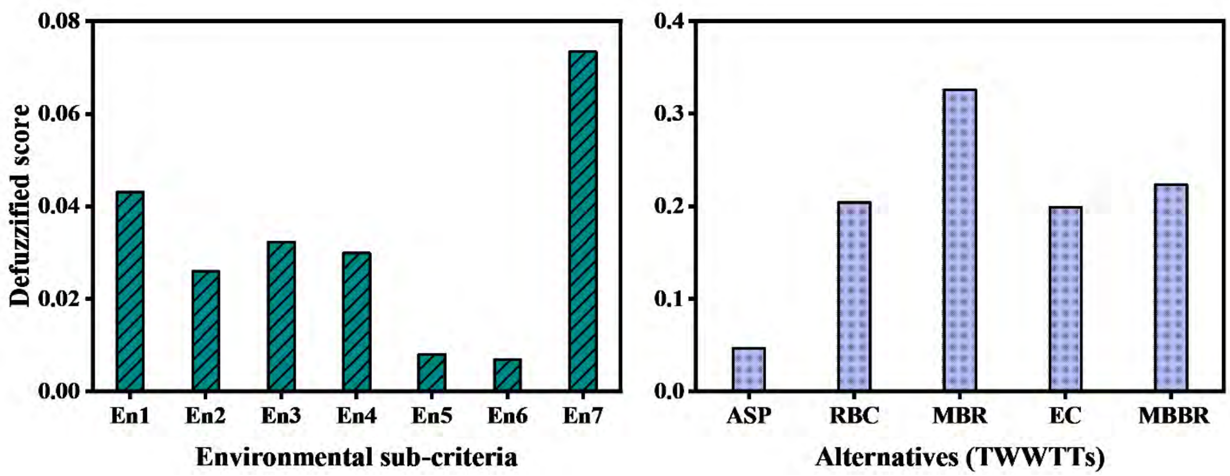


Fig. 3.7 The de-fuzzified score of (a) sub-criteria, (b) alternatives for environmental indicator

3.5.2.4 Social sustainability indicator

The social dimension has scored the fourth rank. In the social dimension, the ranking of sub-criteria is as follows: S3 > S2 > S1 > S4 > S5. Fig. 3.8 (a) summarizes the score of different sub-criteria that makes it into the social dimension. The sub-criteria 'awareness within the industry' is ranked first. It is essential to create awareness among different textile processing units about adequately disposing of untreated effluent and encourage them to follow the rules and regulations. The awareness of TWWTT within industries will help understand the worries and benefits of the treatment technologies. Public safety from the operation of the treatment unit is ranked second and hiring local services that would benefit the community is ranked third. The TWWTTs should operate safely, causing no harmful impacts on the community. The TWWTTs release hazardous gases and generate contaminated sludge, thus causing danger of any occupational disease affecting the employee's health. The acoustic comfort in the treatment unit is also an essential sub-criterion.

The scores of a treatment technique for the sustainability's social dimension are illustrated in Fig. 3.8 (b) and are ranked as follows: RBC > MBR > ASP > EC > MBBR. RBC and MBR treatment technologies are the first and second preferences of the experts. Sawaf & Karaca (2018) have also observed similar results in which the decision-makers and industry managers have preferred the MBR and RBC in the priority ranking. MBBR and EC have performed poorly compared to other treatment techniques due to their limited social characteristics.

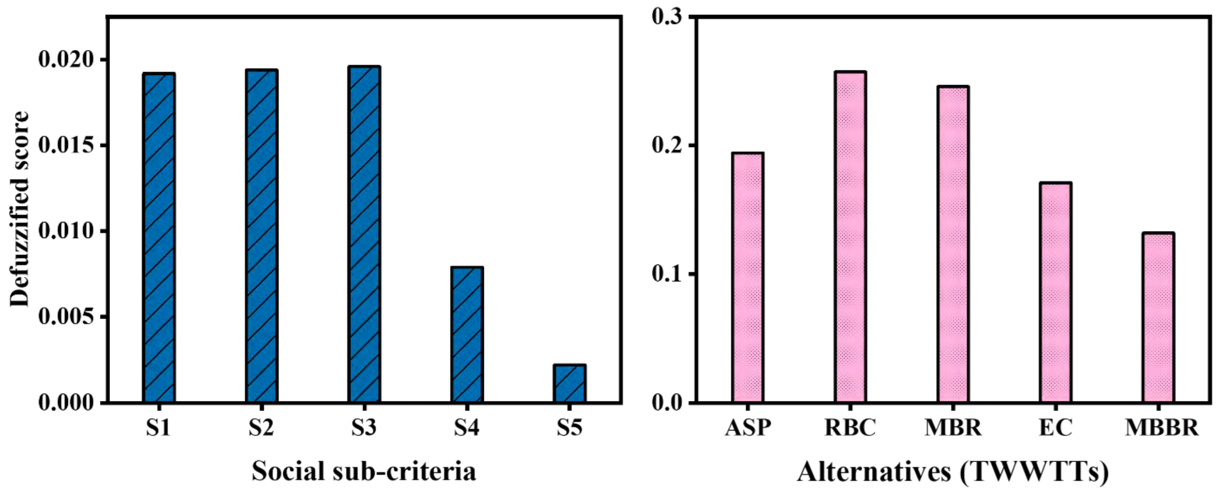


Fig. 3.8 The de-fuzzified score of (a) sub-criteria, (b) alternatives for social indicator

3.5.3 Overall ranking of the alternatives

The different TWWTTs are ranked based on their entropy weights. Table 3.7 shows the entropy weights calculated for all the alternatives for the different levels of confidence (α) and at a different level of optimism (λ) of decision-makers. The entropy weights obtained are good estimators of overall sustainability TWWTTs. The effluent treatment techniques with higher entropy values have better unified performance for all the aspects of sustainability. The final ranking of the alternatives is as follows: MBR > EC > MBBR > RBC > ASP.

Table 3.7 Fuzzy entropy weights for the ranking of alternatives

TWWTs	α= 0.8						α= 0.95					
	λ= 0.25	Rank	λ= 0.5	rank	λ= 0.75	rank	λ= 0.25	rank	λ= 0.5	rank	λ= 0.75	rank
A1: ASP	0.1893	5	0.1893	5	0.1893	5	0.1888	5	0.1887	5	0.1886	5
A2: RBC	0.1942	4	0.1939	4	0.1937	4	0.1943	4	0.1939	4	0.1936	4
A3: MBR	0.2181	1	0.2189	1	0.2196	1	0.2183	1	0.2191	1	0.2198	1
A4: EC	0.2029	2	0.2031	2	0.2032	2	0.2030	2	0.2028	2	0.2027	2
A5: MBBR	0.1955	3	0.1948	3	0.1942	3	0.1957	3	0.1954	3	0.1952	3

However in the past literature, Omran et al. (2021) have ranked the wastewater treatment techniques for the urban areas of Iraq. Conventional treatment, oxidation ditches, aeration lagoon and MBR are the four main techniques considered for the study and MBR followed by oxidation ditches have gained higher importance than aerated lagoons and conventional treatment methods. The ranking is mainly based on higher score of environmental dimension of sustainability. Sawaf & Karaca (2018) have conducted a study in Turkey for finding the sustainability of TWWTTs. MBR, RBC and Sequencing Batch Reactor (SBR) have better sustainability scores than Granule Carbon Coagulants (GAC) and electrocoagulation. In the present chapter, MBR technique has outperformed the other compared techniques and are in conjugation with results from the past studies such as Omran et al. (2021) and Sawaf & Karaca, (2018). The MBR has technical and environmental benefits, such as high COD (95-97.4%), color removal efficiency (97-80%) and high permeate quality which makes it the first choice of decision-makers (Luong et al., 2016; Yigit et al., 2009). This is also apparent from the highest entropy weights of the MBR and its subsequent first rank. The EC, followed by MBBR, have scored the second and third ranks. The higher ranking of MBR than EC and MBBR is because it combines two treatment processes i.e., biological treatment and membrane filtration (ultrafiltration or nanofiltration). The EC and MBBR are single treatment processes and are less effective in a technical aspect. The RBC and

ASP are ranked fourth and fifth as these techniques are biological treatment processes and are less preferred for treating chemically contaminated effluents. Thus, by interpreting the estimated entropy weights, the decision-makers can adopt suitable sustainable TWWTTs.

3.5.4 Sensitivity analysis

The sensitivity analysis is required in the MCDM problem to counter the vagueness and imprecision associated with the data collection process. It also demonstrates the robustness and feasibility of the model with change in time. In this research, the sensitivity analysis has been performed by calculating the entropy weights for the two different levels of confidence (α= 0.8 and 0.95) for the three different types of decision-makers pessimistic (λ= 0.25), nominal (λ= 0.50) and the optimistic (λ= 0.75). Table 8 shows the entropy weights for all the alternatives. The results show that the ranking obtained for each level of optimism and confidence is the same. For the higher value of λ, the MBR (A3) and EC (A4)'s entropy weights are increasing, RBC (A2) and MBBR (A5) are decreasing, while for ASP (A1) are almost constant. From Table 8, it is also evitable that there is no variation in rank with a change in the optimism degree and confidence level, proving that the developed model is robust.

3.6 Summary

This chapter has described the valuable novel framework for decision-makers in assessing TWWTTs based on their suitability index value before selection. It also gives an insight that selecting appropriate technology by evaluating the unified performance of TWWTTs towards social, technical, economic, and environmental sustainability dimensions is of utmost importance. The MBR technique of effluent treatment has outperformed other treatment techniques. However, the MBR technique has not performed well in sustainability's economic dimensions. It is because of membrane fouling which drastically reduces the lifespan and performance of the membrane, which drives up the cost of operation and maintenance (Yang et al., 2020). This demonstrates the necessity for study into pretreatment methods like coagulation/flocculation and adsorption to lessen membrane fouling. According to previous studies, physical effluent treatment through coagulation or adsorption has aided in reducing the fouling of MBR membranes (Asif et al., 2018; Iorhemen et al., 2016; Sabalanvand et al., 2019).

In the subsequent phase of the work, coagulation/flocculation was performed during the treatment of the dyeing industry effluent using different coagulating agents (aluminium sulphate, ferric chloride, ferric sulfate, Poly Aluminium Chloride (PAC)). The results were inappropriate, and an increase in TDS, COD and no color removal was observed in the treated effluent during experimentation. Therefore, further studies were not performed on the coagulation/flocculation treatment process. Adsorption of COD and color from the industrial effluent was tested and found effective in reducing the contaminants. Adsorbent using locally available agricultural waste was prepared and tested in the next phase of the research work. Continuous research has been going on developing more sustainable, efficient, and cost-effective adsorbent materials for treating industrial effluents, and subsequent chapter 4 of the thesis focuses on this aspect.

Chapter 4

Removal of contaminants from textile industrial wastewater using wheat straw activated carbon: An application of response surface and artificial neural network modelling

4.1 Introduction

The researchers have proposed various textile industrial wastewater treatment processes, mainly physical, chemical, and biological, which are already in practice. A brief introduction to the different treatment techniques is presented in chapter 2 of the thesis. The chemical methods are efficient and capable of treating wastewater, but they are cost-ineffective, and the byproduct (chemical sludge) generated is enormous, hazardous, and challenging to store. The biological treatment processes are complex to manage, cannot immediately adapt to pollutant concentration, occupy considerable space, and are costly, as discussed in chapter 3 of the thesis. Hybrid treatment processes such as MBR are effective in treating the effluent and scored the highest sustainability index score, as seen in chapter 3. However, membrane fouling and repetitive requirement for replacing it incur the high cost of operation and maintenance, which are some of the drawbacks of MBR. The adsorption process is used as a pre-treatment process for improving the efficiency of MBR. Adsorption is an efficient, economical, and accessible practice for treating textile wastewater to reduce contaminants and color (Beyan et al., 2021). Additionally, in Chapter 3, COD and color removal efficiencies are the critical sub-indicators for the technical aspects of TWWTTs. Therefore, in the present research work, the contaminant removal efficiency of activated carbon is examined as COD and color removal efficiency.

This work emphasizes using widely available agricultural waste, i.e., wheat straw, as an adsorbent for removing hazardous contaminants from the textile industry wastewater. The experiments are performed following the scheme generated by the CCM. The CCM model considers full factorial design for preparing experimental scheme. The process parameters are optimized to find the ideal condition for contaminants removal by varying the adsorbent dose (g/l), time of contact (min), initial pH and temperature (℃) using the CCM.

The chapter also compares the two prediction models, ANN, and quadratic polynomial regression. RSM method helps in easy optimization of the process parameters and development of polynomial regression model. However, finding the treated effluent quality is paramount for using adsorption technique widely. This study would help the industries reuse the treated wastewater rather than dispose of it to CETP.

The chapter includes an introduction in section 4.1, in which the literature is reviewed, and the gaps are identified. This section also consists of formulating study objectives, followed by a research methodology in section 4.2. Section 4.3 has results and discussion explaining the adsorbent's characterization, experiment design for batch reactor study, mathematical modelling using polynomial regression model and ANN, kinetic study, desorption study and the economic feasibility of the adsorbent. Concluding remarks for this chapter are provided in section 4.4.

4.2 Methodology

An extensive literature review of the existing studies, as given in chapter 2, has helped identify the gaps and design the different parts of the current study. The textile effluent has been collected and preserved for research, and alongside, the adsorbent is prepared. The independent and response variables are selected based on the literature review. Further, the batch reactor experiments are conducted per the CCM experimental scheme. COD and color are measured for the treated effluent. The contaminant removal efficiency by the WSAC for these response variables is calculated. A statistical model is formed, and the optimum condition of the independent variable for the maximum output is determined. Another prediction model using ANN is developed for comparison with quadratic regression. In addition, other studies such as kinetics, desorption, and economic feasibility are also performed. Fig. 4.1 represents the overall outline of the research study.

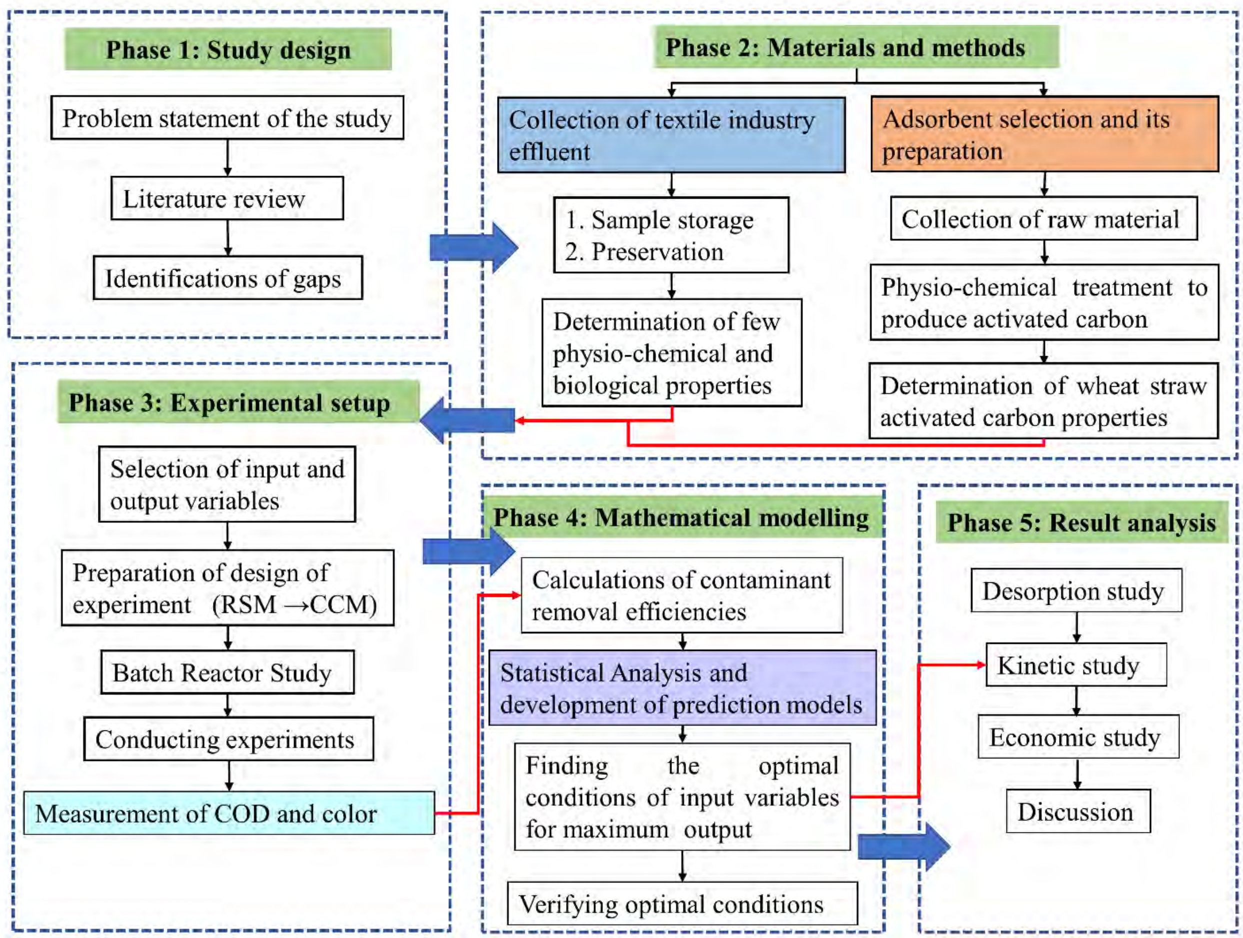


Fig. 4.1 Outline of the research

4.2.1 Material and methods

4.2.1.1 Water source

The textile effluent sample is collected from the cotton dyeing industry in Balotra, Rajasthan, India and is stored at 4 ºC in a cleaned polypropylene bottle. The physicochemical characteristics and the critical constituents of the textile effluent are shown in Table 4.1. The permissible limit for the inland disposal of treated effluent given by the Central Pollution Control Board (CPCB) (1986) is listed in Table 4.1.

Table 4.1 Textile effluent analysis used in this study

Parameters (unit)	Value	Permissible limit for inland
Turbidity (NTU)	9.71	-
pH	5.3	5.5-9.0
COD (mg/l)	1313	250
Temperature (°C)	20°C	shall not exceed 5°C above the receiving water
TDS (mg/l)	7480	-
Color (Platinum Cobalt Unit, PCU)	911	150
BOD – 5 days (mg/l)	157.73	30
Total Organic Carbon (TOC) (mg/l)	331.7	-
Metal ions (Cr^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}) (mg/l)	0.0895, 0.8285, 2.946, 2.498	(0.1, 0.1, 3.0, 5.0)

4.2.1.2 Wheat straw activated carbon preparation

The locally available wheat straw is used to prepare the adsorbent using the physical-chemical treatment process. The wheat straw was washed from the deionized water, dried in the sun for 2 days and then soaked in 0.5M H_2SO_4 in the ratio of 1:3 (w/w) wheat straw for 24 h. The impregnated wheat straw is soaked and cleaned with distilled water to remove the excess acid placed on the sieve for air drying. The acid treatment creates a suitable environment for ring-opening in the lignocellulosic matrix (Gao et al., 2020). The chemically treated wheat straw was soaked in 1M NaOH for 24 h to remove the residual acid and was cleaned with deionized water, followed by air drying. The chemically active wheat straw was air-dried for 24 to 48 h and was carbonized in a muffle furnace at 450 ℃ for an optimal 2 h. The dried particles of the activated carbon are pulverised and sieved through a 250 µm sieve, and the activated carbon of wheat straw is used for experimental purposes. Fig. 4.2 represents the steps involved in the preparation of the absorbent.

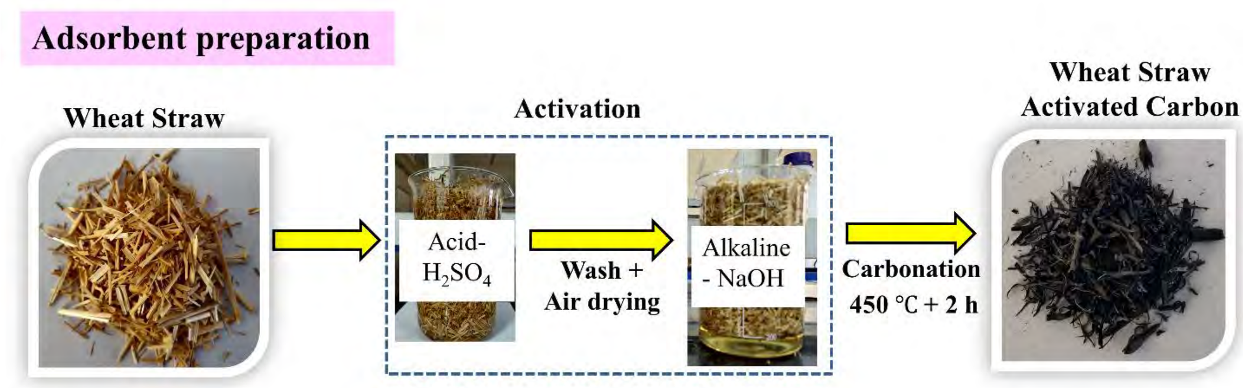


Fig. 4.2 Adsorbent preparation using physio-chemical treatment

4.2.1.3 Characterization of wheat straw activated carbon

FTIR is performed to determine the functional groups on the adsorbent's surface. A PerkinElmer FTIR system ranging from 400 to 4,000 cm^{-1} in the transmittance mode is used to collect the spectra. The morphology of the bio-adsorbent is characterized by FESEM-EDX (FEI, Apreo S LoVac FESEM, Thermo Fisher Ins). The pore volume, specific surface area, and mean pore diameter are also measured using the Bruneuer-Emmett-Teller (BET) surface area analyser (Microtrac Bel, BEL SORP mini II).

The pH for the WSAC at the point of zero charges (pH_{PZC}) was measured by the pH drift method. 50 ml of 0.01M NaCl was added to the flasks, and the initial pH values were adjusted to 2, 3, 4, 5 …12 using 0.1M HCl and 0.1M NaOH solutions. The 0.2 g of WSAC is added to each flask and shaken in an orbital shaker for 24 h. The final pH of the filtered solution is measured (Tran et al., 2016).

4.2.1.4 Biosorption studies on wheat straw activated carbon

Batch experiments are performed to study the interactive effect of the factors, namely contact time, initial pH, the dose of adsorbent (WSAC), and temperature, on the COD and color removal efficiency (%) of the WSAC. The pH of the textile wastewater is adjusted using 0.1M HCl and 0.1M NaOH solutions. After adjusting the pH, 100 ml of textile industry wastewater was taken in a conical flask and placed in a temperature-controlled orbital shaker at 100 rpm. The samples from each experimental run are filtered and tested for COD using the closed reflux colorimetric method (Rice et al., 2012). The Hach COD solution 1 (dichromic acid, silver sulphate, sulfuric acid) and solution 2 (Mercuric sulfate, sulfuric acid) are used for the digestion of standard solution and samples using the Hach COD digestor DRB 200 (2h, 150°C). The five-standard solutions of Potassium Hydrogen Phthalate (PHP) are digested for the preparation of calibration curves. The vials are cooled at the room temperature and are tested using U-V visible spectrophotometer at 600 nm. The measured data is useful for the formation of calibration curve and further COD values determination. The undigested and digested blank are also measured. Similarly, the effluent samples are digested, and the COD is measured. The color was measured by spectrophotometric single wavelength method given in Rice et al. (2012). The color has been measured by preparing 1000 PCU stock solution and then diluting to 5, 20, 40, 80, 200, 500, 800 PCU standard solutions. The absorbance of the different standard solution is measured at 465 nm using U-V spectrophotometer. The calibration curve is prepared for measuring the color of the effluent before and after adsorption. Percentage of color removal is calculated by subtraction in initial PCU value with the PCU after adsorption and divides by the initial PCU value. Fig 4.3 shows the experimental program and the setup for performing the adsorption study.

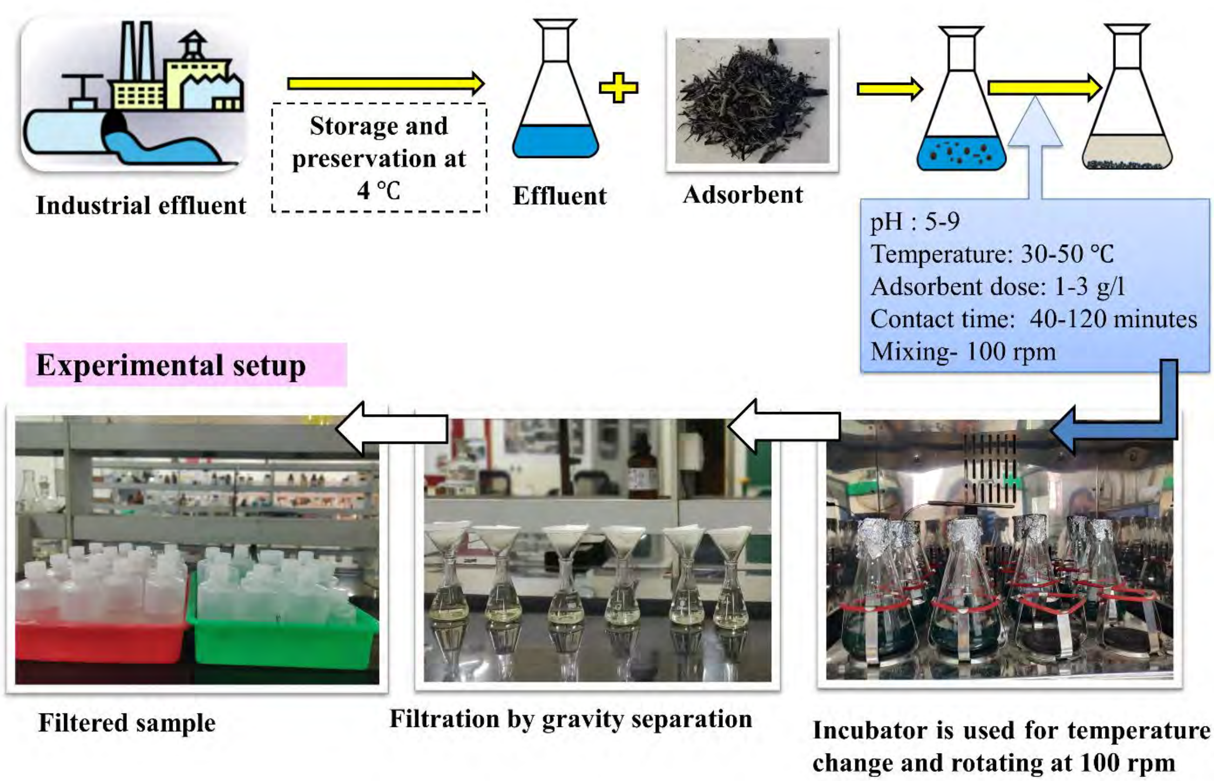


Fig. 4.3 Setup of the experimental program

The WSAC's adsorption capacity for different response parameters is estimated using Eq. (4.1):

$$q_t = \frac{(C_o - C_t)V}{W} \tag{4.1}$$

here, V (l) is the effluent volume; W (g) represents the adsorbent weight and, q_t is the adsorption capacity for COD in mg/g and for color in PCU/g at time t. The percentage removal of the contaminants in the different experimental runs is computed using Eq. (4.2):

$$\%\ \text{removal efficiency} = \frac{C_o - C_t}{C_o} \times 100 \tag{4.2}$$

where C_o and C_t represent the concentration of the COD in mg/l and color in PCU before and after adsorption in the effluent, respectively.

4.2.1.5 Adsorption reversibility study

The adsorption reversibility study was performed using desorbing agents such as methanol, deionized water (pH=2), 0.1M NaCl and 0.1M HCl. The mass 0.05 g (m_2) of contaminant-loaded adsorbent is added to 0.025 l (V_2) of the desorbing agent. The experiments are performed at the equilibrium condition. A mass equilibrium equation Eq. (4.3) is used to find the mass of contaminants remaining on the adsorbent surface after desorption q_o (mg/g), mass while Eq. (4.4) is used to find the percentage of desorption (Leyva-Ramos et al., 2011; Tran, Wang, You, et al., 2017).

$$q_o = q_e - q_d = q_e - \frac{C_2}{m_2} V_2 \tag{4.3}$$

$$\%\ \text{Desorption} = \frac{q_e - q_o}{q_o} \tag{4.4}$$

where, C_2 are the concentration of COD in mg/l and colour in PCU in the desorbing agent; q_e be the COD in mg/g and color in PCU/g adsorbed at the equilibrium condition; and in case of the adsorption is reversible, the q_d represents the desorbed mass of COD in mg/g and color PCU/g.

4.2.2 Experimental design

Response Surface Approach (RSA) is a statistical method for analyzing the combined effect of input variables (process parameters) on responses. The trial version of Design Expert 13 is used to design the batch experiments following the Central Composite Method (CCM) of RSA. The CCM helps reduce the required experimental runs and optimize the process parameters based on the target set (K et al., 2021). The full factorial CCM generates the experiment scheme required to form the quadratic model. The CCM identifies the combined effect of the 5-level 4 factors on the performance of the biochar in removing the color and COD from textile effluent.

The independent variables considered as the performance indicators of WSAC in treating textile effluent are Time of contact (A), Adsorbent dose (B), Initial pH (C) and Temperature (D). Each independent variable is coded with the five levels: -α, -0.5, 0, +0.5, +α where α = 1. The coded level for independent factors in the design of the experiment is presented in Table 4.2. The number of experimental runs for the CCM of RSA is calculated using Eq. (4.5):

$$S = 2s + 2^{s} + s_{c} \tag{4.5}$$

where S is the number of experiments, s represents the number of numeric factors, and s_c is the replicates of the center point. A total of thirty experiments are considered under Eq. (4.5). These consist of sixteen cubical points and eight axial points, followed by the six replicas of center points to estimate the pure error. The experimental design by the CCM is given in Appendix D Table D.1. All the experiments are duplicates, and the mean value of the responses (per cent removal of COD and color) is reported.

Table 4.2 Coded levels for the four independent variables

Factors	**Symbols**	**Coded levels**				
		-α	**-0.5**	**0**	**+0.5**	**+α**
Time of contact (mins)	A	40	60	80	100	120
Adsorbent dose (g/l)	B	1	1.5	2	2.5	3
Initial pH	C	5	6	7	8	9
Temperature (°C)	D	30	35	40	45	50

A mathematical model is created to develop the relationship between the response and process parameters using the observation from each experimental run (Beyan et al., 2021). This empirical model follows the second-order polynomial equation in Eq. (4.6). It also optimizes the process parameters (Solanki et al., 2019). The quadratic polynomial equation is:

$$Y_i = \sum_{j=1}^{k-1} \sum_{l=j+1}^{k} \alpha_{jl} X_j X_l + \sum_{j=1}^{k} \alpha_{jj} X_j^2 + \sum_{j=1}^{k} \alpha_j X_j + \alpha_0 \quad (4.6)$$

Y_i is the response variable (COD and Color (%) removal efficiency), and i ranges from 1 to 9; X_j and X_l are the values of the chosen independent variables (j and l ranging from 1 to k), where k is the number of process parameters considered in the study (k= 4); α_0 is the intercept while α_j, α_{jj} and α_{jl} are the linear, quadratic and interaction coefficients of their respective terms.

ANOVA and determination coefficient (R^2) are used to evaluate the mathematical model created using quadratic regression statistically. Better the value of the coefficient of determination R^2, better is the polynomial equation fit to experimental data (Biswas et al., 2017). The quadratic model is validated using the ANOVA at a 95% confidence level. The adsorbent's performance is optimized by setting the goal of each response variable to maximize, and process parameters are set to be in the range considered in this study. In the case of multiple optimum conditions, the desirability value forms the basis of its selection. In contrast, in the case of a single optimum condition, the desirability value does not play a significant role in its selection. The validation experiment for the optimized condition is also performed.

4.2.3 Artificial Neural Network (ANN) prediction modelling

ANN are computerized models based on the functioning of the human brain and nervous system. The neural network consists of inputs, targets (experimental data) and outputs (the predicted values after training the network). In the present study, the neural network is developed using the nnstart tool of MATLAB 2019a software. Three layered feed-forward network types with backpropagation error consisting of the input, hidden, and output layers are trained using the Levenberg-Marquardt training function (Wali & Tyagi, 2020). The non-linear activation function tansig maps the input layer to the hidden and output layers. In the network, the number of neurons in the input layer depends on the number of process parameters and the number of neurons in the output layer depends on the number of response parameters (Jain et al., 2022).

The input datasets consist of four process parameters (adsorbent dose, contact time, pH, and temperature) that are normalized on a scale of 0 to 1. The output data consists of the experimental results for the COD and color removal efficiency by the WSAC. The neural network randomly divides the dataset of 30 samples into 70% for training, 15% for validation and 15% for testing. The number of neurons is changed to find the optimal number of hidden layer neurons, and the network is trained repeatedly until the best R-value and the minimum Mean Square Error (MSE) are obtained (K et al., 2021). The output values, weights of the trained network and the regression plots data are stored in the Excel file for the best-trained network for different hidden layer neurons.

4.2.4 Kinetic modelling

The kinetic study is essential for determining the pollutant uptake rate by the adsorbent and understanding the controlling mechanism (Aljerf, 2018). The adsorption rate is essential for scaling the adsorption process from the lab scale to the pilot and industrial levels (Lima et al., 2021). The batch adsorption experiments are performed for the kinetic study by varying the adsorbent dose, contact time and pH. The temperature is kept at the optimum condition obtained from the RSA analysis. The experimental data is used to study the non-linear Pseudo-First-Order (PFO) by Lagergren (1898), Pseudo-Second-Order (PSO) kinetic by Blanchard et al. (1984), and intraparticle diffusion models by Weber and Morris (1963). The equations for the non-linear PFO, PSO and intraparticle diffusion models are represented in Eqs. (4.7-4.9)

$$q_t = q_e(1 - e^{-tk_1}) \tag{4.7}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{4.8}$$

$$q_t = k_i(t)^{0.5} + C \tag{4.9}$$

where q_e and q_t are the COD (mg/g) and color (PCU/g) adsorbed at equilibrium and at any time t (min); k_1 (min^{-1}) is the rate constant for the PFO model; k_2 (g/mg× min for COD, g/PCU× min for color) is the equilibrium rate constant for the PSO model; C (mg/g for COD and PCU/g for color) is the intercept describing the boundary layer thickness, k_i (mg/g × $min^{1/2}$ for COD, PCU/g × $min^{1/2}$ for color) is the rate constant for the intra-particle diffusion model

4.3 Results and discussions

4.3.1 Wheat straw activated carbon characteristics

4.3.1.1 FTIR and specific surface area analysis

The FTIR fingerprint of the WSAC before and after the contaminant adsorption is shown in Fig. 4.4 (a). The spectra of WSAC shows the presence of hydroxyl (-OH) carbonyl (-C=O) functional groups on its surface. The band at 3453 cm^{-1} is observed due to hydroxyl group stretching, and the weak peak between 2000-1650 cm^{-1} is associated with the C-H bending of aromatic compounds (Yadav et al., 2021). The peak between 3000-2840 cm^{-1} represents the symmetric C-H stretching vibrations representing the methyl ($-CH_3$) and methylene ($-CH_2-$) groups (Tran et al., 2017b). The prominent peaks at 1443 cm^{-1} show the carboxylic group (-COOH) on the adsorbent surface (Ghosh et al., 2021). The strong and sharp peaks between 1124 to 1087 cm^{-1} are the infrared adsorption band for C-O stretching vibrations for the secondary alcohol. The peaks at 876, 879, 619 and 631 cm^{-1} are attributed to the bending modes of aromatic compounds (Bansal et al., 2009).

