ADSORPTIVE REMOVAL OF COPPER, CADMIUM AND CHROMIUM FROM WASTEWATER: MODELLING AND EXPERIMENTAL STUDY

Ph.D. Thesis

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(2014RCH9064)

DEPARTMENT OF CHEMICAL ENGINEERING
MALAVIYA NATIONAL INSTITUTE OF TECHNOLOGY JAIPUR

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DECLARATION

I, **Renu**, declare that this thesis titled, **“ADSORPTIVE REMOVAL OF COPPER, CADMIUM AND CHROMIUM FROM WASTEWATER: MODELLING AND EXPERIMENTAL STUDY**” and the work presented in it, are my own. I confirm that:

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CERTIFICATE

This is to certify that the thesis entitled **"ADSORPTIVE REMOVAL OF COPPER, CADMIUM AND CHROMIUM FROM WASTEWATER: MODELLING AND EXPERIMENTAL STUDY"** being submitted by **RENU (2014RCH9064)** is a bonafide research work carried out under my supervision and guidance in fulfillment of the requirement for the award of the degree of **Doctor of Philosophy** in the Department of Chemical Engineering, Malaviya National Institute of Technology, Jaipur, India. The matter embodied in this thesis is original and has not been submitted to any other University or Institute for the award of any other degree.

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Signature

ABSTRACT

Due to industrialization, heavy metal has become a serious environmental problem. There are many industries which discharge wastewater containing heavy metals such as textile electroplating, mining, pigments, tanning leather, cement and battery manufacturing. These heavy metals are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg). If the quantity of these heavy metals increases more than their permissible limit they are harmful for living organism.

There are many techniques for heavy metal removal from wastewater such as chemical precipitation, floatation, ion exchange, membrane filtration, and adsorption. But all these techniques have many demerits over adsorption such as chemical precipitation technique produces large amount of sludge, floatation technique requires large initial cost, ion exchange technique causes environmental pollution during regeneration and membrane filtration has membrane fouling problem. Thus, adsorption process is the most efficient and widely used technique for heavy metals removal from wastewater due to its low cost, easy availability and eco-friendly nature. There are two types of adsorbents which are used for heavy metal removal from wastewater such as commercial adsorbents and biosorbents. Commercial adsorbents are costly that’s why there is a necessity to explore biosorbents for heavy metal removal because of their low cost. Different adsorbents such as rice husk, sugarcane bagasse, saw dust, apple pomace, orange peel, grape stalk wastes, peanut shell, hazelnut shell, papaya wood, coffee residue, coconut waste and egg shell etc. were used for heavy metal removal from wastewater.

In the present study, an efficient adsorbent has been developed by acid treatment of wheat bran. The adsorbent was characterised using different characterisation techniques such as scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction analysis (XRD), fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). For optimization study the response surface methodology based box behnken design was used in Design of Experiments (DOE) software for optimization of various parameters such as effect of initial concentration, pH, temperature and adsorbent dose for heavy metal removal from wastewater. A quadratic model was developed for prediction of heavy metals removal such as copper, chromium and cadmium.

The actual R^2 value of model were found to be 0.97 for copper, 0.95 for cadmium, and 0.95 for chromium, respectively, which indicates satisfactory accuracy of the model. The optimum conditions were obtained as follows: initial metal concentration 90.58 mg/L, pH 6, temperature 35.9°C, and adsorbent dose 2.39 g, the removal efficiency of copper, chromium, and cadmium has reached 98.55%, 68.04%, and 54.19%. Adsorption isotherms and rate kinetics were also investigated.

The adsorption followed the pseudo-second order model from the kinetic studies. The equilibrium data fitted well to both Langmuir and Temkin isotherms, with the maximum adsorption capacity of 4.33 mg/g for copper, 9.00 mg/g for chromium, and 3.37 mg/g for cadmium.

From thermodynamic parameters, it is obvious that adsorption process is spontaneous, endothermic for copper and chromium, and exothermic for cadmium. Adsorbent regeneration study was also carried out in batch mode because disposal of saturated adsorbent is harmful for environment. Further, mixed metal ion study and simultaneous removal of metal ions and dye was also carried to predict the synergistic and antagonistic effect of metal ions on metal removal, For mixed metal ion study the actual value of R^2 were found to be 0.95 for copper, 0.97 for cadmium and 0.97 for chromium respectively. For simultaneous removal of metal ions, the actual value of R^2 were found to be 0.80 for copper, 0.82 for cadmium, 0.82 for chromium and 0.80 for dye. Metal complex dyes were also oxidised to release metals and then removed using adsorption process. Similarly, individual metal ions study, mixed metal ions study and study for simultaneous removal of metal ions and dye was also carried out in continuous column. For continuous column study adsorbent pellets were prepared using suitable binders. Then characterisation of adsorbent pellet before and after adsorption process clearly shows that the prepared adsorbent pellets are efficient for removal of copper, chromium and cadmium.

Continuous process was also modelled in fixed bed column by assuming axial dispersion and langmuir isotherm as an equilibrium model. Model equations were solved in MATLAB software by using finite difference technique. It was observed that there is a good agreement in experimental data and model data obtained from MATLAB software. It was also concluded that on increasing bed height, breakthrough time achieved later.

However, on decreasing the flow rate and initial metal concentration, breakthrough time was achieved later. Therefore, it shows that the fixed bed column works efficiently at higher bed height, low flow rate and low initial metal concentration. Continuous study was also carried out for industrial wastewater. Industrial wastewater was collected from various industries such as textile, dye, tannery and electroplating industry. Physico-chemical characterisation of wastewater was done and column experiments were also carried out to analyse the real wastewater sample characteristics.

The result of this study shows that the adsorbent prepared is efficient for heavy metal removal from wastewater at optimum conditions.

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NOMENCLATURE

Abbreviations

SEM	Scanning electron microscope analysis
EDS	Energy dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-Ray diffraction analysis
XPS	X-ray photoelectron spectroscopy
MAPE	The mean absolute percentage error
MWB	Modified wheat bran
RMSE	Root mean square error
TDS	Total dissolved solids
TOC	Total organic carbon

List of Nomenclature

C_0	Initial metal concentration (mg/L)
C_t	Metal concentration at equilibrium (mg/L)
Ce	Equilibrium concentration in the liquid phase (kg/m^3)
R	Heavy metal removal efficiency
R_{Cu}	Removal efficiency of copper
R_{Cr}	Removal efficiency of chromium
R_{Cd}	Removal efficiency of cadmium
df	Degree of freedom
V	Volume of solution (L)
W	Weight of the adsorbent (g)
k_c	Rate coefficient (m^3/kg.s)
B	the adsorption energy constant (mol^2/kJ^2)
ε_P	the Polanyi potential
R	the gas constant (8.314 J/(mol k))
T_a	the absolute temperature (K)
E	the mean free energy (kJ/mol)
b_T	temkin constant (J/mol)
k_T	the Temkin constant related to the equilibrium binding energy (L/mg)
k_1	the rate constant of pseudo first order adsorption
k_2	the rate constant of pseudo second order adsorption (g/mg min)

K_C	Equilibrium constant
C_{AC}	Equilibrium concentration of the metal ion on adsorbent (mg/L)
C_e	Equilibrium concentration of the metal ion in the solution (mg/L)
ΔG	Change in gibbs energy
ΔH	Change in enthalpy
ΔS	Change in entropy
k_m	External mass transfer coefficient (m/s)
Q	Adsorbate concentration (mg/L)
C	Concentration of bulk solution (mg/L)
q_t	the adsorption capacity at time t (mg/g)
t	Time (s)
Z	Axial position from inlet (m)
D_L	Axial dispersion coefficient (m^2/s)
ε_b	Void fraction of bed
C_{os}	Adsorbate concentration in outlet stream (mg/L)
C_{fs}	Adsorbate concentration in the feed stream (mg/L)
ρ_b	Bed density (kg/m^3)
ρ_p	Particle density (kg/m^3)
D_m	Molecular diffusion (m^2/s)
R_p	Pellet radius (m)
U	Interstitial fluid velocity in direction z (m/s)
V	Superficial velocity (m/s)
N	Number of data point
E	Bed porosity
R_e	Reynolds number
Ψ	Association parameter for water = 2.6
M_B	Molecular weight of solvent B
T	Temperature(K)
μ_B	Viscosity of solvent (Kg*s/m)
v_A	Solute molar volume at boiling point (m^3/Kg*mol)
Sh	Sherwood number
Sc	Schmidt number
d_p	Pellet diameter
ν	Kinematic viscosity (m^2/s)

D	Film phase diffusion coefficient m^2/s
D_b	Bed diameter(m)
L	Bed height
a_p	Particle radii
λ_{max}	Maximum wavelength
1/n	Adsorption intensity
k_f	Adsorption intensity
q_e	Adsorption capacity (mg/g)

PUBLICATIONS OUT OF THIS WORK

Journal papers:

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CHAPTER – 1

INTRODUCTION

Enhanced Industrial activities and global population have caused release of huge quantity of effluents in the form of waste gases and waste water streams in the environment leading to contamination of ecosystem especially aquatic system due to discharge of waste water (Aigbe et al., 2018). Release of effluent streams in the environment, without necessary treatment is the major cause of environmental pollution. Water pollution is one of the major pollution of concern worldwide. The release of contaminated water in natural water source not only affects the aquatic life but also causes shortage of pure water for drinking purpose. Availability of pure water is very important for human life because accessibility of pure water is decreasing day by day. Also the consumption of water is increasing with the increasing world population. According to WHO 2003, 1.2 billion people are suffering from scarcity of safe water (Rijsberman 2006). Among all pollutants, heavy metals are considered to be one of the biggest environment threats (Mehdipour et al., 2015) even at low concentration due to their non-biodegradability, toxicity and persistent nature. Various health issues have been reported in human beings due to constant exposure of these toxic metals such as poisoning, organ failure and neurological disorder (Wang et al., 2019; Othman et al., 2012; Ren et al., 2008; Fu et al., 2011).

Therefore, these heavy metals containing streams need be treated for removal of metals, before its discharge into the environment. The effluent streams may carry single heavy metals, multiple heavy metals and heavy metals with other impurities such as dyes, pigments, solvents etc. A detail chemical analysis of heavy metals, their source, toxicity and their health hazards has to be evaluated before adopting any removal mechanism.

1.1 Heavy metals

Heavy metals are those elements which have atomic weights between 63.5 and 200.6 and also specific gravity greater than 5.0 (Srivastava & Majumder 2008). Copper, chromium, cadmium, nickel, zinc, lead, mercury are heavy metals. Heavy metals are present in large amount in the earth’s crust. These metals are mostly used in various industrial processes such as dyeing, printing, electroplating, tanning, etc. The waste water discharged from these industries open water bodies is used for irrigation in many places for agriculture production due to scarcity of pure water. Being non-biodegradable and persistent in nature these heavy metals get accumulated in the aquatic lives and food grains and reaches to human being through food chain (Hapke 1996). Trace amount of heavy metals is essential for human being however, excessive amount of heavy metals is harmful leading to various health problems (Hu et al., 2013; Fu et al., 2011).

1.2 Source and toxicity of heavy metals

Heavy metals discharged from various industrial activities are toxic and carcinogenic and thus harmful to humans and other living species (Clement et al., 1995; Maccarthy et al., 1993; Renge et al., 2012). Heavy metals present in soil and water, enter into human body through plants and animals (Hapke 1996) through food chain. The most concerned heavy metals from various industries include copper, chromium, cadmium, nickel, zinc, lead, mercury (Mehdipour et al., 2015). They originate from sources such as metal complex dyes, pesticides, fertilisers, fixing agents (which are added to dyes to improve dye adsorption onto the fibres), mordants, pigments and bleaching agents from dye industries (Rao et al., 2010). Other Industries such as leather, electroplating, mining, film and photography, metal cleaning, jewellery etc. also discharge considerable amount of heavy metal ions in its effluent stream (Aigbe et al., 2018; Gopalakrishnan et al., 2015; Lin et al., 2017; Wang 2018). In developed countries, legislation is becoming increasingly stringent for heavy metal limits in wastewater. Under section VI of the Environmental (Protection) Rules 1986, central pollution control board, India has set permissible limit for heavy metals discharge in wastewater such as 3, 0.1, 2, 5, 0.1, 0.01, 3 mg/L for copper, chromium, cadmium, zinc, lead, mercury, and nickel respectively. In India, the current maximum contaminant level (ppm) for heavy metals in drinking water is 0.05, 0.01, 0.25, 0.20, 0.80, 0.006, 0.00003 for chromium, cadmium, copper, nickel, zinc, lead, mercury respectively (Gopalakrishnan et al., 2015). Chromium(VI) is an oxidising agent which is carcinogenic in nature and it is also harmful to plants and animals (Barnhart 1997). Chromium is present in two oxidation states, chromium(VI) and chromium(III) (Mohan et al., 2006). Chromium(VI) is more toxic than chromium(III) and is of more concern (Othman et al., 2012). The United States Environmental Protection Agency (USEPA) has set the maximum chromium levels (MCL) in drinking water at 0.1 mg/L. The USEPA has classified cadmium as a human carcinogen and it is known to cause deleterious effects to health and it is listed as a Category-I carcinogen by the International Agency for Research on Cancer (IARC) and a group B-I carcinogen by the USEPA (Friberg et al., 1992). Copper is an essential element and is required for enzyme synthesis as well as tissue and bone development. However, excessive intake of copper (10 mg/day) may lead to liver damage. The USEPA has set the copper limit at 1.3 mg/L in industrial effluents. Similarly, lead is harmful to human health and can damage kidney, liver, reproductive system and brain functions (Naseem & Tahir 2001) as shown in Fig. 1.1. Table1.1 shows the route of exposure, sources and health effects of heavy metals.

Table 1.1: Route of heavy metals exposure and health effects

Heavy Metal	MCL (mg/mL)	Route of exposure	Sources	Health effects	References
Copper	0.25	Food, drinking water	Smelting, mining, electroplating, surface finishing, electric appliances, electrolysis, electrical components	Headache, vomiting, nausea, liver & kidney failure, respiratory problems & abdominal pain	Ren et al., 2008; Hu et al., 2013; Lan et al., 2013
Chromium	0.05	Water, soil, food	Leather tanning, electroplating, nuclear power plants , textile industries	Cancer in the digestive tract & lungs, epigastric pain, nausea, severe diarrhoea, vomiting and haemorrhage	Mohanty et al., 2005
Cadmium	0.01	Food, cigarette smoking	Metal refineries, smelting, mining, the photographic industry	Bone demineralisation	Fu et al., 2011
Nickel	0.20	Drinking water, food, inhalation	Nickel-cadmium batteries ,electroplating industry, Pigments	Kidney, lung problems, gastrointestinal distress, skin dermatitis, pulmonary fibrosis	Borba et al., 2006
Zinc	0.80	Water, soil	Mining, paint, pharmaceuticals, textiles industry	Skin irritation, stomach cramps, vomiting and anaemia	Oyaro et al., 2007
Lead	0.006	Water, soil, paint	Lead based paints, glazed food containers, leaded joints in municipal water systems	Damage kidney, liver, reproductive system, brain functions	Naseem & Tahir 2001; Järup 2003
Mercury	0.00003	Food, fish, dental amalgam	Chlor-alkali industry	Pulmonary, chest pain, dyspnoea	Järup 2003; Namasivayam & Kadirvelu 1999

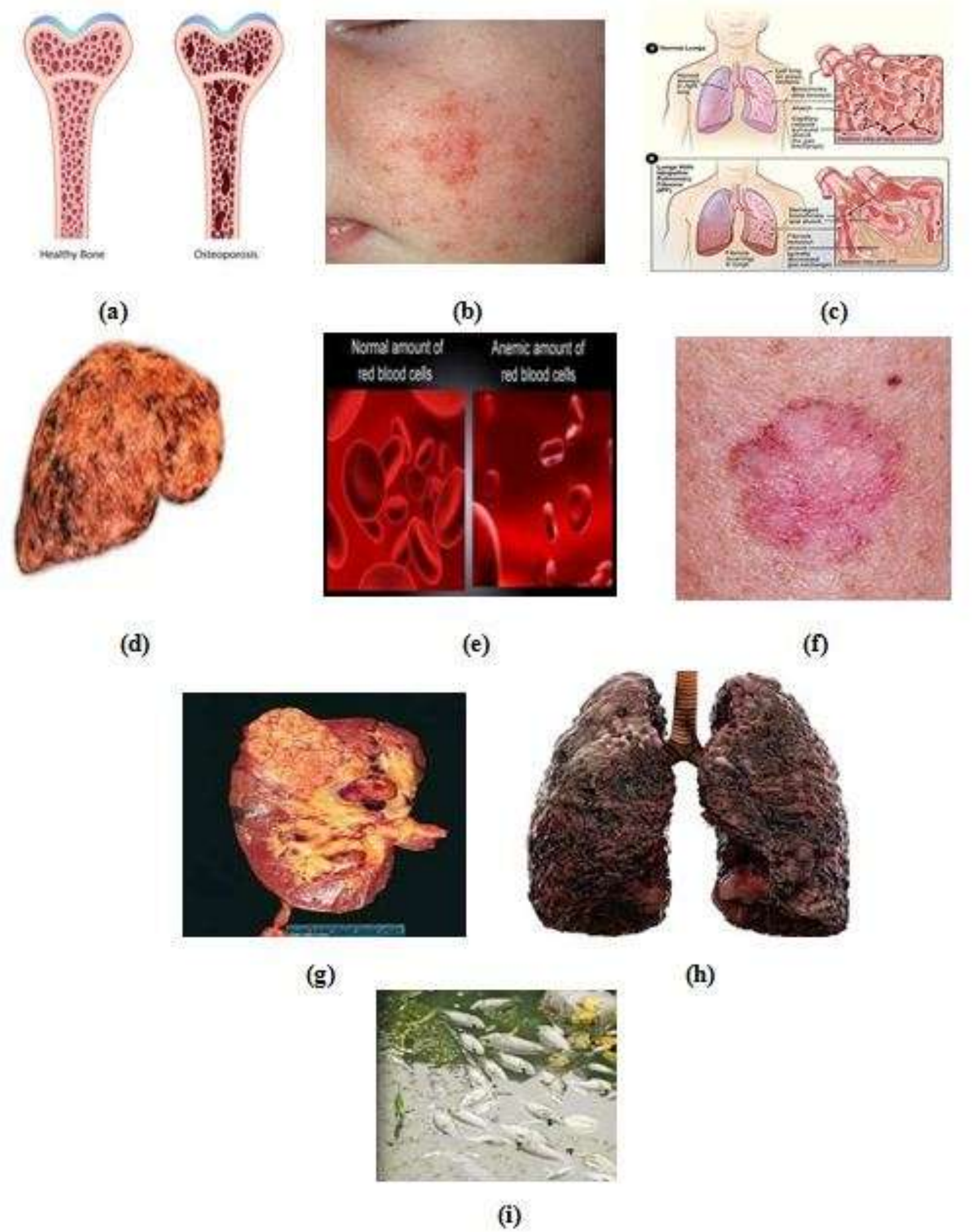


Fig 1.1 Harmful effects of heavy metal on human body (a) Bone demineralizarion (b) Skin dermatitis (c) Pulmonary fibrosis (d) Damaged liver (e) Anaemia (f) Skin cancer (g) Kidney cancer (h) Lung cancer and on aquatic life (i) Death of fish

1.3 Permissible limits of heavy metals

Due to stringent regulations for heavy metals, their removal has become a serious environmental problem. Thus a permissible limit of heavy metals in drinking water and in industrial effluents has been specified by World health organization (WHO) for release of effluents. Presence of heavy metals more than the permissible limit is harmful for living organisms and such limits are given in Table 1.2.

Table 1.2 Permissible limits of heavy metals in industrial effluents (Section VI of the Environmental (Protection) Rules 1986; GSR 801 (E) EPA 1993; Cobbina et al., 2015; Mohod et al., 2013)

Central pollution control board, India Permissible limits (mg/L)		
Metal	**In industrial effluents**	**WHO Limit**
Copper	3	0.05
Chromium (VI)	0.1	0.05
Total Chromium	2	-
Cadmium	2	0.005
Zinc	5	5
Lead	0.1	0.05
Mercury	0.01	0.01
Arsenic	0.2	0.05
Selenium	0.05	-
Nickel	3	-
Cyanide	0.2	-
Fluoride	2	-

1.4 Origin of the problem

Excessive release of heavy metals into environment is a serious problem worldwide. These metals may be released in to the water as natural components of the earth's crust or through industrial effluents. These metals enters into human bodies through food (irrigation by contaminated water), food chain (accumulation in fishes other aquatic animals) and drinking water. Although a small quantity of these metals are required for human metabolism, but excess may cause health problems as specified in Table 1.1. The permissible limit specified by WHO need to be followed strictly. There are many techniques adopted for heavy metal removal such as chemical precipitation, ion exchange, floatation, coagulation and Flocculation, membrane filtration, and adsorption.

These methods have various drawbacks such as, chemical precipitation technique produces large amount of sludge, ion exchange technique causes environmental pollution during regeneration, floatation technique requires large initial cost, coagulation and flocculation has large amount of chemical consumption and membrane filtration has membrane fouling problem. But among all these techniques, adsorption is appropriate because of simplicity in operation, low cost, eco friendly nature, reuse and regeneration possibilities (Fu & Wang 2011; Sabzoi et al., 2015).

In literature quantum of study is available for single heavy metal removal in batch and continuous mode. However, multiple ions and other impurities (dyes) are present in large volume of wastewater discharged by various industries such as textile, electroplating, tannery, dye industries etc. Wastewater contains various heavy metals such as copper, chromium, cadmium, nickel, zinc, lead and mercury. In most of industrial discharge, copper, chromium and cadmium are predominant, that is why these three heavy metals have been selected for heavy metal removal (Mehdipour et al., 2015; Gopalakrishnan et al., 2015). Metallic dyes are also present in the effluent discharged by textile industries. These dyes release heavy metals on oxidation causing increase in concentration of heavy metals in the treated wastewater. Thus an adsorbent capable of removing multiple heavy metals in batch and continuous mode need to be explored.

Commercial adsorbents are costly thus there is a requirement to develop inexpensive adsorbents for heavy metal removal from wastewater. Thus there is requirement to explore biosorbents because they are cheap and available in abundance as waste material. There is always a necessity to increase removal efficiency of biosorbents through suitable modification technique. As stated above waste water containing heavy metals also contain other impurities. These impurities may interfere with removal of heavy metals depending on its concentration. Dye industries discharge is loaded with dyes pigments and heavy metals. Therefore, simultaneous removal of dyes and metals through adsorption can make effluent treatment cost effective provided adsorbent is capable of adsorbing these impurities effectively. A very less study has been reported in the literature for simultaneous removal of multiple heavy metals and dyes. Thus more research is needed in this direction.

1.5 Rationale of study

Various researches have been carried out to remove heavy metals from wastewater using adsorption to keep concentration of these heavy metals in permissible limit in the industrial effluent (Gopalakrishnan et al., 2015). Adsorption has been considered to be one of the effective operations for removal of heavy metals from waste water due to its simplicity, efficiency and ease of operation (Fu & Wang 2011; Sabzoi et al., 2015). In previous work, researchers have used various commercial adsorbents such as activated carbon, carbon nanotubes, alumina, chitosan, graphene oxide and silica gel etc. for removal of heavy metals from wastewater. Activated carbon was used extensively (Chen & Lin 2001; Kannan & Veemaraj 2009; Hydari et al., 2012) for removal of chromium (Cr), copper (Cu), cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni) from wastewater.

Among these adsorbents, activated carbon is commonly used commercial adsorbent for removing heavy metals from wastewater (Hydari et al., 2012). Although a good removal was observed but the process is not feasible because activated carbon is an expensive material due to high cost of production. Therefore, an emphasis has been given by researchers to find alternative adsorbents which are cheap and easily available. Biosorbents developed from waste materials has been explored for heavy metals removal (Semerjian 2018; Kumar et al., 2018). Easy availability of wastes in large quantity may be a solution for process to be economical and feasible. Different biosorbents have been tried for removal of chromium (Cr), copper (Cu), cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni) from wastewater such as marine algae (Bulgariu & Bulgariu 2016; Kumar et al., 2018), peat (Lupea & Bulgariu 2012), saw dust (Semerjian 2018; Mansour et al., 2011) , sunflower leaves (Feizi & Jalili 2015, Jain et al., 2009), orange peel (Feng et al., 2011; Gupta et al., 2012), cashew nut shell (Kumar et al., 2012; Coelho et al., 2014), wheat bran (Renu[b] et al., 2018; Kaya et al., 2014) etc. Although a huge work on adsorption has been reported in literature for heavy metals removal but most of the results are from batch adsorption studies and mostly for single heavy metals. The huge quantity of waste water generated from various industries such as, textile, electroplating, tannery etc. contains multiple heavy metals. Therefore, an eco-friendly adsorbent capable of adsorbing multiple heavy metals with good capacity in continuous mode needs to be explored. Also novel adsorbent capable of removing metals and dyes should be explored in order to eliminate the step for dye removal. Metallic dye containing waste are subjected to dye oxidation (Adams 2015) for reduction of color in the effluent may release heavy metals the effluent causing higher concentration of metals in the effluent stream. Simultaneous removal of dyes and heavy metals can solve this problem. A dynamic model capable of predicting metal removal efficiency of synthesized adsorbent in continuous adsorption column is required before adopting adsorbent for actual Industrial waste water treatment. The model prediction can be compared with experimental findings for continuous column to assess breakthrough curve at different conditions (bed height, initial metal concentration, flow rate).

1.6 Scope of present research

1. Synthesis of an efficient adsorbent for heavy metal removal from wastewater.
2. Optimization of process parameters for adsorption of heavy metals and other impurities such as dye.
3. Study of continuous adsorption for heavy metal removal.
4. Modeling of continuous adsorption operation for heavy metals removal and prediction of break through time
5. Evaluation of removal efficiency of synthesized adsorbent in presence of other metals and dyes.
6. Continuous adsorption experiments on actual effluents collected from various industries using synthesized adsorbent for evaluating its suitability for industrial waste water.

1.7 Structure of thesis

For the convenience of understanding the thesis is divided into five chapters as follows.

Chapter 1: Introduction: This chapter includes information related to heavy metals, their route of exposure in human body, sources in environment and their health effects when exceeds more than permissible limits.

Chapter 2: Literature review: This chapter includes detailed review of heavy metal removal techniques. Adsorption process was compared with other heavy metal removal technique. Available scattered information on different adsorbents has been compiled. Research gaps have been identified and research objectives have been framed.

Chapter 3: Materials and methods: This chapter includes details about experimental methodology adopted in present research. It also includes preparation and characterisation techniques used for various adsorbents. For batch study, isotherm, kinetics and thermodynamics correlation has been included. The design and fabrication of experimental setup was also explained in this chapter alongwith the modelling.

Chapter 4: Result and discussion: In this chapter, an efficient adsorbent was selected for removal of copper, cadmium and chromium and then characterisation analysis of the developed adsorbent was discussed in detail.The removal of individual metal such as copper, cadmium, and chromium using hydrochloric acid-treated wheat bran as an adsorbent in batch and continuous mode was performed. The study was done for individual meal ions, mixed metal ions and then for simultaneous removal of metal ions and dye. In batch study, response surface methodology was used to determine the effect of various parameters on removal efficiency of copper, cadmium, and chromium. However, adsorption isotherms and rate kinetics were also investigated. Adsorption regeneration study was also carried out because disposal of saturated adsorbent is harmful for environment.Further, in continuous study, a model was developed using MATLAB software. Experiments were performed for different parameters and then experimental data was validated with the model data. Further, industrial wastewater was collected from textile, dye, tannery and electroplating industries. Their physico-chemical characterisation was done and continuous experiments were performed.

Chapter 5: Conclusions: This chapter includes summary of key findings along with the recommendations for future studies.

CHAPTER - 2

LITERATURE REVIEW

2.1 Introduction

Heavy metal pollution is one of the biggest problems nowadays. They are discharged into water from various industries. These heavy metals are copper, chromium, cadmium, lead, zinc, mercury, arsenic and nickel. They come out from various industries such as jewellery industries, electronics industry, mining and dye industries etc. They can be toxic or carcinogenic in nature and can cause severe problems for humans (cancer, abdominal pain, nausea and liver damage) and aquatic ecosystems. Central pollution control board, India has set permissible limit for heavy metals discharge in wastewater such as 3, 0.1, 2, 5, 0.1, 0.01, 0.2, 3 mg/L for copper, chromium, cadmium, zinc, lead, mercury, arsenic and nickel respectively (Section VI of the Environmental (Protection) Rules 1986). There are various conventional techniques such as chemical precipitation, flotation, ion exchange, coagulation and flocculation, membrane filtration, reverse osmosis, and adsorption. Among all these techniques, the adsorption process is the most efficient and widely used technique for removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature. Both commercial adsorbents and bioadsorbents are used for the removal of heavy metals from wastewater, with high removal capacity. This chapter aims to provide information on source and toxicity of heavy metals. It also compiles available scattered information on heavy metal removal techniques and on the commercially available and natural bioadsorbents used for removal of chromium, cadmium and copper, in particular.

2.2 Techniques for heavy metals removal

There are various techniques for removal of heavy metal from wastewater such as chemical precipitation, flotation, ion exchange, coagulation and flocculation, membrane filtration, reverse osmosis, and adsorption.

2.2.1 Chemical precipitation

It is an effective technique for remove of heavy metals from wastewater. In this process, chemical react with the heavy metals present in wastewater and there is formation of insoluble precipitates. Further these precipitates are removed using sedimentation technique and the cleared water is decanted (Djedidi et al., 2009; Fu & Wang 2011). Chemical precipitation is categorised as hydroxide precipitation and sulphide precipitation.

2.2.1.1 Hydroxide precipitation:

In hydroxide precipitation process metal hydroxides are formed because of hydroxides reaction with heavy metals (Dupont 1990). Mirbagheri & Hosseini (2005) has utilized $Ca(OH)_2$ and NaOH as a precipitant for removal of Cu(II) and Cr(VI) ions by converting Cr(VI) into Cr(III) using ferrous sulphate and sulphuric acid. Maximum conversion was obtained in the pH range of 2.0-2.3 and maximum precipitation of Cr(III) was obtained at pH 8.7 using $Ca(OH)_2$. The concentration was reduced from 30 mg/L to 0.01 mg/L for chromium and 48.51 mg/L to 0.694 mg/L for copper and removal efficiency was obtained in the range of 98.56-99.9%. However, Chen et al., (2009) has used lime as a precipitant for removal of copper, zinc, chromium and lead from wastewater. Lime was used due to low cost and then fly ash was added as a seed material (Tadesse et al., 2006). Removal efficiency of 99.37%-99.69% was reported between pH of 7 and 11. Hydroxide precipitation has certain disadvantages such as requirement of costly disposal because they produce secondary waste such as metal hydroxide sludge and gypsum (Matlock[a] et al., 2002).

2.2.1.2 Sulfide precipitation:

In sulphide precipitation sulphide compounds form insoluble precipitates when reacts with heavy metals. Sulfide precipitation has several advantages such as, it removes heavy metals selectively, fast reaction rate, better settling properties, sulphide precipitates can be used again by smelting (Azabou et al., 2007; Foucher et al., 2001; Odom 1993; Lewis 2010). Matlock et al[b]., (2002) has used pyridine based thiol ligand for removal of copper, cadmium and it has many advantages such as availability of multiple sites for heavy metal removal and formation of stable metal-ligand precipitates. It is a sulphur containing ligand which binds heavy metals and forms stable precipitates.

This ligand has sufficient length for interaction between heavy metal and each terminal sulphur group. Thus 99.99% removal for copper and 99.88% removal for cadmium were obtained at an optimum pH of 4.5 and 6 respectively.

2.2.1.3 Chelating precipitation:

Excessive use of strong complexing agent such as EDTA (ethylenediaminetetraacetic acid) in wastewater has become environmental problem (Fu et al., 2012). Thatswhy there is a requirement for removal of not only toxic heavy metals but also chelating agent EDTA. For this purpose Fenton-chemical precipitation process was used. In Fenton-chemical precipitation process soluble iron cation interacts with the H_2O_2 (Fu et al., 2012). Because it is difficult to remove Ni (II) by conventional methods. Fu et al., 2009 has used Fenton reactions followed by hydroxide precipitation for removal of Ni (II) from NiEDTA wastewater. Thus the concentration of nickel was reduced from 50 mg/L to 3.6 mg/L and 92.8% of Ni (II) was removed from wastewater. However, Fu et al., 2012 has used advanced Fenton-chemical precipitation process for wastewater containing chelated heavy metal. In this advanced process author has used zero valent ion for treatment of contaminants due to its low toxicity, cost and easy operation. The concentration reduced from 50 mg/L to less than 1 mg/L. At optimum condition, 98.4% removal efficiency was obtained for Ni (II). Comparison of this work with their previous work concludes that advanced fenton process has higher efficiency than the process which was adopted earlier. Table 2.1 summarises workdone related to removal of heavy metal by chemical precipitation.

Table 2.1 Removal of heavy metals by chemical precipitation

Heavy metal	Initial metal conc. (mg/L)	Precipitant	Optimum Ph	Removal (%)	References
Ni	50	Alkali	2.5	98.4%	Fu et al., 2012
Ni	50	Alkali	11	92.8%	Fu et al., 2009
Ni	100mM	FeSO4	3	99.9%	Shih et al., 2013
Cu, Cr	100	Lime	7-11	99.60%	Chen et al., 2009
Cu	25	$Ca(OH)_2$	12-13	>99%	Jiang et al., 2008
Cu, Cd	50	Pyridine based thiol legand	4.5	99.99% 99.88%	Matlock et al[a]., 2002
Zn	200	Sulfate reducing bacteria	6.8	-	Azabou et al., 2007
Cd, Cu	-	Sodium decanoate	4-8	>90%	Mauchauffee & Meux 2007

Cu	100	1,3,5 hexahudrotriazine	3-9	99.6%	Fu et al., 2007
Fe	194	1,3benzenediamidoethanethiol dianion	4.5	>90%	Matlock et al[b]., 2002

2.2.2 Flotation

Flotation is a well known technique for removal of heavy metal from wastewater (Fu et al., 2011). Flotation process has many advantages such as selective metal ion recovery, low sludge generation and high separation efficiency (Rubio et al., 2002). Scorzelli et al., (1999) has used sodium dodecylsulfate (SOS) as a collector and isopropanol, methyl isobutyl carbinol as a frother for cadmium removal from wastewater. Addition of frother at concentration of 0.1% v/v has increased cadmium removal up to 98.8% and 97.7% for isopropanol and methyl isobutyl cabinol. However, Polat & Erdogan (2007) has removed copper, zinc and chromium from wastewater using ion flotation method. Sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide were used as a collector, ethanol and methyl isobutyl carbinol were used as frothers. Removal obtained was 74% and it has increased up to 90% on increasing pH. Ion flotation has several advantages such as less energy requirements, rapid operation, low concentration of metals, small space requirements, and less operating cost (Scorzelli et al., 1999). Blocher et al., 2003 has combined hybrid flotation and membrane filtration technique for copper, nickel and zinc removal. Yuan et al., (2008) has removed cadmium, lead and copper using ion flotation with plant derived bio-surfactant tea saponin. Biosurfactants have high specificity, biodegradability and biocompatibility. Removal of 89.95%, 81.13% and 71.17% was obtained for lead, copper and cadmium respectively with collector to metal ratio 3:1. Table 2.2 summarises workdone related to heavy metal removal using chemical flotation.

Table 2.2 Removal of heavy metals by flotation method

Heavy metal	Initial metal conc. (mg/L)	Frother	Optimum pH	Removal (%)	References
Cd	20	Isopropanol methyl isobutyl	4-5	99.1%	Scorzelli et al., 1999
Cu, Zn, Cr	50	Ethanol and methyl isobutyl carbinol	4-10	90%	Polat & Erdogan., 2007
Pb	2-10	Octadecylamine chloride and cetyltrimethyl ammonium chloride	10	100%	Aldrich et al., 2000
Cd	_	Ethanol	4	92.1%	Salmani et al., 2013

2.2.3 Ion exchange

Ion exchang technique produces less sludge (Lee et al., 2007; Zewail & Yousef 2015). For ion exchange technique different types of resins were used (Dorfner 1991). Resins are categorised as natural resin and synthetic resin. Different resins were used by different authors for removal of heavy metals in ion exchange process. Badawy et al., (2009) has used Purolite C100 resin for separation of lead ions from binary mixtures and 99.71% recovery of lead was observed. However, Thakre & Jana (2015) has removed copper from wastewater using high density ion exchange resin INDION 225H. This high density ion exchange resin provides hydrodynamic advantage when they are used in expanded bed adsorption. Shaidan et al., (2012) has used strong acidic cation exchange resin in a fixed bed for nickel removal from wastewater. It has several advantages such as it can treat large volume of effluents at one time and it is more efficient technique for heavy metal removal from wastewater. However, Zewail et al., (2015) has used spouted bed with AMBERJET 1200 Na resin for nickel and lead removal from wastewater and 99% and 98% removal for lead and nickel were obtained respectively. Table 2.3 summarises workdone related to heavy metal removal using chemical flotation.

Table 2.3: Removal of heavy metals by Ion exchange method

Heavy metal	Initial metal conc. mg/L)	Resin	Optimum pH	Removal (%)	References
Cu, Zn, Cd	_	Amberlite IR-120	_	_	Lee et al., 2007
Ni, Pb	800, 1000,1250	Amberjet 1200 na	_	98%, 99%	Zewail et al., 2015
Ni	1800, 2800,3800	Acidic cation exchange resin	3-7	97%	Shaidan et al., 2012
Cd, Pb	0.1-6 mmol/L	Sargassum multicum loaded with calcium	5	_	Carro et al., 2015

2.2.4 Coagulation and Flocculation

Coagulation is a process which uses coagulants and these coagulants are formed by combination of insoluble particle and/or dissolved organic matter into large aggregates. These coagulants are aluminium sulphate (alum), magnesium chloride ($MgCl_2$), polyaluminium chloride (PACL) and aluminium hydroxide oxides (Lin & Reed 1996; Renault et al., 2009). Pang et al., (2011) has removed lead from wastewater in the existence of other heavy metals such as iron and zinc alongwith aluminium sulphate (alum), polyaluminium chloride, magnesium chloride as a coagulant and korat PA3230 as the polyelectrolyte. The presence of other heavy metals affects removal of lead and it may hinder their removal efficiency. It was reported that maximum removal of lead was 99% at an optimum pH of 6.2-7.8 for alum, 8-9.3 for PACL (Polyaluminium chloride) and 8.7-10.9 for $MgCl_2$. Use of coagulants for removal of heavy metals cause so many problems such as increases heavy metal concentration in wastewater, large volume of sludge is produced and health problems. To eliminate these problems alternative of Coagulants have been considered. Chitosan can be used as an alternative.

Chitosan is a polymer which is natural and biodegradable and works as a coagulating and flocculating agent (Renault et al., 2009, Yang & zall 1984). Assaad et al., (2007) has used chitosan-montmorillonite system for removal of cobalt, nickel and copper from wastewater. Maximum adsorption capacity of 76.3 mg/g for cobalt, 89.3 mg/g for nickel and 112.4 mg/g for copper have been observed. Flocculation is one of the widely used technique to remove heavy metals from wastewater (Staicu et al., 2015).

Shen et al., (2015) has used polymer surfactant complexation and flocculation for removal of chromium, zinc and copper. Poly diallyldimethylammonium chloride

(PolyDADMAC) or polyethylenimine (PEI) was used as a cationic polymer and sodium dodecyl sulphate (SDS) as an anionic surfactant. Maximum removal of 99% was observed at an optimum pH of 6-9. Table 2.4 summarises workdone related to Coagulation/ Flocculation for removal of heavy metals.

Table 2.4 Removal of heavy metals by Coagulation/ Flocculation

Heavy metal	**Coagulant/ Flocculant**	**Initial metal conc. (mg/L)**	**Optimum pH**	**Removal (%)**	**References**
Fe, Zn	Sulphate, polyaluminium chloride, magnesium chloride	25-45	6.2-7.8	99%	Pang et al., 2011
Cr, Zn, Cu	Sodium dodecyl	11.2	6-9	99%	Shen et al., 2015
Cr, Ni, Zn	Tanfloc	20 mg/L	6-7	75%	Heredia & Martin 2009

2.2.5 Membrane filtration

There are different types of membrane filtration techniques based on different kind of membranes. Membrane filtration has several advantages compared to other conventional technique such as it provides high separation efficiency, no phase change, saves energy, easy scaling and environmental friendly (Zhu et al., 2014). Different membrane filtration techniques used for removal of heavy metals are reverse osmosis, ultrafiltration and nanofiltration.