The adsorption isotherm of N_2 for the WSAC, represented in Fig. 4.4 (b), is Type 1 of the International Union for pure and Applied Chemistry (IUPAC) classification system. Type 1 isotherms are the typical characteristic of microporous solids with relatively small external surfaces, mainly activated carbons (Sing, 1985; Thommes et al., 2015). Further, the formation of wide knee hysteria occurs in the adsorption/ desorption isotherms, as given in Fig. 4.4 (b), which is the H-4 type of hysteria loop according to IUPAC nomenclature. This loop type is associated with capillary condensation in the mesopores indicating the presence of micropores and mesopores in the adsorbent structure (Zazycki et al., 2018). The pore size distribution data shown in Fig. 4.4 (c) shows the presence of mesopores and micropores with a diameter greater than 2 nm. The specific surface area (S_{BET}) of the WSAC is 79.285 m^2/g. The mean pore diameter is 2.6025 nm, and the total pore volume is 0.051584 cm^3/g.

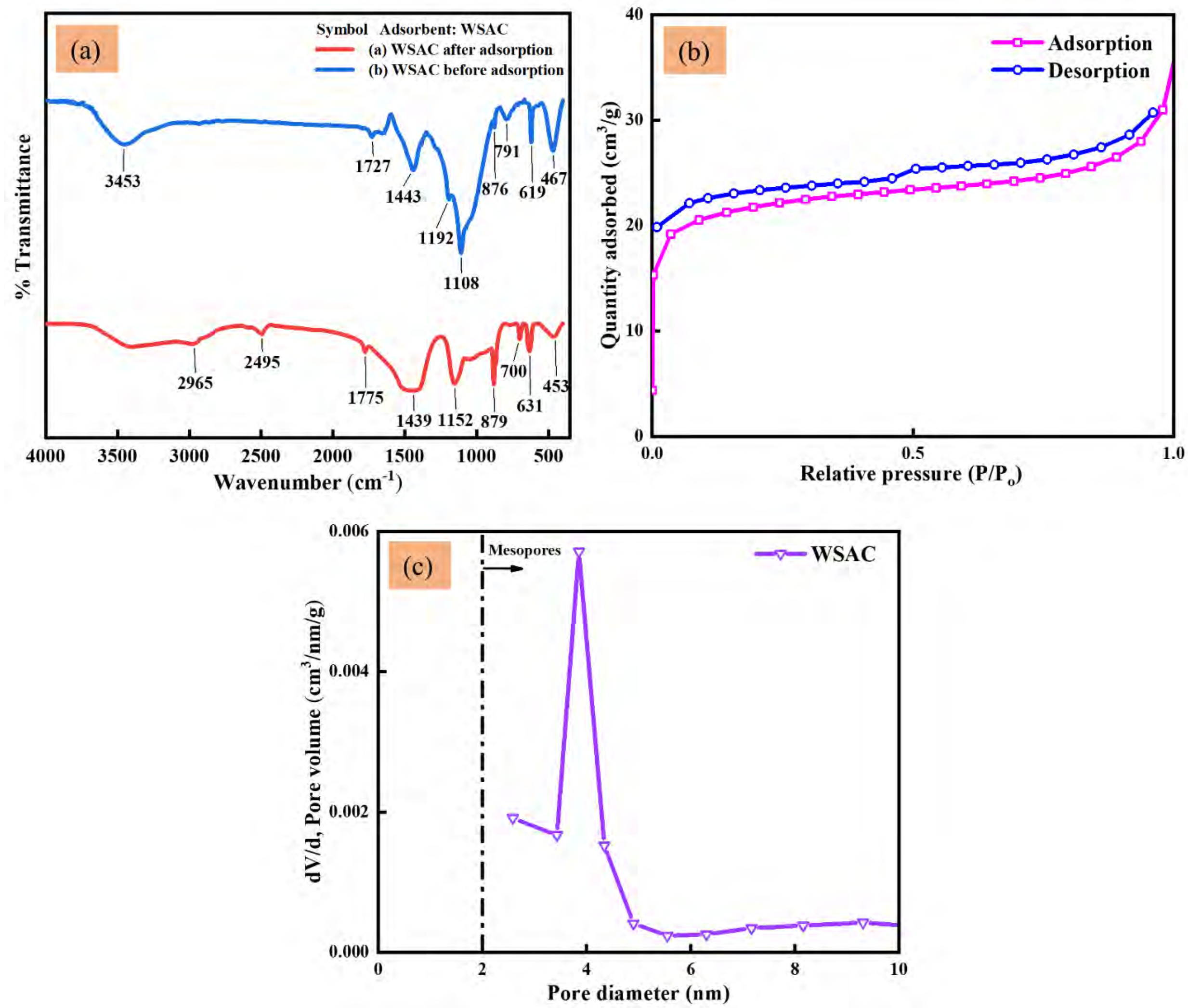
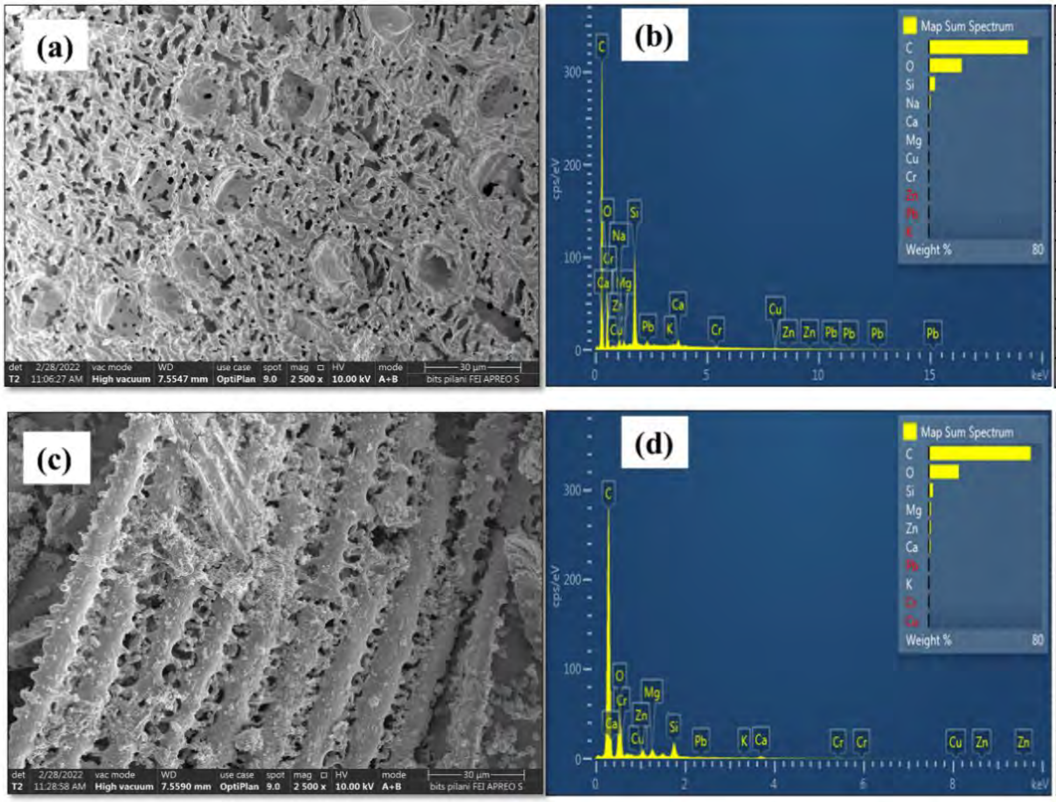


Fig. 4.4(a) FTIR spectrum of WSAC before adsorption and after adsorption; (b) Adsorption-desorption isotherm of N2; (c) Pore size distribution of WSAC

4.3.1.2 Surface morphology

A FESEM-EDX analyzer is used to study the adsorbent's surface morphology and elemental composition. The SEM images of the unused and the used WSAC reveal significant changes in the surface of the WSAC. The micrograph of unused WSAC indicates the highly porous materials mesopores on its surface, as shown in Fig. 4.5 (a). The alkali treatment has aided in developing mesopore (Keey et al., 2018). These pores are numerous sites for adsorption and assist in removing the impurities from the effluent. The micrograph of textile effluent adsorbed WSAC indicates that the dye molecules and the metal ions are absorbed on the pores developed on the surface. The morphology images, EDX spectra and the elemental composition of the WSAC and the contaminants loaded with WSAC are presented in Figs. 4.5 (a, b) and (c, d).



Elements	Wt%
C	70.04
O	23.21
Na	1.11
Mg	0.27
Si	4.4
K	0.01
Ca	0.6
Cr	0.15
Cu	0.18
Zn	0.02
Pb	0.01
Total	100

Elements	Wt%
C	72.01
O	21.1
Mg	1.15
Si	2.31
K	0.33
Ca	1.01
Cr	0.26
Cu	0.29
Zn	1.28
Pb	0.26
Total	100

Fig. 4.5 FESEM images and EDX spectra of the (a, b) unused WSAC and (c, d) contaminants loaded WSAC

4.3.1.3 Effect of dilution factor, pH and pH_{PZC}

pH_{PZC} is the pH at which the surface charge at the adsorbent is zero (Aljerf, 2018). The initial and final pH is plotted in Fig.4.6 (a), and the point at which the initial pH equals the final pH is noted as pH_{PZC}. Determining pH_{PZC} is essential as the adsorbent surface becomes negatively charged when $pH_{solution} > pH_{ZPC}$ and the deprotonation of surface groups containing the oxygen such as -COOH and -OH occurs, increasing the possibility of adsorption of cationic ions from the solutions (Aljerf, 2018). The pH_{ZPC} value of the wheat straw bio adsorbent is 5.8.

The effect of dilution on the adsorption of COD and color is presented in Fig. 4.6 (b). The effluent is diluted to 1%, 2%, 5%, 10%, 15% and 20%. Maximum adsorption is observed at the dilution factor of 10%. The effect of pH on the adsorption of COD and color is illustrated in Fig.4.6 (c). The adsorption of COD and color takes place even at $pH_{solution} < pH_{ZPC}$. The adsorption of COD and color is observed even at a lower pH of 2 to 5. Although at this pH range, intense competition between the COD, color molecules and the H^+ ions occur for adsorption at the active sites. However, the adsorption of COD and color at the lower pH indicates the presence of hydrogen bonding and n-π interaction rather than electrostatic attraction (Tran et al., 2017; Tran et al., 2017a). The maximum adsorption is observed in pH 6 to 8 when $pH_{solution} > pH_{ZPC}$. Similar results are also found in the past literature (Tran et al., 2017).

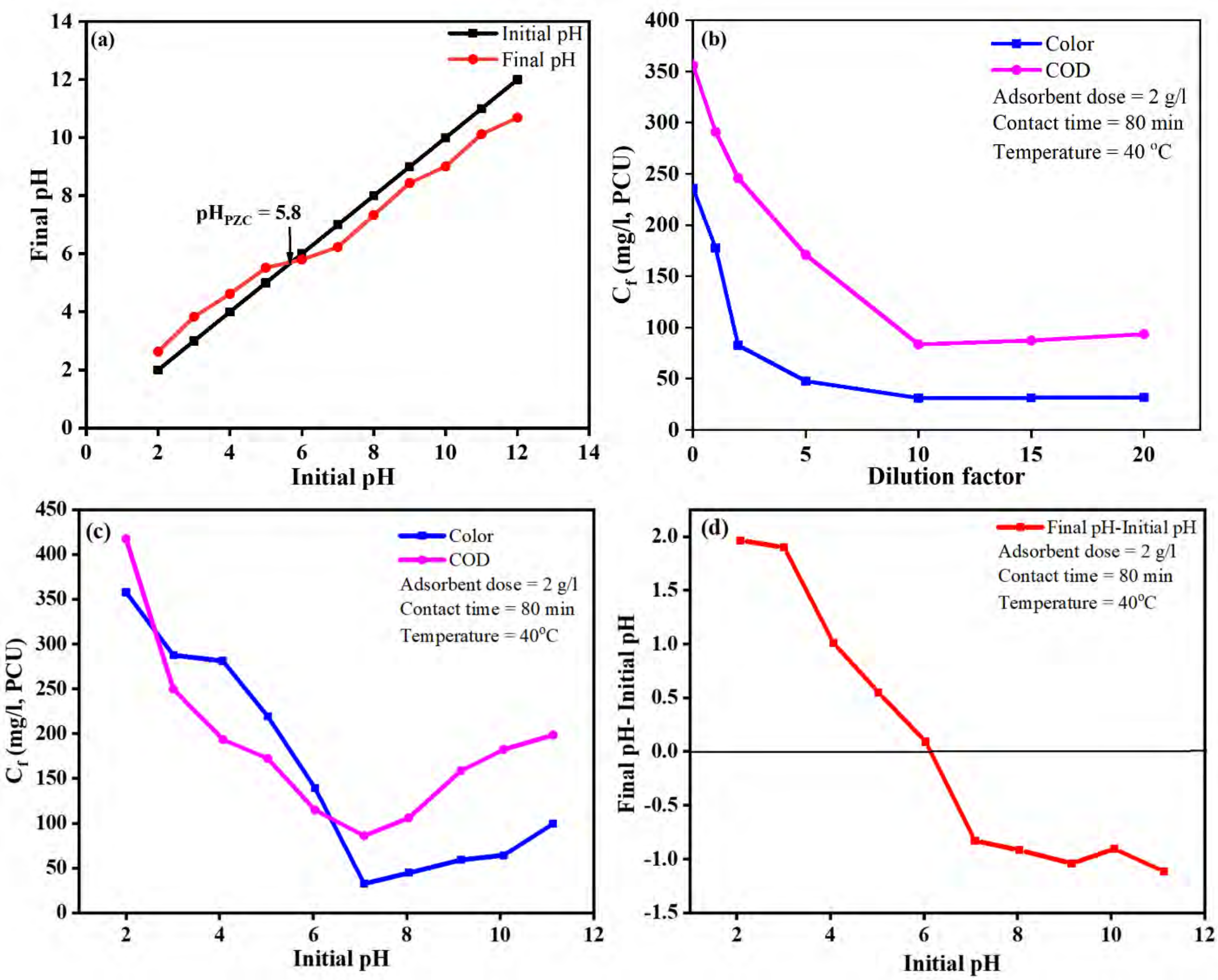


Fig. 4.6(a) The point of zero charge value of the biosorbents, (b) effect of dilution factor on COD and colour adsorption, (c) effect of pH on the COD and colour adsorption, (d) change in pH values after adsorption (Cf = final concentration after adsorption)

4.3.2 Experimental program

The batch experiments are performed to study the effect of contact time and the adsorbent dose on the adsorption of COD and color. The experiment conditions for batch experiments are pH of 7 and temperature of 40 ºC while the adsorbent dose and contact time are varied and are illustrated in Fig. 4.7. From Fig. 4.7 (a), the minimum COD concentration in the effluent after adsorption is observed at the adsorbent dose of 2 g/l and in the contact time of 60 – 80 min. Similarly, the maximum decolorization is observed for the adsorbent dose between 2 g/l- 2.5 g/l for the contact time of 60-100 min, as shown in Fig. 4.7 (b). The initial COD and color removal rate are much higher for all the adsorbent doses for the first 20 minutes, and more than 70% of adsorption takes place during this duration. Because of the rapid rate of adsorption during the initial 10 min, as seen in Fig. 4.7, it is evident that the adsorbents have a high affinity for COD and positively charged dye molecules. It assures efficiency and economy; kinetics plays a vital role in enabling scaling up to small reactor capacities.

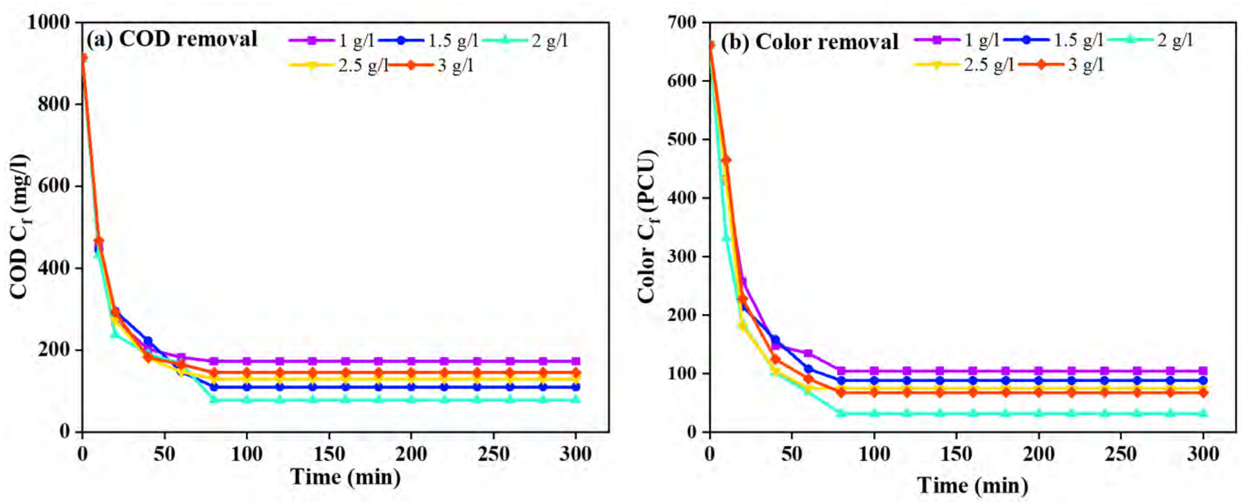


Fig. 4.7 Batch experiments results of the final concentrations of COD and colour adsorption using different doses of WSAC adsorbent

4.3.2.1 Experimental program and modelling of response variables by RSA

The experiments were conducted following the design matrix obtained from the CCM of the RSA. A total of 30 experimental runs are performed in doublets confirming the design matrix for a different range of input factors, i.e. A: contact time, B: adsorbent dose, C: initial pH, and D: temperature. The design matrix for the input factors is given in Appendix D Table D.1. The percentage removal of COD and color by the WSAC for the considered experimental runs is calculated using Eq. (4.4). The results from the 30 experimental runs, the predicted values using the RSM, and ANN are presented in Table 4.3. The experimentally observed maximum COD and color removal efficiency of WSAC is 91.59% and 95.4% at pH of 7, contact time of 80 min, adsorbent dose of 2 g/l and temperature of 40 ºC. The minimum COD and color values after adsorption at the pH of 7 can also be observed in Fig. 4.6 (c). However, a statistical analysis of the experimental data is required to determine the optimum COD and color adsorption conditions.

Table 4.3 Experimental results and the predicted values using the RSA, ANN

Run order	% COD removal			% Color removal		
	Experiment results	Predicted values		Experiment results	Predicted values	
		RSM	ANN		RSM	ANN
1	77.32	77.06	77.23	91.3	92.72	91.1
2	87.28	86.47	87.29	92.3	91.17	92.37
3	91.21	90.24	90.08	95.4	93.9	93.72
4	91.02	89.27	87.2	87.33	86.81	91.34
5	87.6	86.25	87.53	82.5	81.91	82.46
6	90.83	90.17	90.76	82.56	82.95	82.54
7	87.03	85.83	87.04	87.5	88.43	88.41
8	81.51	79.76	81.44	95.09	93.47	95.19
9	89.45	90.24	90.08	94.34	93.9	93.72
10	88.55	88.29	83.88	88.34	88.66	91.38
11	76.94	78.57	76.97	82.77	82.03	82.9
12	75.61	74.97	71.41	82.23	82.16	83.45

Run order	% COD removal			% Color removal		
	Experiment results	Predicted values		Experiment results	Predicted values	
		RSM	ANN		RSM	ANN
13	87.36	87.99	87.26	87.16	87.21	87.4
14	89.69	90.46	89.3	89.16	89.33	89.65
15	91.59	90.24	90.08	94.1	93.9	93.72
16	87.93	87.91	87.85	88.5	88.21	89.01
17	87.17	87.96	88.28	88.13	88.87	90.9
18	89.07	88.68	89.08	91.87	91.27	91.83
19	86.84	87.56	86.88	90.06	90.63	90.24
20	90.93	90.24	90.08	93.45	93.9	93.72
21	86.43	87.26	88.44	90.79	90.69	91.61
22	87.83	90.24	90.08	94.94	93.9	93.72
23	86.6	87.09	86.62	91.63	90.39	91.98
24	84.7	84.52	82.17	89.37	88.61	89.12
25	87.34	87.29	87.3	90.16	90.69	90.21
26	87.17	88.01	87.25	92.73	93.07	92.6
27	82.89	81.71	82.97	85.19	85.22	88.74
28	76.89	79.09	82.58	82.52	83.5	89.19
29	85.55	87.14	85.24	89.16	90.36	89.12
30	90.45	90.24	90.08	91.17	93.9	93.72

The quadratic polynomial regression model helps develop the mathematical correlation between the response parameters and the process parameters by using Eq. (4.6). The quadratic polynomial regression models for the two response parameters (Y_i which represents the response, COD and colour) with input parameters in coded units (A, B, C, and D represent the contact time, WSAC dose, initial pH, and temperature) are presented in Eq. (4.8) and Eq (4.9).

COD (Y_1)

$$Y_1 = 90.24 + 0.3233A - 0.4867B + 1.96C - 1.35D + 0.145AB - 8.63AC + 9.67AD + 2.77BC - 3.29BD + 8.92CD - 4.09A^2 - 1.46B^2 - 2.03C^2 - 11.83D^2 \quad (4.8)$$

Colour (Y_2)

$$Y_2 = 93.9 + 1.37A + 0.9258B + 0.5175C - 0.3792D - 0.3875AB - 3.78AC + 6.78\,AD + 2.06\,BC + 0.0725BD + 9.59\,CD - 4.1A^2 - 6.17B^2 - 11.47C^2 - 0.8054D^2 \quad (4.9)$$

The statistical significance of the regression model is established using the ANOVA test, and the results are given in Table 4.4. The p-value <0.05 for the two-regression model indicates that the model is significant. The R^2 is closer to unity, indicating that the developed regression model can effectively define the experimental data of the adsorption process (Aljerf, 2018). The scatter plots of actual and predicted values by the regression models for the two response parameters are presented in Fig. 4.8. The R^2 value for the COD and color removal efficiencies are 0.9387 and 0.945, respectively. The Fisher's test value (F-value) is the ratio of the mean square of the regression model to the mean square of error. The higher F-value of the model signifies a lower mean square error proving the significance of the model. Insignificant lack of fit and occurrence of a large F-value of 1.36, 0.64 for COD and color regression models indicates a 38.71% and 74.11% possibility of noise.

Table 4.4 ANOVA results for the different physicochemical parameters

Parameters	Sum of squares	Mean square	Degree of freedom	F-value	p-value	Range (%) (Min-max)	R^2
COD							
Model	552.57	39.47	14	16.40	< 0.0001	75.6-91.59	0.93
Residual	36.1	2.41	15	-	-	-	-
Lack of fit	26.38	2.64	10	1.36	0.3871	-	-
Pure error	9.72	1.94	5	-	-	-	-
Color							
Model	447.93	32	14	18.69	<0.0001	82.23-95.4	0.945
Residual	25.68	1.71	15	-	-	-	-
Lack of fit	14.46	1.45	10	0.6445	0.7411	-	-
Pure error	11.22	2.24	5	-	-	-	-

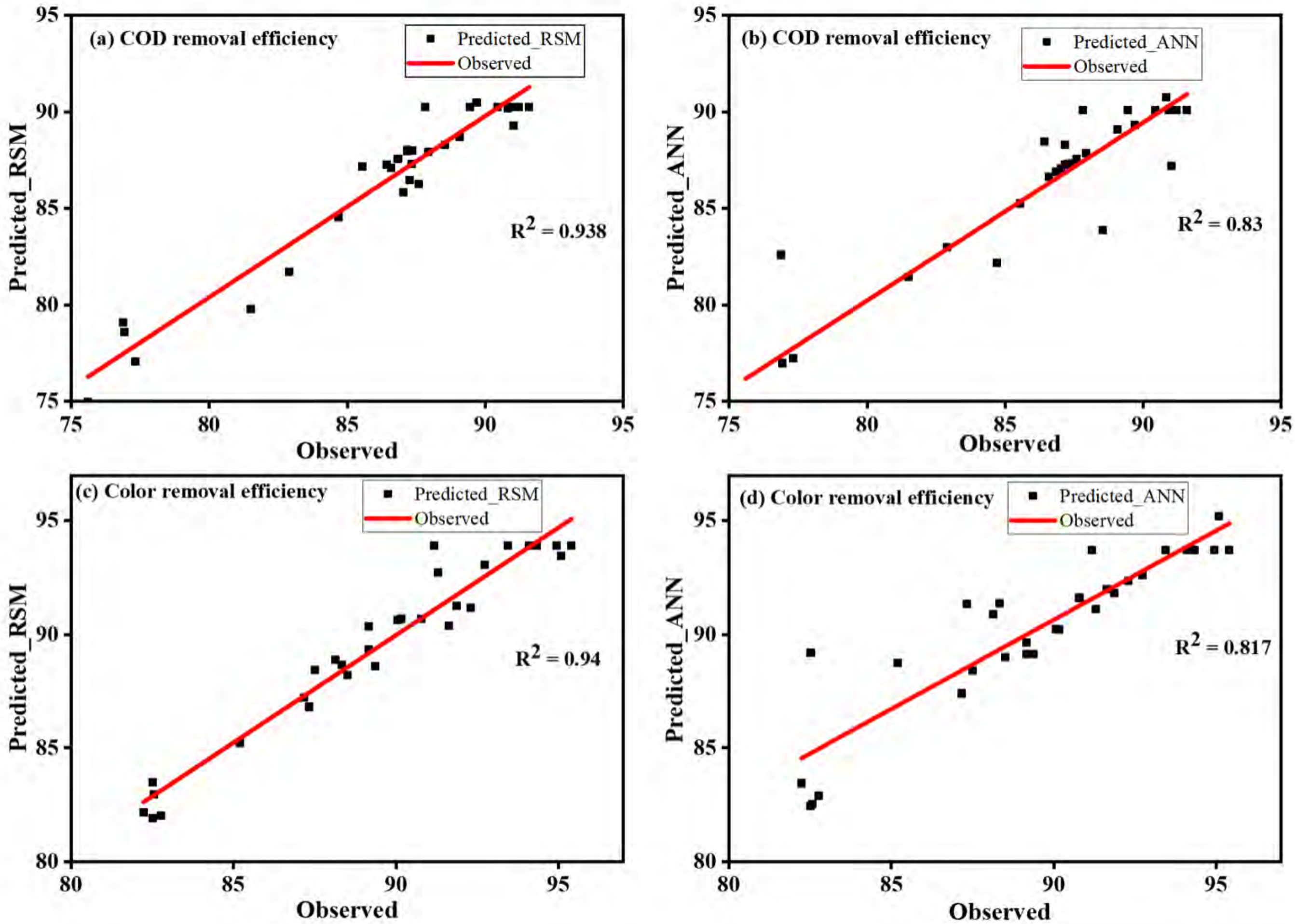


Fig. 4.8 Scatter plots of the predicted and experimental data for the (a) COD and (b) Color removal percentage using WSAC

4.3.3 Development of ANN model

The ANN model consists of four input layer neurons (contact time, adsorbent dose, initial pH and temperature) and two output layer neurons (COD and color removal efficiencies), as presented in Fig. 4.9. The number of hidden layer neurons are changed from 1 to 12 and the relevant data (R value> 0.9) is observed for hidden layer neurons from 5 to 12. The experimental data is used to train the network and find the predicted response parameter values. The predicted values of the COD and color removal efficiencies from this ANN network are presented in Table 4.3. The coefficient of correlation (R) and Root Mean Square Error (RMSE) for the different numbers of hidden layer neurons is given in Table 4.5. It can be observed from Table 4.5 that the ten number of neurons in the hidden layer has R of 0.985 and RMSE for COD is 1.89 while for

Color is 1.873 and is selected as the most optimal number of neurons. The number of epochs demonstrates how the ANN model's training, validation and error have changed over the period (Nayak et al., 2004). The network training terminates when the test error is minimum, and the MSE remains constant for at least nine iterations. The ANN training and performance validation plots at each epoch are shown in Fig. 4.10. The regression plot for the training, validation, test, and overall data sets with the R values 0.985, 0.904, 0.766 and 0.912, respectively, are demonstrated in Fig. 4.11. The R ≈ 1values show a better correlation between the experimental and predicted data.

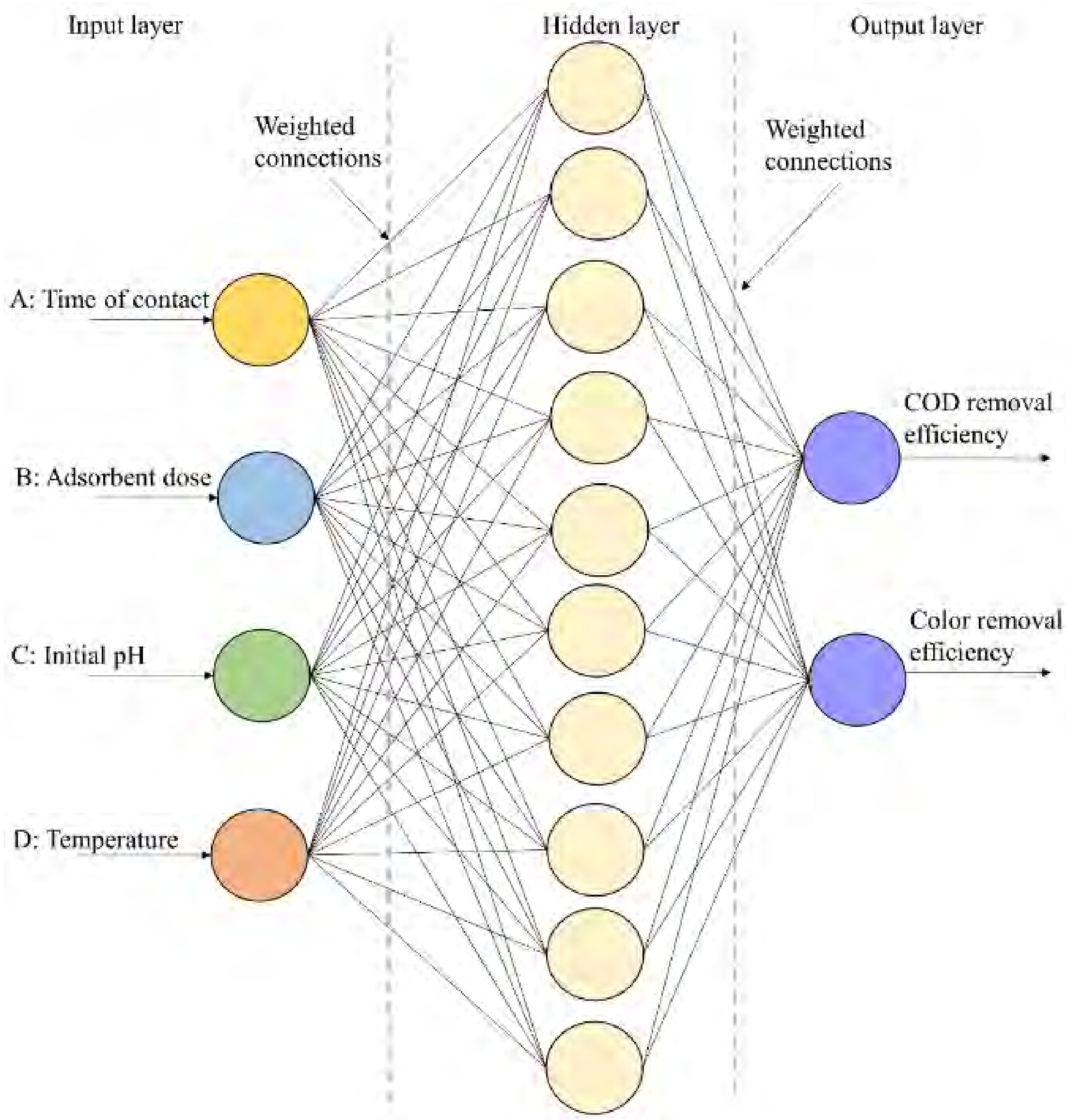


Fig. 4.9 Architecture of the ANN model

Table 4.5 The R and RMSE values for the different hidden layer neurons

Number of hidden layer neurons	Correlation coefficient (R)			Root means square error (RMSE)	
	Training	Validation	Test	COD removal	Color removal
5	0.959	0.631	0.936	1.859	1.859
6	0.989	0.790	0.601	1.510	2.180
7	0.988	0.936	0.309	3.259	2.488
8	0.990	0.616	0.583	2.036	1.695
9	0.988	0.771	0.511	2.927	2.199
10	0.985	0.904	0.766	1.899	1.873
11	0.997	0.744	0.252	2.655	1.707
12	0.972	0.797	0.787	2.069	2.512

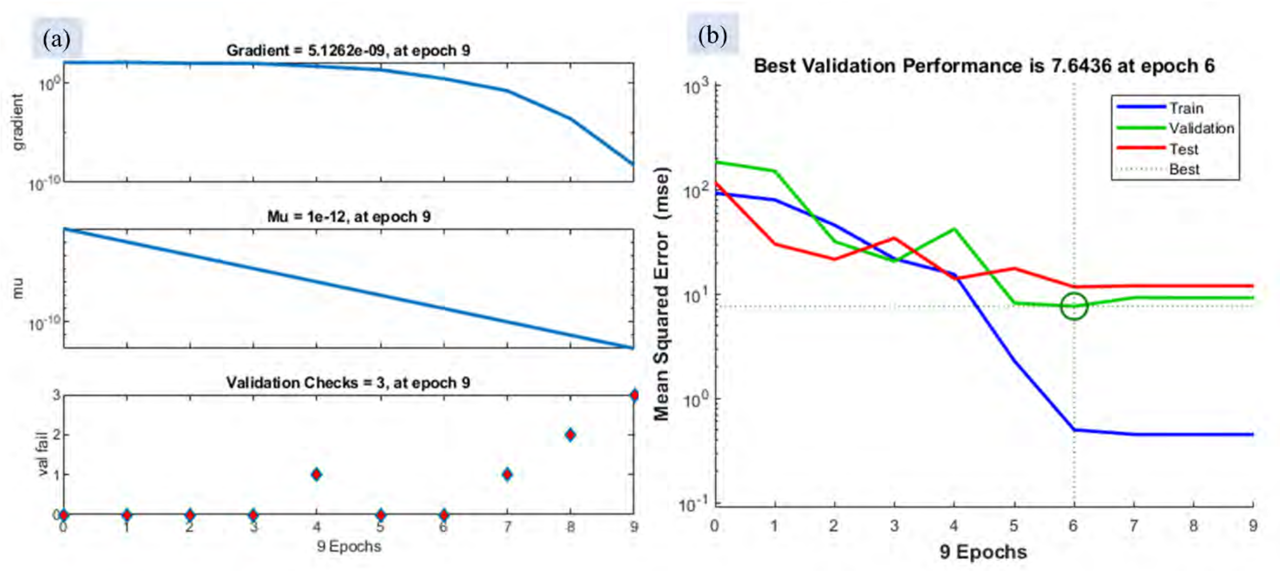


Fig. 4.10 ANN plots (a) training and (b) performance

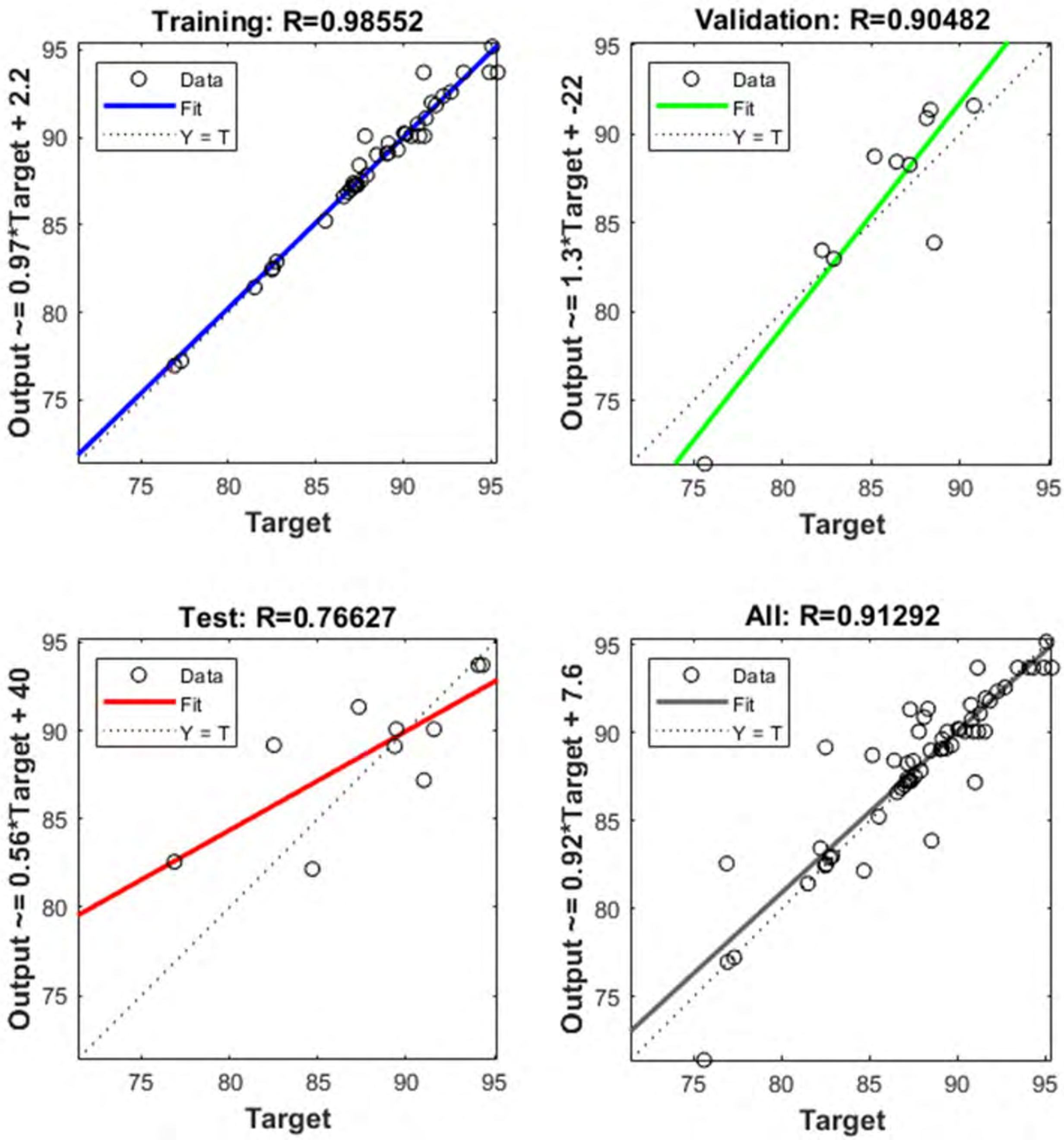


Fig. 4.11 Training, validation, test, and overall regression plots for the ANN model

4.3.4 Comparison of developed RSA, and ANN model

The performance of the developed RSA and ANN models is evaluated using the R, R^2, MSE, and Root Mean Square Error (RMSE) statistical measures. The predicted values from both the models are compared, and the scatter plots are plotted as shown in Fig. 4.8. The R, R^2, MSE, and

RMSE values for the RSA and ANN model for COD and color removal efficiency of WSAC are represented in Table 4.6. From Table 4.6, the R and R^2 values for both RSA models are close to the unit, indicating a better correlation between the experimental results and the predicted values than in the ANN model and are highlighted with green color in Table 4.6. The MSE and RMSE values of color and COD removal efficiency of the RSA model are smaller than the ANN model values indicating that the RSA model is a better fit than the ANN model.

Table 4.6 Performance evaluation of RSA and ANN model

	R	R^2	MSE	RMSE
RSA (COD)	0.969	0.938	1.204	1.097
RSA (Color)	0.97	0.94	0.857	0.926
ANN (COD)	0.911	0.83	3.606201	1.899
ANN (Color)	0.904	0.817	3.508129	1.873

4.3.5 RSA optimization and validation

Optimizing the input variables aims to maximize the contaminant removal efficiency of WSAC statistically. The optimum values for the process parameters and the response variables determined by the RSA optimization are given in Table 4.7 and Table 4.8. The batch experiments are performed at the optimum condition to validate the predicted and observed values of COD and Color. The results show low percentage variation of 0.78 and 0.44 from the RSA and 0.92 and 0.62 from the ANN model resulting in RSA as the reliable prediction and model validation.

Table 4.7 Optimum values of input variables

Time of contact (min)	Adsorbent dose (g/l)	pH	Temperature (^oC)
85.229	2.045	7.181	40.885

Table 4.8 Validation of RSA and ANN predicted and observed values

Parameters	Observed	Predicted		Percentage variations	
		RSM	ANN	RSM	ANN
COD	90.92	90.21	90.08	0.78	0.92
Color	94.48	94.06	93.89	0.44	0.62
Desirability		0.907			

4.3.6 Effect of process parameters on the percentage removal of COD and color

The Response Surface (RS-3D) plots for the developed regression models help study the interactive effect of the variables (pH, adsorbent dose, contact time and temperature) on the response parameters, i.e., the COD and color adsorption by WSAC. In the RS plots, the two parameters are kept constant as the null point, while the other two parameters are varied within the experimental range defined in the study. Each 3-D interaction plot represents an endless number of suitable combinations of the variables (Oberholzer et al., 1997). The 2-D circular contour plots of the response surface represent negligible interaction within the concerned variable Each contour line with different color on the X-Y plane indicates the different COD and Color removal efficiency of WSAC but all the points on the same contour lines indicates same COD and Color removal efficiency (W. Zhao et al., 2011).

At the same time, the elliptical and saddle points show that the interaction between the variables is significant. Figs. 4.12 (a-f) and Figs. 4.13 (a-f) show the response surface plots for the COD and color adsorption, respectively.

4.3.6.1 Effect of adsorbent dose and contact time

Fig. 4.12 (a) and Fig.4.13 (a) show the interaction plot and contour plot for the simultaneous impact of contact time and adsorbent dose on the percentage of COD and color removal, and the initial pH, temperature is kept at the null point. As seen from Fig. 4.12 (a), the maximum COD removal efficiency (91.59%) occurred at the contact time of 80 mins for the adsorbent dose of 1.5-2.5 g/l. Similarly, from Fig. 4.13 (a), the highest decolorization (95.4%) occurs for the contact time of 60-100 min and adsorbent dose between 1.5-2.5 g/l. The circular contour plots show the low interaction between these adsorbent variables. However, there are insufficient sites for adsorption at a lower dose than 1.5 g/l. At a higher dose, the agglomeration of adsorbent occurs and is unsuitable for decolorization (Fito et al., 2020).

4.3.6.2 Effect of initial pH and contact time

Fig. 4.12 (b) and Fig. 4.13 (b) show the removal efficiency of COD and decolorization as the function of initial pH and contact time for the fixed adsorbent dose of 2 g/l and temperature of 40 ºC, respectively. The maximum COD removal occurs when the pH is about 7 and the contact time is 80 min, as depicted in Fig. 4.12 (b). The maximum decolorization efficiency is observed at a pH 7, irrespective of the contact time, as shown in Fig. 4.13 (b). The behaviour of reduction in adsorption with a change in pH is attributed to two properties, the solution's pH and the adsorbent's pH_{ZPC}. The pH_{PZC} of the WSAC is 5.8, as shown in Fig. 4.6 (a). The low adsorption of color and COD in the acidic range is due to the competition of pollutant ions and H^+ for the adsorption sites. The adsorption of cations is preferred at pH > pH_{PZC}. At the pH> pH_{PZC} the adsorbent sites are negatively charged and thus favor the adsorption of positively charged cationic impurities due to electrostatic attraction. However, with a further increase in the pH, precipitation in the form of metal hydroxide may occur, reducing the COD removal and decolorization efficiency of the adsorbent (Assila et al., 2020; Nayl et al., 2017)

4.3.6.3 Effect of contact time and temperature

Fig. 4.12 (c) and Fig. 4.13 (c) display the response surface and contour plots for COD removal and decolorization efficiencies as the function of contact time and temperature at the pH of 7 and adsorbent dose of 2 g/l. The maximum adsorption efficiency for COD (91.59%) can be observed at 40 °C and at a contact time of 60-100 min, as illustrated in Fig. 4.12 (c). The adsorption of COD decreases at a higher temperature, the adsorbent's pore size increases, leading to the breaking of a weak bond on the adsorbent's surface. Fig. 4.13 (c) shows that a temperature higher than 40 °C and a contact time of less than 80 min, and a temperature of 30 °C and a contact time of 100-120 min is unsuitable for decolorization. A possible reason could be the breaking of weak bonds at low temperatures and higher contact time. At high temperatures and low contact time, the increased pore size of the adsorbent reduces the adsorption.

4.3.6.4 Effect of initial pH and adsorbent dose

Fig. 4.12 (d) and Fig. 4.13 (d) represent the 2D and 3D plots for the COD removal and decolorization efficiency, respectively, for the varying adsorbent dose, initial pH, and temperature, contact time are maintained at zero level. Fig. 4.12 (d) illustrates that the higher adsorption is achieved in the range of initial pH (7-9) and adsorbent dose of (1.5-3 g/l). The adsorbent dose of 1 g/l is unsuitable as fewer vacant sites are available for the adsorption leading to incomplete adsorption. Fig. 4.13 (d) represents a pH of 6 to 8, and an adsorbent dose of about 1.5-2.5 g/l is suitable for decolorizing effluent.

4.3.6.5 Effect of adsorbent dose and temperature

The effect of varying adsorbent dose and temperature at the constant contact time of 80 min and initial pH of 7 is shown in Fig. 4.12 (e) and Fig. 4.13 (e) at the COD removal and decolorization efficiency, respectively. It is observed from Fig. 4.12 (e) that maximum adsorption occurs at the temperature of 40 °C and the adsorbent dose of about 1.5-2.5 g/l. A higher temperature than 45°C and a lower temperature than 35 °C, irrespective of the absorbent dose, are not suitable for the adsorption of COD. While Fig. 4.13 (e) shows that the adsorbent dose of 2 g/l is suitable for the adsorption of color irrespective of temperature. However, the maximum decolorization efficiency can be observed at about 40 °C and an adsorbent dose of 2 g/l.

4.3.6.6 Effect of initial pH and temperature

Fig. 4.12 (f) and Fig. 4.13 (f) illustrate the effect of varying temperature and initial pH for the constant adsorbent dose of 2 g/l and contact time of 80 min on the COD and color removal efficiency of WSAC, respectively. It is observed from Fig. 4.12 (f) that maximum COD removal is at pH of 7-9 and temperature of 40-45 °C. The adsorption is effective in the basic range of effluent's pH. From Fig. 4.13 (f), the maximum decolorization is observed at the pH of 5-7.5, irrespective of the temperature.

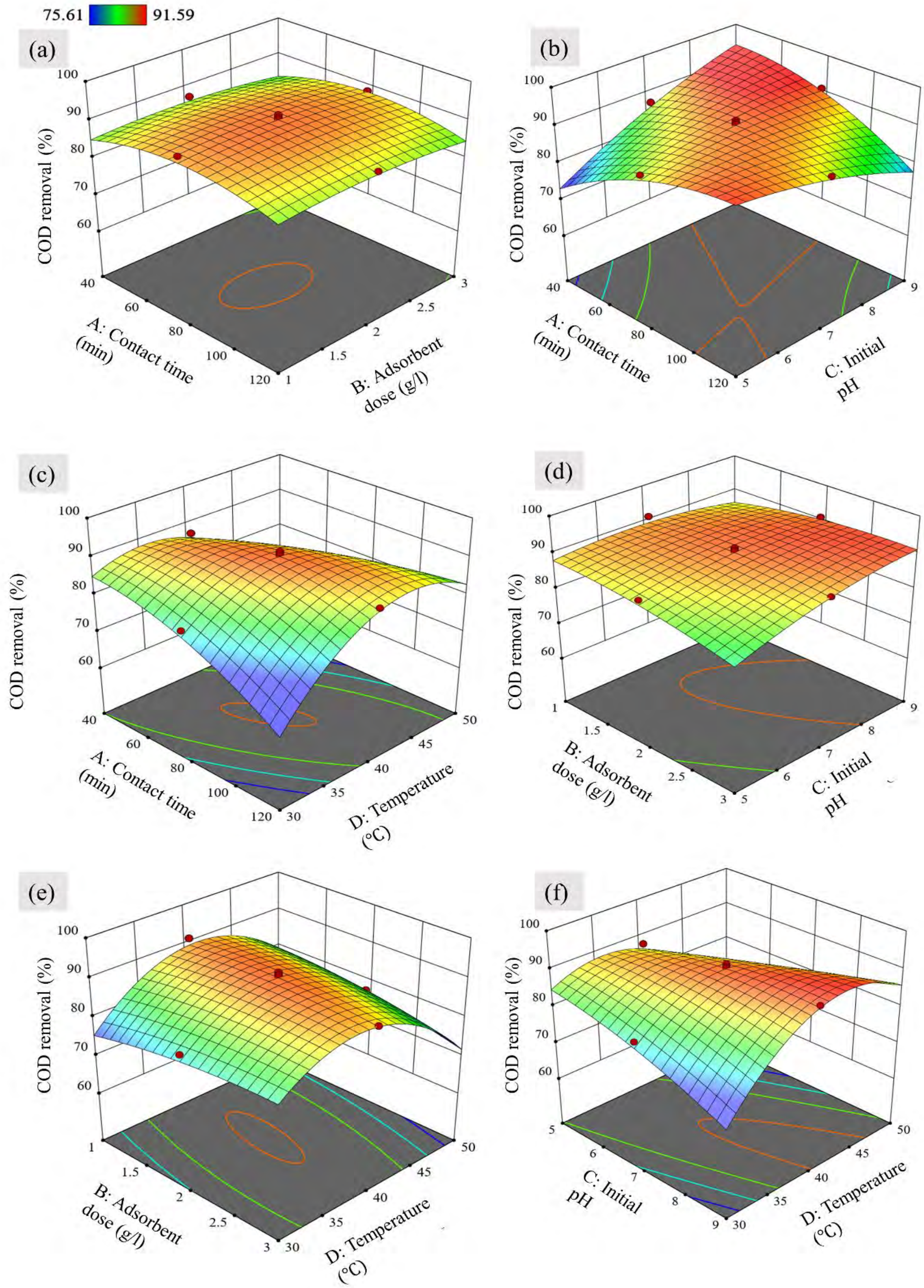


Fig. 4.12 The RS interactive plots for COD removal % by WSAC

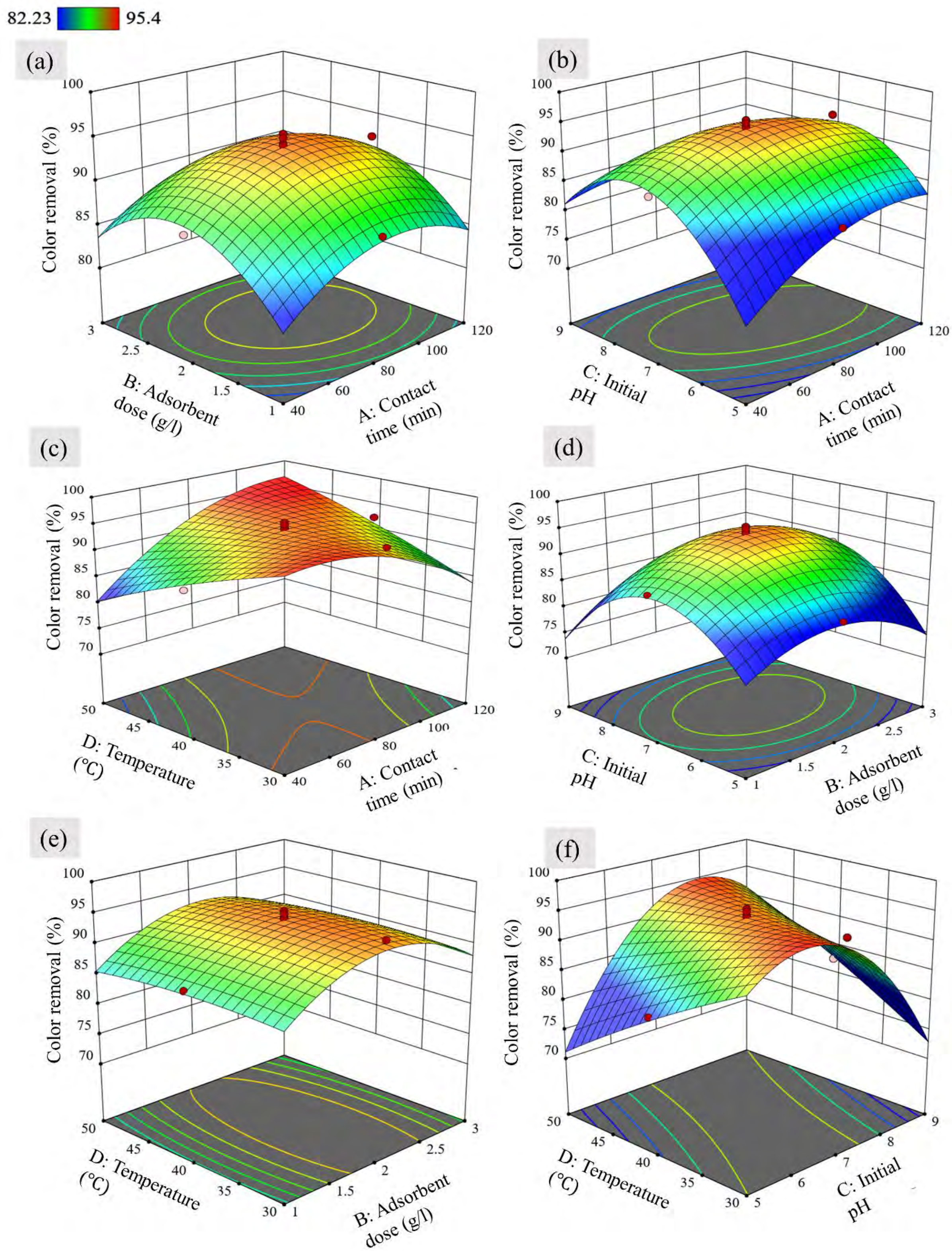


Fig. 4.13 The RS interactive plots for the color removal efficiency of WSAC

4.3.7 Adsorption reversibility

The desorption of contaminants is studied to gain insight into the possible adsorption mechanism for this study. The reversibility of adsorption was examined with desorbing agents such as 0.1M HCl, 0.1M NaCl, deionized water (pH= 2) and methanol. The desorption of contaminants occurs while using the deionized water (pH=2), indicating electrostatic attraction between the negatively charged groups on the adsorbent surface and the cationic contaminants. However, the desorption by the 0.1M NaCl and 0.1M HCl indicates that the ion and cation exchange could be the possible adsorption mechanism. In addition, the desorption by the methanol corresponds to the n-π interaction or hydrogen bonding responsible for adsorption (Tran et al., 2017b). Desorption experiments are carried out for both the COD and color. Fig. 4.14 (a) shows the mass of COD and color desorbed, and Fig. 4.14 (b) represents the desorption percentage. The desorption experiments indicate weak electrostatic attraction and contribute about 71.25 mg/g and 26.33 PCU/g of COD and color desorption, representing 19.65% and 8.629% of desorption of COD and color, respectively, from the WSAC, as shown in Fig. 4.14 (a, b). The 40mg/g and 16.33 PCU/g desorption of COD and color by NaCl, respectively, represents that the cation exchange has a minimal contribution of 10.186% and 5.182% in desorption of COD and color, respectively. The higher desorption of 146.25 mg/g and 122.168 PCU/g by the methanol corresponds to 50.759% and 58.386% for COD and color, showing hydrogen bonding or n-π bond and are significantly responsible for adsorption.

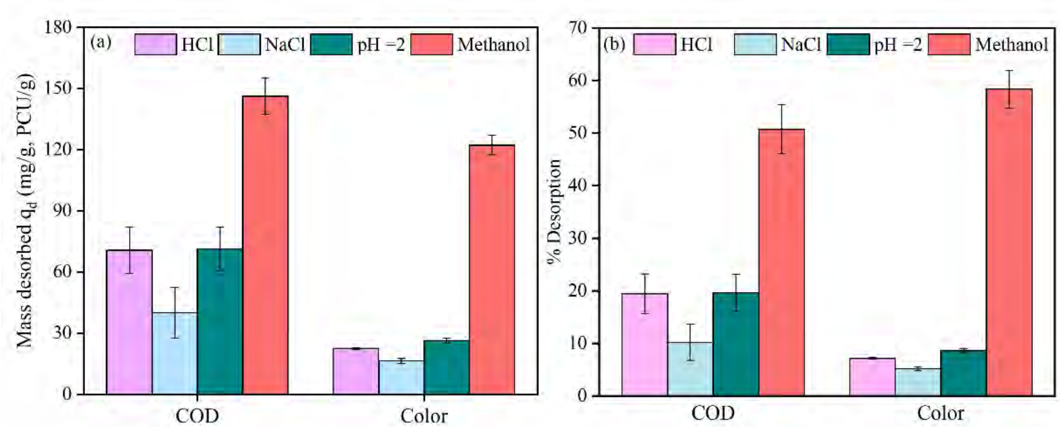


Fig. 4.14(a) mass of color and COD desorbed (b) the percentage of COD and color desorbed

4.3.8 Probable adsorption mechanisms

In general, electrostatic attraction, hydrogen bond formation, n-π interaction, pore filling, and π-π interaction are the probable potential processes of positively charged dye adsorption onto carbonaceous materials (Tran et al., 2017b). The electrostatic attraction and the cation exchange have contributed less than 30% to the adsorption of COD and color on WSAC, as seen in Fig. 4.14.

The negatively charged locations on the surface of WSAC and the cationic contaminants in the solution may exhibit weak electrostatic interactions with one another. After adsorption, the pH of the solution reduces because the oxygen-containing functional groups on the surface of the adsorbent (such as carboxylic and phenolic groups) get ionized when solution pH > pH_{PZC} and the same can be observed from the Fig.4.6 (d). The surface charge of the adsorbents can also be explained by the pKa values of the carboxylic group (-COOH = 2.0-4.0) and the hydroxyl group (-OH = 8-9). When the pH of the solution is higher than the pKa values, these functional groups dissociate and become negatively charged. It has been observed from the experiments and Fig. 4.6 (d) that the maximum COD and color removal occurs at a pH of 7. At the pH of 7, the carboxyl acid dissociates into carboxylate ($-COO^-$) and accounts for the adsorption of COD and color onto the adsorbent surface.

The hydrogen bonding generally occurs between the hydroxyl group of the adsorbent surface and the possible aromatic rings of the dye present in the textile effluent (known as Yoshida hydrogen bonding) and due to dipole-dipole hydrogen bonding between the adsorbent surface hydrogen ion from the hydroxyl group and the nitrogen and oxygen present in the dye. The FT-IR results in Fig. 4.4 (a) the peak of the OH^- group at 3453 cm^{-1} has reduced significantly and changed to broad peaks from sharp peaks. This confirms the presence of dipole-dipole and Yoshida hydrogen bonding interactions in the adsorption mechanism (Blackburn, 2004).

In the case of n-π interactions, the oxygen from the carbonyl groups on the surface of the adsorbent act as electron donors, while the cationic dyes act as electron acceptors. The FT-IR results have demonstrated the reduction in intensity, shifting and broadening of the sharp peak of C-O and C=O after the adsorption of dye molecules and contaminants. The results have been consistent with the previously reported literature (Tran et al., 2017; Tran et al., 2017b).

The contribution of different adsorption mechanisms is summarized as follows: hydrogen bonding and n-π interaction for COD and color desorption by methanol is 50.759% and 58.386%, respectively; electrostatic attraction and cation exchange observed on using NaCl and HCl as desorption agents is 29.3% and 13.811% for COD and color desorption respectively.

4.3.9 Kinetics study

The COD and color adsorption rates are assessed using the non-linear PFO, PSO and intraparticle diffusion model (Sharma et al., 2019; Tran et al., 2017). The kinetic studies are conducted at the maximum adsorption conditions (temperature = 40 °C, pH = 7, adsorbent dose = 2 g/l) and by varying the contact time (10, 20, 40, 60, 80, 100, 120, 140, … 200 min). The specific batch experiment is performed for the kinetic study for COD and color adsorption. These models are shown in Fig. 15 and Table 4.9 for the COD and color adsorption, respectively. The adsorption rate for COD and color is high for the first 20 mins, which later decreases and starts attaining a plateau after 60 min. The higher initial adsorption rate shows the higher affinity of bio-sorbent for the adsorption of cationic dyes (Peng et al., 2021; Rostamian et al., 2022). Table 4.9 lists the kinetic model parameters for both COD and color adsorption. According to the coefficients of determination for the PFO model (R^2 = 0.982, 0.993) and PSO model (R^2 = 0.992, 0.995) and the intraparticle diffusion model (R^2 = 0.71, 0.73). The better fit of the experimental data for the PSO kinetic model suggests the possibility of chemical adsorption. It indicates that the adsorption rate depends on the availability of adsorption sites rather than on the concentration of pollutants. It can be observed that during the initial 20 mins, 74% of the COD and 72% of color removal took place, while with time, sites get gradually occupied with the pollutants, and the adsorption rate decreases. The maximum adsorption capacities for the COD and color at the equilibrium condition observed from the PSO and presented in Table 4.9 are 439.9 mg/g and 337.9 PCU/g, respectively, less than 887.3 mg/g observed for methylene blue adsorption in Zhang et al. (2019).

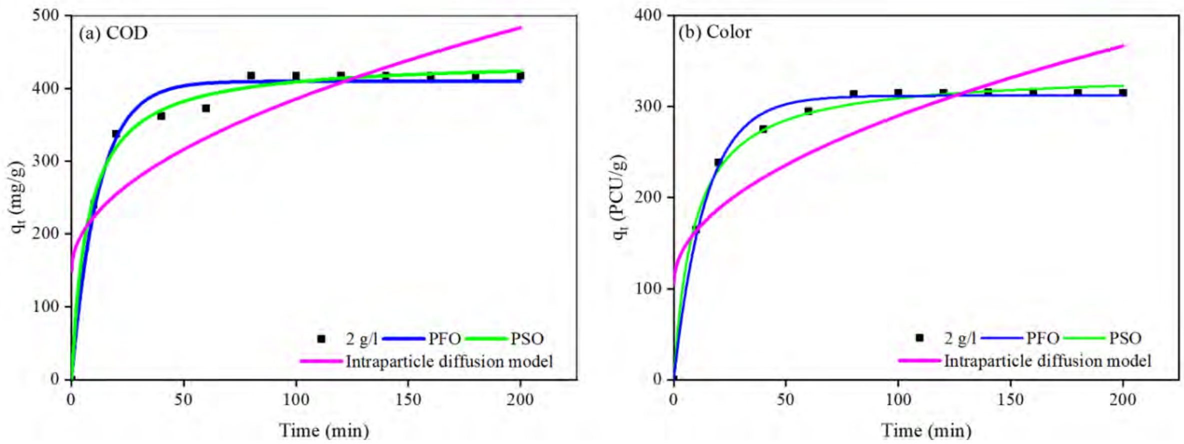


Fig. 4.15 Kinetic study models for (a) COD adsorption (b) Color adsorption by WSAC

Table 4.9 Kinetic parameters for the non-linear methods

Parameters	q_e^{exp}	Pseudo First-Order model (PFO)				Pseudo Second-Order model (PSO)				Intraparticle diffusion model			
		q_e^{cal}	k_1	R^2	χ^2	q_e^{cal}	k_2	R^2	χ^2	k_i	C	R^2	χ^2
COD	417.8	409.8	0.083	0.982	286.5	439.9	3.01E-04	0.992	124.6	23.66	148.7	0.71	4712
Color	315	311.4	0.07	0.993	63.1	337.9	3.19E-04	0.995	45	18.42	106.2	0.73	2588

4.3.10 Economic study

The percentage yield of the WSAC is 10.763%. The WSAC is prepared using the tube furnace, and the maximum amount produced is 0.064 $\pm$0.01 kg from 0.6 kg of wheat straw. At one time, a kg of wheat straw is chemically treated while 1.2 kg is carbonated using two vessels in the tube furnace. The production cost has been computed, including the raw material (wheat straw), the chemical used, distilled water and electricity. The detailed cost for each component is given in Appendix D Table D.2. Commercially available carbon costs 12-15 $/kg, while the overall cost of developing WSAC is 10.71 $/kg which is 16.66% cost-efficient. Also, Zhang et al. (2019) have shown that WSAC is cheaper than commercially available carbon.

4.4 Summary

The current chapter details using locally available agricultural waste, i.e., wheat straw, as an adsorbent. It also discusses the wheat straw-activated carbon's COD and color removal efficiency. The adsorption process is used here to aid the treatment process of MBR techniques. All the treatment techniques generate chemical sludge and treated effluent. This sludge is hazardous. The leaching of heavy metals from the sludge and its impact on human health is studied and discussed in chapter 5.

Chapter 5

Assessment of toxicity characteristics in leachate from the textile industries-based sludge using leachate pollution index

5.1 Introduction

The Common Effluent Treatment Plant (CETP) collects and treats the industrial effluents released by textile manufacturing units using a variety of physio-chemical treatment procedures. One of the end products of CETPs is hazardous sludge (Goyal et al., 2019). Sludge has organic and inorganic salts, heavy metals and other chemicals used in the textile industry and during effluent treatment at CETPs (Paul et al., 2023). The sludge is disposed in the Treatment, Storage and Disposal Facilities (TSDFs) (Patel & Pandey, 2012). However, during the field survey, it was observed that a sizeable amount of sludge lies in CETP, waiting for its disposal at TSDFs. Before being transferred to the TSDF, it could contaminate the surrounding surface and groundwater, thus producing leachate. This highly toxic leachate comprises heavy metals and inorganic and organic chemicals (Ma et al., 2022). Leachate has serious pollution potential, and it is crucial to quantify it and determine possible human health risks (Rajoo et al., 2020). A tool with a mathematical model is required to enumerate the true pollution potential of industrial sludge leachates.

The present chapter consists of a novel framework for developing the Textile-Leachate Pollution Index (T-LPI) using hybrid fuzzy models. The study combines the batch experimental data of the TCLP (Toxicity Characteristic Leaching Procedure) leachate test with the linguistics judgements of the decision makers for developing the T-LPI. The study uses the hybrid Fuzzy Analytical Hierarchical Process (FAHP) infused with Inter-Valued Fuzzy Sets (IVFSs) for calculating the weights of different heavy metals. Additionally, the statistical analysis is performed to determine the correlation between different metal ions, followed by the human health risk assessment concerning the consumption of leachate-contaminated surface water through ingestion and dermal route. The study findings are helpful in solid waste management by ranking sites based on the index for competitive sludge transfer from CETPs to TSDFs sites. The present study effectively estimates the human health risk associated with the textile-effluent treatment plant sludge.

This chapter consists of four sections; the first is section 5.1, which introduces the leaching study. It is followed by section 5.2 of the methodology consisting of the experimental framework, the fuzzy method for T-LPI calculations and human health risk assessment formulations. The third section i.e., section 5.3, has results and a discussion of the case study, followed by section 5.4 of concluding remarks.

5.2 Methodology

The literature survey helped identify the existing types of leachate pollution indices and the importance of developing indices for hazardous sludges such as TCETP sludge. The sludge is collected and processed, followed by the identification of the chemical composition of the sludge. Thirty experiments run for the Toxicity Characterization Leaching Procedure (TCLP) test have been performed to replicate the conditions from the field situation. Leachate has been tested for the metal ions concentration using the ICP-OES. Further, the experimental data is used to develop the Textile-Leachate Pollution Index (T-LPI), assess human health risks, and perform statistical analysis. The detailed outline is given in Fig. 5.1.

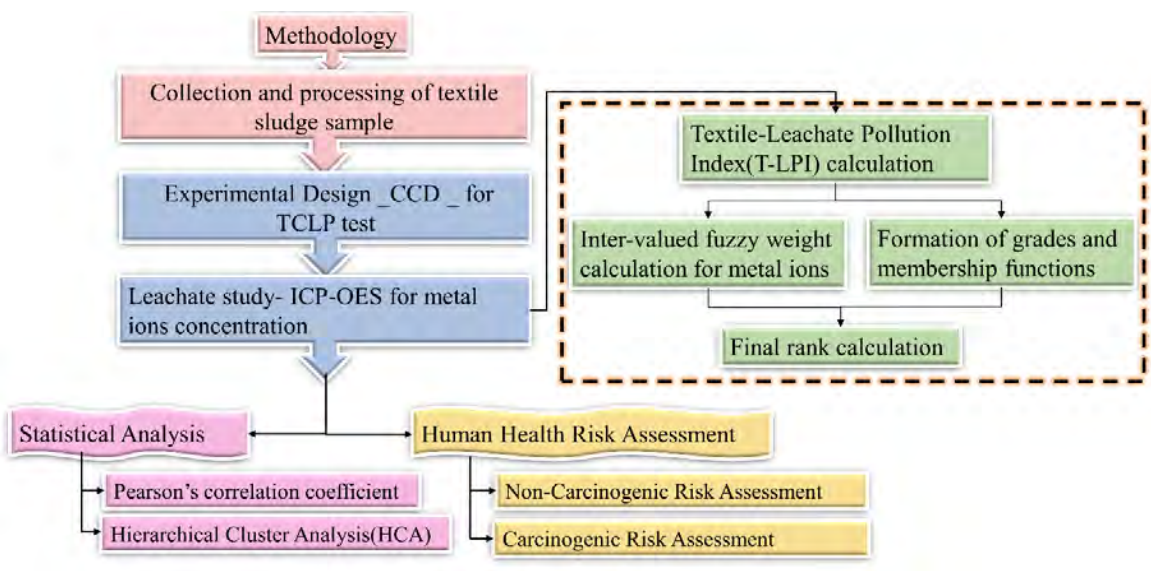


Fig. 5.1 Framework for the leaching study

5.2.1 Material and experimental design

The textile industry-effluent treatment plant sludge was collected from the Balotra industrial cluster in Rajasthan, India. The sludge is bluish-green and is air-dried for a week before being ground using the ball mill. After that, the sludge is sieved through a 90 µm sieve and is used for the study. The primary metal ions in the sludge are identified using X-Ray Fluorescence (XRF). The batch experimental study complied with the TCLP following US EPA method 1311 (1992). As per the TCLP, the glacial acetic acid was diluted to pH =2.88 by mixing 5.7 ml of glacial acetic acid in 1 liter of Millipore water. This study uses diluted acetic acid as the primary leaching agent.

The full factorial Central Composite Design of the Experiment (CCDoE) is used for organizing the effective combination of variables, namely, A: weight of sludge (g), B: time of contact (h), C: the temperature for performing the batch experiment (℃) and D: horizontal rotations (rpm) for the batch reactor study. The CCDoE consists of variables, levels, and responses as their three primary elements. The levels refer to setting the limits for the variables, and the response refers to the measurable output from the experimental runs. Five-level CCDoE is represented in Table 5.1.