2.2.5.1 Reverse osmosis

Reverse osmosis is a process driven by pressure (Ujang & Anderson 1996). Mohsen-Nia et al., (2007) has removed Cu and Ni from wastewater using disodium salt ethylenediaminetetraacetic acid (Na_2EDTA). It was reported that addition of Na_2EDTA has increased the chelated ion size of copper and nickel and their rejection efficiency has been increased up to 99.5%. However, Ozaki et al., (2002) has used aromatic polyamide (ES20) ultralow membrane for removing copper, nickel and chromium from wastewater. Thus the removal of heavy metals was observed greater than 95%. Ipek 2005 has removed nickel and zinc from wastewater by pre-treatment before reverse osmosis process. Removal percent obtained from pre-treatment unit and reverse osmosis is 99.2% and 98.8% for nickel and zinc respectively. Table 2.5 summarises workdone related to reverse osmosis for removal of heavy metals.

Table 2.5 Removal of heavy metals by reverse osmosis

Membrane	Heavy metal	Initial metal conc. (mg/L)	Removal (%)	References
RO	Ni, Zn	44-169	99.2%, 98.8%	Ipek 2005
RO	Cu, Ni, Cr	_	95%	Ozaki et al., 2002
RO	Pb, Ni, Cr, Cu	_	49-100%	Dialynas & Diamadopoulos 2009

2.2.5.2 Ultrafiltration

Ultrafiltration (UF) is a technique which works at low pressures and removes dissolved and colloidal material. There are two types of ultrafiltration technique. One is Micellar enhanced ultrafiltration (MEUF) and another is polymer enhanced ultrafiltration (PEUF). MEUF is a physicochemical membrane separation technique in which there is addition of anionic surfactant in the wastewater. Thus, the monomers of anionic surfactant aggregate and they form micelles. Heavy metals are trapped in outer part of micelle because of electrostatic force. MEUF has several advantages such as it gives high flux, high removal and low energy cost. However, it has disadvantage that it increases operating cost (Landaburu-Aguirre et al., 2010).

Polymer enhanced ultrafiltration uses water soluble polymer in the wastewater. These polymers are retained in the membrane if the size of these polymers is larger than molecular weight cut off of the membrane. PEUF helps in removal of small solute molecules which can not be removed by conventional ultrafiltration (Huang et al., 2010). Landaburu-Aguirre et al., (2010) has removed cadmium and zinc from wastewater using MEUF process and sodium dodecyl sulphate as a surfactant. Removal of 98% for zinc and 99% for cadmium has been observed. However, Camarillo et al., (2012) has used polyethyleneimine for removal of copper from wastewater at an optimum pH of 4-5 and 92% rejection coefficient was obtained. Uzal et al., (2011) has used sulfonated PVA (SPVA) and non sulfonted PVA. Thus 31.81% and 99.98% removal was obtained by using non sulfonated PVA and sulfonated PVA respectively. It was observed that after sulfonation of PVA removal of copper has been increased. However, use of these synthetic surfactant in PEUF cause secondary pollution because of leakage problem. So, that use of biosurfactants can eliminate this problem. In Bio-surfactant based ultrafiltration technique, leakage into permeate of bio-surfactants doesn not cause pollution, because of biodegradability, compatibility and nontoxic nature of biosurfactants (Huang et al., 2015). Table 2.6 summarises workdone related to ultrafiltration for removal of heavy metals.

Table 2.6 Removal of heavy metals by ultrafiltration

UF type	Complexing agent	Heavy metal	pH	Removal (%)	References
PEUF	Polyvinylamine	Hg	_	99%	Huang et al., 2015
PEUF	PVA & sulfonated PVA	Co	5.93-6.5	99.98%	Uzal et al., 2011

2.2.5.3 Nanofiltration

Nanofiltration is one of the membrane filtration process ranging the pore size in between UF and RO (Mehdipour et al., 2015). Commercial nanofiltration membranes are composed of synthetic polymers containing charged groups (Al-Rashdi 2013; Zhu et al., 2014). Positively charged polyethylimine crosslinked polyimide nanofiltration membrane (PEI) has good thermal, chemical and mechanical property. But it has one limitation that it gives higher rejection efficiency only for the multivalent cations. Thus we can modify this membrane for removal of anions also. Gao et al., (2014) has performed adsorption of negatively charged functional group containing chelating polymer over the charged PEI cross linked P84 hollow fiber substrates. Adsorption of these chelating polymers improves membrane performance, change in membrane surface charge, pore size and they become capable of removing multivalent anions. This membrane gives rejection efficiency greater than 98%. However, Zhu et al., (2014) has fabricated membrane by simultaneous co-extrusion of polybenzimidazole (PBI) and polyethersulfone (PES)/ polyvinylpyrolidone (PVP) dopes through a triple orifice spinneret with the help of dry jet wet phase inversion process. This membrane gives 95% rejection for cadmium, 98% for $Cr_2O^-_7$ and 93% for lead respectively. Gholami et al., (2014) has fabricated membrane by combining it with the nanosized ferric oxides in membrane matrix to improve lead removal from wastewater. Mehdipour et al., (2015) has used polyamide NF membrane for lead removal. It was also observed that increase in pressure and initial feed concentration increases removal of lead to 97.5%. Table 2.7 summarises workdone related to nanofiltration for removal of heavy metals.

Table 2.7 Removal of heavy metals by nano-filtration method

Membrane	Heavy metal	Removal (%)	References
NF	Cd, Cr & Pb	95%, 98%, 93%	Zhu et al., 2014
NF	Pb, Cu, Ni, Zn, Cd, Cr	>98%	Gao et al., 2014
NF	Cd, Mn, Pb	74%-99%	Rashdi et al., 2013
NF	Cu, Zn, Cd, Pb	97.5%	Mehdipour et al., 2015

2.2.6 Adsorption

Various conventional techniques were employed for removal of heavy metals such as chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption (Fu & Wang 2011). Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. The adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent and is reversible and the adsorbent can be regenerated (Fu et al., 2011).

Various researchers have used different biosorbents such as rice husk (Sugashini & Begum), black tea waste (Mohammed 2012), orange peel (Lugo-Lugo et al., 2012), sugarcane bagasse (Ullah et al., 2013), saw dust (Politi & Sidiras 2012), apple pomace (Chand et al., 2014), grape stalk wastes (Villaescusa et al., 2004), sunflower leaves (Benaissa & Elouchdi 2007), peanut shell (Al-Othman et al., 2012), hazelnut shell (Cimino et al., 2000) and egg shell (Daraei et al., 2015), etc. for heavy metals removal from wastewater.

2.3 Adsorbents used for removal of heavy metals from wastewater

There are a number of types of adsorbent that are used for the efficient removal of heavy metal removal from wastewater that are both commercial and/or bioadsorbents (Fig. 2.1—2.3). Commercial adsorbents are those adsorbents which are produced commercially on a large scale, such as activated carbon, silica gel, alumina, etc., however they are costly. Natural bioadsorbents are those obtained from biological material and are comparatively cheap. However, cost analysis is an important criterion for selection of an adsorbent for heavy metal removal from wastewater. The cost of the adsorption process depends on the cost of the adsorbent. For instance, the cost of commercial activated carbon is Rs. 500/kg; however, the cost of bioadsorbents is in the range of Rs. 4.4–36.89/kg, which is much less as compared to the commercial adsorbents (Gupta & Babu 2008).

2.3.1 Commercially available adsorbents for chromium removal from wastewater

2.3.1.1 Graphene

Nanomaterials are efficient adsorbents for the removal of heavy metals from wastewater because of their high surface area, enhanced active sites and the functional groups that are present on their surface (Gopalakrishnan et al., 2015; Lv et al., 2014; Wu et al., 2013). Graphene is a carbon-based nanomaterial with a two-dimensional structure, high specific surface area and good chemical stability. It is available in various forms such as pristine graphene, graphene oxide and reduced graphene oxide. Graphene may be oxidised to add hydrophilic groups for heavy metal removal (Sakthivel et al., 2015). Yang et al[a]., (2014) adsorbed chromium onto the surface of graphene oxide and the maximum adsorption capacity found was around 92.65 mg/g at an optimum pH of 5. This adsorption of chromium on graphene oxide was found to be endothermic and spontaneous. Gopalakrishnan et al., (2015) have also oxidised graphene for the addition of –COOH, -C=O and -OH functional groups onto the surface using a modified Hummer’s method (Hummers & Offeman 1958). The novelty of their work is that only 70 mg of graphene oxide has been utilised for 100% removal of chromium from wastewater effectively at an optimum pH of 8. Graphene composite materials have been developed by a number of authors for the removal of heavy metals. Li et al., (2013) functionalised graphene oxide with magnetic cyclodextrin chitosan for the removal of chromium since magnetic cyclodextrin chitosan has favourable properties such as high adsorption capacity and magnetic property which assists in the separation process.

Guo et al., (2014) functionalised graphene with a ferro/ferric oxide composite for chromium removal with a maximum adsorption capacity of 17.29 mg/g which is higher as compared to the adsorption capacity of other magnetic adsorbents, such as Fe@Fe_2O_3 core-shell nanowires (Ai et al., 2008), chitosan-coated $MnFe_2O_4$ nanoparticles (Xiao et al., 2013) and Fe_3O_4- polyethyleneimine-montmorillonite (Larraza et al., 2012), i.e., 7.78 mg/g, 15.4 mg/g, 8.8 mg/g, respectively. Table 2.8 summarises the grapheme-related work that has been reported in this area.

Table 2.8 Chromium removal using graphene, graphine oxide and modified graphine as an adsorbent

Adsorbent	Initial conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsor bent capacity (mg/g)	Removal (%)	References
Graphene oxide based inverse spinel nickel ferrite composite	1,000	4	120	0.125-2.5	45	-	Lingamdinne et al., 2015
Zero-valent iron decorated on graphene nanosheets	15-35	3	90	1.0	-	70%	Li et al.,2016
Copolymer of dimethylaminoethyl methacrylate with graphene oxide	-	1.1	45	-	82.4	93%	Ma et al.,2015
Graphene sand composite (GSC)	8-20	1.5	90	10	2859.38	93%	Dubey et al., 2015
Graphene oxide	52	5	12	-	43.72	92.65%	Yang et al[a]., 2014;

2.3.1.2 Activated carbon

Modern industries began production of active carbon in 1900–1901 to replace bone char in the sugar refining industry (Bansal et al., 1988) and powdered activated carbon was first produced commercially in Europe in the early 19th century, using wood as a raw material (Mantell 1968). Activated carbon can be obtained from any material which has high carbon content (EISikaily et al., 2007). Activated carbon is a good adsorbent for chromium removal because it has a well-developed porous structure and a high internal surface area for adsorption (Anirudhan et al., 2011). However, because coal-based activated carbon is expensive, its use has been restricted and further efforts have been made to convert cheap and abundant agricultural waste into activated carbon (Anirudhan et al., 2011). Activated carbon is now prepared from various agricultural wastes such as rubber wood saw dust (Karthikeyan et al., 2005), moso and ma bamboo (Lo et al., 2012), viticulture industry wastes, grape stalk, lex, pomace (Sardella et al., 2015), hazelnut shell activated carbon (Kobya 2004), coconut tree saw dust (Selvi et al., 2001), coconut shell carbon (Babel & Kurniawan 2004), sugarcane bagasse (Sharma &

Forster 1994), treated saw dust of Indian rose wood (Garg et al., 2004), wood activated carbon (Selomulya et al., 1999), tyre activated carbon (Hamadi et al., 2001), coconut shell activated carbon (Selomulya et al., 1999) and palm shell (Saifuddin & Kumaran 2005; Owlad et al., 2010; Kundu et al., 2015; Nizamuddin et al., 2015, 2016; Sabzoi et al., 2015; Thangalazhy-Gopakumar et al., 2015), etc.

Karthikeyan et al., (2005) removed chromium from wastewater using activated carbon derived from rubber wood saw dust and 44 mg/g maximum adsorption capacity was obtained at an optimum pH 2. Maximum adsorption capacity obtained in their work was higher as compared to other adsorbents such as coconut tree saw dust (Selvi et al., 2001), coconut shell carbon (Babel & Kurniawan 2004), sugarcane bagasse (Sharma & Forster 1994) and treated saw dust of Indian rose wood (Garg et al., 2004), which were only 3.60 mg/g, 10.88 mg/g, 13.40 mg/g and 10 mg/g, respectively. Lo et al., (2012) derived activated carbon from moso and ma bamboo, and 100% removal was obtained using once activated maa bamboo and 91.7% removal using twice activated maa bamboo. Removal efficiency decreases for once activated moso bamboo and twice activated moso bamboo by 20–77% because their average pore diameter is less than 2 nm and major pores were mesopores.

Kobya (2004) prepared activated carbon using hazelnut shell and maximum adsorption capacity of 170 mg/g was obtained at an optimum pH 1 which is higher than adsorption capacity of other adsorbents such as wood activated carbon (Selomulya et al., 1999), tyre activated carbon (Hamadi et al., 2001) and coconut shell activated carbon (Selomulya et al., 1999) which is only 87.6 mg/g, 58.5 mg/g and 107.1 mg/g, respectively. Table 2.9 summarises the reported use of activated carbon for chromium removal from wastewater.

Table 2.9: Chromium removal using activated carbon as an adsorbent

Adsorbent derived from	Metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Acrylonitriledi vinylbenzene copolymer	30	2	420	0.6	101.2	80%	Duranoglu et al., 2010
Syzygium jambolanum nut carbon	20–100	2	240	5	-	100%	Muthukumaran & Beulah 2011

Jatropha wood	30–100	2–10	360	0.6–2	106.4-140.8	-	Gueye et al., 2014
Tamarind wood	10–50	6.5	40	2	-	28%	Acharya et al., 2009
Pterocladia capillacea	5–100	1	120	3–10	66	100%	El Nemr et al., 2015
Zizania caduciflora	10–50	2-3	48	0.8	2.7	84.8%	Liu et al., 2014
Prawn shell	25–125	-	31.4	–	100	98%	Arulkumar et al., 2012

2.3.1.3 Carbon nanotubes

Carbon nanotubes (CNT) are efficient adsorbents for heavy metal removal because they possess chemical stability, large surface area, excellent mechanical and electrical properties, adsorption property and well-developed mesopores (Gupta et al., 2011; Mubarak et al[c]., 2016; Mubarak et al[a]., 2014; Ihsanullah et al., 2015; Luo et al., 2013). They can also be further modified by chemical treatment to increase adsorption capacity (Chen et al., 2009; Mubarak et al[a]., 2013; Mubarak et al[a]., 2016; Ruthiraan et al., 2014). Hu et al., (2009) has removed chromium using oxidised multi-walled carbon nanotubes and 100% maximum removal was achieved at an optimum pH of 2.88. Gupta et al., (2011) combined the adsorptive property of multi-walled carbon nanotubes with the magnetic property of iron oxide. The advantages of this composite are high surface area, can be used for contaminant removal and can be controlled and removed from the medium using a simple magnetic process. A maximum removal of 88% at pH 6 was obtained. Luo et al., (2013) prepared manganese dioxide/iron oxide/acid oxidised multi-walled carbon nanotube (MWCNT) nanocomposites for chromium removal. Manganese dioxide is a scavenger of aqueous trace metals because of its high adsorption capacity but the use of pure manganese dioxide is not favoured because of the high cost and its unfavourable physical and chemical properties. The maximum adsorption capacity of the above nanocomposite was 186.9 mg/g with a maximum removal of 85% at an optimum pH of 2.

Mubarak et al[b]., (2014) functionalised carbon nanotubes for chromium removal using nitric acid and potassium permagnate in 3:1 volume ratio and compared the removal capacity with non-functionalised carbon nanotubes. They found that maximum adsorption capacity for functionalised carbon nanotubes was 2.517 mg/g while for non-functionalised carbon nanotubes it was 2.49 mg/g, and removal capacity for functionalised carbon nanotubes (87.6%) was higher compared to non-functionalised carbon nanotubes (83%). Mubarak et al[b]., (2016) produced carbon nanotubes using microwave heating for comparative study of the removal of chromium with another heavy metal (i.e., lead). Microwave heating provides a fast and uniform heating rate and it accelerates reaction and gives a higher yield. The maximum adsorption capacity obtained for chromium was 24.45 mg/g and removal efficiency obtained was 95% at an optimum pH 8. Table 2.10 summarizes the reported use of carbon nanotubes for chromium removal from wastewater.

Table 2.10: Chromium removal using carbon nanotube as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Nitric acid oxidised CNT	1	7	2	150	0.5	18%	Atieh et al., 2010
CNT & activated alumina composite	100	2	240	2.5	264.5	>95%	Sankararamakrishnan et al., 2014
Nitrogen-doped magnetic CNTs	12.82	8	720	0.2	638.56	>97%	Shin et al., 2011
CNT supported by activated carbon	0.5	2	60	0.04	9	72%	Atieh 2011
Cigarette filter with MWCNT and graphene	4	-	-	4	-	63-79%	Yu et al., 2015
Oxidised MWCNT	2.88	< 2	9,900	75-1.25	4.2615	100%	Hu et al., 2009
Composite of MWCNT & iron oxide	20	6	10–60	0.1–2	-	88%	Gupta et al., 2011

2.3.2 Bio-adsorbents for chromium removal from wastewater

2.3.2.1 Rice husk

Rice husk consists of cellulose (32.24%), lignin (21.44%), hemicellulose (21.34%) and mineral ash (15.05%) (Rahman et al., 1997). This material is not soluble in water and possesses a granular structure, chemical stability and good mechanical strength (Chuah et al., 2005). Silica is derived from rice husk using sol gel technique and has an affinity for chromium (Adam et al., 2006). Thus, Oladoja et al., (2013) incorporated iron oxide into silica derived from rice husk, calling it modified rice husk derived silica. This modified rice husk derived silica has higher adsorption (63.69 mg/g) as compared to the silica derived from raw rice husk. Rice husk in its natural form and in modified form (activated carbon modified using ozone) was used for the removal of chromium(VI) and results compared (Bishnoi et al., 2004; Sugashimi et al., 2015). It was found that ozone modified rice husk shows a higher removal capacity than raw rice husk.

Sugashini et al., (2015) modified rice husk by treating it with ozone to produce activated carbon for chromium removal with 86% removal being reported. Ozone was used for activation because it is a strong oxidising agent, stable and can be regenerated. Rice husk can also be modified by preparation of biochar. Biochar is a carbon-rich solid by-product resulting from the pyrolysis of rice husk under oxygen-free and low temperature conditions (Lehmann 2007; Woolf et al., 2010; Mubarak et al[a]., 2013, Mubarak et al[c]., 2014; Agrafioti et al., 2014; Ruthiraan et al., 2015). Biochar has the ability to adsorb heavy metals because of electrostatic interactions between the negative surface charge and the metal cations, as well as ion exchange between biochar surface protons and metal cations (Machida et al., 2006; Lehmann 2007; Woolf et al., 2010; Xu et al., 2013; Thines et al., 2014, 2015). Agrafioti et al., (2014) modified rice husk by pyrolysis for chromium removal with 95% removal reported. Table 2.11 summarises the reported use of rice husk for chromium removal from wastewater.

Table 2.11 Chromium removal using rice husk as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsor bent capacity (mg/g)**	**Removal (%)**	**References**
Iron oxide incorporated into silica derived from rice husk	50–300	2	120	2.0	63.69	71%	Oladoja et al., 2013
Ozone-treated rice husk	50, 100	2	150	4.0	8.7–13.1	86%	Sugashini et al., 2015
Modified rice husk	190, 850	6.8	5,760	1-16	-	95%	Agrafioti et al., 2014

2.3.2.2 Surfactant modified waste

Various agricultural wastes have been modified using surfactants (Bingol et al., 2004; Namasivayam & Sureshkumar 2008; Nadeem et al., 2009; Jing et al., 2011; Min et al., 2013). Surfactants are amphipathic substances with both lyophobic and lyophilic groups with the capability of forming self-associated clusters. Depending upon the nature of their hydrophilic group they can be cationic (positive charge), anionic (negative charge), non-ionic (no apparent charge) and zwitterionic (both charges are present); because of these characteristics surfactant modified adsorbents are superior in removal efficiency and promote selective adsorption (Nadeem et al., 2006; Rosen 2012). These researchers modified carbon powder obtained from the husks and pods of Moringa oleifera using the surfactant cetyltrimethyl ammonium bromide. This process improved the removal efficiency of the carbon powder with an adsorption capacity of 27 mg/g being reported at an optimum pH of 8. Similarly, Namasivayam & Sureshkumar (2008) has modified coconut coir pith by using hexadecyltrimethyl ammonium bromide surfactant to increase the removal efficiency of chromium. They reported a maximum adsorption capacity of 76.3 mg/g at an optimum pH of 2. Table 2.12 summarises the reported use of surfactant modified waste as an adsorbent for chromium removal.