Table 5.1 The coded level used in the design of the experiment

Independent factors↓ Coded levels→	**Factor Level**				
	-2	**-1**	**0**	**1**	**2**
A: Weight of sample (g)	5	10	15	20	25
B: Time (h)	2	4	6	8	10
C: Temperature (℃)	20	30	40	50	60
D: Horizontal rotations (rpm)	100	120	140	160	180

The experiments are performed following the scheme generated by CCDoE and are given in Appendix E Table E.1. The leachate-sludge mixture is filtered using the gravity filtration techniques using Whatman filter paper No. 42. The leachate is stored in the 50 ml centrifuge tubes. These tubes were cleaned using diluted nitric acid (HNO3) and washed thrice in deionized water, followed by air drying before use. The experiments are performed in duplicates. Nitric acid is added to filtered leachate to stabilize the metal ions in their soluble state. The leachate from each experimental run is tested for metal ions concentration using the ICP-OES.

5.2.2 Statistical analysis

The data's minimum, maximum, mean, and standard deviation are computed considering all the thirty experiments for the eleven metal ions. Multivariate analysis of the detected metal ions is performed using Pearson's correlation coefficient, and Hierarchical Cluster Analysis (HCA) is performed using the software Origin Pro 2022. The correlation between the metal ions was tested at the significance level of $p <= 0.1$. HCA is a commonly used clustering technique that considers the similarities based on the neighbor method on Pearson correlation distance type.

5.2.3 T-LPI development

5.2.3.1 Weights calculation

As the different metal ions have a different impact on the overall assessment of leachate toxicity, weights set, M= {M1, M2, …, Mm} represents the weight coefficient of each metal ion. The weight set has been derived using the hybrid Fuzzy Analytical Hierarchical Process (FAHP) infused with Inter Valued Fuzzy Sets (IVFSs) as proposed by Srinivas & Singh (2018). The IVFSs assign an interval to membership functions when conventional fuzzy membership function such as $\mu: X \rightarrow [0,1]$ fails to allocate a specific numerical value between [0,1] to each element $x \epsilon X$. Therefore, IVFSs can effectively deal with the uncertainty related to experts' judgement. IVFSs can be represented using Eqs. (5.1-5.4) as given below,

$L = \{x, [\mu_L^L(x), \mu_L^U(x)]\}, x \in X$ (5.1)

$\mu_L^L, \mu_L^U: X \rightarrow [0,1] \, \forall \, x \in X, \mu_L^L \leq \mu_L^U$(5.2)

$\bar{\mu}_L(x) = [\mu_L^L(x), \mu_L^U(x)]$(5.3)

$L = \{(x, \bar{\mu}_L(x))\}, x \in (-\infty, +\infty)$ (5.4)

where $\mu_L^L(x)$be the lower limit and $\mu_L^U(x)$be the upper limit of the degree of membership functions. The step-by-step procedure for applying hybrid FAHP-IVFSs is explained below,

a) Selection of criteria

The criteria for developing the T-LPI are selected based on the XRF elemental composition of the textile industry CETP sludge and from the results of experimental data. The existing literature and expert opinion have further helped to select suitable criteria for developing T-LPI for hazardous wastes. Further, the selected criteria are linguistically rated by the expert panel of three members. These experts are members of the CPCB, India, academicians, and researchers. The judgment for the different criteria is recorded in the linguistic form through a questionnaire survey. It is converted into the quantitative score to generate the pairwise comparison matrices of criteria using Table 5.2.

Table 5.2 Linguistic scale and its crisp score

Linguistic terms	**Scale**
Equally toxic	1
Slightly less toxic	2
Less toxic	3
Less moderately toxic	4
Moderately toxic	5
Less strongly toxic	6
Moderately strongly toxic	7
strongly toxic	8
extremely toxic	9

b) Consistency Check

The experts' judgments are collected in the linguistic form in the questionnaire and are converted to a crisp scale using the conversion scale given in Table 5.2. The pairwise comparison matrices have been developed for the different metal ions based on the expert's opinion and checked for consistency. Let $z_1, z_2, \dots, z_n$ be the set of metal ions, the pairwise comparison matrix (Z) of size n x n can be defined in Eq. (5.5) and given below:

$$Z = [z_{ij}] = \begin{matrix} & z_1 & z_2 & z_3 & z_4 \\ z_1 \\ z_2 \\ z_3 \\ z_4 \end{matrix} \begin{bmatrix} 1 & z_{12} & \cdots & z_{1n} \\ 1/z_{12} & 1 & \cdots & z_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ 1/z_{1n} & 1/z_{2n} & \cdots & 1 \end{bmatrix} \tag{5.5}$$

where $i = j, z_{ij} = 1$ $and i \neq j, z_{ij} = \frac{m_i}{m_j}$ $(i, j = 1, 2, 3, \ldots, n)$. In the above matrix 'Z', z_{ij} represents relative toxicity of metal ion' i' (m_i) over metal ion j (m_j) while m_i and m_j, are the crisp values assigned to the linguistic expert's responses. For finding the consistency of decision matrix 'Z', steps 1, 2 and 3 are followed as described below.

Step 1: Find the squared power of matrix 'Z', and its row sum is calculated. Normalize this row sum array to find the vector E_o.

Step 2: Repeat step 1 with the squared matrix and find $(Z^2 \times Z^2)$ followed by calculating the vector array E_1. If the difference between $E_o - E_1$ is close to 'zero', then the E_1 is the eigenvector 'E'. Calculate the eigenvalue λ_{max} using Eq. (5.6)

$$AE = \lambda_{max} E \tag{5.6}$$

Step 3. Calculate the consistency index (CI) using Eq. (5.7) and the consistency ratio (CR) for each decision matrix by using Eq. (5.8)

$$CI = \frac{\lambda_{max} - n}{n-1} \tag{5.7}$$

$$CR = \frac{CI}{RCI} \tag{5.8}$$

where RCI is the random consistency index derived from Saaty (2004). If CR ≤ 0.1, experts are not required to reconsider and revise their judgements.

Step 4. Computation of Interval-Valued Triangular fuzzy Numbers (IVTFN)

After the consistency of the decision matrices is satisfied, IVTFNs are calculated using the Eqs. (5.9-5.14). Each IVTFN number consists of three components: pessimistic, moderate, and optimistic assessment of expert viewpoint for each metal ion.

$$\tilde{L}_{ij} = [(\acute{a}_{ij,} a_{ij}); b_{ij}; (c_{ij}, \acute{c}_{ij})] \tag{5.9}$$

$$\acute{a}_{ij} = Min(L_{ijk}), \forall\, k = 1, \dots, \gamma \tag{5.10}$$

$$a_{ij} = Min(L_{ijk}) + \frac{(\prod_{k=1}^{\gamma} L_{ijk})^{\frac{1}{k}} - Min(L_{ijk})}{2} \tag{5.11}$$

$$b_{ij} = (\prod_{k=1}^{\gamma} L_{ijk})^{\frac{1}{k}} \tag{5.12}$$

$$c_{ij} = Max(L_{ijk}) - \frac{Max(L_{ijk}) - (\prod_{k=1}^{\gamma} L_{ijk})^{\frac{1}{k}}}{2} \tag{5.13}$$

$$\acute{c}_{ij} = Max(L_{ijk}) \tag{5.14}$$

where, $\acute{a}_{ij} \leq a_{ij} \leq b_{ij} \leq c_{ij} \leq \acute{c}_{ij}$; L_{ijk} , represents the relative weight that expert k has given to the toxicity of metal ions ‘i’ over metal ion j, and γ is the total number of experts considered in the study. The single pairwise comparison matrix ($\tilde{Z}^*$) is derived consisting of IVTFN as given in Eq. (5.15).

$$\tilde{Z}^* = \begin{bmatrix} (1,1); 1; (1,1) & (\acute{a}_{12}, a_{12}); b_{12}; (\acute{c}_{12}, c_{12}) & \cdots & (\acute{a}_{1n}, a_{1n}); b_{1n}; (\acute{c}_{1n}, c_{1n}) \\ (\frac{1}{\acute{c}_{1n}}, \frac{1}{c_{1n}}); \frac{1}{b_{1n}}; (\frac{1}{a_{1n}}, \frac{1}{\acute{a}_{1n}}) & (1,1); 1; (1,1) & \cdots & (\acute{a}_{2n}, a_{2n}); b_{2n}; (c_{2n}, \acute{c}_{2n}) \\ \vdots & \vdots & \ddots & \vdots \\ \left(\frac{1}{\acute{c}_{1n}}, \frac{1}{c_{1n}}\right); \frac{1}{b_{1n}}; (\frac{1}{a_{1n}}, \frac{1}{\acute{a}_{1n}}) & \left(\frac{1}{\acute{c}_{2n}}, \frac{1}{c_{2n}}\right); \frac{1}{b_{2n}}; (\frac{1}{a_{2n}}, \frac{1}{\acute{a}_{2n}}) & \dots & (1,1); 1; (1,1) \end{bmatrix} \tag{5.15}$$

Step 5. Estimation of Inter Valued Fuzzy Weight (IVFW) and defuzzification.

The IVFW for the decision criteria from the IVFN is evaluated by Eq. (5.16) and Eq. (5.17). The de-fuzzified weights for each criterion are estimated using Eq. (5.18)

$$\tilde{Y}_i^* = [\tilde{L}_{ij} \otimes \cdots \otimes \tilde{L}_{in}]^{\frac{1}{n}} = (\acute{y}_{1i}, y_{1i}); y_{2i};\ (y_{3i}, \acute{y}_{3i}) \tag{5.16}$$

$$\tilde{M}_i^* = \tilde{Y}_i \otimes \left(\tilde{Y}_i \otimes \cdots \otimes \tilde{Y}_n\right)^{-1} = (\acute{m}_{1i}\,, m_{1i}); m_{2i}; (m_{3i}, \acute{m}_{3i}) \tag{5.17}$$

$$M_i^* = \frac{\acute{m}_{1i} + m_{1i} + 2m_{2i} + m_{3i} + \acute{m}_{31}}{6} \tag{5.18}$$

5.2.3.2 Fuzzy relation matrices and grade functions

The membership functions in the fuzzy set theory are described as $\mu_{ij}(x)$, where x is the actual value of a given metal ion concentration. The membership function $\mu_{ij}(x) = \mu_R(U_i, G_j)$ has two components, G_j represents evaluation class, while U_i is the membership function of the metal ion 'i'. In the Relation Matrix RM, $\mu_{ij}(x)$ represents the value of the membership function for the given metal ion 'i'($i \in [1, m]$ for m number of metal ions) for the evaluation class j ($j \in [1, n]$ for n number of an evaluation class) as is expressed in Eq. (5.19)

$$RM = \begin{bmatrix} \mu_{11}(x) & \mu_{12}(x) & \cdots & \mu_{1n}(x) \\ \mu_{21}(x) & \mu_{22}(x) & \cdots & \mu_{2n}(x) \\ \mu_{31}(x) & \mu_{32}(x) & \cdots & \mu_{3n}(x) \\ \vdots & \vdots & \vdots & \vdots \\ \mu_{m1}(x) & \mu_{m2}(x) & \cdots & \mu_{mn}(x) \end{bmatrix} \tag{5.19}$$

The membership function shape and their value at each grade for all the metal ions concerning TCETP sludge are decided based on the toxicity and previous literature (Bisht et al., 2022) and are represented in Table 5.8. Each criterion is classified into four membership grades G = {G_1: less polluted, G_2: moderately polluted, G_3: severely polluted, and G_4: extremely severely polluted}. For instance, Al, a heavy metal with an acceptable limit in drinking water, is 0.03 mg/l. However, the leachate from the textile sludge is studied, and the concentration of metal ions in the leachate is exceptionally high. Therefore, the opinion of three experts is considered for developing the membership functions and grade classification. Hence, the concentration for Al between 0-22 mg/l is classified into four grades based on expert opinion. The Al concentration is classified into 0-4 mg/l for Less polluted, 2-10 mg/l for medium polluted, 8-22 mg/l for severely polluted and 20-22 mg/l for extremely severely polluted is considered. For the Al, membership functions considered are triangular for grade 1 (i.e., 0, 0, 4), trapezoidal for grade 2 (i.e., 2, 4, 8, 10), trapezoidal for grade 3 (i.e., 8, 10, 20, 22) and triangular for grade 4 (i.e., 20, 22, 22) and is represented in Fig. 5.2. Similarly for all the metal ions considered in this study, the membership functions according to grades based on concentrations are defined in Table 5.3.

Table 5.3 Grade classification of metal ions and their membership functions

Linguistic description of leachate quality	Al	Cu	Cr	Fe	Mn	Ni	Pb	Zn	K	Mg	Ca
Less polluted (LP)	Tri (0, 0, 4)	Trap (0, 0, 0.5, 1)	Tri (0, 0, 0.2)	Trap (0, 0, 0.5, 1)	Tri (0, 0, 2)	Tri (0, 0, 1)	Tri (0, 0, 0.1)	Trap (0, 0, 5, 15)	Tri (0, 0, 200)	Trap (0, 0, 200, 1000)	Trap (0, 0, 400, 1000)
Moderately Polluted (MP)	Trap (2, 4, 8, 10)	Trap (0.5, 1, 3, 3.5)	Trap (0.1, 0.2, 0.9, 1)	Trap (0.5, 1, 3, 3.5)	Trap (1.5, 2, 4, 4.5)	Trap (0.5, 1, 1.5, 2)	Trap (0.05, 0.1, 0.95, 1)	Trap (5, 15, 20, 25)	Trap (100, 200, 400, 500)	Trap (200, 1000, 4200, 5000)	Trap (400, 1000, 4400, 5000)
Severely polluted (SP)	Trap (8, 10, 20, 22)	Trap (3, 3.5, 9.5, 10)	Trap (0.9, 1, 1.9, 2)	Trap (3, 3.5, 5.5, 6)	Trap (4, 4.5, 9.5, 10)	Trap (1.5, 2, 4.5, 5)	Trap (0.95, 1, 1.95, 2)	Trap (20, 25, 30, 35)	Trap (400, 500, 900, 1000)	Trap (4200, 5000, 9200, 10000)	Trap (4400, 5000, 11400, 12000)
Extremely Severely polluted (ESP)	Tri (20, 22, 22)	Tri (9.5, 10, 10)	Tri (1.9, 2, 2)	Tri (5.5, 6, 6)	Tri (9.5, 10, 10)	Tri (4.5, 5, 5)	Tri (1.95, 2, 2)	Tri (30, 35, 35)	Tri (900, 1000,	Tri (9200, 10000,	Tri (11400, 12000,

Linguistic description of leachate quality	Al	Cu	Cr	Fe	Mn	Ni	Pb	Zn	K	Mg	Ca
									1000)	10000)	12000)

LP = Less Polluted, MP = Moderately Polluted, SP = Severely Polluted, ESP = Extremely Severely Polluted, *Tri = Triangular membership function, ** Trap = Trapezoidal membership function.

The membership functions for all the metal ions criteria $(U_1, U_2, U_3 \ldots U_m)$ have been assessed for the four classification grades. The Al membership function value concerning the four grades can be evaluated using Eqs. (5.20-5.23).

$$\mu_{LP}(Al) = \begin{cases} -1 - 0.25\,Al, & 0.0 \le x < 4 \\ 0 & otherwise \end{cases}$$

(5.20)

$$\mu_{MP}(Al) = \begin{cases} 0.5\,Al - 1, & 2 \le Al \le 4 \\ 1 & 4 \le Al \le 8 \\ 5 - 0.5\,Al, & 8 \le Al \le 10 \\ 0 otherwise & \end{cases}$$

(5.21)

$$\mu_{SP}(Al) = \begin{cases} 0.5\,Al - 4, & 8 \le Al \le 10 \\ 1 & 10 \le Al \le 20 \\ 11 - 0.5Al, & 20 \le Al \le 22 \\ 0 & otherwise \end{cases}$$

(5.22)

$$\mu_{ESP}(Al) = \begin{cases} 0.5Al - 10, & 20 \le x \le 22 \\ 1 & x \ge 22 \\ 0 & otherwise \end{cases}$$

(5.23)

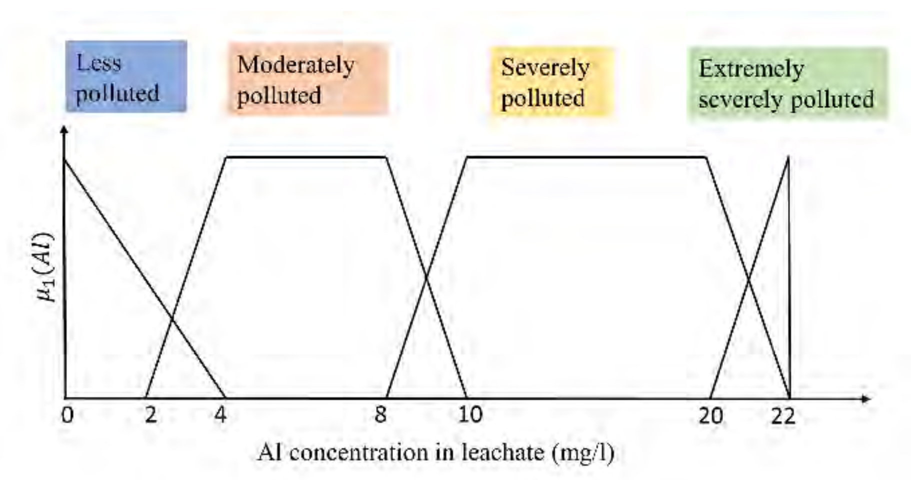


Fig. 5.2 Membership grade function for Al

5.2.3.3 Final rank calculations

After the evaluation of the fuzzy Relationship Matrix (RM) and the Inter Valued Fuzzy Weights (IVFWs), the Fuzzy Assessment Matrix (FAM) is derived. The FAM unifies the collective impact of RM and IVFWs for comparison of different experiment sets. The FAM is derived using Eq. (5.24).

$$FAM = M_i^* * RM = [M_1, M_2, \dots, M_m] * \begin{bmatrix} \mu_{11}(x) & \mu_{12}(x) & \cdots & \mu_{1n}(x) \\ \mu_{21}(x) & \mu_{22}(x) & \cdots & \mu_{2n}(x) \\ \mu_{31}(x) & \mu_{32}(x) & \cdots & \mu_{3n}(x) \\ \vdots & \vdots & \vdots & \vdots \\ \mu_{m1}(x) & \mu_{m2}(x) & \cdots & \mu_{mn}(x) \end{bmatrix} \quad (5.24)$$

$$FAM = \left[F_j\right]_{1\times n} \quad (5.25)$$

where F_j are the elements of FAM for each set of experiments corresponding to all possible grades. The Final Score (FS) at station k is derived using Eq. (5.26).

$$FS_k = \frac{\sum_{j=1}^{n} F_j \alpha_j}{\sum_{j=1}^{n} F_j} \quad (5.26)$$

where α_j are the values assigned to each grade of T-LPI, ranging from 0.25 to 1 based on their comparative importance, as given by Singh et al. (2017). The values for each grade $[\alpha_1, \alpha_2, \alpha_3, \alpha_4 = 0.25, 0.5, 0.75, 1]$ are used for driving the de-fuzzified score for each experimental run. The final score is used for driving the T-LPI and ranking it according to the experimental data. A lower score indicates the less polluted leachate at the considered experiment conditions.

5.2.4 Human health risks assessment

The residents of the textile industry cluster are divided into four categories based on their age, mainly infants (<1 yr), children (1-10 yrs), teens (11-20 yrs), and adults (21-72 yrs). The USEPA HHRA is adopted in this study to measure the health hazard associated with the leaching from textile sludge. The human health risk is evaluated as carcinogenic and non-carcinogenic health hazards considering oral intake and exposure through dermal contact. Each age group and non-carcinogenic risk assessment for each heavy metal is computed. The ingestion risk is associated with the direct intake of polluted water by human beings, and dermal contact by bathing and swimming is considered the direct exposure of polluted water to the skin. The Average Daily

Exposure by Ingestion (ADEI) and Average Daily Exposure by Dermal contact (ADED) was calculated using Eq. (5.27) and Eq. (5.28) in terms of mg/kg/d

$$ADEI_i^j = (C_i^j \times InR \times ExF \times ExD)/(BWt \times AET) \quad (5.27)$$

$$ADED_i^j = \ C_i^j \times SSA \times \ DK_i \times F \times ExF \times ExT \times ExD \times VCF)/(BWt \times AET) \quad (5.28)$$

where, C_i^j is the concentration of ith metal ions in leachate from jth experimental run in mg/l, InR stands for Ingestion Rate, kg/d; ExF is the Exposure Frequency measured in terms of d/yr; ExD is the exposure duration, yr; ExT is the leachate Exposure Time in hr/d; BWt is the Bodyweight of residents of different age group in kg; AET is the Average Exposure Time in d; SSA is the exposed Skin Surface Area in cm^2; DK_i is the Dermal Permeability Coefficient in cm/h; F is the fraction of skin in contact to lecahte and is considered as unitless; VCF is the Volumetric Conversion Factor (l / 1000 cm^3). The input parameter values are adopted from the previous literature and are represented in Appendix E Table E.2 (Mukherjee et al., 2019, 2020; USEPA, 1989).

5.2.4.1 Non-carcinogenic risk assessment

The non-carcinogenic risks of heavy metals are assessed by Hazard Index (HI). The hazard index for the ith metal ion is estimated using Eq. (5.29)

$$HI_i^j = (\ ADEI_i^j\ /RfDing_i) + (ADED_i^j/RfDder_i) \quad (5.29)$$

where $RfDing_i$ and $RfDder_i$ represent the reference dose for the ith heavy metal ions for oral intake and skin absorption. The reference dose ($RfDing_i$ and $RfDder_i$) for Al heavy metals was obtained from Tong et al. (2021), and the other heavy metals were taken from Mukherjee et al. (2020). Dermal permeability coefficient (DK_i) for Pb, Cr, Zn, and Cu are obtained from Zeng et al. (2015), Al, Mn, Fe, and Ni are obtained from Tong et al. (2021) and Wang et al. (2017) as given in AppendixE Table E.3. The HI_i>1 indicates the non carcinogenic adverse impact on human health are likely to occur while HI_i< 1, shows no adverse effect on human health (USEPA, 2004). However the Average Hazard Index ($AvgHI_i$) was calculated by averaging the HQ_i for all the experimental runs for different age groups.

5.2.4.2 Carcinogenic risk assessment

The carcinogenic risk (CR_i) associated with the ith heavy metals for jth experimental run is estimated using Eq. (5.30)

$$CR_i^j = (ADEI_i^j \times CSF_i^{ing}) + (ADED_i^j \times CSF_i^{der}) \quad (5.30)$$

where CSF_i^{ing} and CSF_i^{der} are the ingestion and dermal exposure carcinogenic slope factors for the heavy metals. The ingestion slope factor values of 0.5 and 0.0085 for Cr and Pb $(mg/kg/day)^{-1}$ and the dermal contact slope factor values for Cr and Pb are 13.158 and 0.073 $(mg/kg/day)^{-1}$, respectively. The slope factor values are adopted from the US EPA (2018). The different carcinogenic risk levels are as follows: CR $<10^{-6}$ corresponds to very low risk, $10^{-6} < CR_i < 10^{-5}$ corresponds to low risk, $10^{-5} < CR_i < 10^{-4}$ moderate risk, and $10^{-4} < CR_i < 10^{-3}$ indicates high, and $CR_i > 10^{-3}$ corresponds to very high cancer risk (Ma et al., 2022; Şimşek et al., 2022; US EPA, 1989). The average CR_i is calculated by averaging the CR_i values for all the experimental runs for different age groups.

5.3 Results and discussions

5.3.1 Statistical analysis

The chemical composition, mainly the metal ions in the TCETP sludge, is determined from the XRF analysis in Table 5.4. The metal ions concentration in the leachate is found using the ICP-OES technique. The statistical analysis of metal ions concentrations is represented in Table 5.4 and Fig. 5.3. The average metal ion concentration of the sludge increased in the following order Cr < Pb < Fe < Mn < Ni < Cu < Al < Zn and alkali metal ions K < Ca < Mg. Some heavy metal ions, such as Al, Cu, and alkali metal ions, such as K, Mg, and Ca, have shown higher standard deviations due to differences in the experimental conditions for the TCLP test. The mean concentrations of all the metal ions considered in the study are higher than the admissible concentrations as defined by well-known standards (BIS (2012) and WHO (2011)).

Table 5.4 Metal ions concentration found in the XRF, TCLP test leachate and the corresponding permissible limits.

Elements	XRF	TCLP (mg/l)			Desirable drinking water limit as per WHO	Drinking Water specifications as per BIS (10500:2012)-Acceptable limits (mg/l)
		Minimum	Maximum	Mean ± SD (mg/l)		
Al	3.598	1.4	32.7	17.29 ± 8.44		0.03
Cu	0.495	1.4	9.3	5.25 ± 2.04	2	0.05
Cr	0.090	0.1	0.4	0.19 ± 0.08	0.05	0.05
Fe	3.616	0.1	3.4	0.87 ± 0.84	0.4	0.3
Mn	0.078	1.1	8	2.65 ± 1.44	0.04	0.1
Ni	0.011	1.1	9.1	2.75 ± 1.047	0.07	0.02
Pb	0.006	0.1	1.6	0.69 ± 0.509	0.01	0.01
Zn	0.686	11.8	22	17.48 ± 2.75	4	5
K	0.639	106	1135	484.9 ± 217.09	12	-
Mg	12.612	1592	11857	6483 ± 2827.67	150-300	-
Ca	55.621	1153	12962	6433.9 ± 3565.2	150-300	75

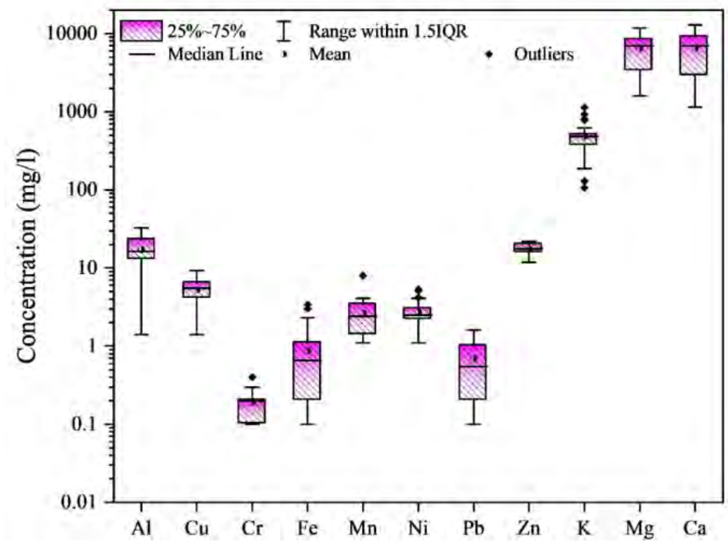


Fig. 5.3 The variation of heavy metal and alkali metal ions in textile sludge TCLP leachate

As demonstrated in Fig. 5.4, Pearson's correlation analysis examines the positive and negative association between the metal ions. The color symbolizes the correlation coefficient, red denotes the positive, white suggests no correlation and blue indicates the negative correlation. The bubble size shows the correlation coefficient value (r). The significant positive correlations at (p <= 0.1) are observed between Al and Cr (0.35), Cu and K (0.39), Mn and Ca (0.58), Mn and Mg (0.49), K and Mg (0.34), Fe and Ni (0.32) Mg and Ca (0.74). The positive correlation signifies a common source of origin and identical behavior(Elif Yakamercan et al., 2021). Significant negative correlations at p <= 0.1 were observed between Al and Cu (-0.38), Fe and Ca (-0.42), Fe and Mg (-0.37), Ni and Ca (-0.36), and Fe and Mn (-0.39). The Pb does not show any significant correlation with other metal ions. A negative correlation indicates the existence of different sources, mainly different chemicals and dyes (Jiang et al., 2022). However, in the study, the low Pearson's correlation coefficient value for the heavy metal ions and alkali metal ions K signifies different sources for their existence. The high correlation between Mg and Ca indicates common sources of their existence.

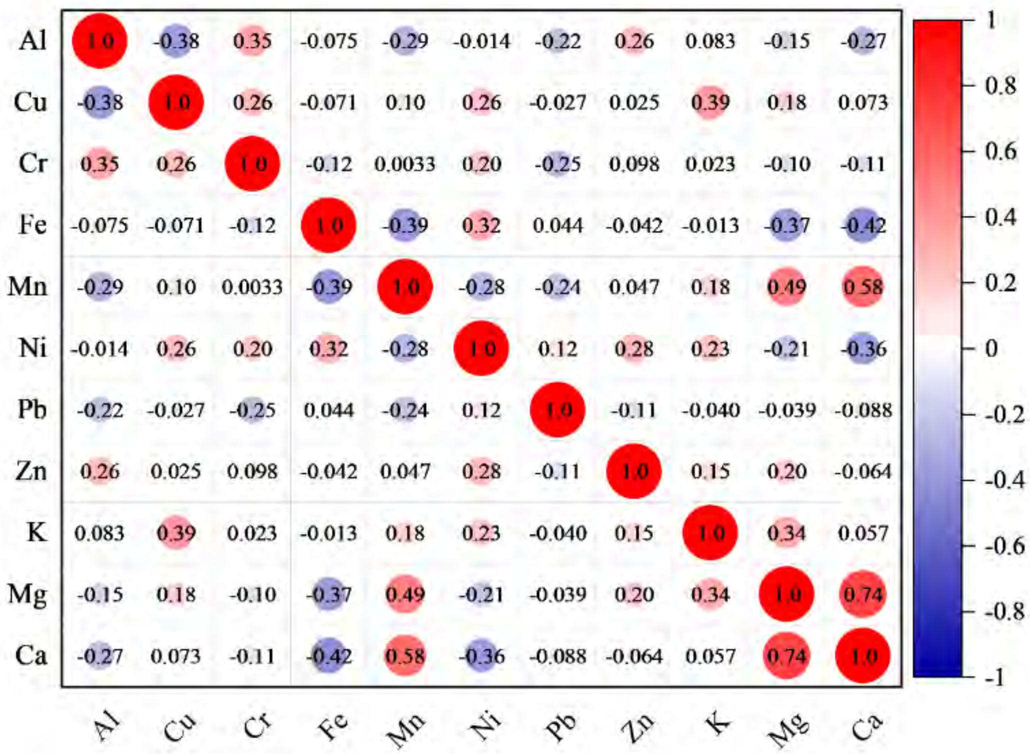


Fig. 5.4 Pearson's correlation analysis of metal ions in leachate from TCETP sludge

This study used the HCA to cluster the metal ions and identify their possible source. The HCA clusters are formed, and the nearest neighbor method is applied to Pearson's correlation distance type. The HCA dendrogram is shown in Fig. 5.5. The heavy metal and alkali metal ion content based on the dendrogram can be divided into one cluster with four groups, and a singleton is formed. Al and Cr have less distance and are clustered in one group, Fe, Ni and Zn are clustered in the second group, Cu and K in the third group, while Mn, Mg and Ca are clustered in the fourth group. The Pb is a singleton joining at the end to form one cluster.

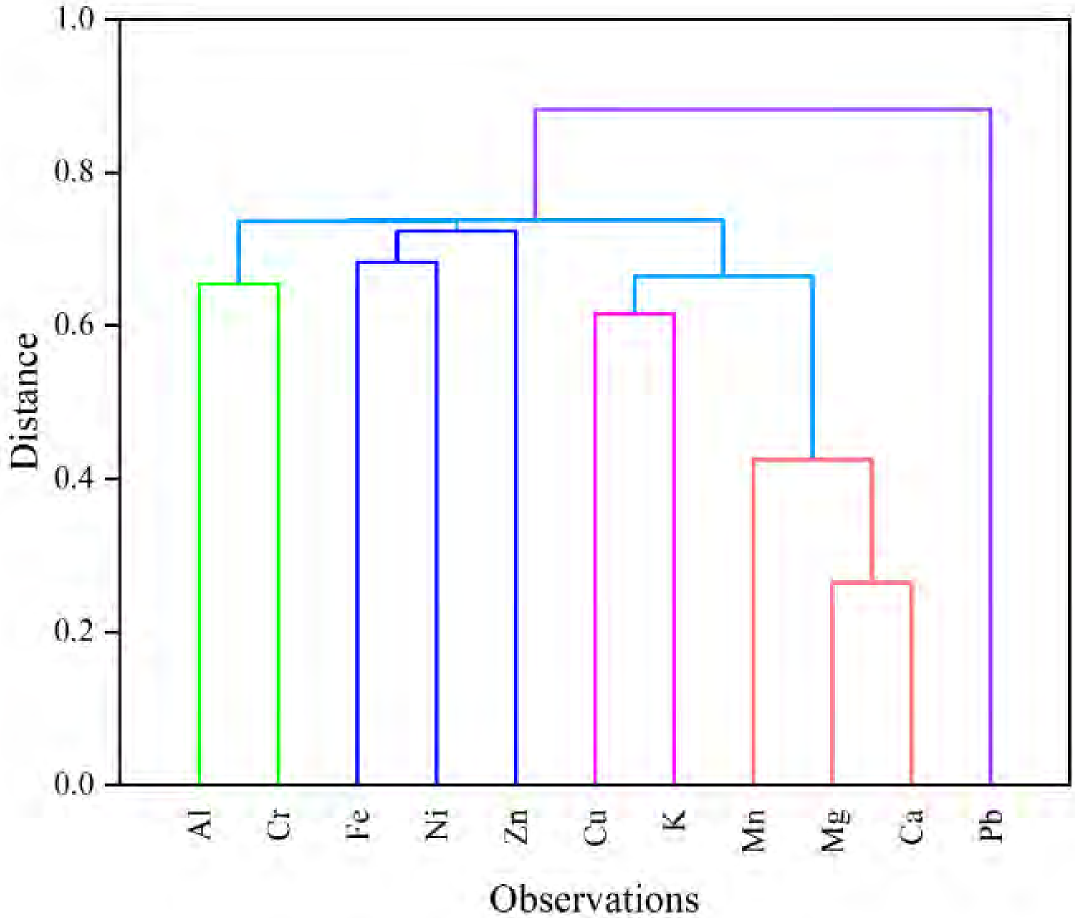


Fig. 5.5 Dendrogram for the metal ions found in leachate

5.3.2 Textile-leachate pollution index

The stakeholder opinion is gathered through the questionnaire in linguistic form and converted to numerical form using Table 5.2. Three pairwise comparison matrices are constructed, and the consistency of each matrix is checked using Eqs. (5.5-5.8). Finally, the IVFW is calculated by applying Eqs. (5.9-5.14), and the single pairwise matrix is constructed. The de-fuzzfied weights for the metal ions are presented in Table 5.5 and Fig. 5.6. The weights are evaluated on a scale of 0-1, with 0 being "least important" and 1 being "extremely important". It is evident from the findings that the relative weight scores are as follows: Al > Pb > Ni > Fe > Cr > Cu > Mn > K > Zn > Mg > Ca. The higher Al score is mainly due to Al's excessive presence in sludge, as alum is used extensively in coagulation and flocculation procedures while treating the textile industry effluent. Therefore, a higher amount of Al concentration is found in all thirty TCLP test results.

Table 5.5 The fuzzy weights matrix (M_i^*)for the metal ions obtained using the IVTFN

Metal ions	Fuzzy weight using IVTFN	De-fuzzified weights	Rank
Al	(0.162, 0.16, 0.11, 0.175, 0.175)	0.1502	1
Cu	(0.094, 0.086, 0.092, 0.089, 0.089)	0.0912	6
Cr	(0.115, 0.118, 0.101, 0.111, 0.109)	0.1086	5
Fe	(0.121, 0.13, 0.102, 0.123, 0.123)	0.1153	4
Mn	(0.083, 0.076, 0.091, 0.078, 0.078)	0.0838	7
Ni	(0.154, 0.148, 0.111, 0.136, 0.132)	0.132	3
Pb	(0.14, 0.138, 0.124, 0.168, 0.178)	0.147	2
Zn	(0.042, 0.041, 0.073, 0.039, 0.038)	0.051	9
Mg	(0.024, 0.027, 0.06, 0.02, 0.019)	0.0344	10
Ca	(0.022, 0.027, 0.06, 0.02, 0.019)	0.0338	11
K	(0.043, 0.05, 0.076, 0.04, 0.039)	0.0526	8

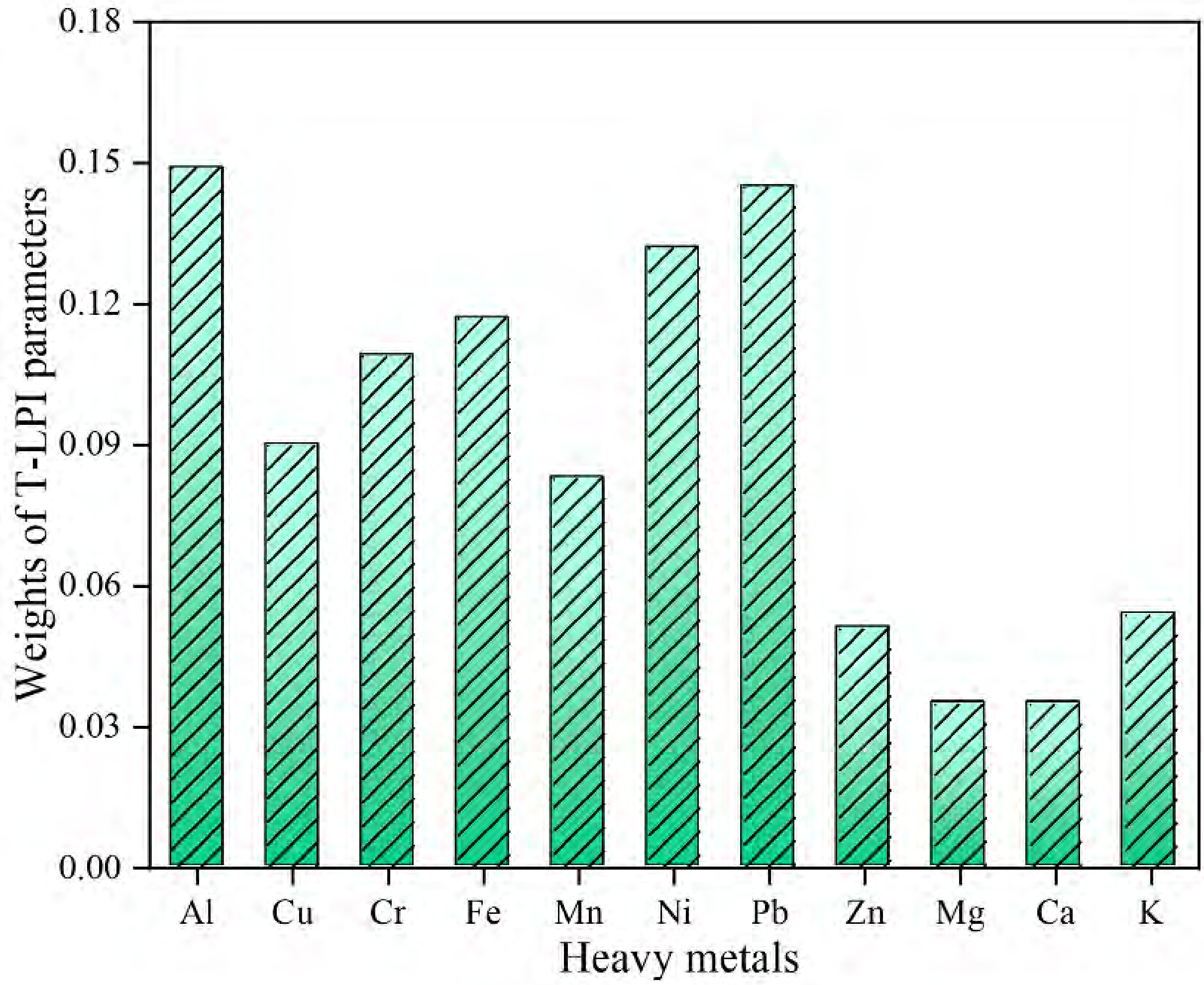


Fig. 5.6 The de-fuzzified IVFWs of the metal ions present in leachate

The membership functions corresponding to four classification grades for all the pollutants considered have been derived as given in Table 5.3. The membership function value of the criteria U_i (metal ions) for each grade, G_j corresponds to different experimental runs (S_i) for the different metal ions, and the fuzzy relation matrix is constructed as given in Eq. (5.19). It is worth mentioning that the data set of thirty experimental data can be considered as thirty different sites, and the ranking of sites for earlier disposal of sludge can be performed. The membership function value for the four metal ions concerning grade classifications is represented in Table 5.6. For instance, the Al concentration for the S_1 is 19.1 mg/l which belongs to the severely polluted grade, i.e., G_3. The membership function value for the G_3 between 10-20 mg/l is 1.

Table 5.6 Fuzzy relation matrix values for each sampling data (S_i) for each heavy metal

Metal ions	Fuzzy relation matrix
Al	$\begin{array}{c} \\ G_1 \\ G_2 \\ G_3 \\ G_4 \end{array}\begin{array}{c} \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{bmatrix} 0 & 0.65 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ 1 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 1 \end{bmatrix} \end{array}$
Cu	$\begin{array}{c} \\ G_1 \\ G_2 \\ G_3 \\ G_4 \end{array}\begin{array}{c} \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{bmatrix} 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ 1 & 1 & \cdots & 1 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$
Cr	$\begin{array}{c} \\ G_1 \\ G_2 \\ G_3 \\ G_4 \end{array}\begin{array}{c} \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{bmatrix} 0 & 1 & \cdots & 0 \\ 1 & 0 & \cdots & 1 \\ 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$
Fe	$\begin{array}{c} \\ G_1 \\ G_2 \\ G_3 \\ G_4 \end{array}\begin{array}{c} \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{bmatrix} 0 & 0 & \cdots & 1 \\ 0 & 0.2 & \cdots & 0 \\ 1 & 0.8 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$

The IVFWs obtained for the metal ions are used to calculate the Fuzzy Assessment matrix (FAM) by substituting the weights in the fuzzy relation matrix in Eq. (5.24). The FAM for the four metal ions Al, Cu, Cr and Fe is given in Table 5.7. For instance, FAM matrix calculations for the experimental run S_1, S_2, S_3, S_4, S_5, …, S_{30} for the Al ions are given in Eq. (5.31).

$$FAM = M_i * RM = [0.152*1, 0.152*0.65, 0.152*1, 0.152*1, 0.152*1, \ldots, 0.152*1] \qquad (5.31)$$

Table 5.7 Fuzzy assessment matrix for the heavy metal

Metal ions	Fuzzy Assessment Matrix (FAM)
Al	$\begin{array}{c c} & \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{array}{c} G_1 \\ G_2 \\ G_3 \\ G_4 \end{array} & \begin{bmatrix} 0 & 0.09763 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ 0.1502 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0.1502 \end{bmatrix} \end{array}$
Cu	$\begin{array}{c c} & \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{array}{c} G_1 \\ G_2 \\ G_3 \\ G_4 \end{array} & \begin{bmatrix} 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ 0.0912 & 0.0912 & \cdots & 0.0912 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$
Cr	$\begin{array}{c c} & \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{array}{c} G_1 \\ G_2 \\ G_3 \\ G_4 \end{array} & \begin{bmatrix} 0 & 0.1086 & \cdots & 0 \\ 0.1086 & 0 & \cdots & 0.1086 \\ 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$
Fe	$\begin{array}{c c} & \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{array}{c} G_1 \\ G_2 \\ G_3 \\ G_4 \end{array} & \begin{bmatrix} 0 & 0 & \cdots & 0.1153 \\ 0.1153 & 0.2306 & \cdots & 0 \\ 0 & 0.9224 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{bmatrix} \end{array}$

The elements of the matrix a $F_j * \alpha_j$ and $\sum_{j=1}^{n} F_j$ for the calculations of the final FS, the matrix is given in Eq. (5.32) and Eq. (5.33)

$$F_j * \alpha_j = \begin{array}{c c} & \begin{array}{cccc} S_1 & S_2 & \cdots & S_{30} \end{array} \\ \begin{array}{c} G_1 \\ G_2 \\ G_3 \\ G_4 \end{array} & \begin{bmatrix} 0.0048 & 0.0599 & \cdots & 0.0288 \\ 0.2457 & 0.0711 & \cdots & 0.2293 \\ 0.5074 & 0.3267 & \cdots & 0.3453 \\ 0 & 0.132 & \cdots & 0.1502 \end{bmatrix} \end{array} \tag{5.32}$$

$$\sum_{j=1}^{n} F_j = [0.999 \quad 0.8970 \quad \ldots \quad 0.999] \tag{5.33}$$

The final score (FS) is calculated using Eq. (5.26) and is represented in Table Z. The sample calculation for estimating the final score for FS_1 is shown in Eq. (5.34). The final scores for the different experimental runs are presented in Table 5.8.

$$FS_1 = (0.00408 + 0.245778 + 0.507468 + 0) / 0.9999 = 0.757 \quad (5.34)$$

Table 5.8 Final score for the different experimental runs

Experiment no.	De-fuzzified weights	Rank
FS_1	0.757	10
FS_2	0.657	26
FS_3	0.634	28
FS_4	0.735	14
FS_5	0.781	4
FS_6	0.734	15
FS_7	0.779	5
FS_8	0.755	11
FS_9	0.762	8
FS_{10}	0.654	27
FS_{11}	0.772	6
FS_{12}	0.76	9
FS_{13}	0.797	3
FS_{14}	0.836	1
FS_{15}	0.693	25
FS_{16}	0.731	16
FS_{17}	0.729	18

Experiment no.	De-fuzzified weights	Rank
FS_{18}	0.768	7
FS_{19}	0.729	17
FS_{20}	0.722	21
FS_{21}	0.727	19
FS_{22}	0.724	20
FS_{23}	0.75	13
FS_{24}	0.812	2
FS_{25}	0.63	29
FS_{26}	0.703	24
FS_{27}	0.62	30
FS_{28}	0.721	22
FS_{29}	0.707	23
FS_{30}	0.754	12

The de-fuzzified score for the different experiment runs is presented in Table 5.8. The first five rankings are $FS_{14} > FS_{24} > FS_{13} > FS_5 > FS_7$. The higher de-fuzzified score for FS_{14}, FS_{13}, FS_5 and FS_7 is due to higher Al, Ni, and Pb content in the leachate of the sludge. The higher weights for these three metals contribute to the higher score indicating higher toxicity. The higher score for the FS_{24} is mainly due to high Al, Cr, Ni, and Pb concentrations in the leachate.

The concentration of Al, Ni, and Pb heavy metal ions is mainly responsible for the higher score of the experiment run. Further, heavy metals in the sludge could contaminate the groundwater and surface water. The ingestion of these heavy metals may result in carcinogenic, respiratory, skin, and gastrointestinal diseases, congenital disabilities, and nervous system disorders (Izah et al., 2016).

5.3.3 Human health risk assessment

A human health risk assessment was performed to quantify the risk level of heavy metals in leachate and possible surface water contamination. The estimated average hazard index values ($AvgHI_i$) for Cu, Ni, Fe, Mn, Al, Ni, Pb, and Zn and the average carcinogenic risk ($AvgCR_i$) of Cr and Pb values for the four different age groups considering the ingestion and dermal pathways are presented in Fig. 5.7 (a) and Fig. 5.7 (b), respectively. The hazard index values decreased in the order of Pb> Mn> Ni> Cu>Zn>Cr>Al>Fe. The level of risk is maximum for infants and children, while the risk is almost similar for teens and adults. It indicates that children and infants are more susceptible to non-carcinogenic health than adults. The hazard index for Fe and Al for all the age groups is less than 1, which indicates no potential non-carcinogenic impact. In a similar vein, other metal ions may produce a potential non-carcinogenic impact on human health.

The CR values due to Pb for all age groups lie in the $10^{-4}< CR < 10^{-3}$, indicating the high-risk level. The CR values for all age groups aremore significant than $CR > 10^{-3,}$ lying in a very high carcinogenic risk level. The long-term consumption of leachate-polluted surface water and its dermal contact may result in cancer.

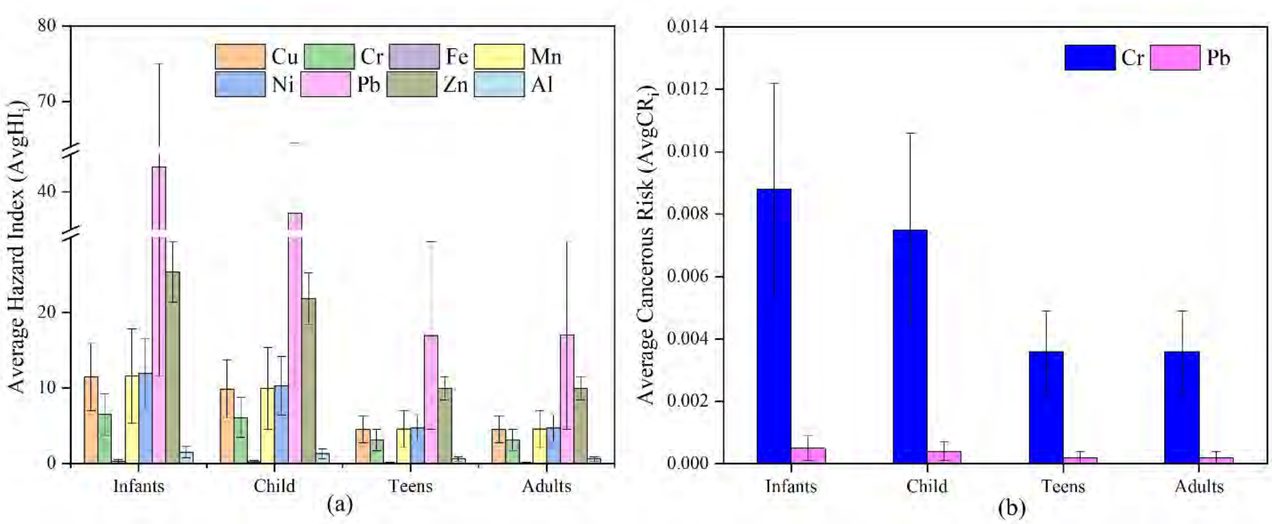


Fig. 5.7(a) Average hazard index and (b) average carcinogenic risk of the metal ions for different age groups

5.4 Summary

This research study on textile sludge examines the possible potential of heavy metal dissolution from it. TCLP experiments were performed, and the pollution potential of the leachate was calculated using T-LPI. T-LPI is a mathematical model developed using hybrid FAHP to estimate the toxicity behavior of leachate. This chapter also describes the human risks associated with dermal contact and ingesting leachate-contaminated surface water. Results indicate carcinogenic risk for all the age groups considered in the study. It suggests that stabilization/solidification of sludge is necessary to reduce the dissolution of heavy metals. The next chapter of the thesis focuses on utilizing this sludge as a building material to provide an environment-friendly solution for reducing the sludge amount and using it as a resource.

Chapter 6

Effective re-utilization of textile sludge from common effluent treatment plant with mineral admixture in cement mortar mixes

6.1 Introduction

The TCETP sludge has chromium (Cr), zinc (Zn), lead (Pb), and other hazardous chemicals, as discussed in Chapter 5. The typical discarding methods, such as open dumping, landfilling, and incineration, are not recommended due to the hazardous nature of the textile sludge since they result in secondary pollution in the form of leachates. This leachate is carcinogenic for all age groups considered for the study, as examined in Chapter 5. Therefore, finding a distinct approach to reduce immobilizing hazardous compounds and heavy metals through solidification and stabilization is crucial (Patel & Pandey, 2012). It is, therefore, imperative to find a sustainable use by converting industrial waste into a resource and its reuse such that it stabilizes hazardous chemical compounds (Goyal et al., 2022). One such approach is to use the TCETP sludge as a partial substitute for construction materials. Over the years, researchers have investigated the reuse potential of the TCETP sludge as a partial replacement for several building material components such as fine aggregate, clay in bricks and cement in mortar and concrete.

In the literature review discussed in Chapter 2, textile sludge is reported to have lower silica, which results in poor pozzolanic activity on addition in the cement mixes (Goyal et al., 2019). However, the mineral admixture from the agricultural waste rich in silica, i.e., Sugarcane Bagasse Ash (SBA), is added to improve the pozzolanic activity by providing silica needed for converting CH into secondary CSH in the later stages of mortar mixes. SBA is responsible for developing secondary CSH gel and improving the cement mixes' strength, permeation and durability properties (Minnu et al., 2021).

The use of TCETP sludge and SBA as the building material might benefit society in several ways; (1) the stabilization and safe disposal of hazardous textile effluent sludge and conversion into a stable product; (2) the use of agricultural waste SBA as a mineral admixture in mortar mixes reduces the landfill issue of the SBA; (3) the study curbs exploitation of natural resources as the construction material by using the sludge and SBA as a replacement for conventional building material;(4) the majority of earlier research has been on weight replacement of building materials with TCETP sludge and SBA despite the difference in the specific gravity of cement and sludge, SBA.

This chapter consists of four sections; the first is section 6.1, which introduces the need for sludge solidification/stabilization. It is followed by section 6.2 of the methodology consisting of the physio-chemical characterization of materials, mix proportion, and the test procedures for determining strength, leaching and durability properties. The third section, i.e. section 6.3, has results and discussion for the experimental study and is followed by section 6.4 of concluding remarks.

6.2 Methodology

6.2.1 Material

The study uses commercially available Ordinary Portland Cement (OPC) 43 as the binder material for cement mortar mixes (IS:8112, 2013)**.** Textile sludge was obtained from the CETP of Balotra and is blue. Sludge preprocessing includes air drying followed by over-drying for 24 h at 105 ℃ to remove excess moisture and ground using the tumbling mill. It is sieved through 90 µm (Goyal et al., 2019). The raw and processed TCETP sludge is presented in Fig. 6.1. SBA was obtained from Awadh Sugar Mills Ltd. company in Uttar Pradesh. The SBA was also dried for 24 h in the oven at 105 ℃ and sieved through 90 µm, as depicted in Fig. 6.2 (Patil et al., 2020). Dried sludge, cement and SBA samples are investigated for their chemical composition using X-Ray Fluorescence (XRF) analysis. The physicochemical properties of the binder materials (cement, TCETP sludge, and SBA) are given in Table 6.1. Mineralogical constituents of sludge and SBA, determined by the X-Ray Diffraction (XRD) technique, are given in Fig. 6.3. The XRD peak analysis of the sludge shows the presence of calcium carbonate, silica oxide, zinc oxide, ferric oxide, chromium, and aluminium oxide. The fingerprint of the SBA shows that silica oxide is the main component. Fig. 4 depicts the Scanning Electron Microscopy (SEM) analysis of sludge and the SBA. The SEM images show the irregular-shaped particles for the sludge and the porous, flaky particles for the SBA. The specific surface area of the cement, sludge, and SBA is measured by the Brunauer-Emmett-Teller (BET) analyser. The specific gravity was measured per IS 4031 (part 11) (1988). Results indicate that sludge has low specific gravity and high specific surface area.

Coarse aggregate, mainly sand comprising of three grades of particles passing through a 2 mm, 1 mm, and 500 µm sieve and retained on a 1 mm, 500 µm, and 90 µm sieve, respectively, are used in the study to prepare the mortar mixes (IS:650, 1991). All these three sizes of sand are mixed in equal proportion for each mortar mix. The mortar mixtures use potable water (IS: 456, 2000).

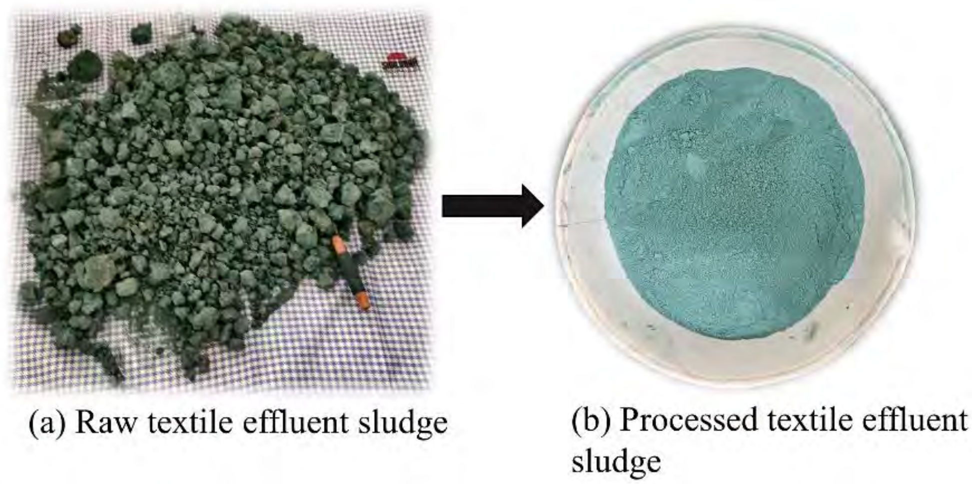


Fig. 6.1 TCETP sludge (a) raw (b) processed

Fig. 6.2 Sugarcane bagasse ash (a) sieved (b) flaky particles

Table 6.1 Physicochemical properties of binder materials (cement, TCETP sludge and SBA)

Chemical Properties			
Compounds	**Cement**	**TCETP sludge**	**SBA**
CaO	64.91	52.222	6.829
SiO_2	20.62	13.403	70.529
Al_2O_3	4.794	5.590	3.025
Fe_2O_3	3.409	3.222	4.424
K_2O	1.025	0.534	8.338
MgO	3.6	-	-
Na_2O	1.04	-	1.482
P_2O_5	0.10	-	3.939
TiO_2	0.21	0.217	0.479
Loss on ignition	2.18	29.74	13.32
Physical Properties			
Specific Surface area	0.3291	22.89	2.14
Specific Gravity	3.17	2.29	1.78
Color	Grey	Blue-green	Dark grey

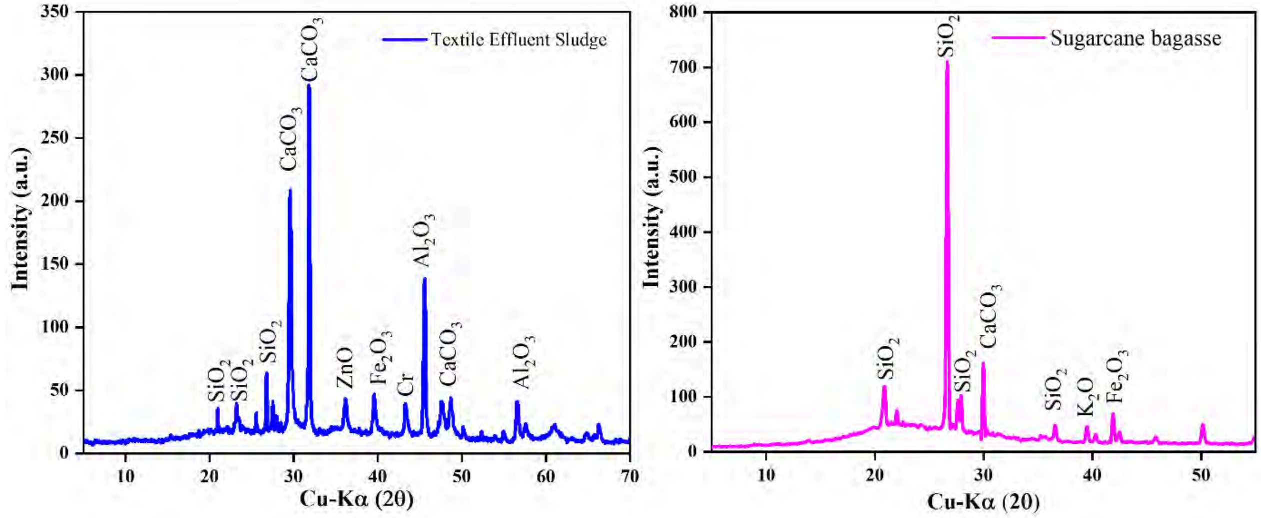


Fig. 6.3 XRD fingerprints of (a) TCETP sludge (b) Sugarcane Bagasse Ash

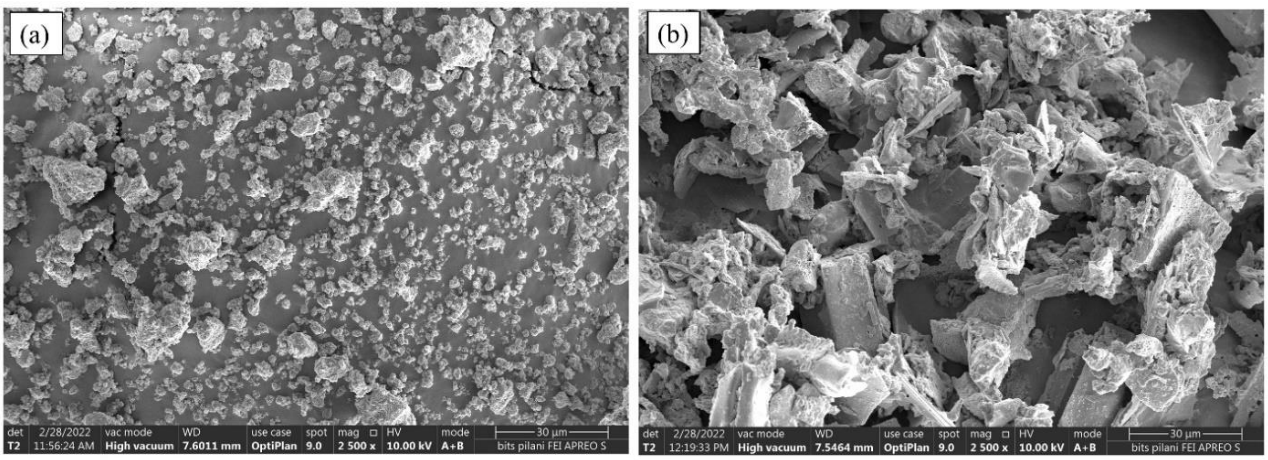


Fig. 6.4 SEM images of (a) TCETP sludge (b) Sugarcane Bagasse Ash

6.2.2 Mortar mix proportions

Thirteen mortar mixes are prepared to study the feasibility of partial cement replacement with TCETP sludge and sludge-SBA in mortar mixes. The control mix is designated as CM. The cement was replaced by sludge at 2.5%, 5%, 7.5%, and 10%, whereas SBA at 5% and 10% by volume. The mortar sample preparation, mixing and curing were performed as per IS: 4031 (Part 8) (2005). The prepared mortar specimens were investigated for their strength, permeation, durability, and microstructure properties. The water-to-cement (w/c) ratio for the 13 mortar mixes is maintained at 0.44, 0.46, and 0.48 based on the standard consistency test performed on the cement-sludge-bagasse pastes under IS: 4031 (Part 4) (1988). During the preliminary study, the sludge and SBA absorb the water due to the high specific surface area, reducing the consistency of the mixes. Therefore, excess water is required for adequate standard consistency of the mixes at high replacement. The binder to the sand ratio (b/s) is maintained constant at 1: 3 following the IS: 4031 (Part 6) (2005). The details of the considered mixes are given in Table 6.2.

Table 6.2 Mix proportions of mortar mixes

Mix Notations	% cement replaced		Mix proportion (g)				
	TCETP sludge	SBA	Cement	Sand	TCETP sludge	SBA	water/cement
CM	0	0	200	600	0	0	0.44
2.5T	2.5	0	195	600	3.61	0	0.44
5T	5	0	190	600	7.22	0	0.44
7.5T	7.5	0	185	600	10.83	0	0.46
10T	10	0	180	600	14.44	0	0.46
2.5T5S	2.5	5	185	600	3.61	5.61	0.46
5T5S	5	5	180	600	7.22	5.61	0.46
7.5T5S	7.5	5	175	600	10.83	5.61	0.46
10T5S	10	5	170	600	14.44	5.61	0.46
2.5T10S	2.5	10	175	600	3.61	11.23	0.48
5T10S	5	10	170	600	7.22	11.23	0.48
7.5T10S	7.5	10	165	600	10.83	11.23	0.48
10T10S	10	10	160	600	14.44	11.23	0.48

6.2.3 Test procedures

The strength, durability, and leaching properties of the 13 cement mortar mixes are evaluated. The following describes the test methods used to investigate each property:

6.2.3.1 Strength testing

The performance of mortar mixes is examined for compressive, flexural, and split tensile strength tests at 7, 28 and 90 days of immersed water curing. For compressive strength, nine cubes of 70.6 mm were cast for each mix and tested per the procedure mentioned in IS: 4031 (Part 6) (2005). Split tensile strength is an alternate method to measure tensile strength, and flexural strength is the measure of tensile strength during bending. The prismatic specimens (beams) of size 160 mm × 40 mm × 40 mm were prepared and tested for flexural strength, and 100 mm × 50 mm (diameter × height) cylindrical samples were prepared and tested for split tensile strength test (Abraham & Ransinchung, 2019; ASTM C78, 2019). It is worth mentioning that an average of three specimens are considered for strength testing. Fig. 6.5 depicts the experimental setups for the strength testing. A total of 351 specimens having 117 cubes, beams and cylinders each, were prepared for the strength test.

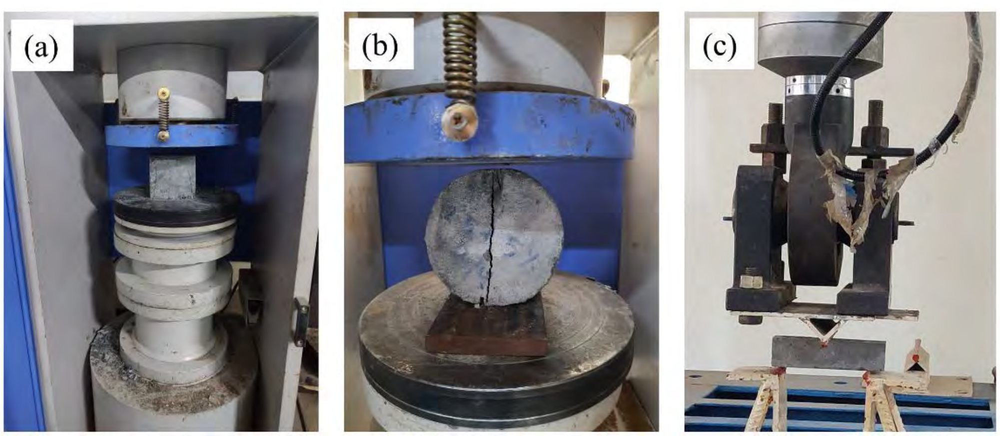


Fig. 6.5 Strength test setup (a) compressive (b) tensile (c) flexural

6.2.3.2 Permeation study

The permeation characteristics of the mortar mixes are assessed using the sorptivity test was conducted as per ASTM C1585 (2013). For sorptivity tests, two cylindrical specimens of 100 mm × 50 mm (diameter × height) are prepared for each mix. The experimental setup for the sorptivity test is represented in Fig. 6.6.

For the sorptivity test, the specimens are placed in the environment chamber (temperature of 50 ± 2 °C,relative humidity of 80 ± 3%) for 3 days. Then the samples are placed in the sealable container for the remaining time. The age of the samples at the time of testing is 28 days. The circumference of the specimens is covered with Aluminium tape, and the top surface is covered with silicon sealant so that capillary water absorption can take place from only one surface, which is in contact with the water.

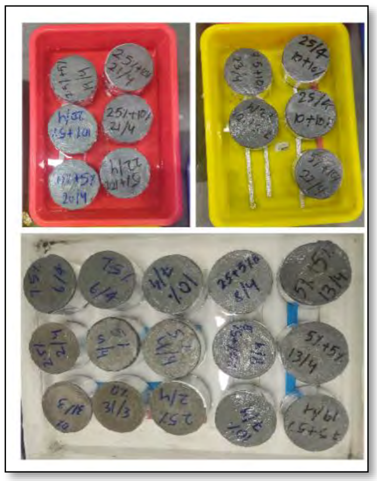


Fig. 6.6 Experimental setups for the sorptivity test.

6.2.3.3 Durability study

The durability study is mainly performed to study the resistance to adverse conditions to which the mortar may be exposed during its service life. The cement mortar mixes could deteriorate in contact with sulphate present in water or soil. The durability study for sulphate resistance is done by immersing the three cubes of 70.6 mm in a 5% magnesium sulfate ($MgSO_4$) solution for 90 days, including 28 days of moist curing per ASTM C1012 (2004). The experimental setup for the durability test is presented in Fig. 6.7

Fig. 6.7 Experimental setup for a durability test

6.2.3.4 Alkalinity, carbonation, and leaching study

Measuring the pH of mortar mixtures is crucial because their acidic nature may degrade the passive layer around the steel rebars in reinforced concrete. The pH of the mortar mixes is tested by mixing 30 gm of crushed samples from the 28 days compressive strength (passing through a 300 µm sieve) in 100 ml of deionized water (Goyal et al., 2022). The pH is measured using the pH electrode manufactured by Hanna instruments. The carbonation of the mortar mixes is checked by spraying the solution of phenolphthalein indicator (1% solution) on the freshly split beam surfaces after the flexural test at 28 and 90 days (Abraham & Ransinchung, 2022). The phenolphthalein indicator changes colour in the pH range of 8.2-10.

The Toxicity Characteristics Leaching Procedure (TCLP), in compliance with USEPA method 1311, 1992, was used to conduct the leaching investigation of the heavy metals from all cement mortar mixtures (US EPA, 1992). As per the USEPA 1311, for the sample with initial pH > 5, the extraction fluid is made by diluting 5.7 ml of glacial acetic acid with 1 L of millipore water. The pH of the extraction fluid should be preserved at 2.88 ± 0.5. The 5 g of mortar specimens from each mix from the 28-day compressive strength test are crushed and sieved through the 300 µm standard sieve. The solid crushed sample to extraction fluid ratio for each batch experiment is kept at 1:20. The batch experiments are performed by mixing 5gm of the sample with 100 ml of extraction fluid in a 250 ml Erlenmeyer flask. Each flask is kept in the orbital shaker for horizontal shaking at 180 r.p.m and 18 h at 25 °C. After shaking, the mixture is filtered through a 0.45µ filter paper, as shown in Fig. 6.8, followed by filtration using 0.22 µ syringe filters. This filtrate is acidified using the HNO_3 to a pH of less than 2 and is preserved in 50 ml centrifuge tubes. Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES) is used to detect the presence and concentration of heavy metals in the filtered leachate. Data is compared to WHO and Indian Standard Drinking Water Specification, 2012 (BIS, 2012).

Fig. 6.8 Experiments performed for heavy metals leaching from mortar mixes

6.2.3.5 Microstructure of the mixes

The microstructure properties of the mortar mixes were studied on the broken specimens of the 28-day compressive strength test. These broken samples are stored in bottles containing acetone. The SEM analysis assists in studying the modification in the morphology of mortar mixes with the addition of TCETP sludge and SBA. Image J software is used to analyse SEM images and pore area is calculated for the mixes. Similarly, XRD fingerprinting for the mortar mixes is also performed. After the 28-day compressive strength test, the mortar mixes are ground using mortar and pestle and sieved through a 75 μm sieve before testing for XRD.

6.3 Result and Discussions

6.3.1 Strength properties

The strength of modified mortar mixes at 7, 28 and 90 days of moist curing is depicted in Fig. 6.9. As seen from Fig. 6.9, there was an increase in the strength of the mortar specimen with age; though, there was a decrease in strength for all the modified mortar mixes. The 28 days stipulated compressive strength for the cement mortar mixes using the OPC 43 cement is 43 MPa (IS: 456, 2000). Mixes 5T5S and 7.5T5S have achieved 93.27% and 95.66% of characteristic strength of 43MPa of the control mix strength. The binary mixes 2.5T, 5T, 7.5T and 10T with only the sludge as cement replacement material have gained compressive strength of 85.03%, 84.38%, 84.81% and 75.92 % of the control mix. The tertiary mixes 2.5T5S, 5T5S, 7.5T5S, and 10T5S have achieved strength of 91.75%, 93.27%, 95.66% and 91.5% of the control mix, respectively. The tertiary mixes 2.5T10S, 5T10S, 7.5T10S and 10T10S have a compressive strength of 89.80%, 89.37%, 73.75% and 68.54% of the control mix, respectively. The addition of 5% of SBA with sludge has improved the strength of the mixes, and a significant increase is observed in long-term strength (90 days).