Table 2.12 Chromium removal using surfactant modified waste as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsor bent capacity (mg/g)**	**Removal (%)**	**References**
Coconut coir pith modified by using surfactant cetyltrimethyl ammonium bromide	30	8	120	1	29.96	98%	Nadeem et al., 2006
Coconut coir pith modified by using hexadecyltrimethyl ammonium bromide surfactant	20–60	2	90	0.5–6.0	76.3	96%	Namasivayam & Sureshkumar 2008

2.3.2.3 Modified sugarcane bagasse

Sugarcane bagasse is a by-product of agricultural wastes that consists of cellulose (50%), polyoses (27%) and lignin (23%). Due to these biological component polymers, sugarcane bagasse is rich in hydroxyl and phenolic groups and these groups can be chemically modified to improve adsorption capacity (Ngah et al., 2008). Sugarcane bagasse is obtained from the fibrous material left after cane stalk crushing and juice extraction. Sugarcane bagasse originates from the outer rind and inner pith (Ullah et al., 2013) and has been used in the natural form as well as in a modified form. Ahmad et al., (2013) reported chromium removal using chromium-resistant reducing bacteria Acinetobacter haemolyticus inside sugarcane bagasse; this bacteria converts Cr(VI) into Cr(III) which is less toxic and less soluble as compared to Cr(VI), and a removal of more than 90% was obtained. Chemicals used for modification of sugarcane bagasse are succinic anhydride, EDTA dianhydride (EDTAD), xanthate, pyromellitic anhydride, sulphuric acid, citric acid, sodium bicarbonate, ethylenediamine, etc. These acids work as good chelating agents, so they become polymerised with sugarcane bagasse because it increases the number of chelating sites and helps in heavy metal removal from wastewater.

Garg et al., (2009) used succinic acid for modification of sugarcane bagasse and reported 92% removal obtained at an optimum pH of 2. Cronje et al. (2011) removed chromium by activating sugarcane bagasse with zinc chloride, and >87% chromium was reported at an optimum pH of 8.58. Table 2.13 summarises the reported use of sugarcane bagasse as an adsorbent for chromium removal.

Table 2.13 Chromium removal using modified sugarcane bagasse as an adsorbent

Adsorbent	Metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Removal (%)	eReferences
Acinetobacter haemolyticus bacteria inside sugarcane bagasse	10-100	7	2,880	-	>90%	Ahmad et al., 2013
Succinic acid modified sugarcane bagasse	50	2	60	20	92%	Garg et al., 2009
Sugarcane bagasse activated with zinc chloride	77.5	8.58	60	6.85	>87%	Cronje et al., 2011

2.3.2.4 Modified wheat bran

Wheat bran (WB) is an agricultural by-product which can be used for the removal of heavy metals and is obtained from the shell of flour mill wheat seeds. It is economically viable, biodegradable and consists of many nutrients such as protein, minerals, fatty acids and dietary fibres (Kaya et al., 2014). It has various organic functional groups with a surface area of 441 m^2/g and a fixed carbon content of 31.78% (Singh et al., 2009). It has various functional groups, such as methoxy, phenolic hydroxyl and carbonyl that have the ability to bind heavy metals (Ravat et al., 2000; Renu[a] et al., 2017). Farajzadeh et al., (2004) demonstrated the removal of chromium using wheat bran with a maximum adsorption capacity of 93 mg/g and a maximum removal of 89%.

Wheat bran can be modified by using different acids to increase removal capacity. The thermo-chemical interaction between wheat bran and acids increases with temperature. Thus, Ozer et al., (2006) modified wheat bran using sulphuric acid and demonstrated chromium removal with an adsorption capacity of up to 133 mg/g at an optimum pH of 1.5.

Kaya et al., (2014) used tartaric acid for modification of wheat bran and reported a 51% removal without modification, while after modification, removal was up to 90% at pH 2 and the maximum adsorption capacity was reported to be 4.53 mg of Cr(VI)/g and 5.28 mg of Cr(VI)/g at pH 2.2, without and with modification, respectively. Table 2.14 summarises the reported use of modified wheat bran as an adsorbent for chromium removal.

Table 2.14 Chromium removal using modified wheat bran as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
WB	20	5	20	80	93	89%	Farajzadeh et al., 2004
WB modified using sulphuric acid	50, 100	1.5	300	2.0	133	99.9%	Ozer et al., 2006
WB modified using tartaric acid	52	2, 2.2	15-1,440	20	5.28	90%	Kaya et al., 2014

2.3.2.5 Modified coconut waste

Coconut waste is also used as an adsorbent for chromium removal. Its sorption properties are due to the presence of coordinating functional groups such as hydroxyl and carboxyl (Tan et al., 1993). Coconut coir pith and coconut shell are coconut wastes suitable for heavy metal removal. Coir pith is a light fluffy biomaterial and is generated during the separation process of fibre from coconut husk (Namashivayam et al., 2008). Notably, 7.5 million tons per year of coconut is produced in India (Chadha et al., 2003).

Raw coir pith consists of 35% cellulose, 1.8% fats, 25.2% lignin and resin, 7.5% pentosans, 8.7% ash content, 11.9% moisture content and 10.6% other substances (Dan 1993).

Namashivayam et al., (2008) modified coir pith using the surfactant hexadecyltrimethylammonium bromide for chromium removal. The maximum removal obtained with this material was reported as being higher than 90% at an optimum pH of 2 and the maximum adsorption capacity was 76.3 mg/g. This was higher than the maximum adsorption capacity obtained using raw coir pith which was only 1.24 mg/g (Sumathi et al., 2005). This demonstrates that the adsorption capacity obtained after modification was much higher. Similarly, Shen et al. (2012) removed chromium using coconut coir and derived char and reported a maximum removal of 70%. Table 2.15 summarises the reported use of modified coconut waste as an adsorbent for chromium removal.

Table 2.15 Chromium removal using modified coconut waste as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
Modified coir pith using the surfactant hexadecyltrimethylammonium bromide	20–100	2	30–90	50	76.3, 1.24	>90%	Namashivayam et al., 2008
Coconut coir and derived char	10–500	3	7,200	1.0	70.4	70%	Shen et al., 2012

2.3.2.6 Modified orange peel waste

Orange peel (OP) is used as an adsorbent for the removal of chromium from wastewater because it contains cellulose, hemicelluloses, pectin (galacturonic acid) and lignin (Feng et al., 2011). These components also have various coordinating functional groups including carboxylic and phenolic acid groups which can bind heavy metals. Orange peel is an attractive adsorbent because of its availability and low cost (Feng et al., 2011).

Marin et al., (2010) studied the role of three major functional groups (amine, carboxyl and hydroxyl) on chromium removal where the bioadsorbent (orange peel) was chemically modified by esterification, acetylation and methylation in order to selectively block the functional groups. Thus, esterification decreased removal capacity, which indicates that the carboxylic groups present in the adsorbent are important for chromium removal and that the amine and hydroxyl groups have a negligible effect. The maximum adsorption capacity reported by these researchers was 40.56 mg/g.

Lugo et al., (2012) has biosorbed chromium on pre-treated orange peel in both single (presence of chromium only) and binary mixtures (presence of chromium along with iron) and it was observed that in the binary mixture removal of chromium was interfered by presence of iron as more than one heavy metal in mixture may increase, decrease or may not affect removal performance of the adsorbent. The removal per cent and adsorption capacity obtained in single phase (presence of chromium only) was 51% and 4.79 mg/g while for the binary system (presence of chromium along with iron) it was 79% and 7.60 mg/g. Tellez et al., (2011) removed chromium by preparing a composite that incorporates iron nanoparticles into orange peel pith. It was found that for this composite the percentage removal and adsorption capacity were 71% and 5.37 mg/g, respectively, as compared to raw orange peel, i.e., 34% and 1.90 mg/g, respectively. Table 2.16 summarises the reported use of modified orange peel waste as an adsorbent for chromium removal from wastewater.

Table 2.16: Chromium removal using modified orange peel waste as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
Modified OP	0-500	4	4,320	4.0	40.56	82%	Marin et al., 2010
Pre-treated OP	10	3	260	10.0	4.79, 7.60	51%, 79%	Lugo et al., 2012
Composite of iron nanoparticles into OP pith	10-50	1	60	5.0	1.90, 5.37	34% 71%	Tellez et al, 2011

2.3.2.7 Modified saw dust

As a solid waste, sawdust is produced in large quantities at sawmills. It contains primarily lignin and cellulose. Sawdust has been used as an adsorbent for heavy metal removal and shows good removal (Shukla et al., 2002). Sawdust is obtained by cutting, grinding, drilling, sanding or by pulverising wood with a saw or other tool producing fine wood particles. Argun et al., (2007) used hydrochloric acid modified oak saw dust (Quercus coccifera) for the removal of chromium. This treatment increases the proportion of active surfaces and prevents the elution of tannin compounds that would stain treated water. The maximum removal efficiency reported was 84% for Cr(VI) at pH 3 and the maximum adsorption capacity was 1.70 mg/g for Cr(VI) at pH 3.

Politi & Sidiras (2012) used pine sawdust modified with 0.11–3.6 N sulphuric acid for the removal of chromium and reported a maximum adsorption capacity of 20.3 mg/g and 86% removal at pH 2. Table 2.17 summarises the reported use of modified saw dust as an adsorbent for chromium removal from wastewater.

Table 2.17 Chromium removal using modified saw dust as an adsorbent

Adsorbent	Inital metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
HCl-acid modified oak saw dust	0.1-100	3	0–720	60	1.70	84%	Argun et al., 2007
Sulphuric acid modified pine sawdust	15–75	2	240	4	20.3	-	Politi & Sidiras 2012

2.3.2.8 Modified egg shell

Although chicken eggs are a worldwide daily food they also pose environmental problems. For example, in the United States, about 150,000 tons of this material is disposed of in landfills every year (Patricio et al., 2007). Egg shell has an outstanding mechanical performance, such as an excellent combination of stiffness, strength, impact resistance and toughness. The composition is about 95% calcium carbonate (which occurs in two crystal forms: hexagonal calcite and rhombohedral aragonite) and 5% organic materials. The amine and amide groups of the proteins on the surface of particulate egg shell are a potential source of hardening agent and help in chromium removal via chelation (Guru & Das 2012) and this hardening agent (providing strength to the adsorbent) has an affinity for chromium. Egg shells have been used for the removal of chromium from water in both modified and non-modified forms. Modification is carried out by calcinating at high temperatures. After calcination the structure changes due to the development of pores via the emission of carbondioxide gas (Rohim et al., 2014). Daraei et al., (2015) used egg shell for chromium removal and reported 93%

removal at an optimum pH 5 and 1.45 mg/g of maximum adsorption capacity. Liu & Huang (2011) modified egg shell using polyethyleneimine (PEI). The PEI functionalises the eggshell membrane (ESM) via cross-linking reactions between various functional groups. The prepared bioadsorbent is reported as interacting strongly with chromium(VI), and the uptake capacity of the PEI–ESM was increased by 105% compared with the unmodified egg shell with a maximum removal of 90% and a maximum adsorption capacity of up to 160 mg/g at an optimum pH of 3. Table 2.18 summarises the reported use of modified egg shell as an adsorbent for chromium removal from wastewater.

Table 2.18 Chromium removal using modified egg shell as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
Egg shell	5-30	5	90	3.5	1.45	93%	Daraei et al., 2015
Egg shell modified using polyethyleneimine	100	3	10-1,440	10-40	160	90%	Liu & Huang 2011

Fig 2.1 Commercial adsorbents (a) activated carbon (b) graphene (c) carbon nanotube and Bio adsorbents (d) rice husk (e) coconut coir pith (f) sugarcane bagasse (g) wheat bran (h) coconut shell (i) orange peel (j) saw dust (k) egg shell for chromium removal from wastewater

2.3.3 Commercially available adsorbents for cadmium removal from wastewater

2.3.3.1 Mesoporous silica

Mesoporous silica is a highly ordered material which possesses a regular two-dimensional hexagonal array of channels. Mesoporous silica is efficient for cadmium removal because of its high surface area and 2–10 nm pore size (Bhattacharyya et al., 2006; Machida et al., 2012). Mesoporous silica may be chemically modified via the attachment of groups including carboxylic acid, sulfonic acid and amino-carbonyl. Javadian et al., (2014) prepared polyaniline/ polypyrrole/ hexagonal type mesoporous silica for cadmium removal and reported a removal of 99.2% cadmium at an optimum pH of 8. Hajiaghababei et al., (2011) modified SBA-15 nanoporous silica by functionalising it with ethylenediamine. SBA-15 is a highly ordered material with a regular two-dimensional hexagonal array of channels with a pore diameter of the order of 7–10 nm. The reported removal was 98% at pH > 4.5.

Similarly, Burke et al., (2009) also used aminopropyl and mercaptopropyl, functionalised and bi-functionalised, large pore mesoporous silica spheres for the removal of chromium from wastewater. These researchers reported a maximum sorption capacity of 43.16 mg/g for Cr. Pérez-Quintanilla et al., (2007) modified silica and amorphous silica using 2-mercaptopyridine and reported maximum adsorption capacities of 205 mg/g and 97 mg/g, respectively. Table 2.19 documents the available data for mesoporous silica for cadmium removal from wastewater.

Table 2.19 Cadmium removal using mesoporous silica as an adsorbent

Adsorbent functionalised with	**Metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
Amino functionalised silica	50	5	120	5	18.25	90%	Heidari et al., 2009
Amino functionalised mesoporous silica	5–300	-	1,440	1.11	93.30	100%	Aguado et al., 2009
Iminodiacetic acid-modified mesoporous SBA-15	50-1,000	5.6	1,440	4.0	-	99.8%	Gao et al., 2007
Polyamine-functionalised	100	5.5-7	2,880	-	-	70%	Alothman& Apblett 2010

2.3.3.2 Chitosan

Chitosan is a derivative of the N-deacetylation of chitin which is a naturally occurring polysaccharide obtained from crustaceans. Chitosan is an efficient adsorbent for the removal of heavy metals (Ren et al., 2008).

Chitosan is cheap, hydrophilic and biodegradable and it also offers ease of derivatisation. It contains amino and hydroxyl groups that may form chelates with heavy metals (Huo et al., 2009; Hu et al., 2011). Chitosan has the advantage of being cheap yet effective, but has the disadvantages of being mechanically weak, soluble under acidic conditions and may leach carbohydrate when used in raw form (Ren et al., 2008; Huo et al., 2009). Various efforts have been made to stabilise chitosan using cross-linking agents, but this results in a decrease in adsorption capacity (Wang et al., 2011). Thus, Chen et al., (2012) have developed ‘ion imprint technology’ for achieving higher adsorption capacity and stability. This involves the development of a novel adsorbent that is a thiourea-modified magnetic ion imprinted chitosan /TiO_2 composite for the removal of cadmium. The maximum adsorption capacity obtained for this material was reported to be 256.41 mg/g at an optimum pH of 7. Chitosan has also been modified by a coating process involving ceramic alumina. Coating helps increase accessibility of binding sites and improves mechanical stability. Maximum adsorption capacity obtained was reported to be 108.7 mg/g at an optimum pH of 6 and the maximum removal reported was 93.76% (Wan et al., 2004). Similarly, Hydari et al., (2012) modified chitosan by coating with activated carbon and reported an adsorption capacity of 52.63 mg/g adsorption capacity at an optimum pH of 6 with 100% removal. Table 2.20 presents cadmium removal data for chitosan as an adsorbent from wastewater.

Table 2.20 Cadmium removal using chitosan as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Removal (%)	References
α-Ketoglutaricacid-modified magnetic chitosan	100-500	6	90	0.04	93%	Yang et al^{b}., 2014
Electrospun nanofibre membrane of PEO/chitosan	50-1,000	5	120	-	72%	Aliabadi et al., 2013
Nano-hydroxyapatite/chitosan composite	100–500	5.6	90	5.0	92%	Salah et al., 2014
Polyaniline grafted cross-linked chitosan beads	40–220	6	120	4.5	99.6%	Igberase et al., 2015
O-carboxymethyl functionalisation of chitosan	675	10	1,440	-	95%	Borsagli et al., 2015
Multi-walled carbon nanotubes modified with chitosan	-	6-7	-	-	>90%	Salam et al., 2011

2.3.3.3 Zeolite

Zeolite has good ion exchange properties, a high surface area and a hydrophilic character which makes them suitable for sequestration of cadmium. Modified zeolite provides a higher adsorption capacity compared to natural zeolite. There are different methods for zeolite modification. For example, nanosized zeolite has more accessible pores which make it more suitable for heavy metal removal. Among nanosized zeolite adsorbents, NaX nanozeolite (Ansari et al., 2014) (in molar ratio of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O) is widely used for cadmium removal from wastewater (Choi et al., 2016; Erdem et al., 2004; Jha et al., 2008; Ibrahim et al., 2010, 2012; Aliabadi et al., 2013; Rad et al., 2014).

Rad et al., (2014) synthesised NaX nanozeolite using a microwave heating method, and then polyvinylacetate polymer/NaX nanocomposite nanofibres were prepared using electrospinning method; the potential of these composite nanofibres was then investigated for cadmium. The reported maximum adsorption capacity was 838.7 mg/g with 80% removal at an optimum pH of 5. Choi et al., (2016) modified zeolite by replacing Si(IV)and Al(III) sites in the lattice with exchangeable cations such as sodium, magnesium, potassium, or calcium, leading to a net negative charge. Mg-modified zeolite has certain advantages such as non-toxicity, low cost, abundance (and hence availability) and large pore size of 40–50 nm compared to the non-modified adsorbent. This Mg-modified adsorbent has a cadmium removal of more than 98% at an optimum pH of 7. In addition, the adsorption capacity of Mg-zeolite was found to be 1.5 times higher than that of zeolite modified with Na or K and 1.5 to 2.0 times higher than that of natural zeolite.

Coal, which is used in many industries as a fuel, produces fly ash as a by-product which causes air pollution and presents disposal problems. Due to its low cost fly ash can be used for zeolite formation using the hydrothermal process (Hui et al., 2005). Javadian et al., (2015) converted fly ash into amorphous aluminosilicate adsorbent and reported a maximum adsorption capacity for cadmium of 26.246 mg/g with 84% removal at an optimum pH of 5. Similarly, Visa et al., (2016) converted fly ash into zeolite for cadmium removal through a hydrothermal process using sodium hydroxide. These researchers reported that this product has high surface area and is rich in micropores and demonstrates more than 80% cadmium removal at an optimum pH of 7–8. Table 2.21 summarises the removal parameters for the sequestering of cadmium using zeolite.

Table 2.21: Cadmium removal using using zeolite as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Synthetic zeolite A	100-2,000	-	180	1.0	315.65	-	El-Kamash et al., 2005
Zeolite	25-100	6	90	25	-	76%	Rao et al., 2006
Zeolite from fly ash	1124.1-3372.3	6.6	1,440	10	57–195	95.6%	Izidoro et al., 2013
Oil shale into zeolite	100	7	60-1,440	-	95.6	-	Shawabkeh et al., 2004
Natural zeolite	9–90	5	1,440	-	9	71%	Hamidpour et al., 2010

2.3.3.4 Red mud

Red mud is a waste material from the aluminium industry that may be converted into an efficient adsorbent for cadmium removal from waste water (Gupta & Sharma 2002; Ma et al., 2009; Ju et al., (2012; Zhu et al., 2007). However, Zhu et al., (2007) developed red mud as a novel adsorbent for cadmium removal from wastewater. In this regard, the adsorption process onto granular red mud was found to be spontaneous and endothermic in nature. A maximum adsorption capacity of 52.1 mg/g was reported at a pH of 3 to 6.