The modified mortar mixes are also tested for split tensile and flexural strength, as depicted in Fig. 6.9 (b, c) and are compared with the 28-day strength of the control mixes. The binary mixes 2.5T, 5T, 7.5T and 10T have achieved 91.15%, 89.2% 68.368% and 62.234%, tertiary mixes 2.5T5S, 5T5S, 7.5T5S, 10T5S have 92.64%, 95.44%, 98.05%, 91.347% and the mixes 2.5T10S, 5T10S, 7.5T10S and 10T10S have 90.142%, 78.97%, 56.364% and 51.632% of the control mix split tensile strength (4.565 MPa) respectively. The maximum and minimum split tensile strength of 4.556 MPa and 2.357 MPa is achieved by the 7.5T5S and 10T10S mortar mixes, respectively. The binary mixes 2.5T, 5T, 7.5T and 10T have achieved 89.314%, 88.4% 71.02% and 64.074%, tertiary mixes 2.5T5S, 5T5S, 7.5T5S, 10T5S have 94.11%, 95.469%, 97.073% and the mixes 2.5T10S, 5T10S, 7.5T10S and 10T10S have 89.98%, 81.49%, 56.076% and 52.849%. of the control mix flexural strength (14.655 MPa). The results of split tensile and flexural strength test exhibit similar patterns to those of compressive strength test.

The compressive strength of binary mixes containing 2.5% and 5% of sludge is at par with the CM due to the filler effect of the sludge. Further increasing sludge content has resulted in a decrease in compressive strength of mortar mixes which indicates slow hydration reaction with the incorporation of sludge compared to cement (Balasubramanian et al., 2006; Goyal et al., 2019). TCETP sludge has less lime and silica oxide than cement as observed from XRF results in Table 1. This results in less hydration products and insufficient pozzolanic activity. Therefore, with the increasing sludge content, CH formation may occur but will not get converted to CSH gel due to the absence of silica in sludge. The high LOI content of the sludge also results in a reduction of strength. Organic matter decomposes during the mixing which impedes the further hydration of cement (Rahman et al., 2017; Zhan et al., 2020). Further the presence of heavy metals in sludge retards the hydration process and reduces the compressive strength (Goyal et al., 2022; Patel &Pandey, 2012). Therefore, supplementary cementitious material (SBA) is added in 5% and 10% to enhance the hydration and conversion of CH into CSH.

In the case of tertiary mixes with 5% SBA and 2.5-10% sludge, presence of additional silica may have improved the pozzolanic activity and have compressive strength at par with the CM. The presence of free lime in cement and sludge may have resulted in formation of additional CSH gel, thus improving the strength of the mortar mixes (Gupta et al., 2021). However, further increasing the SBA to 10% and sludge content to 7.5% and 10% results in reduced strength of mortar mixed. Sludge and SBA both contribute to slow hydration of the mortar mixes. The presence of organic matter in both SBA and sludge also retards the hydration of cement (Arenas-Piedrahita et al., 2016; Zhan et al., 2020). The sludge particles are finer than cement as act as the filler material and at 10% bagasse ash, the silica is available but free lime reduces due to decrease in cement content. Less availability of cement of hydration leads to less formation of CSH gel and reduced conversion of free lime, portlandite to secondary CSH gel. This leads to the formation of a highly porous matrix which is being studied using the sorptivity test. Additionally, the existence of heavy metals (zinc, iron, chromium and copper) in the TCETP sludge prevents the cement particles from hydration by forming a membrane of compounds such as calcium hydroxyl zincate ($CaZn_2(OH)_6.2H_2O$) around them (Goyal et al., 2022; Zhan et al., 2020).

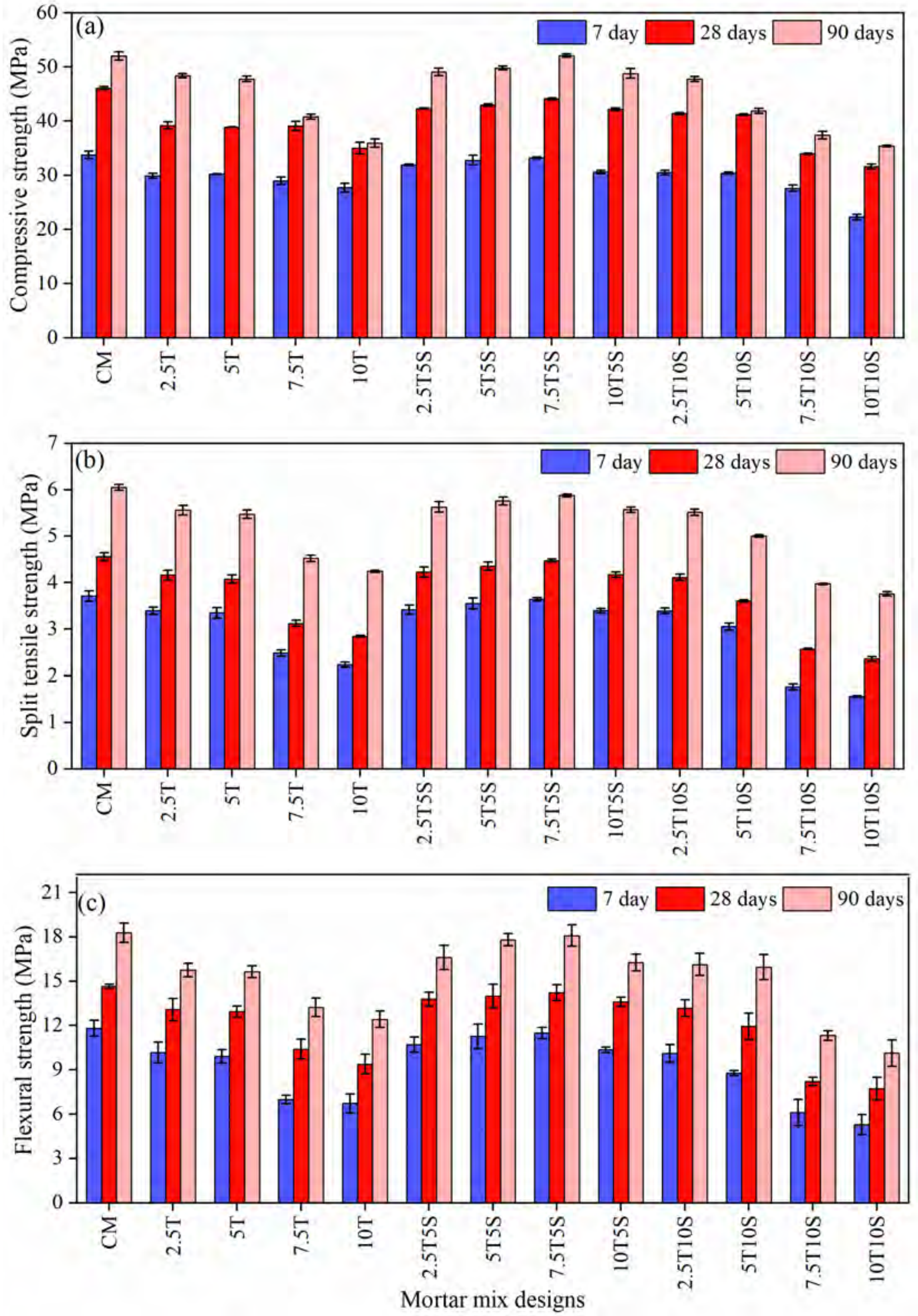


Fig. 6.9 Strength behaviour of the different mortar mix designs (a) compressive strength, (b) split tensile strength and (c) flexural strength

6.3.2 Permeability test

The mortar samples at 28 days of age are evaluated to comprehend the capillary suction behaviour. The capillary suction through a surface in contact with the water determines the sorptivity, which controls the propensity of water absorption by the mortar mixtures. The pore shape and surface properties of the specimens significantly impact their capillary suction behaviour (Bahurudeen et al., 2015). The sorptivity indices for the 13 mortar mixtures are depicted in Fig. 6.10.

When compared to CM, the 2.5T and 5T specimens showed decreases in sorptivity index of 8.68%, 13.79%, respectively. This shows that the sludge effectively filled the pores and reduced the size of the big pores. In the tertiary mixes 2.5T5S, 5T5S, and 7.5T5S, the sorptivity indices decreased by 23.56%, 29.14%, and 26.35%, respectively. This is attributed to the filler effect and the potential for secondary CSH gel formation with the addition of SBA, which would reduce large size pores and increases the denseness of the structure (Goyal et al., 2019; Quedou et al., 2021). However, the sorptivity indices were increased by 0.15% and 4.96% for the 7.5T and 10T mixes due to the lack of hydration of cement and increased size of pores. The sorptivity indices increased by 0.15%, 0.62%, 3.25%, 7.75%, 6.97% for the 10T5S, 2.5T10S, 5T10S, 7.5T10S and 10T10S mortar mixes respectively. The increased capillary water absorption of the mixes is caused by the lack of cement hydration as a significant portion of cement is replaced by sludge and SCBA, thus forming voids. Further, the mixes 2.5T10S, 5T10S, 7.5T10S and 10T10S with 10% SBA require more water to form paste of standard consistency thus, on drying large size pores are formed which contributes to increase in sorptivity (Gupta et al., 2021).

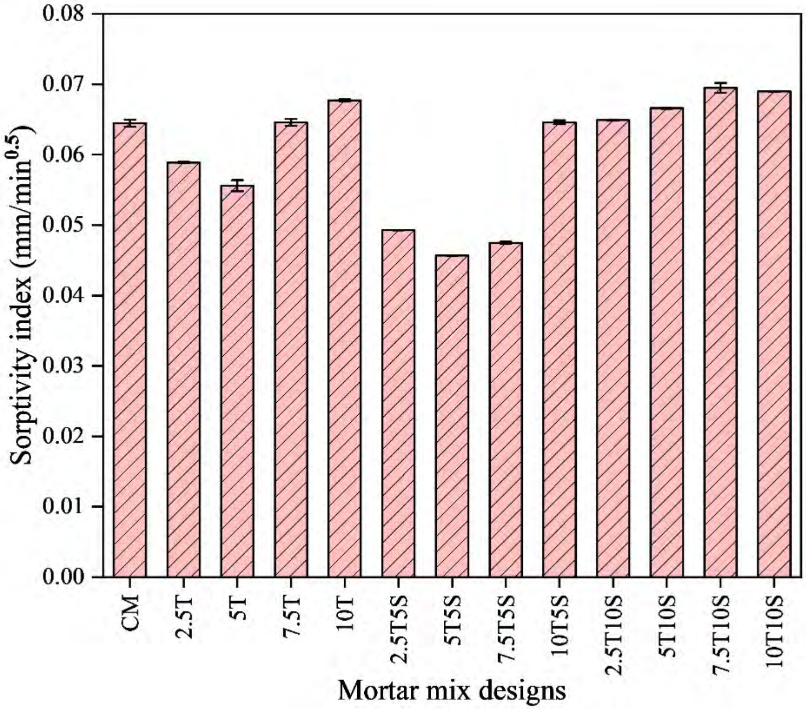


Fig. 6.10 Sorptivity index of the different mortar mix design

6.3.3 Durability

The resistance to the sulfate ions attack of the different mortar mixes is investigated by submerging the 28-day specimens in the 5% $MgSO_4$ for 90 days (including 28 days). The 5% $MgSO_4$ solution is revived every two weeks, and after the completion of 90 days, samples are washed in clean water. The compressive strength of the sulfate attack specimens is tested and compared with the specimens of moist curing for 90 days IS: 4031 (Part 6) (2005).

The reduction in compressive strength due to the sulfate attack is observed for the CM and the other specimens. It is demonstrated in Fig. 6.11 that salt crystallisation is predominantly responsible for the sulfate attack. Gypsum and ettringite are produced when the sulfate ions interact with calcium hydroxide (CH) and calcium aluminum hydrate (C_3A). The ettringite is responsible for the volume expansion, and gypsum can cause softening and loss of mass. Initially, the formation of gypsum and ettringite in the micro-cracks and pores increases compressive strength. In the later stages, with the gradual increase in these products, the development of new cracks and fractures affects the compactness of the mixes (Abraham & Ransinchung, 2019). However, there is 25% change in the strength of the CM, and 35.8%, 34.96%, 32.9 %, 33.7 % and 35.9 % for 2.5T, 5T, 2.5T5S, 5T5S and 7.5T5S, respectively. The reduced change in strength in the mixes is due to the filler action of sludge and the development of secondary CSH gel leading to a compact structure. It leads to the availability of fewer pores for the formation of ettringite and gypsum, thus reducing the compactness of mortar specimens. However, for the mixes 7.5T, 10T, 10T5S, 2.5T10S, 5T10S, 7.5T10S, and 10T10S, a change in the strength of 20% to 30% is observed. The lesser reduction in strength may be due to a large volume of pores and voids in these mixes leading to the greater availability of space for forming gypsum and ettringite. The pores and cracks are filled by these products, forming compact mortar.

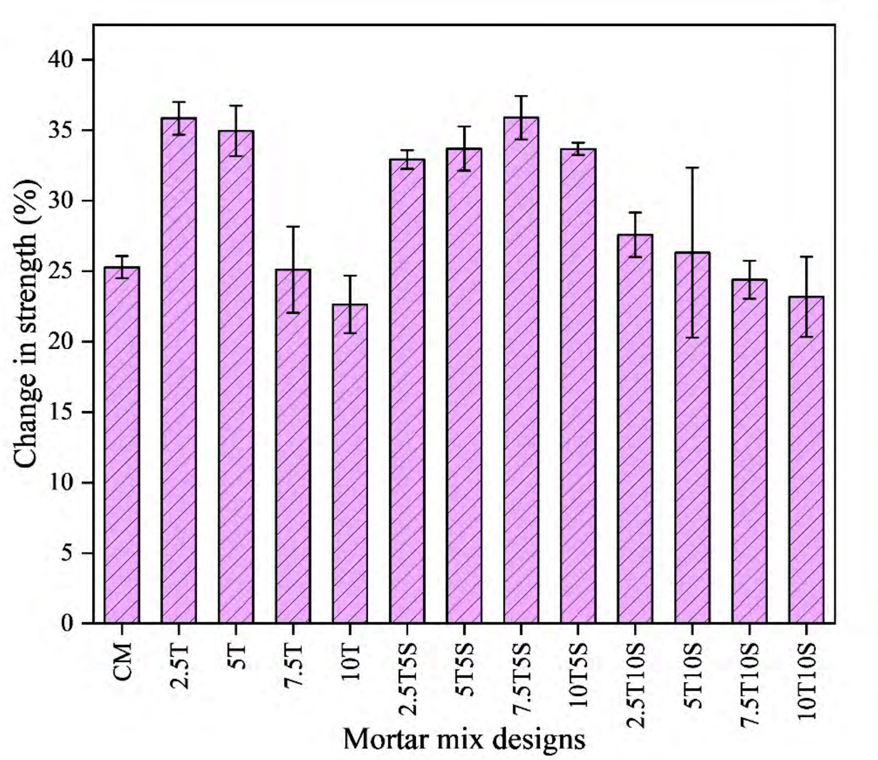


Fig. 6.11 Change in the strength (%) of the mortar mixes due to sulfate attack

6.3.4 Alkalinity, carbonation, and leaching tests

The pH of all the mortar mixes is determined and is reported in Table 6.4. The pH of the mortar mixes should lie between 12.0 and 13.0 to prevent corrosion of the reinforcement bars (M. Singh et al., 2020). The pH of all the mixes under consideration is within the acceptable range and is represented in Table 6.4. However, compared to CM, pH increases with adding sludge and SBA in the mixes.

The carbonation study is essential as the passive layer of the reinforcement deteriorates on the reaction of atmospheric CO_2 with the moisture present in the pores. As a result, the pH of pore moisture decreases due to the formation of carbonate and bicarbonate ions. After the flexural strength test, the phenolphthalein indicator is sprayed on the freshly split specimens. The sprayed surface turns pink, indicating the absence of carbonation (De Weerdt et al., 2019). All the mix designs, including the control mix, were observed to have no carbonation. Fig. 6.12 represents the carbonation test performed on the beams.

In the present work, the heavy metal analysis for the four primary heavy metals (Cu, Cr, Fe, Zn) found in the XRF results of the sludge was analyzed for the 13 mortar mixes using the TCLP test. The amount of heavy metal in the sludge is determined by the digestion using concentrated HNO_3(Goyal et al., 2022). Table 6.3 provides the results of the TCLP test analysis of the leaching of heavy metals in the TCETP sludge. Table 6.4 displays the TCLP test results for the various mortar mixtures. It is observed that the heavy metal content in the leachate of mortar mixes with 2.5%, 5%, and 7.5% of the sludge is under the permissible limit. The leaching of zinc is under the permissible limit indicating the formation of the compound (calcium hydroxyl zincate) with cement. However, the leaching of heavy metal from the mortar mixes rises with an increase in sludge content. The addition of SBA has no definite pattern that can be observed in the leaching of heavy metals, as it depends mainly on the sludge content in the mortar mixes.

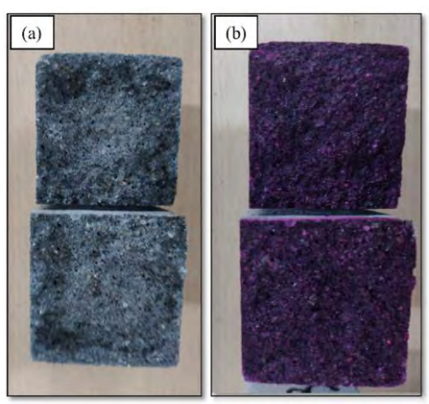


Fig. 6.12 Carbonation test (a) the freshly broken beams (b) the specimen after the phenolphthalein indicator is sprayed

Table 6.3 Heavy metal determination in the raw sludge using XRF after digestion and TCLP leaching test

Heavy metals	XRF (TCETP) %	ICP-OES - Digested sludge (mg/Kg)	ICP-OES (TCLP Test) (mg/l)
Fe	3.616	442.4	3.4
Cu	0.495	68.8	1.6
Zn	0.686	225.9	11.8
Cr	0.090	11.2	0.4

Table 6.4 The observed pH values and the heavy metal concentration of the mortar mixes

Mortar mixes designs	Observed pH values	Cu (mg/l)	Cr (mg/l)	Fe (mg/l)	Zn (mg/l)
CM	12.48	0.027	0.065	0.194	0.097
2.5T	12.46	0.029	0.083	0.267	0.089
5T	12.51	0.033	0.088	0.285	0.177
7.5T	12.55	0.046	0.084	0.228	0.151
10T	12.57	0.081	0.089	0.353	0.184
2.5T5S	12.59	0.038	0.076	0.283	0.109
5T5S	12.61	0.039	0.081	0.297	0.066
7.5T5S	12.68	0.047	0.075	0.298	0.088
10T5S	12.72	0.059	0.117	0.303	0.069

Mortar mixes designs	Observed pH values	Cu (mg/l)	Cr (mg/l)	Fe (mg/l)	Zn (mg/l)
2.5T10S	12.77	0.041	0.091	0.264	0.059
5T10S	12.78	0.043	0.088	0.272	0.083
7.5T10S	12.85	0.045	0.095	0.267	0.057
10T10S	12.89	0.061	0.163	0.371	0.104
WHO standards	-	2	0.05	NA	NA
CPCB	-	0.05	0.1	0.3	5

6.3.5 Microstructure study

XRD and SEM analysis is performed to analyse the components formed and the microstructure of the different mortar mixes. SEM images help study the microstructure changes in the mortar by adding sludge and SBA. Fig. 6.13-16 depicts the SEM and processed images for the CM, 5T, 7.5T5S, and 7.5T10S mortar mixes. The significant compounds observed in SEM analysis are Calcium Hydroxide (CH), Calcium Silicate Hydrate (CSH), Voids (V), and Ettringite(E).

It can be inferred from SEM analysis of mixes CM and 5T in Fig. 6.13 and Fig. 6.14, the addition of sludge has led to the decrease in large-size pores due to its filler effect. Additionally, as shown in Fig. 6.15, adding 5% SBA such as 7.5T5S promotes the formation of CSH which further reduces the pore area. It indicates the densification of the pore structure and, consequently, improved strength, and permeation properties. However, with increase in SBA to 10% and sludge to 7.5% in the mix such as 7.5T10S, has led to the formation of large-size pores, as observed in Fig. 6.14. Therefore, the SEM analysis results corroborate well with the strength and permeation test performed in this study. The pore area for each of the different mortar mixes is estimated using the Image J software and is represented in Fig. 6.17. The analysis of the pore area shows decreases in pore area with the addition of sludge and SBA but at the higher replacement amount, such as in the 7.5T10S mix; pore area significantly increases.

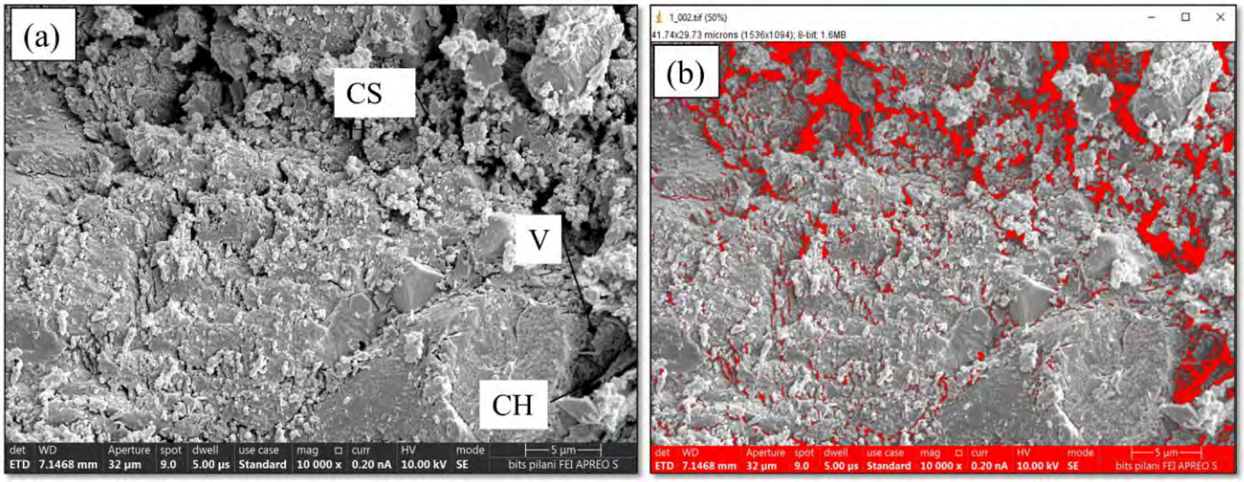


Fig. 6.13(a) SEM analysis and (b) processed image of the CM mortar specimen

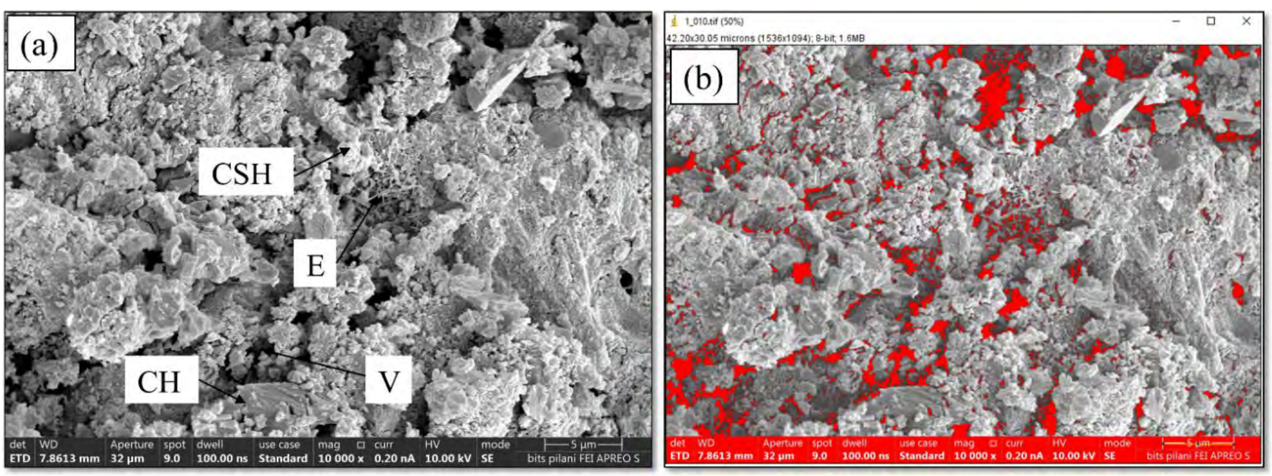


Fig. 6.14(a) SEM analysis and (b) processed image of 5T mortar mix

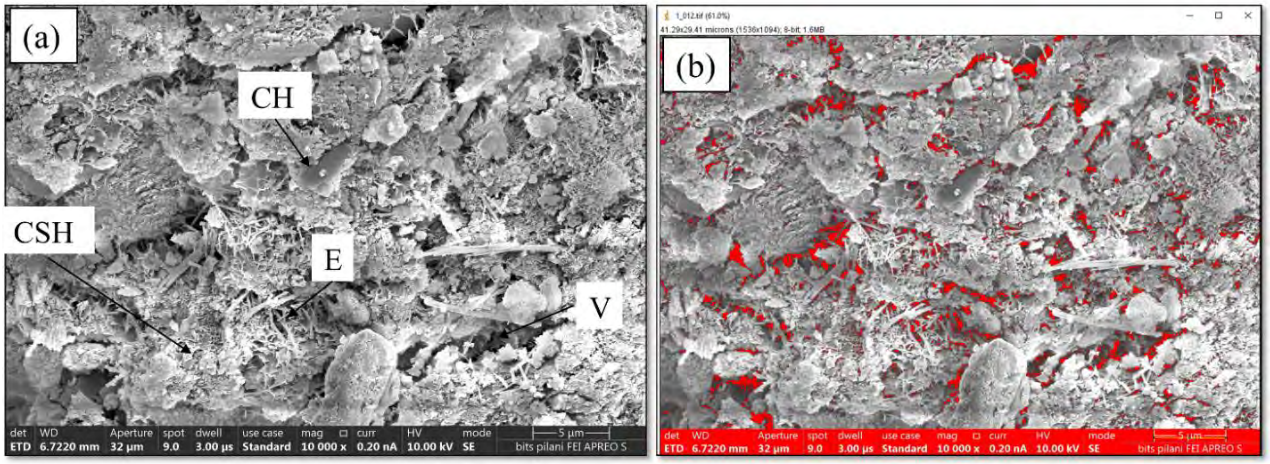


Fig. 6.15(a) SEM analysis (b) processed image of 7.5T5S mortar mix

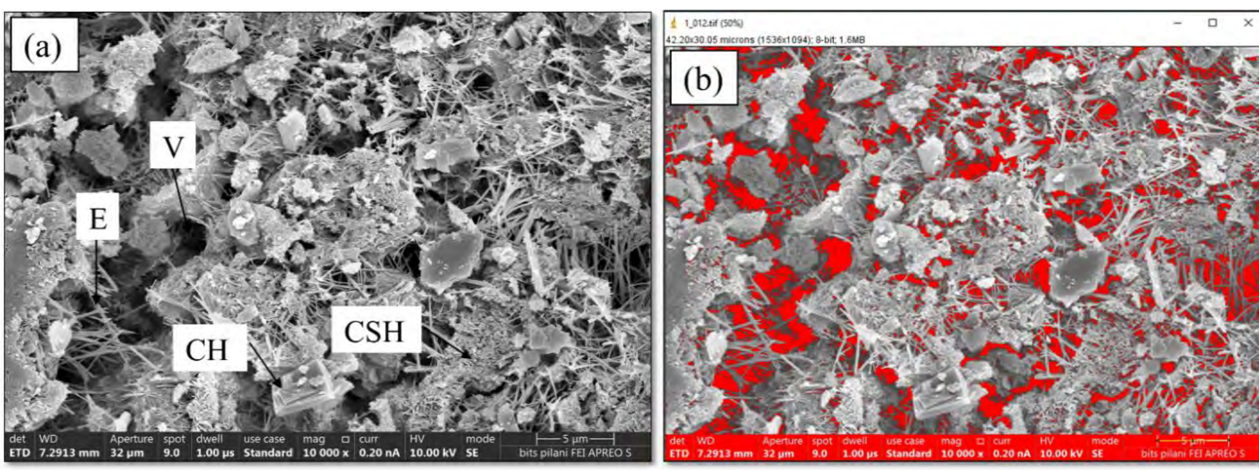


Fig. 6.16(a) SEM analysis and (b) processed image of 7.5T10S mortar mix (CH- Calcium Hydroxide, CSH – Calcium Silicate Hydrate, V- Voids, E- Ettringite)

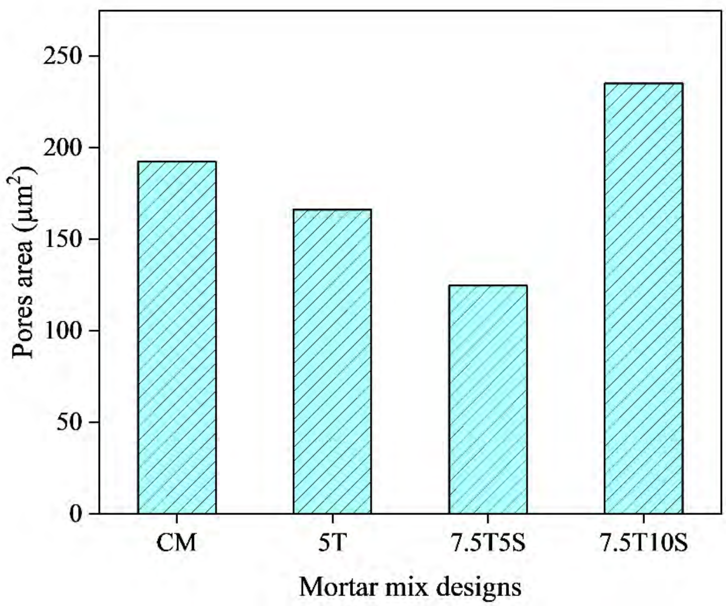


Fig. 6.17 Pore area of the mortar mixes based on SEM image analysis

XRD analysis of the four mortar mixes CM, 5T, 7.5T5B, and 7.5T10B is presented in Fig. 6.18. The major compounds observed in the XRD fingerprint analysis are tricalcium silicate, dicalcium silicate, quartz, calcium hydroxide, calcium silicate hydrate, and ettringite. It is observed from the XRD analysis that the fingerprints of the mixes containing cement only, cement with sludge, and cement with sludge and SBA have not changed much. However, significant changes in the intensities of the compounds are observed for the mixes. The addition of sludge shows the increased intensity of the peak of calcium carbonate and calcium silicate, as can be observed from Fig. 6.18(a, b) as compared to CM. However, the increased CSH and CH hydration products are observed in the 5T and 7.5T5B mix. The reduction in the peak intensity of hydration products is found in the XRD fingerprint of the 7.5T10S mix in Fig. 6.18(d) as compared to CM. The replacement of cement with sludge and SBA in a higher considerable amount leads to lesser hydration products.

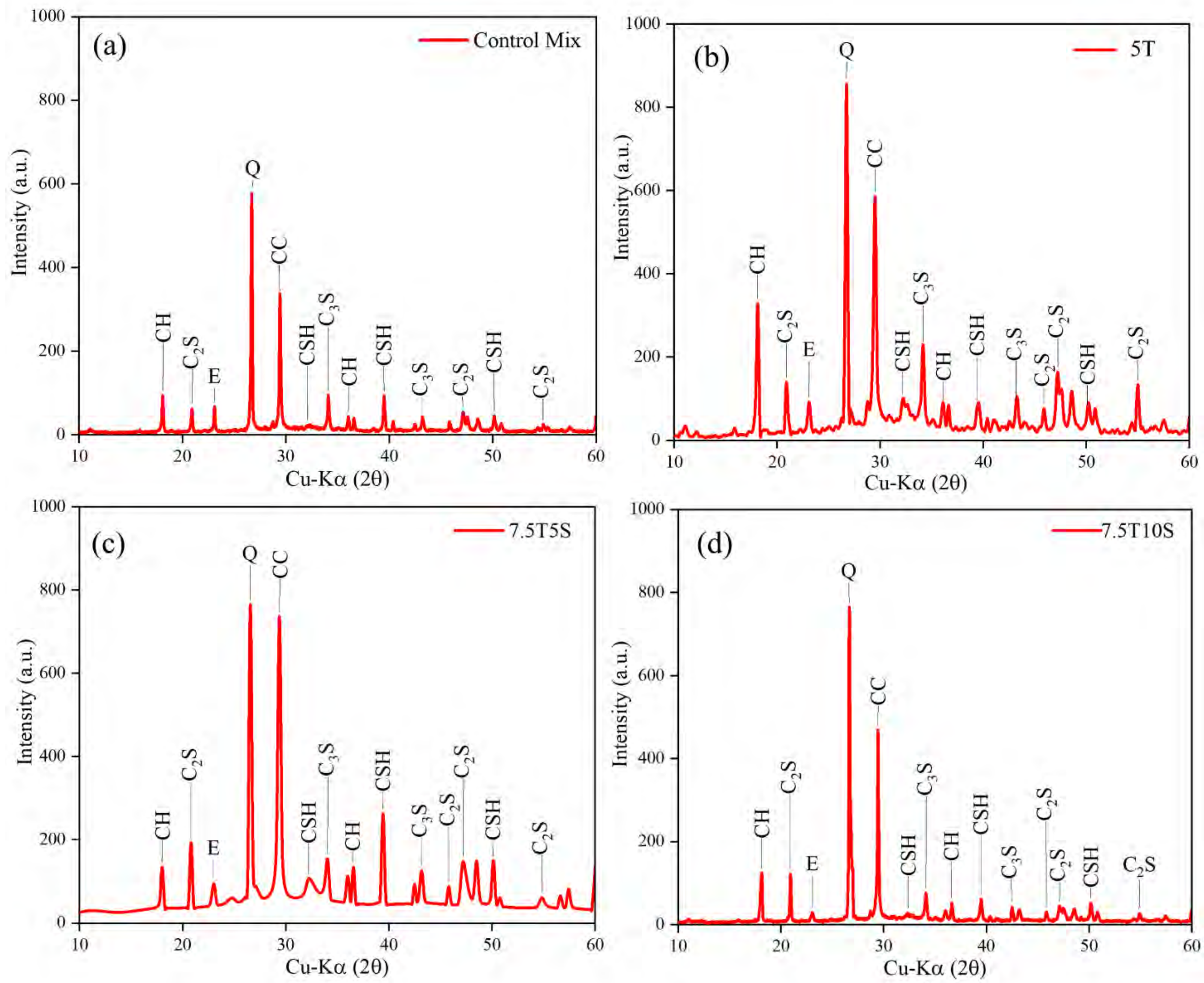


Fig. 6.18 XRD analysis of the mortar mixes (a) CM (b) 5T (c) 7.5T5S (d) 7.5T10S (CH = Calcium Hydroxide, Q = Quartz, E= Ettringite, C_3S = Tri-Calcium Silicate, C_2S = Di-Calcium Silicate, CSH = Calcium Silicate Hydrate)

6.4 Summary

This chapter uses TCETP sludge in mortar mixes, considering binary mixes (sludge-cement) and tertiary mixes (sludge-bagasse ash-cement) as binder material. Few of the mixes, 5T and 7.55T5S, have strength performance equivalent to the CM. Other properties such as durability, water absorption, sorptivity, and RCPT of 5T and 7.55T5S mixes are also at par with the CM. However, the environmental impact of using TCETP sludge and SBA in mortar mixes must be studied. Therefore, chapter 7 deals with the mortar mixes' LCA.