Similarly, Gupta & Sharma (2002) also used red mud for cadmium removal from wastewater and complete removal was obtained at the lower concentration $(1.78 \times 10^{-5} \text{ to } 1.78 \times 10^{-4} \text{ Molar})$ while 60–65% removal was obtained at the higher concentration $(1.78 \times 10^{-4} - 1.78 \times 10^{-3} \text{ Molar})$ at an optimum pH between 4 and 5

2.3.4 Bio-adsorbents for cadmium removal from wastewater

2.3.4.1 Coffee residue

Coffee residue has been reported as an efficient adsorbent for the removal of cadmium from wastewater. For example, Boonamnnayvitaya et al., (2004) used coffee residues for cadmium removal and also blended them with clay to prepare an adsorbent with a negative charge which promotes cadmium complexation and removal. The prepared adsorbent contains hydroxyl, carbonyl and amine groups and has a pyrolysis temperature of 500 °C (this temperature gives maximum adsorption capacity) and a particle size diameter of 4 mm.

A weight ratio of coffee residue to clay of 80:20 was found to be the most suitable blend. Oleveira et al., (2008) employed coffee husks that comprise the dry outer skin, pulp and parchment as these are likely to represent the major residue obtained from the handling and processing of coffee. For this material, the maximum adsorption capacity was reported to be 6.9 mg/g at an optimum pH of 4 with a removal of 65–85%. Kaikake et al., (2007) soaked and degreased coffee beans in water and methanol to produce an adsorbent. The prepared degreased coffee beans (DCB) material behaved as a cation exchanger with 90% removal at an optimum pH 8. Azouaou et al., (2010) used waste material from cafeterias as an adsorbent for cadmium removal and reported an adsorption capacity of 15.65 mg/g with more than 80% removal at an optimum pH of 7. Table 2.22 presents cadmium removal data for coffee residue as an adsorbent.

Table 2.22 Cadmium removal using coffee residue as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Coffee residues blended with clay	25–250	1.6–2.5	30	10	17.5–17.9	88–92%	Boonamnnayvitaya et al., 2004
Coffee husks	50–100	4	4,320	6.7	6.9	65–85%	Oleveira et al., 2008
Coffee beans	6–202	8	1,440	10	3.80	90%	Kaikake et al., 2007
Coffee grounds from cafeterias	10–700	7	120	9	15.65	>80%	Azouaou et al., 2010

2.3.4.2 Rice husk

Rice husk is an agricultural waste obtained from rice mills and it consists of cellulose, hemicelluloses, mineral ash, lignin and a high percentage of silica (Rahman et al., 1997). It contains groups such as –OH, Si-O-Si and -Si-H which have an affinity for cadmium coordination and hence removal. It may be useful as an adsorbent for cadmium removal because it is cheap and easily available.

Chemicals that are used for the modification of rice husk in order to increase adsorption capacity include the bases sodium hydroxide, epichlorohydrin and sodium carbonate (Kumar et al., 2006). Ye et al., (2010) modified rice husk by constant stirring with sodium hydroxide for 24 hours and reported an adsorption capacity for cadmium removal of 125.94 mg/g, which is higher than the non-modified rice husk at 73.96 mg/g, at an optimum pH of 6.5.

Kumar et al., (2006) modified rice husk using epichlorohydrin, sodium hydroxide and sodium bicarbonate, and the adsorption capacity increased from 8.58 mg/g for raw rice husk to 11.12 mg/g, 20.24 mg/g and 16.18 mg/g, respectively, with the removal increasing from 75% to 86.2%, 97% and 97.2%, respectively, at an optimum pH of 9. It was also reported that the equilibrium time was reduced from 600 min to 120 min, 240 min and 60 min, respectively. Ajmal et al., (2003) treated rice husk using phosphate, and a maximum removal of 99% was reported at an optimum pH of 12. Srivastava et al.,

(2006) used mesoporous rice husk with an 80% pore area (ratio of rice husk's unoccupied area to its total area) and reported a 23.3% cadmium removal along with some other heavy metals at an optimum pH of 6. Sharma et al., (2009) used polyacrylamide grafted rice husk for cadmium removal from wastewater, and 85% removal was reported at an optimum pH of 9. Table 2.23 summarises the removal parameters for the sequestering of cadmium using rice husk.

Table 2.23 Cadmium removal using rice husk as an adsorbent

Adsorbent	**Metal conc. (mg/L)**	**Optimum pH**	**Bestmodel fit**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorption capacity (mg/g)**	**Removal (%)**	**References**
Rice husk ash	10-100	6	Freundlich, Redlich-Peterson	5	1–10	3.04	29.8%	Srivastava et al., 2008
Sulphuric acid-treated rice husk	50, 100	4	Langmuir	60	1.0	41.15, 38.76	-	El-Shafey 2007
Activated rice husk	8.9–89 M	6	Freundlich, Langmuir & D-R	20	4.0	-	97%	Akhtar et al., 2010

2.3.4.3 Powdered olive stones

Olive stones form part of the waste produced from the oleic industry and are available in olive oil producing countries (Bohli et al., 2015; Aziz et al^{b}., 2009). Thus, the olive stone is a plentiful by-product of the olive oil industry and is a candidate for use as an adsorbent for the removal of cadmium. Olive stones can be modified using succinic anhydride, sulphuric acid, nitric acid or sodium hydroxide to increase adsorption (Blazquez et al., 2005; Aziz et al^{a}., 2009). Aziz et al^{a}., (2009) modified olive stones using succinic anhydride that chemically functionalises it with succinate moieties that have an affinity for cadmium. This adsorbent was synthesised by esterifying the lignocellulosic matrix of the olive stone with succinic anhydride in the presence of toluene in basic medium. The adsorption capacity reported for this material was 200 mg/g at an optimum pH of 4. Blezquez et al., (2005) used olive stones for cadmium removal and observed the effect of different parameters on the percentage removal. Thus it was found that for a smaller size of adsorbent particles (250–355 nm) the removal capacity increases up to 90% at an optimum pH of 11, and the maximum adsorption capacity was reached within

20 minutes, which is fast compared to the equilibrium time achieved in cadmium removal using olive stones prepared by $ZnCl_2$ activation (Kula et al., 2008) and by using olive cake (Anber & Matouq 2008). Olive stone can also be used as an adsorbent by converting it into activated carbon using chemicals such as $ZnCl_2$, H_3PO_4 and H_2O_2 with a subsequent improvement in pore distribution that increases the surface area of the adsorbent.

Kula et al., (2008) used 20% zinc chloride as an olive stone activating agent for cadmium removal and 95% removal was reported and compared with raw olive stone (43%) at an optimum pH of 9. Valencia et al., (2014) prepared activated carbon from carbon aguaje and olive fruit stone using phosphoric acid solution, and a maximum adsorption capacity of 8.14 mg/g and 9.01 mg/g and a removal capacity of 61% and 68% was obtained for aguaje and olive fruit stones, respectively. Hamadaoui (2009) compared the adsorption capacity of olive stone in the absence of ultrasound (42.19 mg/g) and in the presence of ultrasound (55.87 mg/g) and with combined ultrasound/stirring (64.94 mg/g). Ultrasound increases adsorption capacity of olive stone due to acoustic power which enhances mass and heat transfer at films and within the pore. Further, combination of stirring with ultrasound leads to intensification of the removal of cadmium. Table 2.24 summarises the removal parameters for the sequestering of cadmium using powdered olive stones.

Table 2.24 Cadmium removal using powdered olive stone as an adsorbent

Adsorbent functionalised/ composite with/modified	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Removal (%)**	**References**
Olive cake	100	6	1,440	0.3	66%	Al-Anber et al., 2008
Zinc chloride activated olive stone	15-45	9	60	20	95%	Kula et al., 2008
Microwaved olive stone activated carbon	20	5	7	0.25-2	95.32%	Alslaibi et al., 2013
Activated carbon from olive stones	56-562	5	200	6	23%	Bohli et al., 2015
Olive stone waste	33-16,861	5.5-6	60	13.33	49.2%	Fiol et al., 2006

2.3.4.4 Apple pomace

Apple pomace is a waste product from the apple juice industry and is usually dumped at industrial sites in very large quantities (Chand et al., 2015). An apple (solid residue part) consists of the flesh 95% (wt%), seed 2–4% (wt%) and stem 1% (wt%) (Chand et al., 2014). Apple pomace is the solid residue part of the apple which is obtained during its processing (Chand et al., 2014). Apple pomace contains 7.24 g kg^{-1} of total polyphenol which includes epicatechin (0.64 g/kg), caffeic acid (0.28 g/kg), 3-hydroxyphloridzin (0.27 g/kg), phloretin-20-xyloglucoside (0.17 g/kg), phloridzin (1.42 g/kg), quercetin-3-galactoside (1.61 g/kg), quercetin-3-galucoside (0.87 g/kg), quercetin-3-xyloside (0.53 g/kg), quercetin-3-arbinoside (0.98 g/kg) and quercetin-3-rhamnoside (0.47 g/kg).

Thus, apple pomace behaves as a metal chelator because of these polyphenols, amine and carboxyl groups (Foo & Loo 1997). Chand et al., (2014) chemically modified apple pomace with succinic anhydride via a simple ring opening mechanism that provides a larger surface area on the material. The surface area is reported to increase by 18%, and consequently, 50 times less apple pomace was required as an adsorbent. The adsorption capacity of modified apple pomace (91.74 mg/g) was increased 20 times compared to non-modified apple pomace (4.45 mg/g) and for the modified apple pomace a removal of 90% was obtained compared to 70% for non-modified apple pomace at an optimum pH of 4. Table 2.25 presents cadmium removal data for apple pomace as an adsorbent.

Table 2.25 Cadmium removal using apple pomace as an adsorbent

Adsorbent	**Initial metal conc. (mg/L)**	**Optimum pH**	**Contact time (min)**	**Adsorbent dose (g/L)**	**Adsorbent capacity (mg/g)**	**Removal (%)**	**References**
Succinic anhydride modified apple pomace	10-80	4	10-180	0.8 & 40	4.45, 91.74	70%, 90%	Chand et al., 2014
Xanthate moiety into apple pomace	10-120	4	5–60	0.2-8	112.35	99.7%	Chand et al., 2015

2.3.4.5 Modified coconut waste

Seven and a half million tons of coconut per year is produced in India alone and the waste by-products have been used as adsorbents for cadmium removal (Chadha et al., 2003). The sorption properties are due to the presence of functional groups such as hydroxyl and carboxyl and this material demonstrates a high affinity for metal ions (Tan et al., 1993). Coconut coir pith and coconut shell are waste by-products that can be used for cadmium removal.

Coir pith is a light fluffy biomaterial generated during the separation of the coconut fibre from the husk (Namashivayam & Sureshkumar 2008). Raw coir pith consists of 35% cellulose, 1.8% fats, 25.2% lignin and resin, 7.5% pentosans, 8.7% ash, 11.9% moisture and 10.6% other substances (Dan 1993). Kadirvelu et al., (2003) prepared activated carbon using coconut coir pith and reported a maximum adsorption capacity of 93.4 mg/g at a pH of 5.

For cadmium removal, along with some other heavy metals, Jin et al., (2013) converted coconut into activated carbon and then grafted it with tetraoxalyl ethylenediamine melamine chelate using a pressure relief dipping ultrasonic method. The maximum adsorption capacity reported was 26.41 mg/g at an optimum pH of 5.5. Pino et al., (2006) used green coconut shell powder and reported removal of cadmium over a large concentration range of 20 to 1,000 ppm with a maximum adsorption capacity of 285.7 mg/g and 98% removal at pH 7. Similarly, Sousa et al., (2010) used green coconut shell for cadmium removal, along with other heavy metals, and the maximum adsorption capacity found for the single component system (presence of cadmium only) was reported to be 37.78 mg/g and for the multicomponent system (presence of lead, nickel, zinc and copper along with cadmium), 11.96 mg/g at pH 5. Table 2.26 presents cadmium removal data for modified coconut waste as an adsorbent.

Table 2.26 Cadmium removal using modified coconut waste as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Optimum pH	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Activated carbon from coconut shell	5-40	5	120	0.3921	93.40	98%	Kadirvelu et al., 2003
Activated carbon from coconut shell	1,124	5.5	240	2	26.41	93.4%	Jin et al., 2013
Green coconut shell	20-1,000	7	120	5	285.70	98%	Pino et al., 2006
Green coconut shell	100	5	1.33-9.98	1.620	37.38, 11.96	-	Sousa et al., 2010

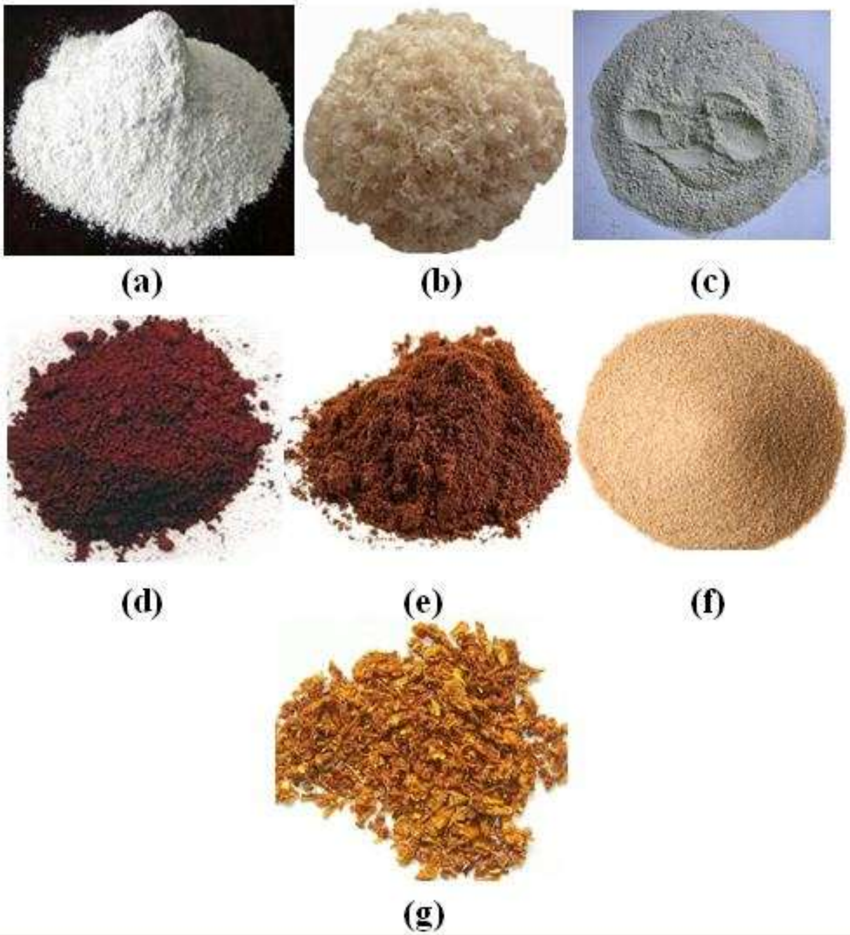


Fig. 2.2 Commercial adsorbents (a) silica (b) chitosan (c) zeolite (d) red mud and biosorbents (e) coffee residue (f) powdered olive stone (g) apple pomace for cadmium removal from wastewater

2.3.5 Commercially available adsorbents for copper removal from wastewater

2.3.5.1 Magnetic adsorbents

Various magnetic adsorbents have been used or show potential for the effective removal of copper from wastewater, including ‘magnetic’ adsorbent micro- and nano-sized particles (Yin et al., 2012). These latter adsorbents show high adsorption capacity and can be harvested from aqueous solution in the presence of a suitable magnetic field. In addition, such material is potentially reusable (Mehta et al., 2015).

A problem with the use of unmodified magnetic particles is the formation of aggregates due to magnetic dipolar attraction between the particles. To prevent this, a layer of various polymer compounds or the inorganic oxide may be coated on the surface of the particles (Yin et al., 2012). Ren et al., (2008) prepared a novel adsorbent by using waste fungal mycelium obtained from industry (industries dealing with fungal products such as antibiotics, citric acid and enzymes), chitosan and iron oxide nanoparticles utilizing metal imprinting technology. Fungal mycelium has been used because of its low cost, abundance and high efficiency. However, its direct use is difficult because of its limited reusability, relative low adsorption and low mechanic intensity (mechanical strength). Chitosan is considered useful since it is a polysaccharide and contains -NH_2 and -OH functional groups, which have an affinity for copper removal, and iron oxide is used because it is magnetic. In metal ion imprinting technology, selective binding sites are made on synthetic polymer using metal ion templates, and after removal of these templates, polymer become more selective for heavy metal removal from wastewater.

Thus, binding of chitosan and industrial waste fungal mycelium on iron oxide nanoparticles produces a novel adsorbent known as magnetic Cu(II) ion imprinted composite adsorbent (Cu(II)-MICA). Ren et al., 2008 reported that the Langmuir isotherm fits the experimental data well and a maximum adsorption capacity of 71.36 mg/g was reported. It was also shown that this adsorbent can be reused up to five times with a regeneration loss of 14%–15%. Lan et al., (2013) used hyaluronic acid supported magnetic microspheres for copper removal, and their adsorption capacity is reported to increase from 6 mg/g to 12.2 mg/g as the pH is increased from 2 to 6.8, and slowly decreases to 11.6 mg/g up to pH 8. The corresponding adsorption equilibrium study showed that the copper adsorption of the hyaluronic acid-supported magnetic microspheres had the best fit to the Freundlich isotherm model.

Gong et al., (2012) used a pectin-coated iron oxide magnetic nanocomposite as an adsorbent for removal of copper from wastewater. This nanocomposite adsorbent was synthesised using an iron salt co-precipitation method followed by direct encapsulation with a coating of pectin and in the absence of calcium cross linking. The experimental data are reported to fit both Langmuir and Freundlich models and a maximum adsorption capacity of 48.99 mg/g was reported. The adsorbent can be further regenerated using EDTA and a removal of 93.70% was obtained after the first regeneration cycle and a removal of 58.66% remained even after a fifth cycle. Hu et al., (2013) used sulfonated graphene oxide for removal of copper from wastewater. The introduction of the sulfo functional group to graphene oxide is reported to increase the copper adsorption with an adsorption capacity of 62.73 mg/g at pH 4.68 and the experimental data fit the Langmuir isotherm.

2.3.5.2 Alumina

Alumina may be used for copper removal from wastewater and several authors have utilized alumina for this purpose either in nanoparticulate form or via loading with cation exchangers (Mahmoud et al., 2010; Fouladghar et al., 2015). For example, Fouladghar et al., (2015) used Ɣ-alumina nanoparticles for removal of copper alongwith nickel. Nanoparticles are useful because of their high adsorption capacity due to the high number of metal coordination sites. These researchers have a best fit for the Freundlich isotherm and a maximum adsorption capacity of 31.3 mg/g for copper removal from wastewater. Ghaemi (2016) used a phase inversion method to prepare a mixed matrix membrane using PES (polyethersulfone) and varying amounts (1 wt %) of alumina nanoparticles. Such mixed matrix membranes have shown higher water permeation compared to a pristine PES membrane that is facilitated by the addition of small amounts of nanoparticles. This results in an increase in porosity and hydrophilicity. The mixed matrix membrane has shown the highest removal of copper from wastewater of 60% compared to the PES membrane (around 25%).

Mahmoud et al., (2010) removed copper from wastewater using three new alumina adsorbents of acidic, neutral and basic nature and their surface was modified by loading with 1-nitroso-2-napthol as a cation exchanger. After modification, alumina adsorbents become stronger towards acid leaching and thermal decomposition. The adsorption capacities obtained were 27.96 mg/g, 28.58 mg/g and 28.59 mg/g for the acidic, neutral and basic adsorbents, respectively. Conventional porous solids such as fly ash, clay and silica materials have the disadvantage of having non-uniform pores and low adsorption capacity. Thus, Rengaraj et al., (2004) prepared aminated and protonated mesoporous alumina for copper removal from wastewater. Mesoporous alumina have several advantages over conventional porous solids such as a large surface area, uniform pore size distribution with a sponge-like interlinked pore system, high stability and high metal uptake capacity (Lee et al., 2001). Ion exchange takes place between copper and the hydrogen ions that are present on the surface of mesoporous alumina, and the maximum adsorption capacity obtained for aminated mesoporous alumina is 7.924 mg/g compared to 14.535 mg/g for protonated mesoporous silica.

2.3.5.3 Clay

Clay may be used for removal of copper from wastewater due to high surface area (Singh et al., 2001; Krikorian & Martin 2005; Asci et al., 2007; De Almeida Neto et al., 2014; Futalan et al., 2011; Oubagaranadin et al., 2010).

Thus, researchers have studied different types of clay, either in raw form or after its modification, for copper sequestration. For example, Bertagnolli et al., (2011) employed bentonite clay after calcination at 400–500 °C. Bentonite has several advantageous properties as an adsorbent including low cost, good ion exchange capacity, selectivity and regenerability. This material showed a maximum adsorption capacity of 11.89 mg/g.

Vengris et al., (2001) modified clay using hydrochloric acid followed by neutralisation of resultant solution with sodium hydroxide for copper removal from wastewater. Initially, the chemical composition (wt %) of clay was: iron oxide 6.9, silicon oxide 44.2, aluminium oxide 15.3, calcium oxide 13.8 and magnesium oxide 4. After treatment with hydrochloric acid, aluminium, iron and magnesium compounds of clay had increased because acid treatment causes dissolution of iron, calcium, magnesium and aluminium oxides and during the neutralisation process many dissolved metals (except calcium) reprecipitate in the form of hydroxides and their amount in the modified adsorbent increases. This leads to an increase in metal uptake capacity of modified clay compared to unmodified clay. This acidic treatment led to the decomposition of the montmorillonite structure. The maximum adsorption capacity obtained for single component solutions was 0.75 mg/g, for ternary component solutions 0.80 mg/g and the experimental data fitted the Langmuir isotherm.

2.3.6 Bio-adsorbents for copper removal from wastewater

2.3.6.1 Fungal biomass

Fungal biomass has been explored by several researchers for its potential to remove copper from wastewater. The use of fungal biomass for such purposes has been hindered due to problems such as small particle size, poor mechanical strength, low density and rigidity (McHale & McHale 1994; Volesky & Holan 1995). However, the use of a suitable matrix can potentially overcome these problems.

Thus, Iqbal & Edyvean (2004) used a low cost, physically strong and highly porous matrix, namely ‘loofah sponge’ for the immobilized biomass of Phanerochaete chrysosporium, and a maximum adsorption capacity of 50.9 mg/g at pH 6 with 98% removal was reported. Formaldehyde inactivated Cladosporium cladosporioides, Gliomastix murorum and Bjerkandera fungi, at optimum conditions, can also be used for copper removal. These fungi are highly porous; their mesh structure provides ready access and a large surface area for the biosorption of copper. Thus, Li et al., (2009) obtained maximum adsorption capacities of 7.74 mg/g, 9.01 mg/g and 12.08 mg/g, and removals of 93.79%, 85.09% and 81.96%, for C. cladosporioides, G. murorum and Bjerkandera fungi, respectively. The biosorption data of all fungal species fitted well with the Langmuir model. Ertugay & Bayhan (2010) used Agaricus bisporus fungi and 73.3% removal was obtained at pH 5 with a preferred fit to the Freundlich model compared to other adsorption models. Table 2.27 summarises the parameters for the sequestration of copper using fungal biomass.

Table 2.27 Copper removal using fungal biomass as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	pH	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal (%)	References
Aspergillus niger	10-100	6	-	-	23.60	-	Mukhopadhyay 2008
Mucor rouxii	10-1,000	5-6	4,320	0.25	52.60	96.3%,	Majumdar et al. 2008
Fungal cells	20-100	5-9	4,320	0.2	-	95.27%	Hemambika et al., 2011
Aspergillus niger	25-100	5	10, 200	15	15.60	-	Dursun et al., 2003
Rhizopus oryazae filamentous fungus	20-200	4-6	200	1	19.40	-	Bhainsa & D’souza 2008
Pleurotus pulmonarius CCB019 and Schizophyllum commune	5-200	4	12	3	6.20, 1.52	-	Veit et al., 2005
Chlorella sp. & Chlamydomonas sp.	5	7	12	25	33.4	-	Maznah et al., 2012
Trametes versicolour	37-80	5.51	80	1	60.98	-	Sahan et al., 2010
Aspergillus niger	10-100	6	30	2-5	23.62	30%	Mukhopadhyay 2007
Penicillium citrinum	10-90	5	30	1.5	-	76.2%	Verma et al., 2013

2.3.6.2 Yeast

Yeast has been successfully used as an adsorbent for the sequestration of copper (Wang & Chen 2009). Waste beer yeast is a by-product of the brewing industry that is a cheap and promising adsorbent for copper removal from wastewater (Han et al., 2006).

These researchers reported a maximum uptake of copper of 1.45 mg/g with a preferred fit to the Langmuir and Freundlich isotherms; bisorption was reached in equilibrium in 30 minutes. The sorption capacity of beer yeast was found to be a function of the initial metal ion concentration, the adsorbent dose, pH, contact time and the amount of salts added and the process best fits the Langmuir and Freundlich adsorption models (Han et al., 2006). Table 2.28 summarises the parameters for the sequestration of copper using yeast.

Table 2.28 Copper removal using yeast biomass as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	Ph	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal (%)	References
Caustic-treated Succharomyces cerevisiae yeast biomass	16-18	5	2,160	2.0	9.01	-	Lu et al., 1996
Saccharomyces cerevisiae biomass	25-200	3-4	-	15	2.59	43.08%	Cojocaru et al., 2009
Baker's yeast	100	2.7-6	250	1	65	-	Yu et al., 2008

2.3.6.3 Algal biomass

Algae may be used for the removal of copper because of their high capacity, low cost, renewability and ready abundance (Chen 2012; Loutseti et al., 2009). There are different types of marine algae, such as red algae, green algae and brown algae that are used for copper removal from wastewater and the main difference in these algae is in their respective cell walls where biosorption occurs (Romera et al., 2007; Solisio et al., 2006; Kratochvil & Volesky 1998; Herrero et al., 2011).

The cell walls of brown algae contain cellulose (as a structural support), alginic acid and polymers of mannuronic and guluronic acids complexed with metals such as sodium, magnesium, potassium, calcium and other polysaccharides (Romera et al., 2007). Green algae mainly have cellulose in the cell wall with a high content of bonded proteins. Therefore, this material contains various functional groups such as carboxyl, amino, sulfate and hydroxyl. Red algae contain cellulose in the cell wall, but their biosorption capacity is attributed mainly to the presence of sulfated polysaccharides called galactans (Romera et al., 2007). Brown algae, Turbinaria ornate, and green algae, Ulothrix zonata, have shown a maximum copper removal of 176.20 mg/g and 147.06 mg/g from wastewater at pH 6 and pH 4.5, respectively (Nuhoglu et al., 2002; Vijayaraghavan & Prabu 2006). Industrial algal waste has also been used for copper removal with a maximum adsorption of 16.7 mg/g at pH 5.3 (Vilar et al., 2008). Under hydrated and dehydrated conditions, micro algae Spirulina platensis has also been reported to remove up to 90% of copper from aqueous solution (Solisio et al., 2006). The dried biomass of Spirogyra neglecta has a reported maximum adsorption capacity for copper of 115.5 mg/g at pH 4.5–5 (Singh et al., 2007). Table 2.29 summarizes the removal parameters for the sequestering of copper using algal biomass as an adsorbent.

Table 2.29 Copper removal using algal biomass as an adsorbent

Adsorbent	Initial metal conc. (mg/L)	pH	Contact time (min)	Adsorbent dose (g/L)	Removal (%)	References
Sargassum sp., Padina sp., Ulva sp. and Gracillaria sp.	64	5	60	1	90%	Sheng et al., 2008
Padina sp.	127	5	30	2	90%	Kaewsarn 2002
Gelidium	317	5.3	60	1–20	97%	Vilar et al., 2007
Cystoseira crinitophylla biomass	25, 40, 50	4.5	720	2.5	100%	Christoforidis et al., 2015
Sargassum, Chlorococcum and GAC	1-100	4.5	60, 90, 300	0.1	87.3%	Jacinto et al., 2009
Codium vermilara	10-150	5	120	0.5	-	Romera et al., 2007
Spirogyra insignis	10-150	4	120	5	-	Romera et al., 2007

2.3.6.4 Microbial (bacteria)

Bacteria and cyanobacteria remove heavy metal because the cell wall has the ability to capture the heavy metals due to negatively charged groups within its fabric (Uslu *& Tanyol* 2006; Tunali et al., 2006; Schut et al., 2011; Pagnanelli et al. 2003). There are several processes to remove heavy metals, such as transport across the cell membrane, biosorption to cell walls, entrapment in extra cellular capsules, precipitation, complexation and oxidation/reduction (Rai et al., 1981; Brady & Duncan 1994; Veglio et al., 1997).

Bacteria are the most abundant and versatile of microorganisms (Mann 1990) and bacteria species such as Bacillus sp., Micrococcus luteus, Pseudomonas cepacia, Bacillus subtilise and Streptomyces coelicolor have been used for copper removal from wastewater (Nakajima 2002; Ozuturk et al., 2004; Hassan et al., 2009). Veneu et al., (2013) used Streptomyces lumalinharesii for copper removal from wastewater and a removal of 81% was reported at an optimum pH of 5 with best fit to the Freundlich model. Ozuturk et al., (2004) used S. coelicolor for copper removal and reported 21.8% removal at an optimum pH of 5 with a good fit to the Langmuir model.

Uslu & Tanyol (2006) used P. putida for copper removal as a single component (in the presence of copper only) or as binary component (in the presence of copper along with other heavy metal, i.e., lead here) and reported an endothermic and spontaneous process with 50% copper removal from wastewater. Lu et al., (2006) used Enterobacter sp. J1 for copper removal and an adsorption capacity of 32.5 mg/g and a removal of 90% of copper removal was reported at pH > 2. Even after four repeated adsorption and desorption cycles, the Enterobacter sp. J1 biomass achieved 79% removal. Nakajima (2002) studied removal of copper using Arthrobacter nicotianae bacteria from wastewater by electron spin resonance method, and found that copper ions present in bacterial cells are of octahedral structure with nitrogen and oxygen as ligand atoms and most copper in bacterial cells is combined with amino acid residues present in cell surface protein. Table 2.3 summarises the removal parameters for the sequestering of copper using bacteria as an adsorbent.

Table 2.30 Copper removal using bacteria as an adsorbent

Adsorbent	Initial conc. (mg/L)	pH	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal (%)	References
Paenibacillus polymyxa	25-500	6	120	-	112, 1,602	-	Acosta et al., 2005
Escherichia Coli	32-64	-	-	-	8.846, 10.364	-	Ravikumar et al., 2011
Pseudomonas stutzeri	30-100	5	30	1	36.2	-	Hassan et al., 2009
Pseudomonas putida	0.1	5	10	1	6.6	80%	Pardo et al., 2003
Sphaerotilus natans	100	6	150	3	60	-	Beolchini et al., 2006

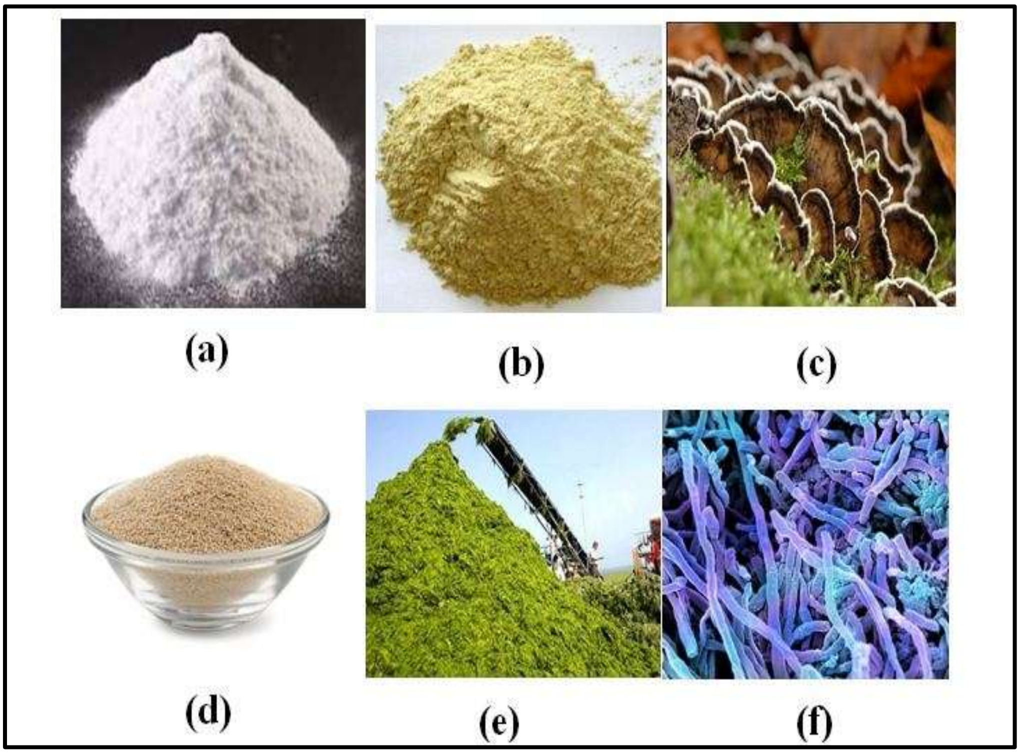


Fig. 2.3 Commercial adsorbents (a) alumina (b) clay; and biosorbents (c) fungal biomass (d) yeast (e) algal biomass (f) Microbial (bacteria) for copper removal from wastewater

2.3.7 Comparison of adsorption with alternative technologies

Table 2.31 shows comparison of adsorption with alternative technologies for Cu(II), Cr(VI) and Cd(II) removal from wastewater and good removal percent was observed.

Table 2.31 Comparison of adsorption with alternative technologies for heavy metal removal from wastewater

Technique	Heavy metal	% Removal	Reference
Chemical precipitation	Cu, Cr	99.60%	Chen et al., 2009
Flotation	Cu, Cr	90%	Polat & Erdogan., 2007
Ion Exchange	Cu, Cr	25%, 30%	Vinodh et al, 2011
Coagulation and Flocculation	Cu, Cr, Cd	77-91%	Zazouli & Yousefi 2008
Membrane filtration	Cu, Cr	95%	Ozaki et al., 2002
Adsorption	Cu, Cr, Cd	99.55%, 98.56%, 98.03%.	Present study

2.4 Single metal adsorption

In batch study, adsorbent and adsorbate remain in contact for a long time until they reaches to the equilibrium stage. Batch study has various advantages such as simplicity and flexibility in operation and low cost. They also have various drawbacks such as in batch operation, large scale effluent can not be treated and it is difficult to control outlet concentration (Treybal R. E., 1980).

Chromium was removed in batch mode using egg shell, coir pith, sugarcane bagasse and maximum removal of 93%, 96%, 80.6% was obtained respectively (Daraei et al., 2015; Namasivayam & Sureshkumar 2008; Ullah et al., 2013). Similarly, copper was removed in batch mode using coffee grounds, Agaricus bisporus fungi and >80%, 73.3% removal was obtained. However, Machida et al., 2012, Alothman & Apblett 2010 and Gao et al., 2007 has removed cadmium in batch mode using mesoporous silica and 80%, 70% and 99.8% removal was obtained.

2.4.1 Optimization of operating parameters

There is a necessity of optimum parameters to make batch study effective for heavy metal removal. As the rate of adsorption depends on operarting parameters such as initial concentration, temperature, adsorbent dose, pH, contact time and stirring speed (Sahu et al. 2009). Zulkali et al., 2006 has optimized a batch process for lead removal for various parameters (initial concentration, temperature, adsorbent dose and pH) using central composite design in Response Surface Methodology by Design Expert Version 5.0.7 (StatEase, USA). The optimum conditions obtained were 50 mg/L initial concentration, 60°C temperature, 0.2 g adsorbent dose and pH 5 for 98.11% lead removal.

Similarly Kataria & Garg 2018 has removed lead and cadmium using ZnO and optimized with central composite design in response surface methodology, observed optimum conditions were 0.8 g/L adsorbent dose, 100 min contact time, 6 pH and 10 mg/L metal concentration. But for Cr(VI) and total Cr removal using Wicherhamomyces anomalus biofilm supported on wood husk, optimum conditions such as pH of 3.72 and 5.48, initial chromium concentration 10 and 16.91 mg/L and adsorbent dose of 6.95 and 8.20 g/L were obtained by central composite design (Asri et al., 2018). However, Lung et al., 2018 has used Box-Behnen Design for optimization of batch process for heavy metal removal (cadmium, lead and arsenic) and 20 mg/L initial ion concentration, 5 g/L adsorbent dose and pH 5.5 was obtained as an optimum condition. Similarly Box-Behnen Design was used by Rahman & Nasir 2018 for optimization of batch process for cadmium removal using poly(o-phenylenediamine)/hydrous zirconium oxide composite and optimum conditions obtained were 50 mg/L initial metal concentration, 25 mg/mL adsorbent dose, pH 6 and contact time 45 min for 99.6% cadmium removal. Khobragade et al., 2016 has removed nickel, copper using surfactant modified alumina using a three-factor, three-level Box–Behnken experimental design. The optimum values found for nickel were pH 8.2 adsorbent dose 5 g/L and contact time 60 min for 93.83% removal and for copper the optimum values were pH 5.3 adsorbent dose 4 g/L and contact time 75 min for 97.23 % removal. For lead, copper and cadmium removal optimal conditions obtained were 25 mg/L initial metal concentration, pH 6 and 2 g/L of adsorbent dose using pseudomonas azotoformans bacterium and Box-Behnken design (Choińska-Pulit et al., 2018) for 63.32% copper, 78.23% lead, % 44.67% cadmium removal. For optimization, use of Box-Behnken design is useful over central composite design because it requires less munber of experiments (Rakic et al., 2014).

2.4.2 Design of experiments

In experimental optimization technique, it is difficult to understand the effect of interacting parameters on removal. Therefore nowadays various statistical methods have been adopted for optimization such as design of experiments, Mini tab.

Design of experiments is a statistical technique being used since 1990s. Experimental design includes experimental statistics and it can produce explicit results. Main effects and interaction effects can be calculated using design of experiments (Lee et al., 2006). Cao et al, 2014 has used central composite design in design of experiments with four variables (temperature, pH, initial concentration and adsorbent dose) and 30 expermiments for chromium removal using amine-functionalized MCM-41.

From ANOVA analysis, it was clear that the predicted results are close to the experimental results and optimum values obtained were temperature 40^0 C, pH 3.5, initial metal concentration 10 mg/L and removal 98.70% and adsorbent dose 5 g/L. Similarly, Singh et al., 2010 has used Box–Behnken design in design of experiments with three levels, four variables (temperature, pH, initial conc. and adsorbent dose) and 29 experiments for lead, cadmium and copper removal using Trichoderma viride as an adsorbent and ANOVA ensures that model is significant because probability value is less than 0.05 and predicted and adjusted R-square value are in the range of 0.84-0.99.

Simlarly, zinc, lead and cadmium were removed from wastewater using Box-Behnken design in design of experiments with three levels, four factor (temperature, pH, initial metal concentration and adsorbent dosage) and 29 experiments (Ahmadi et al., 2014) using maghemite nanoparticles. ANOVA found that for cadmium removal pH and initial metal concentration, for lead removal pH, adsorbent dose, interaction effects and for zinc removal interaction of pH and intial metal concentration are significant factors. Nickel and copper was removed by surfactant modified alumina using Box–Behnken design with three-factor, three-level and a second-order polynomial equation (Khobragade et al., 2016). Similarly, chromium was removed from wastewater using Box-Behnken design for two levels, three variables (pH, metal concentration and temperature) and 29 experiments were performed. ANOVA shows that the models are significant because it gives low probability value and precision value greater than 4.

2.5 Multimetal adsorption

Most of the work is available for single metal system thus researchers has also worked on multimetal adosorption. In a mixed metal system, heavy metals are present together. These heavy metals can affect adsorption process and this is called competitive adsorption. Presence of heavy metals together affects adsorption process antagonistically, synergistically or non-interactive. For example, antagonistic effect of lead was observed during adsorption of nickel, cadmium and lead on mesoporous silica (Heidari et al., 2009). The maximum adsorption capacity in ternary system for nickel, cadmium and lead observed were 12.36, 18.25 and 57.74 mg/g, respectively. Langmuir model was fitted for adsorption of nickel, cadmium and lead. For cadmium and lead pseudo second order kinetics was followed however for nickel pseudo first order kinetics was followed.