Chapter 7

Life Cycle Assessment of mortar mixes having textile industry effluent treatment plant sludge and sugarcane bagasse ash

7.1 Introduction

Chapter 5 of the thesis examines the leaching behaviour of TCETP sludge. chapter 6 gives the solution for the environmental problem of storing and disposing of sludge by utilizing sludge in mortar mixes. The current chapter quantifies the environmental aspects of using TCETP sludge and SBA in mortar mixes. Mortar is one of the essential products used during building construction, and the raw materials used for mortar production are cement, sand, and water. The critical ingredient construction material, i.e., cement, is the primary emitter of Green House Gases (GHGs). It has been estimated that the production of 1 ton of cement emits 0.85-0.95 tons of CO_2 into the atmosphere (Hendriks et al., 1998). However, waste products such as TCETP sludge and SBA do not require a separate production process and must be disposed of at the TSDF site and landfills. Lifecycle assessment is a proven technique to quantify the environmental benefits of using TCETP sludge and SBA. The impacts are assessed for endpoint indicators such as human health, ecosystem quality, and resources and the midpoint indicators such as fossils depletion, human toxicity, agricultural land occupation, climate change or global warming potential. This chapter quantifies the impact at both endpoint and midpoint categories of life cycle assessment.

7.2 Materials and methods

This section of the chapter explains LCA approach in detail, its goal and scope, framework, for the mix proportion considered for the various mortar mixes.

7.2.1 Life Cycle Assessment (LCA)

LCA is the compilation and evaluation of a product system's inputs, outputs, and potential environmental impacts throughout its lifecycle (Dandautiya & Singh, 2019). LCA of a product or scheme quantifies the ecological impacts throughout its life cycle (Jiménez et al., 2015). LCA method ascertains the sustainability of using textile sludge and bagasse ash as partial cement substitutes in mortar mixes. LCA is performed following the guidelines of the International

Standard Organization (ISO) 14040:2006 (ISO, 2006). LCA method as per ISO 14040:2006 consists of four steps: namely (1) defining of goal and scope, (2) inventory analysis, (3) impact assessment, and (4) interpretation of the LCA model results. Life cycle studies can be performed using various approaches such as cradle to the gate (from raw materials until factory gate), cradle to grave (from raw materials until disposal) and gate to gate (consider only manufacturing processes) (Paz et al., 2023). These four steps of LCA procedure are discussed in the following sections.

7.2.1.1 Goal and scope of the LCA

This study's foremost aim is to evaluate the environmental impacts of using the TCETP sludge and SBA in mortar mixes in different compositions w.r.t the control mix. UMBERTO NXT LCA software is used to model the different life cycle phases of mortar production. These life cycle phases considered in the study are raw materials, transportation of raw materials, manufacturing, and disposal of mortar. Cradle to grave approach is used for the analysis. The constituents of mortar (materials) are measured for the functional unit of $1m^3$ mortar. Mortar comprises fine aggregate, binder material (cement, TCETP sludge, bagasse ash), and water. Due to the difference in the specific gravity of each ingredient, the material volume will be different for the equal mass of materials. Therefore, for comparative analysis of different mortar mixes, constant volume, i.e., $1m^3$ of mortar, is considered for LCA models. The study uses wastes such as TCETP sludge and sugarcane bagasse ash in mortar mixes. The study doesn't consider the production process for these wastes but only considers their transportation impact. These waste materials are recycled in the study. Fig. 1 represents the LCA model framework and consists of four life cycle phases: raw material, transportation, manufacturing, and disposal.

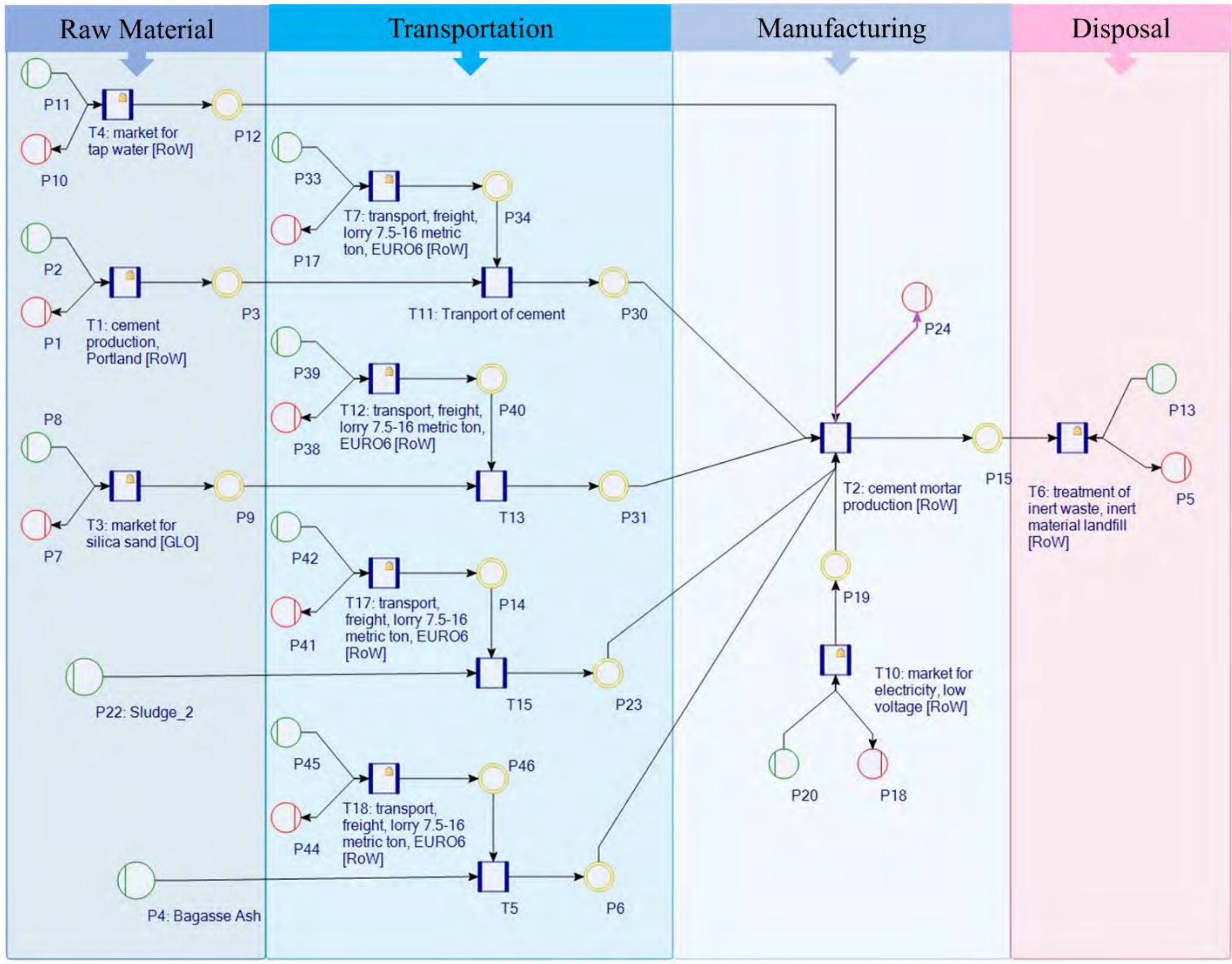


Fig. 7.1 Framework of the LCA model

7.2.1.2 Inventory analysis

Experiments on maintaining the standard consistency of the thirteen mixes are performed in accordance with IS: 4031 (Part 4) (1988). The water-to-cement ration is maintained at 0.44, 0.46 and 0.48 based on the results of standard consistency. The inventory data on the environmental impacts of cement, sand, inert waste, tap water production, low voltage electricity was taken from the Rest of the World (RoW) category of Ecoinvent 3.0 and Ecoinvent 3.1 database (Bajpai et al., 2020). TCETP sludge and bagasse are considered inert waste in this study. In all the inventory calculations for LCA, 1 m^3 of mortar and 1 kWh of power are considered functional units. The inventory data for raw materials is presented in Table 7.1.

7.2.1.2.1 Materials and mortar mix proportion

The materials used to perform the analysis mainly comprise of (i) TCETP sludge, (ii) SBA, (iii) OPC 43, (iv) sand and (v) potable water. The details of chemical and physical properties of material used are already discussed in Chapter 6, Table 6.1 of the thesis. Thirteen mixes prepared by volumetric replacement of cement with TCETP sludge and SBA and their mix design proportion, preparation, mixing, and curing of samples are presented in Chapter 6. Table 7.1 shows the composition of the mix used for the preparation of 1m^3 volume of the mortar and the Ecoinvent 3.0 data used for the LCA study.

Table 7.1 Composition of the mix for 1m^3 of the mortar

Mix Notations	**Mix proportion (kg)**					
	Cement	**Sand**	**TCETP**	**SBA**	**w/c**	**Water**
Ecoinvent	Portland	Silica sand	Inert waste	Inert waste		Tap water
CM	568.35	1705.05	0	0	0.44	250.07
2.5T	554.14	1705.05	10.26	0	0.44	250.07
5T	539.93	1705.05	20.53	0	0.44	250.07
7.5T	525.72	1705.05	30.79	0	0.46	261.44
10T	511.5	1705.05	41.05	0	0.46	261.44
2.5T5S	525.723	1705.05	10.26	15.95	0.46	261.44
5T5S	511.51	1705.05	20.53	15.95	0.46	261.44
7.5T5S	497.31	1705.05	30.79	15.95	0.46	261.44
10T5S	483.09	1705.05	41.05	15.95	0.46	261.44
2.5T10S	497.31	1705.05	10.26	31.91	0.48	272.80
5T10S	483.1	1705.05	20.53	31.91	0.48	272.80
7.5T10S	468.88	1705.05	30.79	31.91	0.48	272.80

Mix Notations	Mix proportion (kg)					
	Cement	**Sand**	**TCETP**	**SBA**	**w/c**	**Water**
10T10S	454.68	1705.05	41.05	31.91	0.48	272.80

*Textile Sludge = T, * SBA = S, *Cement = c, * Water = w, *Control Mix =CM

The product is formed at Balotra, Rajasthan state, India, near the TSDF site for storing TCETP sludge. The distances for transporting raw materials required for manufacturing mortar are summarized in Table 7.2.

Table 7.2 Transport distances considered for the study

Raw Material	Cement	TCETP sludge	SBA	Sand
Distance (Km)	200	5	800	50

7.2.1.3 Life Cycle Impact Assessment (LCIA)

Life cycle impact assessment quantifies the environmental impacts associated with a product during its life cycle. The ecological consequences of the product may include the vast number of resource extraction and by-product emissions. The main aim of the LCIA is to improve the understanding of the LCA study by converting the impact of resource extraction and by-product emissions into manageable scores/points. LCIA is measured using the ReCiPe midpoint and endpoint methods. Endpoint impact assessment is a top-down approach, and the environmental consequences are measured in a single standardized point score. The endpoint method has three damage categories: ecosystem quality, human health, and resources. Damage to human health is measured in terms of Disability Adjusted Life Years (DALYs). The term "DALYs" represents the number of years a person loses due to early death or sickness that degrades their quality of life (Ahmad Kiadaliri et al., 2016). Ecosystem quality is defined as the Potentially Disappeared Fraction (PDF) of species integrated over area and time (PDF*m^2 *year) (Goedkoop et al., 2009). The third category in the endpoint method is resource scarcity, measured in dollars ($), representing the extra costs for future mineral and fossil resource extraction.

The midpoint category has eighteen ecological factors that cumulate into three endpoint damage categories. Impacts of ReCiPe midpoint categories are measured in terms of absolute and independent units. Environmental impacts for the eight midpoint categories, namely agricultural land use (m^2a), climate change (kg CO_2-Eq), fossils depletion (kg oil-Eq), freshwater ecotoxicity (kg 1,4-DCB-Eq), human toxicity (kg 1,4-DCB-Eq), ozone depletion (kg CFC-11-Eq), particulate matter formation (kg PM10-Eq), water depletion (m^3) are measured in this study considering the past literature (Bajpai et al., 2020; Dandautiya & Singh, 2019).

7.3 Results and discussion

7.3.1 Mechanical properties

The performance of mortar mixes is tested using the compressive strength test. Three cubes of 70.6 mm were casted for each mix to measure compressive strength and tested as per the procedure mentioned in IS: 4031 (Part 6) (2005). Compressive strength is measured at 28 days of immersed curing and is depicted in Fig. 7.2. The details of the compressive strength test results are described in Chapter 6 section 6.3.1. However, the comparison of only 28days compressive strength test results is presented in Fig. 7.2.

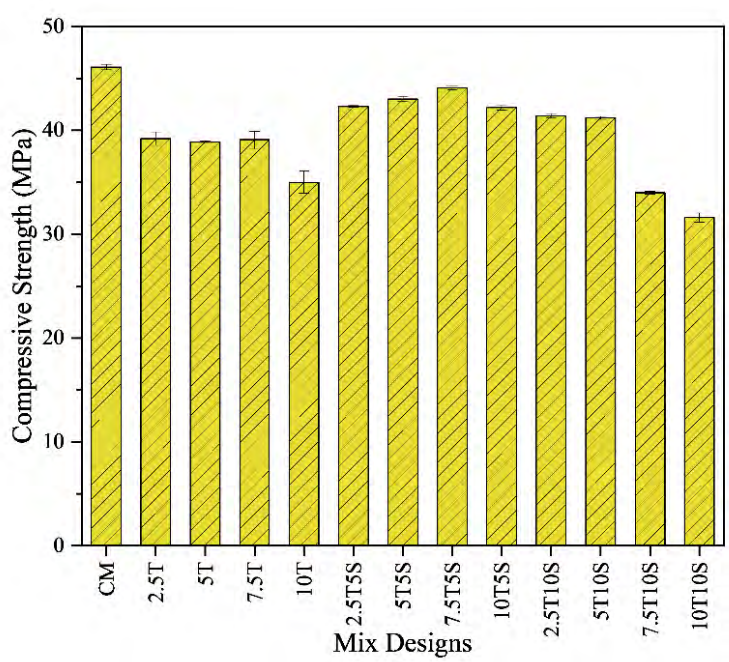


Fig. 7.2 Compressive strength results of the mortar mixes

7.3.2 Endpoint and midpoint assessment

The detailed results of environmental impact assessment by the endpoint indicators of the ReCiPe method of Life Cycle Impact Assessment (LCIA) have been summarized in Fig. 7.3. Along with this, the effect of different lifecycle phases, raw material, transportation, manufacturing, and disposal of the thirteen mortar mixes on the ecosystem quality, human health and resources are depicted in Fig. 7.3. The lifecycle phases of the mortar have a similar adverse impact on the ecosystem quality and human health category, followed by the less adverse impact on resources. The environmental impact of the control mix (mortar without any sludge and SBA) is highest in all three endpoint damage categories. The impact on ecosystem quality has reduced from 33.6 points and 31.13 points to 29.64 points for CM, 7.5T5S and 10T10S mix, respectively. For the human health endpoint category, the impact reduces from 33.26 points and 29.98 points to 28.06 points for CM, 7.5T5S and 10T10S mix, respectively. Similarly, for the resource category, the impacts reduced from 13.4 points and 12.49 points to 11.9 points for CM 7.5T5S and 10T10Smix, respectively.

No notable variation in the scores was observed for the manufacturing phase among the four life cycle phases. A similar trend for all the mortar mixes could be attributed to constant energy use in their manufacturing. Transportation and disposal are also not affected by the different compositions of the mixes. However, the raw materials phase has the highest impact among all the product lifecycle phases. The raw materials used for mortar manufacturing are sand, cement, water, sludge, and SBA. The sand quantity is constant for all the mixes, and the change in the water-to-cement ratio is minimal. Hence, cement mainly contributes to adverse impacts in all three endpoint categories. The impacts have decreased with reduced cement requirements by adding sludge and sugarcane bagasse ash. This can be attributed as the manufacturing of 1 ton of cement releases about 0.95-0.85 ton of CO_2 in the atmosphere (Hendriks et al., 1998). The CO_2 emission is mainly contributed by burning fossils to heat the kiln to 1400^{o}C and calcinating limestone to produce lime in the kiln (Huntzinger & Eatmon, 2009). However, sludge is waste generated from CETP, and sugarcane bagasse ash is the waste generated from the cogeneration plants of sugar mills. Therefore, it does not require a separate production process, thus emitting fewer Green House Gases (GHGs) (Charitha et al., 2021). Moreover, utilizing TCETP sludge and SBA in mortar mixes resolves the disposal problem and thus benefits the environment.

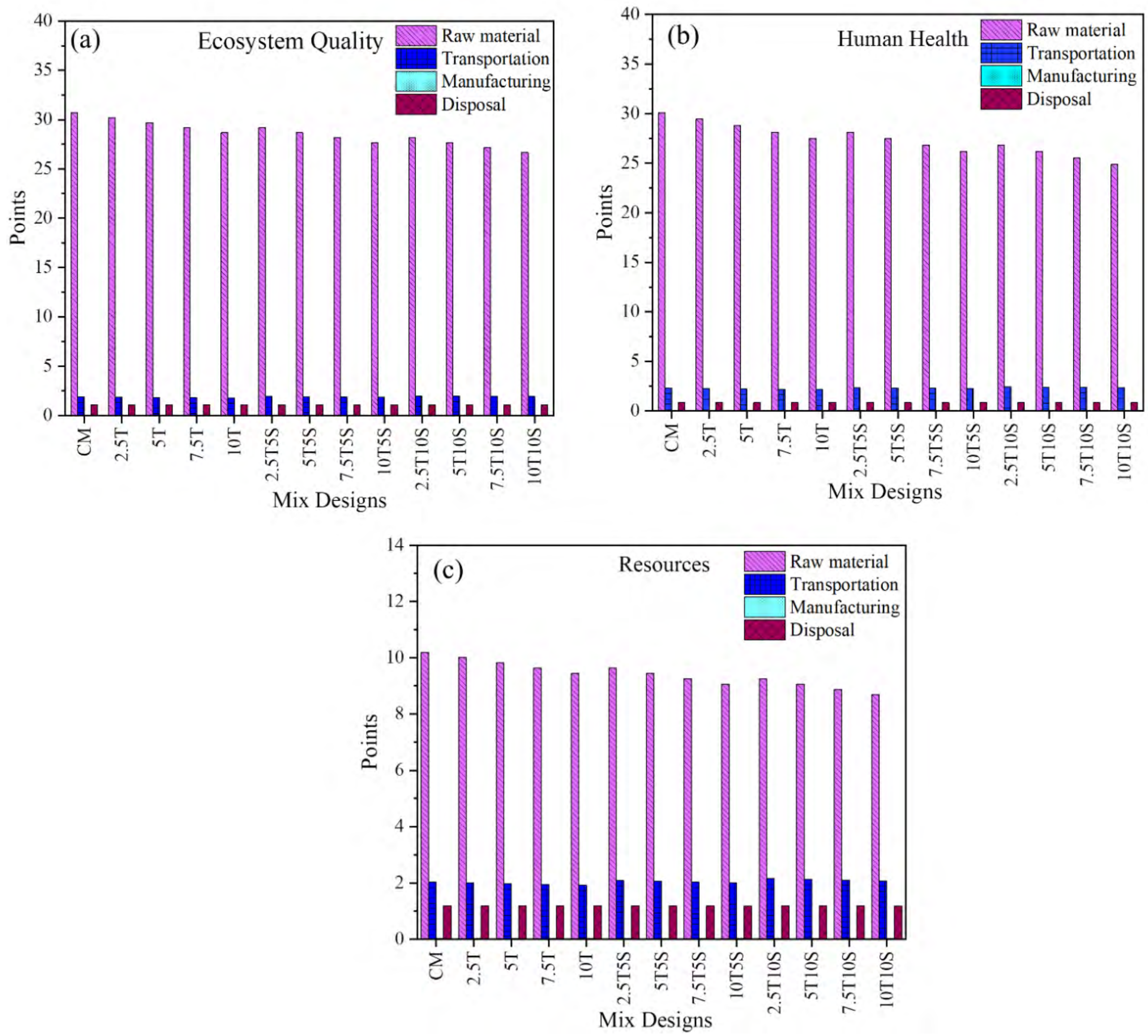
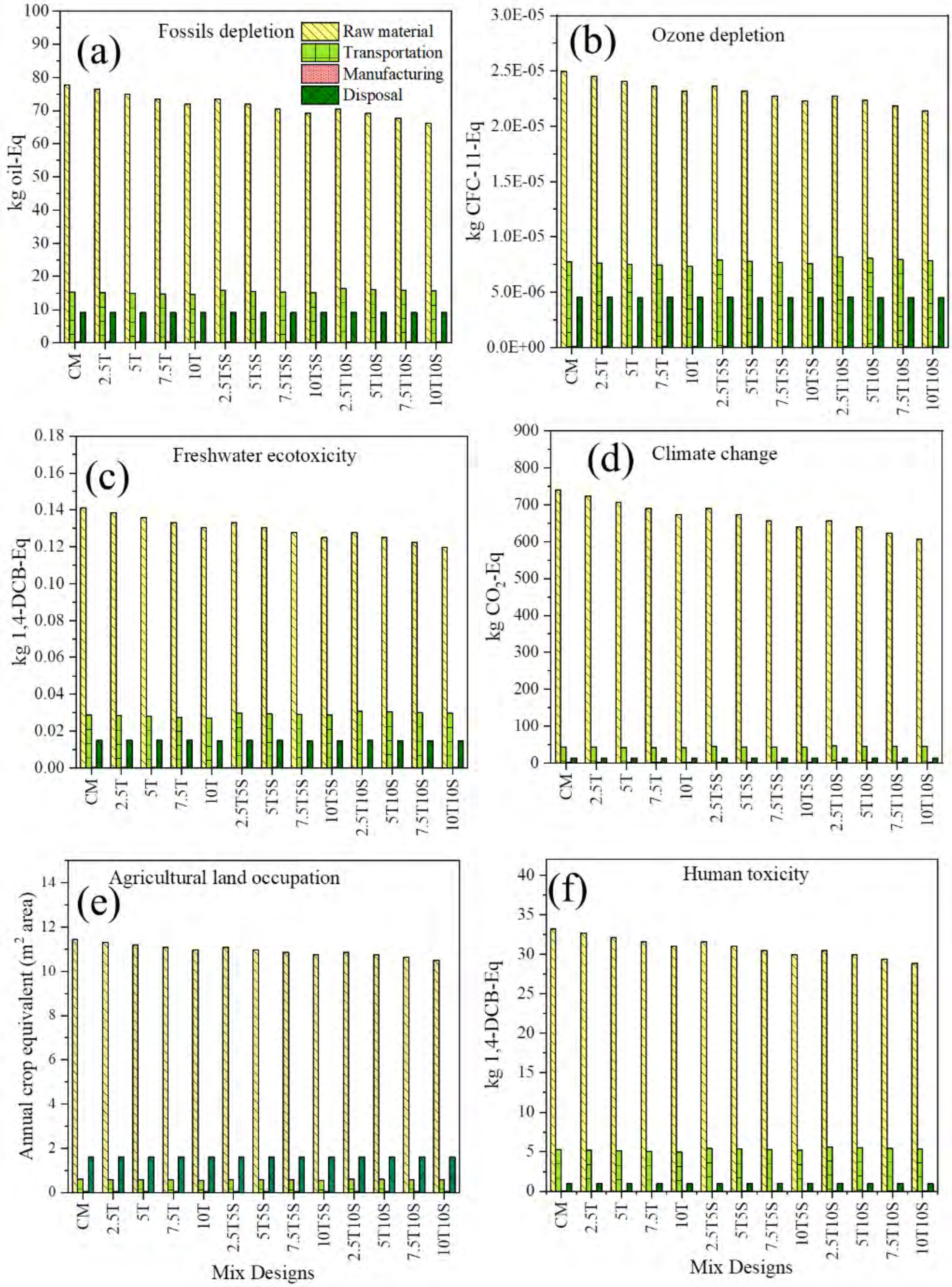


Fig. 7.3 Scores for the ecosystem quality for the life cycle phases of mortar mixes

The results of the impact of modified mortar mixes for the midpoint indicators of LCA, namely fossils depletion, ozone depletion, freshwater ecotoxicity, climate change, agricultural land use, human toxicity, particulate matter formation, and water depletion, are summarized in Fig. 7.4. The variation is observed mainly in the raw material phase of the LCA model. Of the eight categories, climate change or global warming potential, human toxicity and fossil depletion are the most influenced by replacing cement with sludge and SBA in mortar. The impact of mortar production on climate change varies from 798.12 kg of CO_2 Eq to 665.56 kg of CO_2 Eq for CM and 10T10S mix. The impact of the 7.5T5S mix, whose compressive strength is at par with the

CM on climate change, is 714.52 kg of CO_2 Eq. In the case of fossil depletion, manufacturing modified mortar mixes have reduced 102 kg oil-Eq, 95.23 kg oil-Eq to 91.22 kg oil-Eq for CM, 7.5T5S, and 10T10S mixes.

Similarly, the adverse impact on human toxicity has decreased from 39.50 kg of 1,4-DCB-Eq and 36.79 kg of 1,4-DCB-Eq to 35.27 kg of 1,4-DCB-Eq for the CM, 7.5T5S and 10T10S respectively. The reduction in the adverse impact of the mid-point category is mainly due to the reduced cement requirement in modified mortar specimens. Cement production contributes to GHGs emission and thus have a significant adverse effect on fossil depletion, human toxicity, and climate change. Mortar manufacturing does not produce any severe adverse impact on any mid-point category, as seen in Fig. 4. No variation in manufacturing is mainly due to the consumption of equal electricity in producing mortar mixes. However, the impact of transportation almost balances as cement and bagasse both need to be transported from distant places for mortar production in the Balotra district; therefore, variation is not observed in the mixes.


(a)
Fossils depletion
Raw material
Transportation
Manufacturing
Disposal
kg oil-Eq
(b)
Ozone depletion
kg CFC-11-Eq
(c)
Freshwater ecotoxicity
kg 1,4-DCB-Eq
(d)
Climate change
kg CO_2-Eq
(e)
Agricultural land occupation
Annual crop equivalent (m^2 area)
(f)
Human toxicity
kg 1,4-DCB-Eq
CM
2.5T
5T
7.5T
10T
2.5T5S
5T5S
7.5T5S
10T5S
2.5T10S
5T10S
7.5T10S
10T10S
Mix Designs

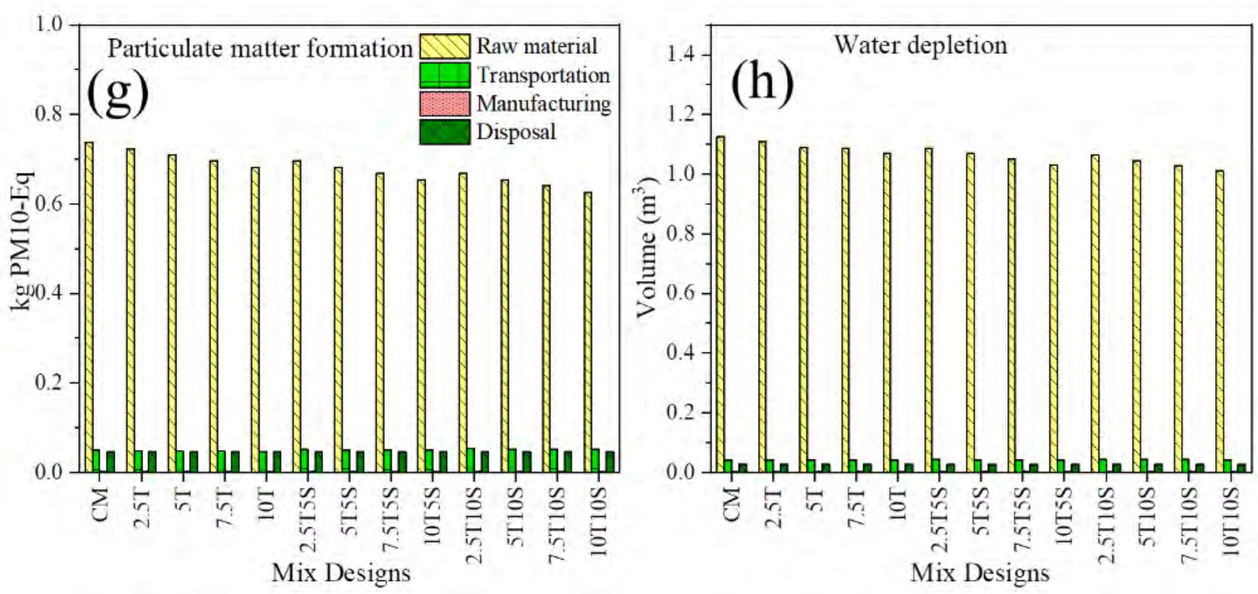


Fig. 7.4 Midpoint indicators of lifecycle assessment of the different mortar mixes

7.3.3 Cost estimation of the modified mortar mixes (Economic viability)

The economic feasibility of incorporating TCETP sludge and SBA as a partial replacement for cement in mortar mixes is essential. The details of the cost estimate of all the modified mortar mixes and the control mix are presented in Table 7.3. The cost is calculated in (Rs) for the quantity of raw material required for making one cu m volume of mortar. The rates of each raw material have been taken from the scheduled rates followed in district Balotra, Rajasthan, India, for the year 2023. The total expenditure for making one cu m for each modified mix is compared with the cost of the control mix.

From the cost analysis, the reduction in the cost of the modified mixes is observed with the partial replacement of cement by sludge and SBA in mortar mixes. In Fig.7.5 relative reduction in the cost of modified mixes compared to control mixes is presented. The production cost for one cu m of modified mixes compared to the control mix has reduced by 1.2%, 2.4%, 3.6%, and 4.8% for the binary mixes 2.5T, 5T, 7.5T, and 10T. For the tertiary mixes, the reduction in production cost of modified mixes is 2.7%, 3.9%, 5.1%, 6.3%, 4.1%, 5.4%, 6.6%, and 7.8% for 2.5T5S, 5T5S, 7.5T5S, 10T5S, 2.5T10S, 5T10S, 7.5T10S, 10T10S mixes respectively.

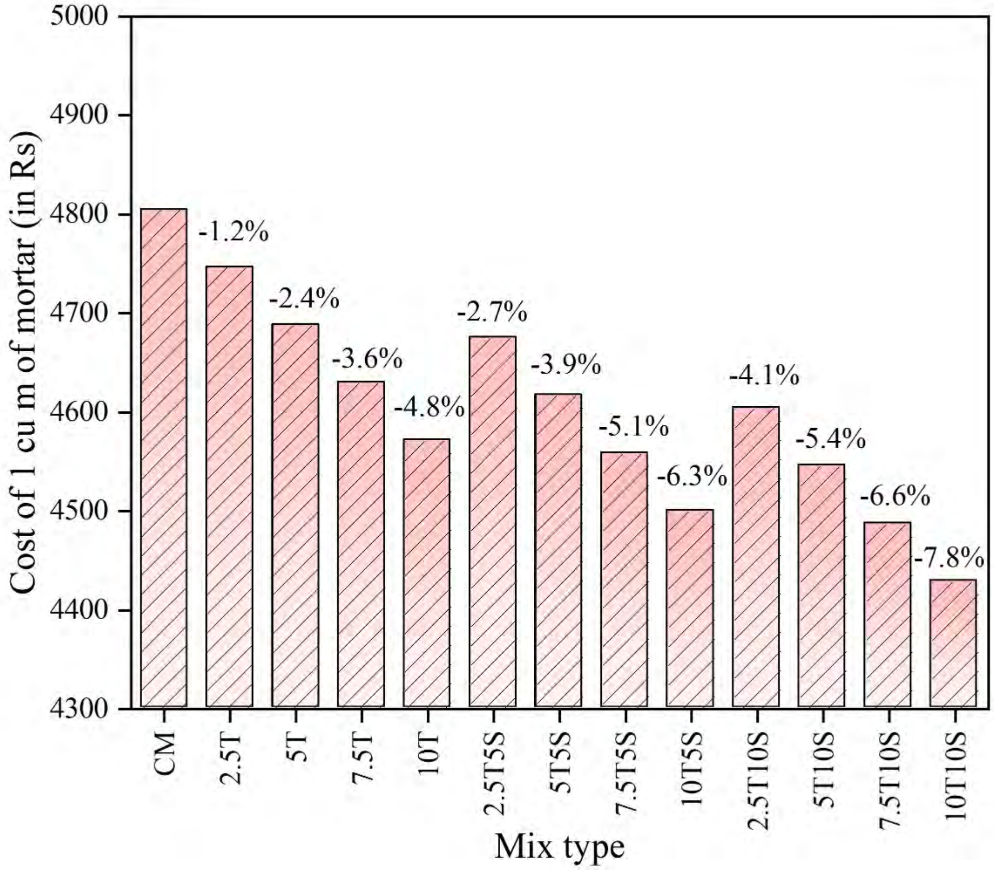


Fig. 7.5 Cost reduction in percentage for the different modified mortar mixes

Table 7.3 Cost analysis of one cu m of mortar for the different mix combinations

Mix notations	Cement	Sand	TCETP sludge (transportation)	SBA (transportation)	Total Cost of 1 cu m of mortar
CM	3978.45	826.26	0	0	4804.7
2.5T	3878.98	826.26	41.04	0	4746.3
5T	3779.51	826.26	82.12	0	4687.9
7.5T	3680.04	826.26	123.16	0	4629.5
10T	3580.5	826.26	164.2	0	4571

Mix notations	Cement	Sand	TCETP sludge (transportation)	SBA (transportation)	Total Cost of 1 cu m of mortar
2.5T5S	3680.06	826.26	41.04	127.6	4675
5T5S	3580.57	826.26	82.12	127.6	4616.6
7.5T5S	3481.17	826.26	123.16	127.6	4558.2
10T5S	3381.63	826.26	164.2	127.6	4499.7
2.5T10S	3481.17	826.26	41.04	255.28	4603.8
5T10S	3381.7	826.26	82.12	255.28	4545.4
7.5T10S	3282.16	826.26	123.16	255.28	4486.9
10T10S	3182.76	826.26	164.2	255.28	4428.5

*Textile Sludge = T, * SBA = S, *Cement = c, * Water = w, *Control Mix =CM

7.4 Summary

In this chapter, the environmental impact of utilizing TCETP sludge and SBA in cement mortar mixes in different proportions is discussed. A detailed overview of the LCA process is discussed in the sub-section of the chapter. The endpoint and midpoint indicators are used for LCA analysis, and the cradle-to-grave approach (raw material to disposal as inter waste to landfills) is considered for the study. The results of the LCA analysis show that modified mortar mixes have a less adverse impact on the environment (endpoint and midpoint categories) than the control mix. The economic feasibility of incorporating sludge and SBA as partial replacements for cement in mortar mixes has also been evaluated. In the next chapter of the thesis, the conclusion, limitations, and the future scope of the research are discussed.