In an another study of ternary metal system, Kim et al., 2003 has shown influence of lead, cadmium and chromium on adsorption process using crab shells as an adsorbent. Lead, cadmium and chromium has synergistic effect on adsorption process. Similarly in adsorption of cadmium, nickel and cobalt on iron oxide, nickel has more antagonistic affect than cobalt (Roy & Bhattacharya 2013). The selectivity order of these metals was Cobalt>Nickel>Cadmium and adsorption followed langmuir isotherm and pseudo second-order kinetic model. However, Corami et al., 2007 has removed copper and zinc present in binary system using hydroxyapatite as an adsorbent. Presence of copper and zinc in binary system has reduced the efficiency 13–76% and 10–63% for Cu and Zn respectively because of competitive adsorption of heavy metals. The adsorption capacity obtained for copper was 0.016–0.764 mmol/g and for zinc was 0.015–0.725 mmol/g and Langmuir model was fitted well. Further, removal of cadmium and chromium by Marine Alga Sargassum sp was decreased due to the presence of lead (Sheng et al., 2007). Modified Langmuir model and modified Jain-Snoeyink model both of them fitted well. For copper and lead removal using algal cells (Chlamydomonas reinhardtii) in binary metal system, no competitive adsorption was observed (Flouty et al., 2012). This means copper and lead are adsorbing at different binding sites.

2.6 Simultaneous removal of heavy metals and dyes

Wastewater which comes out from various industries (Textile, electroplating and tannery) contains dyes alongwith heavy metals. Thus there is a necessity to remove heavy metals and dye simultaneously.

Less literature is available for simultaneous removal of heavy metals thus more work is required in this direction. Tovar-Gómez et al., 2012 has removed heavy metals such as nickel, cadmium, zinc and acid blue 25 dye simultaneously using $Ca(PO_3)_2$-modified carbon adsorbent. It was reported that presence of acid blue 25 dye has increased removal of heavy metals in binary mixture of dyes and heavy metals. Simlarly, Aguayo-Villarreal et al., 2013 has removed cadmium, zinc and acid blue 25 simultaneously using activated carbons and it was observed that acid blue 25 has synergistic effect on cadmium and zinc removal and in its presence cadmium and zinc removal has increased 60 times as compared to the results obtained in monometal system. Further, in simultaneous removal of dyes (methyl orange, methylene blue) and heavy metals (copper, cadmium, nickel) using fly ash, dyes were competing with heavy metals.

The removal order was dye > copper > cadmium > nickel and pseudo second order kinetics was fitted well (Visa et al., 2010). However, variuos dyes such as basic violet 3, Acid blue 25, basic blue 9 and heavy metals such as nickel, lead, cadmium and zinc were removed simultaneously using Clinoptilolite (CL) and ER (Erionite). In this system, there is competition between heavy metals and dyes for same adsoption sites and it reduces adsorption capacity of both dye and eavy metals (Hernández-Montoya 2013). Deng et al., 2013 has removed cadmium and dyes (methylene blue and orange G) simultaneously. Methylene blue was affecting cadmium antagonistically but cadmium has no effect on methylene blue dye in Cd(II)–Methylene blue binary system. However, the adosorption capacity of orange G increases with cadmium concentration but cadmium has no effect on orange G dye. Pseudo-second-order kintetics and langmuir model was fitted well. Taştan et al., 2010 has removed dye and heavy metals (copper. nickel) using Aspergillus versicolor. Presence of dye decreases removal of both dye and chromium. However, in presence of copper and dye together, copper has no effect on dye but removal rate of copper is increasing from 29.06% to 37.91%.

2.7 Heavy metal removal in continuous adsorption bed

Various industries such as as textile, electroplating, tannery etc. generates large amount of wastewater containing multiple heavy metals. Therefore, to treat large volume of wastewater, continuous operation is needed. For example, Vijayaraghavan et al, 2006 has removed copper in continuous operation using Sargassum wightii biomass and the highest bed height (25 cm), and highest inlet copper concentration (100 mg/L) and lowest flow rate (5 ml/min) gives highest copper(II) removal of 52.6 mg/g. Copper, lead and zinc was removed by Mohan et al, 2008 in fixed bed column using phosphate treated rice husk and it was reported that the breakthrough time was increasing with bed height. Nickel was removed by Malkoc & Nuhoglu 2006 using tea factory waste and best performance of column was at low flow rate. Sousa et al., 2010 has removed lead, copper, cadmium, zinc and nickel using green coconut shell in fixed bed column and 2 mL/min of flow rate and 10 cm of bed height were found most feasible. However, chitosan immobilized on bentonite was used for copper removal from wastewater (Futalan et al., 2011) and it was found that the breakthrough time decreases with increase in flow rate and intial concentration, and decrease with bed height.

Johnson et al., 2002 has used peanut hull pellets for copper removal from wastewater. Peanut hulls were converted into pellet form for fixed column because pellet should have good physical and structural strength, does not clog in fixed bed column and they should have less head loss in the column. Hoever, Copper, lead, cadmium and zinc were removed using adsorbent in combination of maple leaves, mandarin peel and tea waste and effect of various parameters such as initial metal concentration, bed height and flow rate were observed at pH 5.5. For copper, cadmium, zinc and lead, at flow rate of 10 mL/min, initial concentration of 20 mg/L and bed height of 31 cm, maximum adsorption capacity obtained were 63.37, 8.25, 35.23 and 108.12 mg/g (Abdolali et al., 2017). Sooksawat et al., 2017 has conducted breakthrough study at various parameters such as bed height (3.29, 6.29 cm) and flow rate (20, 30, 40, and 60 mL/min) for lead and cadmium removal using Chara aculeolata biomass in fixed bed column and it was observed that largest breakthrough time was obtained at highest bed height and lowest flow rate.

2.8 Modelling of adsorption

2.8.1 Adsorption isotherm model

In our work, Freundlich, Langmuir, Dubinin–Radushkevich (D–R) and Temkin models were used to analyse the adsorption data (Table 2.1). Langmuir isotherm is based on the assumption that adsorption takes place on specific site of the adsorbent and no further adsorption takes place once adsorbent site has been occupied. However, Freundlich isotherm is for multilayer adsorption and for adsorption on heterogeneous surfaces. In Dubinin–Radushkevich (D–R) isotherm model assumption is not based on homogenous surface, it gives the information of biomass porosity as well as the adsorption energy. Temkin's isotherm shows the effects of the heat of adsorption that decreases linearly with coverage of the adsorbate and adsorbent interactions (Gopalakrishnan et al., 2015).

Various researchers have used these models to analyse equilibrlium data. Freundlich isotherm was fitted well for copper, lead and cadmium removal from wastewater using mesoporous silica with amine and melamine-based dendrimer amine (Shahbazi et al., 2011). Similarly Freundlich isotherm was well fitted for cadmium removal using poly(o-phenylenediamine)/hydrous zirconium oxide composite (Rahman

& Nasir 2018). However Freundlich, Langmuir and Temkin models well fitted for cadmium, lead and arsenic removal from wastewater using magnetite nanoparticles. Kataria & Garg 2018 has removed cadmium and lead from wastewater using ZnO nanoflowers and fitted equilibrium data with four isotherms such as Langmuir, Freundlich. Temkin and Dubinin–Radushkevich (D–R) but among them Freundlich model was well fitted with the adsorption data.

Table 2.32 Isotherm models (Rahman & Nasir 2018; Kataria & Garg 2018)

Isotherms	**Linear equation**
Freundlich	$\log q_e = \log k_f + \frac{1}{n} \log C_e$
Langmuir	$\frac{1}{q_e} = \frac{1}{k_L q_m C_e} + \frac{1}{q_m}$
Dubinin–Radushkevich (D–R)	$\ln q_e = \ln q_m - \beta\varepsilon^2$ $\varepsilon_p = RT_a \ln\left[1 + \frac{1}{C_e}\right], E = \frac{1}{\sqrt{2\beta}}$
Temkin	$q_e = B\ln k_T + B\ln C_e, B = \frac{RT}{b_T}$

2.8.2 Adsorption kinetics model

Adsorption kinetics determines the rate of adsorption. Various researchers have used Pseudo-first order and second order kinetics for experimental data fitting. Pseudo first order kinetics was well fitted for experimental data obtained from copper, lead and cadmium removal using mesoporous silica with amine and melamine-based dendrimer amine (Shahbazi et al., 2011). However, Kataria & Garg 2018 has removed cadmium and lead from wastewater using ZnO nanoflowers and pseudo-first order, pseudo-second order and intraparticle diffusion model were fitted with experimental data and it was observed that pseudo second order model had well fit with experimental data. Similarly Pseudo second order kinetics was well fitted for experimental data obtained from cadmium removal using poly(o-phenylenediamine) /hydrous zirconium oxide composite.

Pseudo-first order is given as follows (Gopalakrishnan et al., 2015)

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \ldots..(2.1)$$

Similarly, Pseudo-second order kinetic rate equation in linear form can be expressed as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{t} q_e \ldots..(2.2)$$

However, this model provides information about the kinetic behaviour of adsorption with chemical sorption as rate controlling step

2.8.3 Adsorption thermodynamics modelling

Adsorption process depends on temperature and this dependency can be explained by several thermodynamic parameters. Thermodynamic study determines whether adsorption process is spontaneous or not. Various researchers have performed adsoprtion thermodynamics modelling for heavy metal removal from wastewater. Cadmium was removed using chitosan as an adsorbent and from thermodynamics parameters it was observed that adsorption of cadmium was spontaneous, feasible and endothermic in nature (Madala et al., 2017). Ogundipe & Babarinde 2017 has removed cadmium, lead and zinc from wastewater using plantain flower and adsorption of each metal was endothermic. Order of spontaneity was Cd(II) > Zn(II) > Pb(II) and positive change in entropy shows disorderness for each metal.

Various thermodynamic parameters such as change in Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are related as follows (Gopalakrishnan et al., 2015).

$$\Delta G = \Delta H - T\Delta S \ldots \ldots.(2.3)$$

Further, the Change in Gibbs free energy can be calculated from the following relation (Wu et al., 2011).

$$\Delta G = -RT \ln K_C \ldots \ldots (2.4)$$

$$K_c = \frac{C_{AC}}{C_e} \ldots..(2.5)$$

ΔH and ΔS were calculated from the slope and intercept of ΔG verses T.

2.9 Modelling of continous adsorption column

In continous column, mathematical models are required to explain kinetic behanviour of adsorption. Babu & Gupta 2010 has developed a mathematical model for fixed bed column for adsorption process with variation in fluid velocity. Internal mass resistances are also included in this model. To solve partial differential equations, finite difference technique was used and a mathematical program was prepared in MATLAB (v.6.1) software to solve coupled equations. However, Gupta & Babu 2009 has removed chromium using saw dust in a fixed bed column and developed a model which includes both internal and external mass transfer resistances and also velocity variation in the column. Explicit Finite Difference technique was used to solve partial differential equations numerically and coupled equations were solved by MATLAB (v.6.1) program.

Maheshwari & Gupta 2015 has removed chromium using neem bark in a fixed bed column and Yoon-Nelson and Yan mathematical models were used to determine dynamic behaviour of continous column. Kinteic parameters were calculated using these models and non-linear regression method was used to fit experimental data in Origin 6.0. Xavier et al., 2018 has removed copper, nickel and cobalt using carboxylated sugarcane bagasse in fixed bed column and two models such as Thomas and Bohart-Adams were used for breakthough curve modelling. Both of the models fits experimental breakthrough curves well with high value of root mean square and R-square and adsorption capacity obtained for these models is also closed to the experimental value. Vijayaraghavan & Prabu 2006 has removed copper in continuous operation using Sargassum wightii biomass in continous operation and used various models Yoon-Nelson, modified dose-response and Thomas model. Breakthrough curves obtained using Thomas and Yoon-Nelson model are satisfactory.

2.10 Future perspective and challenges in removal of heavy metals

As per the above literature survey, the bioadsorbents used for removal of chromium, cadmium and copper are low-cost adsorbents and are beneficial replacements for commercially available adsorbents. In some studies, removal efficiency of adsorbents for heavy metal removal from wastewater has been reported to increase after modification. However, less work has been carried out in this direction. Hence, the study to increase removal efficiency of bioadsorbents after modification (at minimum requirements of acid, bases and heat), regeneration of adsorbents, recovery of metal ions and application of bioadsorbents at commercial level is highly desirable. The challenge in heavy metal removal from wastewater is that it may require large amounts of bioadsorbents and extra chemicals to maintain a pH that provides suitable conditions for adsorption.

2.11 Summary of the literature survey and research gap identified

On the basis of literature survey, following research gaps were identified

1. Literature is available for individual removal of copper, chromium and cadmium from wastewater. Less work has been done on mixed metal removal from wastewater. Wastewater which comes out from various industries mostly contains mixed metals, therefore, there is a requirement to work on removal of mixed metals and to investigate their effects on each other.
2. There are many industries which discharge dyes and heavy metals together. Thus there is a necessity to work on simultaneous removal of heavy metals and dyes.
3. From literature survey it was found that various conventional techniques were used for removal of heavy metals from wastewater. But they have many disadvantages such as high cost and production of significant amount of sludge material (in chemical precipitation) which is to be disposed off. But adsorption process has many advantages such as low cost, minimizes biological and chemical sludge, high efficiency and regeneration of adsorbents. So in our work we have adopted adsorption process for heavy metal removal.
4. Till now different types of adsorbents have been used for removal of heavy metals from wastewater. Use of commercial adsorbents for heavy metal removal is costly. Thus, need of low cost and safe adsorbents necessitated to explore bio-adsorbents. The use of an agricultural waste as an adsorbent with low cost and high removal efficiency may solve this problems. In this regard attempts to identify and develop efficient adsorbent for heavy metal removal is necessity of time.
5. A huge quatity of wastewater containing heavy metals is discharged by various industries. In order to handle this wastewater continuous metal removal operation has to be adopted. Therefore packed bed adsorption column may be used for treating large amount of wastewater.

OBJECTIVES OF PRESENT RESEARCH

Based on the literature survey the following objectives have been formulated.

1. Synthesis and characterisation of an efficient adsorbent for heavy metal removal from wastewater.
2. Batch study for heavy metal removal from synthetic wastewater containing single/multiple metals/metals plus dyes to evaluate adsorption capacity of the synthesized adsorbent and optimum process parameters.
3. Removal of color from metal dyes by oxidation and adsorption study of released metals.
4. Modeling of fixed bed column for heavy metal removal from wastewater and simulation using MATLAB software.
5. Design and fabrication of experimental set up for continuous study of heavy metal removal from synthetic wastewater containing single, mixed metals and both heavy metals and dye.
6. Performance evaluation of developed adsorbent for actual industrial wastewater samples.

CHAPTER - 3

MATERIALS AND METHODS

3.1 Introduction

This chapter explains materials and methods for preparation of different adsorbent with and without modification for removal of copper, chromium and cadmium. This chapter also includes design of experiments. Design of experiments (DOE) is a method to determine the relationship between factors affecting a process and output of the process. The design and fabrication of experimental setup was also explained in this chapter. This experimental setup was fabricated at the Chemical Engineering Department, Malaviya National Institute of Technology (MNIT), Jaipur. Various correlation and model parameters were also discussed. Characterisation techniques for adsorbent was also included. All the characterization was carried out in Material Research Center (MRC), Malaviya National Institute of Technology MNIT Jaipur.

3.2 Materials and Chemicals used

Activated carbon, Alumina balls, Potassium dichromate ($K_2Cr_2O_7$), Cupric sulphate pentahydrate ($CuSO_4.5H_2O$), Sodium hydroxide (NaOH), Bentonite clay and Chitosan (Merck, Germany) were purchased from local market. Egg shell and wheat bran were collected from local bakery shop and flour mill at Jaipur. Hydrochloric acid (HCl, Rankem) of analytical reagent grade was purchased from local market. Chitosan, Bentonite clay and Cadmium chloride monohydrate ($CdCl_2.H_2O$) were purchased from Sigma Aldrich, New Delhi, India.

3.3 Adsorbent preparation

3.3.1 Egg shell powder and calcined egg shell

The egg shells were collected from the bakery shop. Then these egg shells were thoroughly washed with tap water and rinsed several times in DI water (De-ionized water) and membranes were removed. Washed egg shells were dried in an oven for 12 hrs at 70°C. Finally egg shells were crushed into fine powder. Further, Calcined egg shells were prepared by calcinating egg shell at 700°C in muffle furnace (Fig. 3.1). The complete procedure for egg shell modification is shown in Fig. 3.3(a).

3.3.2 Wheat bran and modified wheat bran

Wheat bran has been collected from local flour mill at Jaipur, India. The collected wheat bran was washed with DI water (De-ionized water) to remove soluble impurities. The washed wheat bran was dried in oven at 70°C for 1-2 h. The dried wheat bran was subjected to screening. A 300-micron size fraction was collected after screening for preparation of adsorbent. 50 gram of screened wheat bran fraction was taken in a 250 ml conical flask and treated with 100 mL of concentrated hydrochloric acid for 1 hour. The hydrochloric acid treated adsorbent after 1 hour was washed with DI water and filtered. Finally, the adsorbent (Modified wheat bran) was dried in oven at 100°C for 2 h to remove water and stored for further processing i.e. adsorbent pellet preparation (Fig. 3.2). The complete procedure for modification of wheat bran is shown in Fig. 3.3(b).

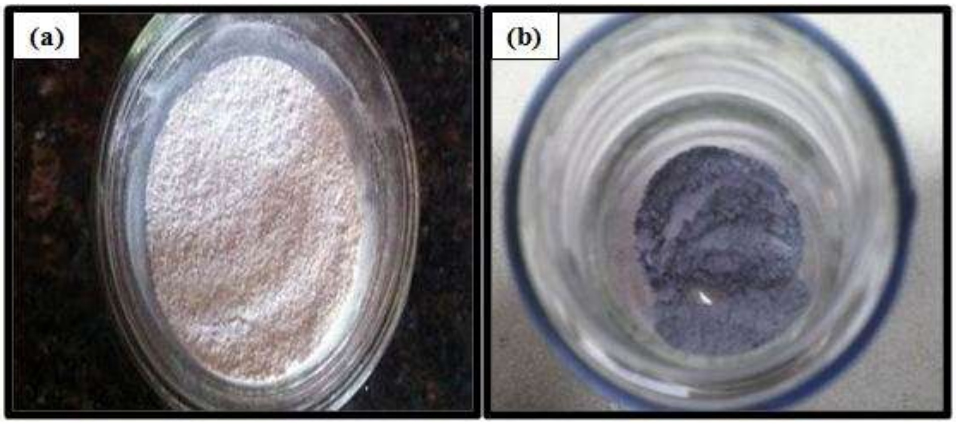


Fig. 3.1 Adsorbent prepared in the laboratory
(a) Egg shell (b) Calcined egg shell