Chapter 8

Conclusions, limitations, and future scope

8.1 Conclusions

Based on the results and summary presented at the end of each chapter, it can be concluded that the study can potentially reduce pollution discharged by textile industries. The research is expected to remarkably encourage clean and sustainable practices for treating effluent and stabilization of TCETP sludge produced by the textile industry. The objectives, scope, and significance of the study are presented in Chapter 1. The literature review signifies the different treatment techniques available, the application of multi-criteria techniques such as a hybrid fuzzy analytical hierarchical approach, and the need for adsorption-based effluent treatment, which is cost-effective and environmentally friendly. Chapter 2 also provides a broader perspective and a review of previous studies on the adverse impact of improper handling of TCETP sludge, its utilization in the construction industry and the environmental impact of using TCETP sludge in the construction industry in mortar mixes. Chapters 3, 4, 5, 6, and 7 illustrate the contributions made through this thesis in dealing with the environmental concerns of the wastes generated by textile industries and provides sustainable solutions contributing to clean production.

The summary section at each chapter's end also highlights the essential findings and contributions of the studies in that subsequent thesis chapter. In accordance with the above discussions and the research work performed, the following are the conclusions drawn from the research work:

8.1.1 Performance evaluation of TWWTTs

- The research work in chapter 3 aims to develop a novel methodology for evaluating the sustainability of different TWWTTs. Discussions presented in this work precisely explain the challenges faced while planning for any TWWTTs due to the multitude of governing factors, some of which are often ignored.
- The sub-indicators with higher scores from each category are the color removal efficiency, COD removal efficiency, the quantity of sludge generated from the treatment units, the effluent suitability for reuse, operation/maintenance cost, awareness within industries and hiring of local services.

- The ASP and RBC have low indices values showing poor sustainability. This is due to the poor integrated performance in COD and color removal efficiency, poor treated effluent quality requiring further treatment before reuse, low social acceptance and being economically infeasible.
- The poor sustainability indicates its lesser contribution to the cleaner production of fabric. Therefore, selecting appropriate technology will help the industries advance the quest for a cleaner environment and support the industries for efficient products at an economical cost.
- The MBR, EC and MBBR have higher sustainability scores and are the competitive alternatives showing better overall performance. It is important to note that MBR technology is recommended as it integrates the biological treatment process with membrane filtration, demonstrating high contaminants removal efficiency. The high effluent quality of the permeate from MBR makes it suitable for reuse in the textile industry with no negative impact on finished fabric quality. Industries' high social acceptance of the MBR technique will reduce uncontrolled and illegal waste disposal practices.
- Reusing recycled water in different textile processes will ultimately contribute to cleaner production by decreasing the textile effluent quantity and reducing the requirement for groundwater. The sensitivity analysis result indicates no rank reversal; thus, the model is robust.
- The methodology provides a broad scope to decision-makers as one can customize (add or delete) the alternatives according to the problem and the data availability. Therefore, the proposed methodology is highly beneficial for planning and decision-making problems.

8.1.2 Removal of contaminants using WSAC

- Research work in chapter 4 shows the use of agricultural waste product wheat straw as a low-cost, efficient, environment-friendly adsorbent for removing pollutants from the textile industrial effluent.
- The amount of pollutants uptake on the treated wheat straw activated carbon increases with increasing process parameters and becomes stationary—however, the rapid adsorption of COD and colour within 10 minutes of the addition of WSAC. In the first 10 min of the addition of WSAC, more than 70% of adsorption takes place.

- The main advantage of the research is that it gives a practical solution for treating wastewater at a meagre cost without generating harmful sludge.
- WSAC is characterized using the FTIR, pH_{PZC}, FESEM-EDX, BET and the XRD, which describes the adsorbent properties. The morphology of the WSAC shows the development of a highly porous structure consisting of mesopores.
- Polynomial quadratic regression and ANN models are compared using statistical measures such as R, R^2, MSE and RMSE. The RSA model is a better fit than the ANN model, as MSE and RMSE values for both models by RSA are less than the ANN model values.
- Further, the COD and colour removal efficiency at the optimum conditions (contact time- 85.229 mins, WSAC dose- 2.045 g/l, initial pH- 7.181, and temperature- 40.885 ℃) were 90.92% and 94.48%, respectively.
- The non-linear PSO model is better suited to the experimental adsorption data than the non-linear intraparticle diffusion and PFO models. This signifies that the adsorption does not depend on the concentration but on the availability of vacant adsorbent sites.
- The results of the desorption study indicate that hydrogen bonding and n-π interaction are the predominant adsorption mechanism rather than electrostatic attraction.
- The economic study also shows the cost-effectiveness of the proposed approach. Hence, using WSAC could be one economic and environment-friendly solution for treating textile industry wastewater.

8.1.3 Assessment of toxicity characteristics in leachate

- Chapter 5 provides a novel flexible framework to develop a leachate pollution index for hazardous sludges. The study is imperative in distinguishing the different sludges based on their toxicity index. It is hence helpful in establishing the priority among different sludge sites for sludge disposal at TSDFs.
- The number of metal ions based on their preliminary investigation can be increased or reduced based on the requirement of the study and the availability of heavy metals in the sludges.
- The study is helpful for finding the toxicity of sludges and categorizing them based on their toxicity level. These T-LPI scores are essentially helpful in determining the least hazardous

sludge and could provide an alternative sustainable method for its disposal, such as its use in the construction industry.

- These scores could also help us in finding the probable reason. For instance, coagulation and flocculation are chemical-based effluent treatment processes at CETP. They could be considered as one of the significant contributors of heavy metals (Al and Fe) in CETP sludge.
- Based on the T-LPI score, one can also plan for the best waste management practices and disposal strategies. The sludges with high T-LPI scores cannot be disposed of in the open for a few days before their final disposal at TSDF sites. But the sludges with low T-LPI scores can be disposed of later after the disposal of sludges with high T-LPI scores.
- These indices will also be functional in decision-making about sludge disposal. The T-LPI is helpful in selecting the CETP site from where the sludge needs to be disposed of at first to TSDF based on their toxicity scores.
- The statistical analysis and the human health risk assessment of the metal ions in leachate are also performed to correlate the metal ions and the possible non-carcinogenic and carcinogenic impact of leachate-contaminated surface water consumption.
- The low Pearson's correlation coefficient values of the sludge metal ions data indicate the presence of different sources for their existence. The human health risk assessment results indicate the potential non-carcinogenic impact by Pb, Mn, Ni, Cu, Zn, and Cr and the carcinogenic impact by Pb and Cr.

8.1.4 Effective re-utilization of TCETP sludge and SBA in cement mortar mixes

- In the Chapter 6, textile effluent sludge and SBA have partially replaced cement in cement mortar mixes. The strength, durability, permeation, carbonation, alkalinity,and leaching tests are performed on the 13 different mortar mixtures. Microstructural analyses are also performed on the broken 28-day compressive test samples. The investigation reached the following specific conclusions.

- The strength of a few of the modified mortar mixes is comparable to the CM, and the later age strength (90 days) of the 2.5T, 5T, 5T5S and 7.55T5S is equivalent to the CM. However, the compressive strength of the mortar mixes declines with increasing sludge and SBA content such as in 7.5T10S, 10T10S mixes.

- The sorptivity test of the modified mortar mixes 2.5T5S, 5T5S and 7.5T5S, 2.5T, and 5T are less than the CM. It indicates the decline in capillary water absorption and thus reduced pores.
- The durability test results using the $MgSO_4$ show contradictory results to compressive strength results as the mixes 2.5T, 5T, 2.5T5S, 5T5S, 7.55T5S and 10T5S have higher loss of strength compared to other mixes.
- The pH of all the mortar mixes is between 12-13. The carbonation test shows that the mixes are carbonation free. The finding of the leaching test results indicates stabilization of sludge, and the presence of metals ions in the leachate for a few of the sludge and SBA blended mixes is below the admissible limit.
- SEM images demonstrate the densification of pores with the addition of sludge and SBA. However, the excessive formation of ettringite and large voids occurred at higher replacement levels. This also agrees with the conclusion drawn from the results of the compressive strength tests.

8.1.5 Environmental Impact Assessment of mortar mixes

- Chapter 7 examines the environmental impacts of utilizing TCETP sludge and SBA as an alternative for partially replacing cement in mortar. The environmental sustainability of the mortar mixes was found using the life cycle assessment approach.
- The results of the LCA analysis show a decrease in the adverse environmental impact of the manufacturing of modified mortar for the endpoint and mid-point categories.
- LCA results indicate a decreased emission of GHGs, thus positively impacting the environment and reducing the endpoint scores for ecosystem quality, human health, and resource categories.
- The progressive decrease in fossil depletion, ozone depletion, global warming potential, and human toxicity is observed with increasing sludge and SBA content in mortar mixes. This indicates that the production of cement is a primary GHG emission process.
- The results also indicate a significant reduction in the emission of GHGs to the environment for the modified mixes. It will reduce the landfill disposal of waste materials and thus decreases environmental implications.

- The cost analysis of the modified mixes results indicates a reduction in cost compared to the control mix, which suggests the economic feasibility of the modified mortar. The maximum cost reduction is about 8% for the modified mix.

  Finally, the planned approach could be implemented in a real scenario considering the administrative complexities, as it is challenging task to ask the industry for a heavy investment to develop the necessary infrastructure to address liquid and solid (sludge) wastes and a long-term operation. The technical advancements mainly recovery of value-added products such as sodium sulfate, sodium carbonate and potassium nitrate by osmotic membrane contactors, hydrogen and methane by hydrothermal gasification, energy by using microbial fuel cell, photocatalytic cells etc and use of water free dyeing process could be one way to reduce liquid and solid waste (Varjani et al., 2021; Khattab et al., 2020). However, the government intervene, and their policies could also help in encouraging industries for such huge investments. Further the government should provide subsidies in installing ZLD plant at various industries. Tax relaxation, development of guidelines are other few methods to encourage use of natural fibres, natural dyes and water free dyeing process.

8.2 Limitations and future scope of the work

Based on the research work and its contributions, this thesis can be distinguished as a unique and innovative attempt to improve the sustainability of the textile industry. Attempts have been made to make a decision-making framework for the selection of TWWTTs, and considering the results of it, the adsorption of contaminants before the MBR technique is suggested. Furthermore, sludge generated from the effluent treatment plant is hazardous and has pollution potential. Developing the leachate pollution index is useful in assessing sludge toxicity, as discussed in Chapter 6. The research also focuses on using sludge in mortar mixes and assessing the environmental impacts using the LCA approach. However, there is tremendous scope of research that can be performed for treating effluents and managing toxic sludge generated from the treatment plants. Considering the work performed, certain limitations and work that can be considered for future research are mentioned below:

- The limitation of Chapter 3 and the methodology adopted is that the target group is all from the same region. The selection of these techniques may have economic, social, environmental, and technical constraints that may impact the study's outcome.

- Chapter 4 considers using wheat straw-activated carbon for COD and color removal for real textile dyeing industry effluent. However, the flexibility of materials and the other parameters (temperature, pressure) can be considered in the extension of this research work.
- The research work in Chapter 4 doesn't consider dye aggregation, equilibrium isotherms and thermodynamic studies; the study was performed on industrial effluent. Therefore, it is not appropriate to form standard solutions of known concentrations as can be prepared from the artificially prepared dye solutions. The variation of initial concentrations is essential for the equilibrium isotherm study. The equilibrium constant value from the isotherm study is used for the thermodynamic study. However, the study on the artificial dye solution and the isotherm, the kinetic and thermodynamic study, could be considered one of the most crucial future works.
- There are several challenges associated with practical application of adsorbents such as extreme variability in industrial effluent and changes in the type of dyes produced and used in the industry, exhaustion of adsorbents in few days and weeks leading to its continuous demands and regeneration and large-scale requirement of raw materials.
- The end use of media is another limitation of using activated carbon in removing contaminants from effluents. There are three possible methods of disposal of active carbon: landfill, incineration for energy recovery and reduction of waste biomass volume and reactivation. Regeneration is necessary to keep the cost of treatment low, to recover the adsorbate, to conserve natural resources and to minimize the amount of waste. Reactivation of the spent AC is a sustainable approach. However, cost-effective methods are not yet available (Oladejo et., 2020). Ashes derived to some agricultural waste have pozzolanic properties when they are burnt under controlled temperature and residence time and can be used as supplementary cementitious materials (Martirena & Monzó, 2018). However, it is expected that exhausted media (wheat straw activated carbon) may consist of hazardous materials. Hence there is a need to study the characteristics of exhausted media using XRF to know about the chemical composition. It will help in appropriately planning its effective use. This is the future scope of our work.
- Chapter 5 considers the leaching effect of sludges from textile effluent treatment plants. However, the sludge from the different CETPs can be taken to study the leaching potential and ranked based on the toxicity and T_LPI index. This provides a vast scope of the study.

- In Chapter 6, the sludge and SBA are utilized in mortar mixes. However, further investigation can be done using different agricultural waste ashes and sludge in mortar mixes.
- In Chapter 7, the sensitivity analysis can also be performed to find the optimized distance based on global warming potential for using sludge and SBA in mortar mixes.

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Appendix: A

Response sheet: 1

At the outset, we thank you for your time in sharing your opinion.

1. This study aims to identify sustainable sub-criteria for evaluating the performance of textile wastewater treatment techniques in India. Extant literature is reviewed, and the list of sub-indicators that are valid in a global context is given below.
2. A total of 38 sustainable sub-indicators corresponding to four sustainable indicators are identified. We want your expertise to choose the list of sub-indicators that are more relevant in the Indian scenario.
3. Please fill the response sheet as given in Table A. 2 and give each sub-criterion score from (1 to 7) by using the linguistic scale as given in Table A.1 to determine the importance of selected sub-indicators. Given below are the sub-indicators for selecting the textile treatment technique.

Table A.1 Linguistic scale with score

Linguistic Scale	Score
Very Low (VL)	1
Low (L)	2
Medium Low (ML)	3
Medium (M)	4
Medium High (MH)	5
High (H)	6
Very High (VH)	7

Please fill your response in the table below

Table A.2 Response table for collecting data of sub-criteria for fuzzy Delphi analysis

Name of Respondent			**Date**
Designation			
S. No.	**Sustainable**	**Sub-criteria**	**Data Score**
1	Technical	Energy consumption	
2		Maintenance frequency	
3		Hydraulic Retention time	
4		BOD removal efficiency	
5		COD	
6		TSS	
7		Color	
8		Turbidity	
…		…	
17		Upgradability ease	
18		Accessibility ease	
19	Economic	Technology Cost	
20		Construction Costs	
21		Operation/ maintenance costs	
22		Capacity up-gradation	
23		Use of Locally available material.	
24	Environmental	Space requirement	
25		Soil contamination	

Name of Respondent			Date
Designation			
S. No.	Sustainable	Sub-criteria	Data Score
26		Surface water contamination	
…		…	
32		Effluent suitability for reuse	
33	Social	Public safety	
34		Employee Health	
35		Community participation	
36		Awareness to industries	
37		Acoustic/visual comfort	
38		Hiring local services	

Response sheet: 2

At the outset, we thank you for your time in sharing your opinion.

1. The objective of this study is to evaluate the performance of textile wastewater treatment techniques in India. Extant literature is reviewed, and the list of critical sub-indicators are given below.
2. A total of 28 critical sustainable sub-indicators corresponding to four sustainable indicators are identified. We want your expertise to compare the sustainable indicators, sub-indicators and alternatives corresponding to each sub-indicator based on their relative importance with each other.
3. Please give each sub-criterion score from (1 to 9) using the linguistic scale given in Table A.3.

Please fill the response tables for pairwise comparison of sustainability indicators and sub-indicators as given in Table A.4 and Table A.5. Also fill the response tables for comparison of alternatives for each sub-indicator

4. The value filled at the left side column shows the relatively higher importance of the left side parameter than right and the vice-versa.

Table A.3 Linguistic scale for fuzzy analytical hierarchical approach

Definition	Crisp
Equally important	1
Judgement value amid equally and weakly important	2
Weakly important	3
Judgement value amid weakly and strongly importance	4
Strongly important	5
Judgement value amid strongly and very strongly important	6
Very strongly important	7
Judgement value amid very strongly and extremely strongly important	8
Extremely strongly important	9

First round: Comparison of sustainability indicators

Table A.4 Response matrix for pairwise comparison of sustainability indicators

Left indicators	Left (1-9)	Right (1-9)	Right indicator
Technical			Social
			Economic
			Environment
Social			Economic
			Environment
Economic			Environment

Second round: Comparison of sub-indicators

1. **Technical**

Table A.5 Response matrix for pairwise comparison of sub-indicators

Left sub-indicator	Left (1-9)	Right (1-9)	Right sub-indicator
Energy consumption			BOD removal
			COD
			TSS
			Color
			Turbidity
			Sludge generated
			Durability
			Flexibility
			Complexity
			Upgradability ease
			Maintenance frequency
BOD removal			COD
			TSS
			Color
			Turbidity
			…
…			
Complexity			Upgradability ease
			Maintenance frequency

2. Social

Left sub-indicator	Left (1-9)	Right (1-9)	Right sub-indicator
Hiring local services			Public safety
			Employee health
			Awareness to industries
			Acoustic comfort to
…			
Awareness to			Acoustic comfort to

3. Economical

Left sub-indicator	Left (1-9)	Right (1-9)	Right sub-indicator
Technology cost			Construction costs
			Operation /maintenance
			Capacity up-gradation
…			
Operation/maintenance			Capacity up-gradation

4. Environmental

Left sub-indicator	Left (1-9)	Right (1-9)	Right sub-indicator
Space requirement			Surface water contamination
			Effect on the surrounding
			Footprint requirements
			Odour problems
			Poor aesthetics
			Effluent suitability for reuse

Left sub-indicator	Left (1-9)	Right (1-9)	Right sub-indicator
…			
Poor aesthetics			Effluent suitability for reuse

Third round: Comparison of alternatives for each sub-indicator

Alternatives

1. ASP: Activated Sludge Process
2. RBC: Rotating Biological Contractors
3. MBR: Membrane Bioreactors
4. EC: Electro-Coagulation
5. MBBR: Moving Bed Biofilm Reactor

Table A.6 Response matrix for comparison of alternatives for each sub-indicator

1.Energy Consumption

Left alternatives	Left (1-9)	Right (1-9)	Right alternatives
ASP			RBC
			MBR
			EC
			MBBR
…			
EC			MBBR

…

28.Poor Aesthetics

Alternatives	**Left (1-9)**	**Right (1-9)**	**Right alternatives**
ASP			RBC
			MBR
			EC
			MBBR
…			
EC			MBBR

Appendix: B

Fuzzy Delphi Technique

Step A: Data collection

In this first step of the study, the sustainability sub-criteria are identified from the extant literature and the expert opinion. Later, the list is circulated among the chosen experts from different backgrounds so that the analyst can capture the subjective and the objective aspects of the experts' judgement.

Step B: Conversion of expert opinion into TFN

The experts' judgement was collected from the questionnaire using the linguistic scale for which the fuzzy score is associated and is given in Table 2 of section 1, step 3.

Let G_{ij} is the fuzzy score corresponding to the linguistic scale given for the i^{th} sub-criterion of 'm' sub-criteria and by the j^{th} expert of 'n' experts. Then the score can be represented using Eq. (1).

$$G_{ij} = \left(a_{ij,} b_{ij,} c_{ij}\right) \; where, i = 1,2,3 \ldots\ldots m; j = 1,2,3 \ldots\ldots n \quad (1)$$

The ith sub-criterion overall fuzzy weight, considering the 'n' experts' scores, can be computed using Eq. (1). The lower bound and the upper bound are the minimum and maximum value among the $a_{i\,j=1}^{n}$ and $c_{i\,j=1}^{n}$ respectively. The middle bound is estimated by geometric mean of all the b_{ij} for each sub-criterion for n experts.

$$G_i = \left[\min\left(a_{ij}\right), \left(\prod_{j=1}^{n} b_{ij}\right)^{1/n}, \; \max\left(c_{ij}\right)\right] \quad (2)$$

Step-C: Defuzzification of fuzzy score

The de-fuzzified weight of each sub-criterion is estimated using the mean method given in Eq. (3).

$$G_i^d = \left[\frac{\min\left(a_{ij}\right) + \left(\prod_{j=1}^{n} b_{ij}\right)^{1/n} + \max\left(c_{ij}\right)}{3}\right] \quad (3)$$

Appendix C

The final assessment and the ranking of alternatives are done using Cheng's Entropy method of FAHP. The calculated fuzzy synthetic extent analysis of alternatives for each criterion is used to find the α-cut performance matrix at the confidence level (α=0.8) and the optimism index (λ = 0.5). This matrix is called the total fuzzy judgement matrix and is shown in Table C.1.

Table C.1 The total fuzzy judgement matrix for $\alpha = 0.8,\ \lambda = 0.5$ of alternatives and the sub-indicators.

	T1	**T2**	**T3**	**T4**	**T5**
A1: ASP	[0.0025,0.0027]	[0.004,0.0043]	[0.004,0.0043]	[0.0008,0.0009]	[0.0023,0.0025]
A2: RBC	[0.0044,0.0048]	[0.0033,0.0036]	[0.0164,0.0174]	[0.0057,0.006]	[0.008,0.0084]
A3: MBR	[0.0018,0.002]	[0.0092,0.0099]	[0.0123,0.0131]	[0.0132,0.014]	[0.0086,0.0091]
A4: EC	[0.0004,0.0005]	[0.0023,0.0024]	[0.0076,0.0082]	[0.006,0.0064]	[0.0188,0.0198]
A5: MBBR	[0.0051,0.0054]	[0.0016,0.0018]	[0.0013,0.0014]	[0.005,0.0054]	[0.0062,0.0065]
	T6	**T7**	**T8**	**T9**	**T10**
A1: ASP	[0.0017,0.0018]	[0.001,0.0011]	[0.0013,0.0014]	[0.0026,0.0028]	[0.0015,0.0017]
A2: RBC	[0.0041,0.0044]	[0.0139,0.0148]	[0.0031,0.0034]	[0.0006,0.0006]	[0.0008,0.0009]
A3: MBR	[0.0087,0.0092]	[0.0064,0.0068]	[0.0055,0.006]	[0.0023,0.0025]	[0.0007,0.0008]
A4: EC	[0.0089,0.0094]	[0.0127,0.0134]	[0.0005,0.0005]	[0.0022,0.0024]	[0.0003,0.0004]
A5: MBBR	[0.0006,0.0007]	[0.0034,0.0037]	[0.0045,0.0048]	[0.0088,0.0094]	[0.0018,0.002]
	T11	**T12**	**S1**	**S2**	**S3**
A1: ASP	[0.0013,0.0014]	[0.0019,0.0021]	[0.003,0.0037]	[0.0019,0.0023]	[0.0011,0.0013]
A2: RBC	[0.0012,0.0013]	[0.0023,0.0025]	[0.003,0.0036]	[0.0044,0.0053]	[0.0005,0.0006]
A3: MBR	[0.0042,0.0045]	[0.0004,0.0004]	[0.0025,0.003]	[0.0037,0.0045]	[0.0037,0.0045]

A4: EC	[0.0003,0.0004]	[0.0008,0.0009]	[0.0022,0.0027]	[0.0013,0.0016]	[0.0034,0.0041]
A5: MBBR	[0.0014,0.0015]	[0.0011,0.0012]	[0.0015,0.0019]	[0.0009,0.0011]	[0.0035,0.0042]
	S4	**S5**	**E1**	**E2**	**E3**
A1: ASP	[0.0014,0.0017]	[0.0002,0.0002]	[0.0008,0.0009]	[0.0005,0.0005]	[0.0009,0.001]
A2: RBC	[0.0015,0.0018]	[0.0004,0.0005]	[0.0052,0.006]	[0.0024,0.0028]	[0.0071,0.0084]
A3: MBR	[0.0003,0.0004]	[0.0004,0.0005]	[0.0022,0.0026]	[0.0083,0.0095]	[0.0064,0.0076]
A4: EC	[0.001,0.0012]	[0.0001,0.0001]	[0.0089,0.0102]	[0.002,0.0023]	[0.0025,0.003]
A5: MBBR	[0.0005,0.0006]	[0.00004,0.0001]	[0.0145,0.0165]	[0.0054,0.0062]	[0.0059,0.007]
	E4	**E5**	**E6**	**E7**	**EC1**
A1: ASP	[0.0011,0.0013]	[0.0003,0.0004]	[0.0002,0.0003]	[0.0014,0.0016]	[0.0012,0.0014]
A2: RBC	[0.0055,0.0064]	[0.001,0.0012]	[0.001,0.0012]	[0.0067,0.0048]	[0.0042,0.0049]
A3: MBR	[0.0099,0.0114]	[0.0021,0.0025]	[0.0008,0.0009]	[0.0266,0.0221]	[0.0006,0.0007]
A4: EC	[0.0009,0.0011]	[0.0014,0.0017]	[0.002,0.0024]	[0.0051,0.004]	[0.0073,0.0086]
A5: MBBR	[0.0041,0.0048]	[0.0002,0.0002]	[0.0002,0.0002]	[0.0162,0.0131]	[0.0082,0.0096]
	EC2	**EC3**	**EC4**		
A1: ASP	[0.0039,0.0046]	[0.0278,0.0313]	[0.0003,0.0003]		
A2: RBC	[0.0129,0.0148]	[0.0578,0.0646]	[0.001,0.0012]		
A3: MBR	[0.0022,0.0026]	[0.0114,0.013]	[0.0029,0.0035]		
A4: EC	[0.0272,0.0311]	[0.0035,0.004]	[0.0019,0.0023]		
A5: MBBR	[0.0256,0.0291]	[0.0458,0.0513]	[0.0043,0.0051]		

Appendix D

Table D.1 CCM matrix for the experimental run with input factors

Run order	Coded values				Uncoded Values			
	A	B	C	D	A = contact time (min)	B = adsorbent (g/l)	C = pH	D = Temp (°C)
1	0	0	0	1	80	2	7	50
2	1	0	0	0	120	2	7	40
3	0	0	0	0	80	2	7	40
4	0	-1	0	0	80	1	7	40
5	0	0	-1	0	80	2	5	40
6	0	0	1	0	80	2	9	40
7	-1	0	0	0	40	2	7	40
8	0	0	0	-1	80	2	7	30
9	0	0	0	0	80	2	7	40
10	0	1	0	0	80	3	7	40
11	-0.5	-0.5	-0.5	0.5	60	1.5	6	45
12	-0.5	0.5	-0.5	0.5	60	2.5	6	45
13	-0.5	-0.5	0.5	-0.5	60	1.5	8	35
14	-0.5	0.5	0.5	-0.5	60	2.5	8	35
15	0	0	0	0	80	2	7	40
16	-0.5	-0.5	0.5	0.5	60	1.5	8	45
17	0.5	-0.5	-0.5	0.5	100	1.5	6	45
18	0.5	-0.5	0.5	0.5	100	1.5	8	45
19	-0.5	-0.5	-0.5	-0.5	60	1.5	6	35
20	0	0	0	0	80	2	7	40

Run order	Coded values				Uncoded Values			
	A	B	C	D	A = contact time (min)	B = adsorbent (g/l)	C = pH	D = Temp (ºC)
21	-0.5	0.5	-0.5	-0.5	60	2.5	6	35
22	0	0	0	0	80	2	7	40
23	-0.5	0.5	0.5	0.5	60	2.5	8	45
24	0.5	0.5	-0.5	0.5	100	2.5	6	45
25	0.5	-0.5	-0.5	-0.5	100	1.5	6	35
26	0.5	0.5	0.5	0.5	100	2.5	8	45
27	0.5	0.5	0.5	-0.5	100	2.5	8	35
28	0.5	-0.5	0.5	-0.5	100	1.5	8	35
29	0.5	0.5	-0.5	-0.5	100	2.5	6	35
30	0	0	0	0	80	2	7	40

Table D.2 Cost estimation for production of 1 kg WSAC.

Components	Consumption	Unit cost	Cost ($)
Wheat Straw	9.375 kg	0.0014 $/kg	0.013
Acid	1000 ml	0.24 $/l	0.24
NaOH	750 g	5.7 $/kg	4.2
Furnace run/Furnace run	8 run/2h/1kW	7 kWh	1.6
Water	32l	0.14 $/l	4.5
Total			10.71

Appendix E

Table E.1 Experiment design for the TCLP test of Textile industry common effluent treatment plant sludge

Experiment No.	A= Weight (g)	B=Time (hour)	C= Temp (℃)	D= RPM	A= Weight	B=Time	C= Temp	D= RPM
S1	1	1	1	1	20	8	50	160
S2	-1	1	-1	1	10	8	30	160
S3	1	1	1	-1	20	8	50	120
S4	1	1	-1	1	20	8	30	160
S5	-1	-1	1	1	10	4	50	160
S6	0	0	0	0	15	6	40	140
S7	-1	1	-1	-1	10	8	30	120
S8	1	-1	-1	-1	20	4	30	120
S9	0	0	0	0	15	6	40	140
S10	-1	-1	1	-1	10	4	50	120
S11	1	1	-1	-1	20	8	30	120
S12	-1	1	1	-1	10	8	50	120
S13	1	-1	1	-1	20	4	50	120
S14	-1	-1	-1	1	10	4	30	160
S15	-1	1	1	1	10	8	50	160
S16	0	0	0	0	15	6	40	140
S17	1	-1	-1	1	20	4	30	160
S18	1	-1	1	1	20	4	50	160
S19	0	0	0	0	15	6	40	140

Experiment No.	A= Weight (g)	B=Time (hour)	C= Temp (℃)	D= RPM	A= Weight	B=Time	C= Temp	D= RPM
S20	-1	-1	-1	-1	10	4	30	120
S21	0	0	0	-2	15	6	40	100
S22	0	0	0	0	15	6	40	140
S23	0	0	0	2	15	6	40	180
S24	2	0	0	0	25	6	40	140
S25	0	-2	0	0	15	2	40	140
S26	0	2	0	0	15	10	40	140
S27	-2	0	0	0	5	6	40	140
S28	0	0	-2	0	15	6	20	140
S29	0	0	2	0	15	6	60	140
S30	0	0	0	0	15	6	40	140

Table E.2 Value of the parameters used for determining Human Health Risk Assessment (HHRA) (Mukherjee et al., 2020)

Parameters	Infants	Children	Teens	Adults	Unit
Exposure Frequency (ExF)	365	365	365	365	d/yr
Exposure Duration (ExD)	1	6	6	6	yr
Exposure Time (ExT)	0.08	0.13	0.13	0.13	hr/d
Body Weight (BWt)	7	16.68	46.25	57.03	kg
Average Exposure Time (AET)	365	2190	2190	2190	d
Exposed Surface Area (SAF)	3416	7422	14321	18182	cm2
Skin fraction in contact with	0.9	0.9	0.9	0.9	unitless

Ingestion Rate (InR)	0.61	1.25	1.58	1.95	kg/d

Table E.3 Value of the coefficients used for computing Hazard Quotient Index (HQI)

Heavy	Dermal permeability	Reference Dose	Reference Dose	Reference
Al	0.001	1	0.2	(Tong et al.,
Cu	0.001	0.04	0.012	(Mukherjee et al., 2020)
Cr	0.002	0.003	0.000015	
Fe	0.001	0.3	0.045	
Mn	0.001	0.02	0.008	
Ni	0.0002	0.02	0.0054	
Pb	0.0001	0.0014	0.00042	
Zn	0.0006	0.06	0.06	

List of publications

JOURNALS

1. **Agarwal, S.,** Singh, A.P. (2022). Performance evaluation of textile wastewater treatment techniques using sustainability index: An integrated fuzzy approach of assessment, Journal of Cleaner Production. 337. 130384.https://doi.org/10.1016/j.jclepro.2022.130384 **(SCIE and SCOPUS indexed) (I.F. 11.072).**

2. **Agarwal, S.,** Singh, A.P. & Mathur, S. (2023). Removal of COD and colour from textile industrial wastewater using wheat straw activated carbon: an application of response surface and artificial neural network modelling, Environmental Science and Pollution Research. https://doi.org/10.1007/s11356-022-25066-2 **(SCIE and SCOPUS indexed) (I.F.: 5.190).**

3. **Agarwal, S.,** Singh, A.P. Assessment of Toxicity Characteristics in Leachate from the Textile Industry–Based Sludge Using Leachate Pollution Index. *Water Air Soil Pollut* 234, 774 (2023)**. https://doi.org/10.1007/s11270-023-06785-9 (SCI and SCOPUS indexed) (I.F.: 2.90).**

CONFERENCES

1. Agarwal, S., Singh, A.P., Mathur, S. (2022). Utilizing the Potential of Textile Effluent Treatment Sludge in Construction Industry: Current Status, Opportunities, Challenges, and Solutions. In: Kanwar, V.S., Sharma, S.K., Prakasam, C. (eds) Proceedings of International Conference on Innovative Technologies for Clean and Sustainable Development (ICITCSD – 2021). pp. 279–290, Springer, Cham. https://doi.org/10.1007/978-3-030-93936-6_22 (SCOPUS indexed).

Research work under review

1. Effective reutilization of textile sludge from common effluent treatment plant with mineral admixture in cement mortar mixes (Journal of material cycles and waste management)

2. Environmental Impact Assessment of using textile industry effluent treatment plant sludge and bagasse ash in mortar (submitted)

Brief biography of the candidate

Somya Agarwal is a Research Scholar in the Department of Civil Engineering at Birla Institute of Technology & Science (BITS) Pilani, Rajasthan. She has completed her B.E in Civil Engineering from Galgotia College of Engineering and Technology, Greater Noida and M.E Civil with Infrastructure Engineering and Management from Birla Institute of Technology and Science, Pilani. Her research interest lies in treatment and providing sustainable solutions for industrial wastes, use of fuzzy logic in selection of wastewater treatment technique and development of leachate pollution index. Liquid and solid waste sample collection, storage, its characterization using various analytical techniques such as UV-VIS spectrophotometer, XRD, XRF, FE-SEM are few of the area of expertise of her. Additionally, design of experiments, batch experiments, development of adsorbents, leaching study for sludges, life cycle assessment and testing various properties of mortar mixes such as mechanical, durability, microstructure, and permeation property are the areas in which she has worked during her Ph.D. She has published three research papers in the journals of international repute and two paper in an international conference.

Brief biography of supervisor

Prof. Ajit Pratap Singh is currently working as a Senior Professor of Civil Engineering Department and Dean, Academic- Undergraduate Studies (University Wide) at Birla Institute of Technology and Science, Pilani, Rajasthan India. He obtained his B.E. (Hons) Civil, M.E. (Civil), Ph.D in Environment and Water Resource Planning and Management from BITS Pilani, Rajasthan, India. He is Fellow of the Institution of Engineers (India), Fellow of Inidan Association of Hydrologist (FIAH) and Member of Eastern Asia Society for Transportation Studies (EASTS), Japan etc. He has been actively reviewing various research papers submitted in his fields to more than 25 Journals of International and National reputation. His administrative appointments at BITS include Dean, Instruction Division (Campus wide), Dean Admissions (University wide), Assistant Dean, Instruction Division and Head of Department, Civil Engineering Department (Dubai Campus). He has more than 25 years of teaching and research experience in the area of sustainable water resource management, hydraulic and water resources engineering with special focus on surface water-quality modelling, and advanced computer applications: water quality and quantity assessment, water pollution analysis, solid waste management, prediction and management of surface water, groundwater contaminants, transport modelling, climate change, soft computing techniques, fuzzy-based decision making , simulations and modelling and pavement management systems. Dr. Singh has worked on various important projects as third-party expert funded under JNNURM, PMGSY, NHAI, PCI verification schemes of Central and State governments, working group expert member of National Institute of Hydrology, Roorkee, Government of India, Coordinator, PTA (PMGSY roads), Rajasthan state, National Rural /Infrastructure Development (NRIDA), Ministry of Rural Development, Government of India, New Delhi, etc. He has also worked as commissioner for Hon'ble National Green Tribunal, New Delhi for assessing the status of environmental quality in different rivers.

He has published more than **150** research papers in different journals and international conference proceedings of repute in his area of research. Prof. Singh has guided **9** doctoral theses and over **50** master's dissertations and currently guiding **3** Ph.D. students in research areas of real-life importance. Prof. Singh has also evaluated **20** Ph.D. thesis.