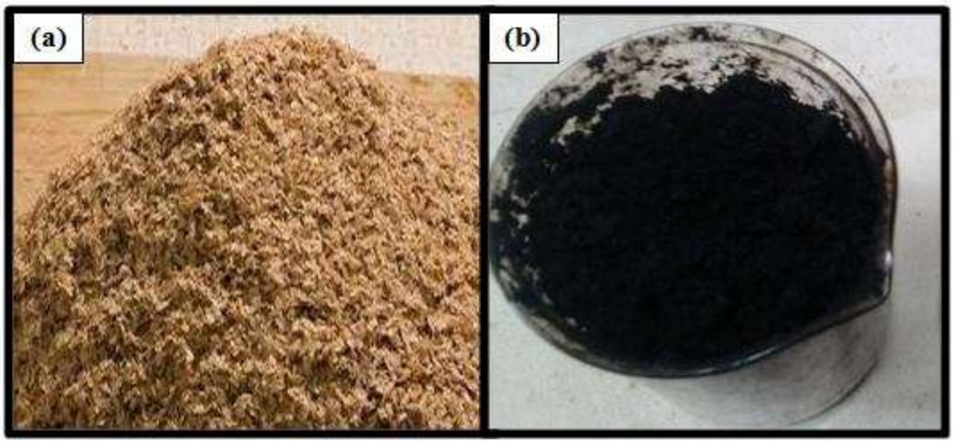
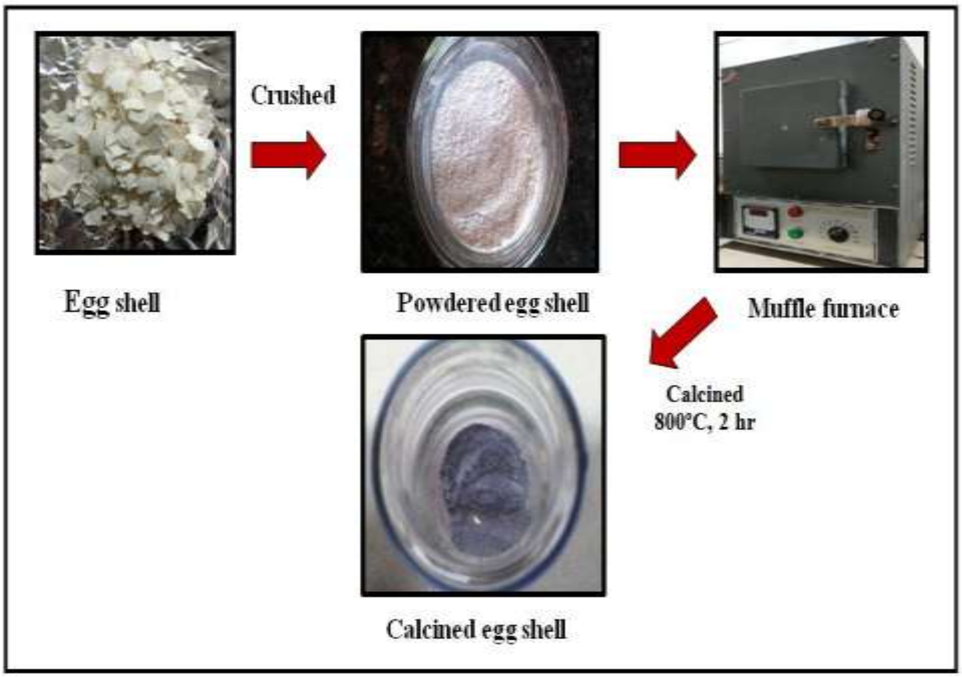


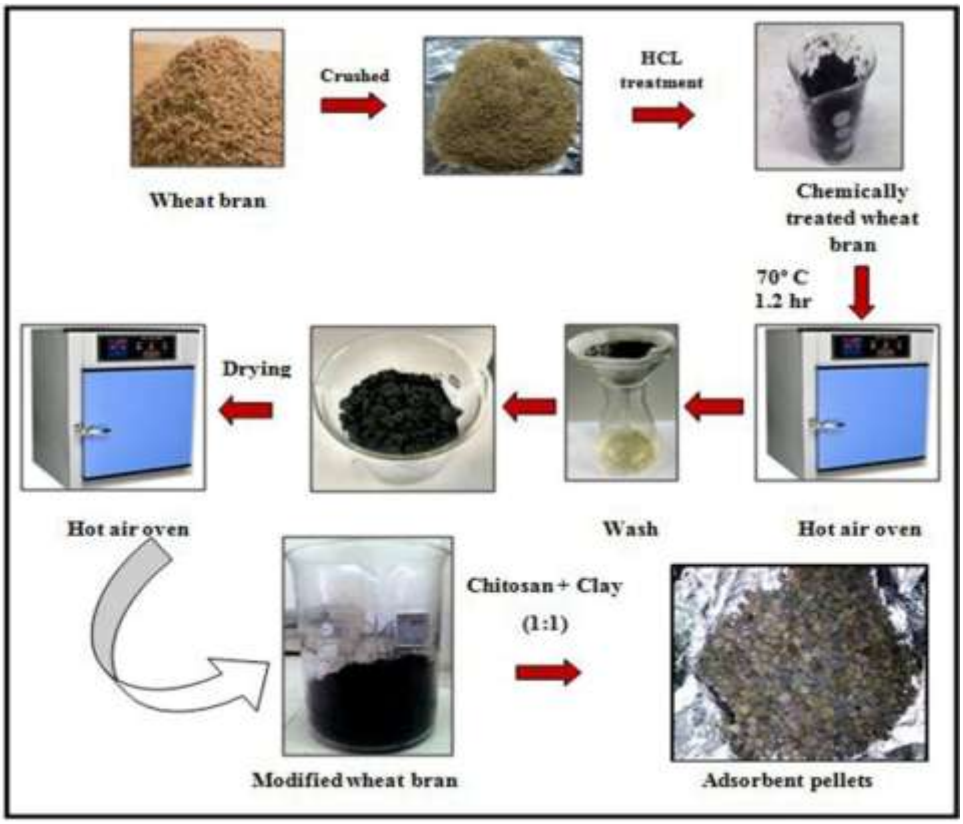
Fig. 3.2 Adsorbent prepared in the laboratory
(a) raw wheat bran (b) Modified wheat bran

3.3.3 Adsorbent pellet preparation

One gram of chitosan was taken in 250 mL beaker and 10 mL of 2 wt% of acetic acid solution was added to it, the mixture was stirred on magnetic stirrer at 300 rpm for 1 hour. The mixture obtained was (1 part) mixed with the synthesised adsorbent (3 part) and bentonite clay (1 part) in the ratio of 1:3:1 by weight. A dough was prepared by proper mixing of all the three ingredients together. Suitable consistency of this dough was maintained for pellet formation. Pellets of diameter 2.5 cm were prepared from this dough by passing it through the press machine (Fig. 3.3(b)). Chitosan and clay was used as a binder in adsorbent pellet formation. Chitosan and clay are highly biodegradable and also nontoxic in nature. Thus the prepared adsorbents are eco-friendly in nature. Chitosan as a binder provides adhesiveness, plasticity and flexibility to the pellet however clay as a binder provides the mechanical strength to the pellet (Carvalho et al., 2006; Ilium, 1998).



(a)



(b)

Fig. 3.3 (a) Egg shell modification by calcination

(b) Wheat bran modification using hydrochloric acid

3.4 Characterisation techniques for prepared adsorbents

Developed adsorbents were analysed for their physical, chemical properties using different characterisation techniques. The methodology for characterization and analysis are discussed as follows,

3.4.1 Scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDS):

Scanning electron microscopy (SEM) images and Energy dispersive spectroscopy of prepared adsorbent was recorded by SEM-EDS system (Nova Nano 450) at MNIT, JAIPUR (Fig. 3.4). Scanning electron microscope was used for adsorbent surface analysis and Energy dispersive spectroscopy (EDS) was used for surface elemental analysis of prepared adsorbent.

In scanning electron microscope a high energy electron beam is passed across the adsorbent surface. Usually, this sample is coated with gold or platinum to improve contrast and signal to noise ratio. As the beam passes through the adsorbent surface, interaction between electron beam and adsorbent surface takes place and it resulted in various electron signals. These electronic signals are collected, processed, and converted into pixels form, on a monitor. This forms an image of the adsorbent surface. Energy dispersive spectroscopy (EDS), is a technique for the elemental analysis.

3.4.1.1 Principle of SEM and EDS:

Accelerated electrons in SEM carry kinetic energy and this energy is released in the form of signal when interaction between electron and sample takes place during deceleration of electron inside the sample. These electrons have secondary electrons, backscattered electrons and diffracted backscattered electrons. Secondary and backscattered electrons are helpful in imaging samples, secondary electrons are important for showing morphology and topography on sample. Backscattered electrons are helpful in showing contrast in composition of sample. X-ray is generated when collisions of incident electrons with electrons in shells of atoms in the sample takes place. In SEM analysis generated X-rays do not lead to volume loss of sample thus same material can be analysed repeatedly. In EDS analysis sample is bombarded with a beam of electrons and it emits X-ray spectrum for elemental analysis.

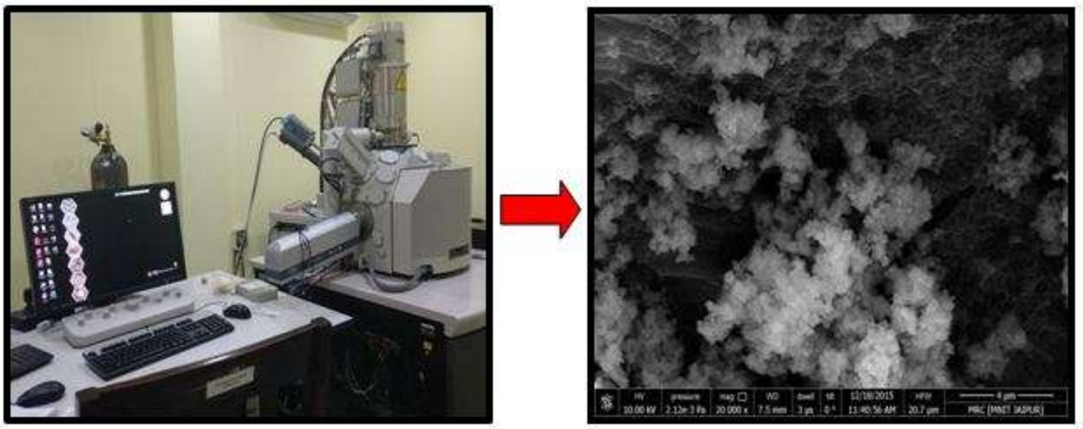


Fig. 3.4: NOVA NANSEM -450 for surface morphology analysis

3.4.2 Fourier Transform Infra-Red (FTIR) spectroscopy:

Fourier Transform Infra-Red (FTIR) spectrophotometer (Perkin Elmer, Model- FT-IR spectrum 2) was used for identification of functional groups present in prepared adsorbent at MNIT, Jaipur. Fourier Transform Infra-Red (FTIR) spectroscopy was recorded by FTIR spectroscope (PerkinElmer) as shown in Fig. 3.5. Fourier-transform infrared spectroscopy technique is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. In FTIR, analysis, infrared radiation is passed through the adsorbent, a portion of radiation is absorbed by the adsorbent and other portion passes through the adsorbent (is transmitted). A spectrum is obtained on detector which represents molecular structure of the adsorbent.

3.4.2.1 Principle of FTIR

In FTIR technique, there is an interaction between infrared radiation and sample. FTIR gives information about vibration and rotation of chemical bonding and molecular structure. FTIR analysis is the fingerprint of sample with absorption peaks showing frequency of vibration between bonds of the atom. The size of FTIR peak shows the amount of material present. The infrared region is commonly divided into three smaller areas: near – Infrared region (400 - 10 cm^{-1}), mid – Infrared region (4000 - 400 cm^{-1}), and far infrared region (14000 – 4000 cm^{-1}).

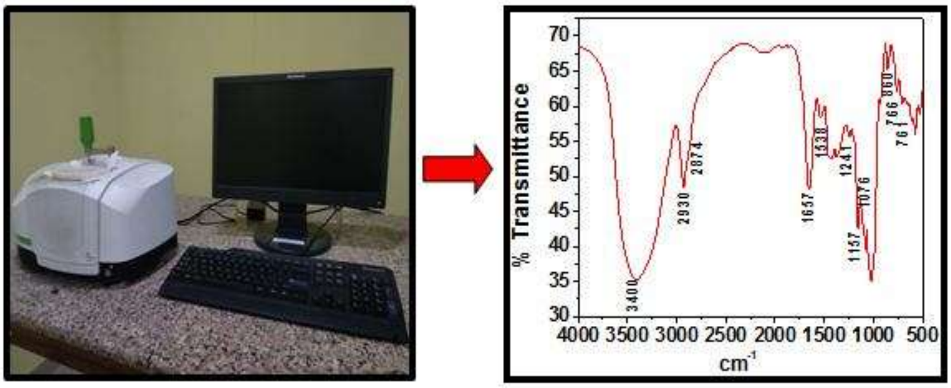


Fig. 3.5 Perkin Elmer, Model- FT-IR spectrum 2 for FTIR analysis

3.4.3 X-ray diffractometer

X-ray diffractometer (Pananalytical, Model- Xpert pro) was used to determine crystallinity of prepared adsorbent at MNIT, Jaipur. X-ray diffraction is used mainly to identify crystalline material, distinguish between crystalline and amorphous material and to quantify the percent of crystallinity in a sample. X-ray diffraction was recorded by X-ray diffractometer (Pananalytical, Model- Xpert pro) as shown in Fig. 3.6. X-ray diffractometer is used to study the structural properties of crystalline and amorphous materials. X-ray diffractometers has three basic elements- an X-ray tube, a sample holder, and an X-ray detector. XRD analysis is used in pharmaceutical Industry, forensic Science, microelectronics Industry and glass Industry. XRD have strengths and limitations. XRD is a powerful and rapid technique for identification of any material, requires less sample preparation and it also provides straightforward data. However, the limitations are that homogeneous material is best for identification, detection limit is nearly 2% for mixed material and peak overlay problem may occur.

3.4.3.1 Principle of X-ray diffractometer

First of all, X-rays are generated in a cathode ray tube by heating filament to produce electrons. After application of voltage, electrons are accelerated towards the adsorbent and bombarded the adsorbent with electrons. When electrons gain sufficient energy to dislodge inner shell electrons of adsorbent (sample), X-ray spectra is produced.

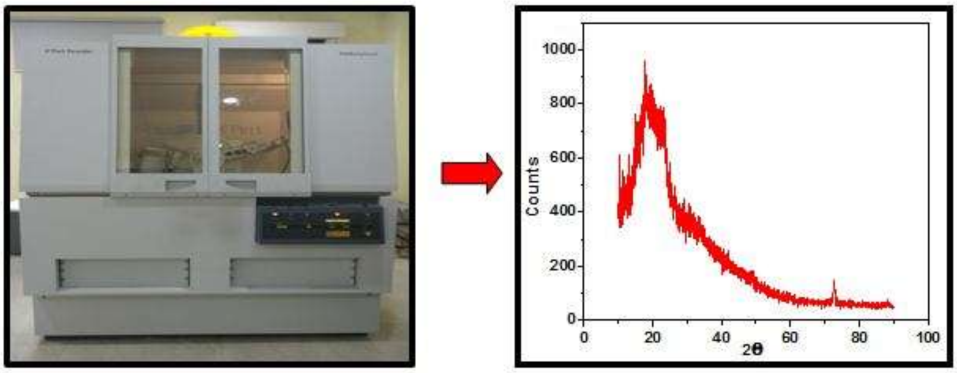


Fig. 3.6 X-ray diffractometer (Pananalytical, Model- Xpert pro)

3.4.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectrometer (model Physical Electronics 5700) was used to measure the elemental composition (in parts per thousand ranges) of prepared adsorbent at MNIT, Jaipur. The XPS (X-ray photoelectron spectroscopy) measurements were carried out with a spectrometer (model Physical Electronics 5700), using an Mg-Ka source (300 W, 15 kV and 1253.6 eV) with a multi-channel detector as shown in Fig. 3.7. XPS is used in analysis of nanoparticles, catalysis and corrosion studies and also in characterisation of paints, polymer, glass and ceramic. XPS has limitation for curved surfaces and surface with dimensions of the order of nanometres cause in handling and in quantification.

3.4.4.1 Principle of XPS:

In XPS, sample is irradiated with X-rays and it emits electrons from atoms. Photoelectron energies determine specific atom which is present in < 10 nanometres depth. The measured photoelectron kinetic energies are diagnostic of the specific atoms which constitute the sampled depth (< 10 nanometres), since each atom in the periodic table is characterised by a unique set of electron energy levels.

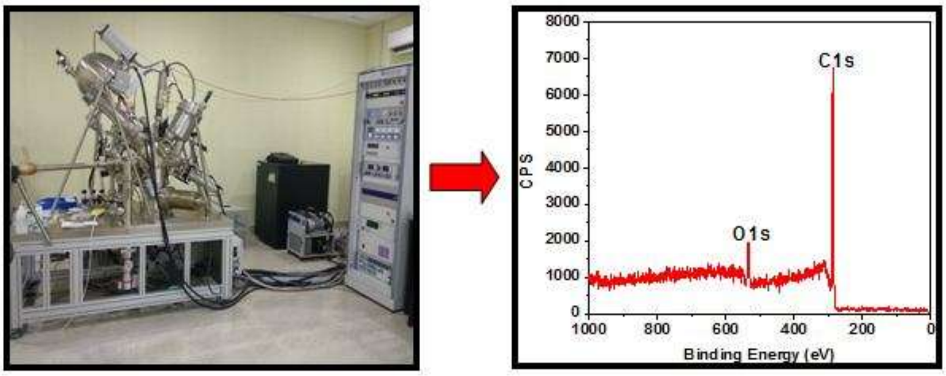


Fig. 3.7: X-ray photoelectron spectrometer (Model Physical Electronics 5700)

3.4.5 Brunauer-Emmett-Teller (BET) Surface Area Analyser

BET surface area analyser (NOVA touch LX1) was used for evaluation of specific surface area of prepared adsorbent at MNIT, Jaipur. Surface area is determined by nitrogen multilayer adsorption as a function of relative pressure using a fully automated analyzer. The technique includes external area and pore area calculation to determine the total specific surface area in m^2/g. BET surface area analyser has its application in ceramics, dye, paint, pigment, textile, pharmaceuticals, toothpaste manufacture and cosmetic industries. For BET analysis of adsorbent the adsorbent was dried with nitrogen purging or in a vacuum applying elevated temperatures. The value of P/P0 is used as a standard measurement points. The volume of gas adsorbed on the surface of the particles is measured at the boiling point of nitrogen (-196°C). The amount of adsorbed gas is correlated with the total surface area of the particles alongwith the pores in the surface (Fig. 3.8).

3.4.5.1 Principle of BET surface area analyser

BET surface area analyser works on the concept of extended Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption. This theory has following hypothesis such as gas molecules physically adsorb on a solid in layers and gas molecules only interact with adjacent layers. The specific surface area of any material is determined by physical adsorption of a gas on the surface of the material. Then the amount of adsorbate gas was calculated corresponding to a monomolecular layer on the surface. Surface area analysis is carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

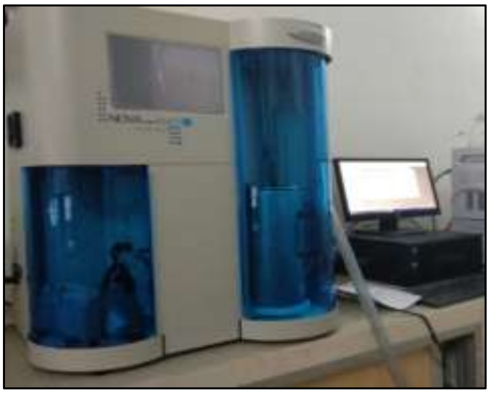


Fig. 3.8: BET surface area analyser (NOVA touch LX1)

3.4.6 Zeta potential analyser

Zeta potential analyser was used to determine the point of zero charge of prepared adsorbent at MNIT, Jaipur. The value of zeta potential determines dispersion stability. Higher value of zeta potential shows that there is good dispersion stability. Point of zero charge is calculated by determining the zeta potential at different pH value. Point of zero charge is that value of pH at which electrical charge density on a surface is zero. (Fig. 3.9)

3.4.6.1 Principle of zeta potential analyser

When nanoparticles are in a suspension they have surface charge. These particles start moving on application of electric field. Velocity of particle is measured by observation of Doppler shift in scattered light. Hence, motion of the particle under electric field helps in determining zeta potential. The value of these zeta potentials at different pH values give an idea of point of zero charge.

Fig. 3.9: Laboratory zeta potential analyser (Delsa TM nano)

3.5 Preparation of stock solution

The stock solution containing 1000 mg/L of chromium (VI), copper, and cadmium was prepared by dissolving 2.835 g of potassium dichromate, 3.9294 g of cupric sulphate pentahydrate, and 1.791 g of cadmium chloride monohydrate in 1000 mL of DI double-distilled water. The absorbance was measured using atomic absorption spectrophotometer.

3.6 Calculation of percent removal and adsorption capacity

The percent removal of each metal ion was calculated using the following equation.

$$\%\mathrm{R} = \frac{\mathrm{C_0} - \mathrm{C_t}}{\mathrm{C_0}} \times 100 \ldots\ldots (3.1)$$

Where R is the heavy metal removal efficiency, C_0 is the metal ion concentration in solution before reaching equilibrium (mg/L), and C_t is the metal ion concentration in solution after reaching equilibrium (mg/L). The amount of heavy metal adsorbed on adsorbent at equilibrium is called adsorption capacity and calculated using following equation.

$$\%\mathrm{q_e} = \frac{(\mathrm{C_o} - \mathrm{C_e})\mathrm{V}}{\mathrm{W}} \ldots\ldots (3.2)$$

Where, q_e, C_o and C_e are the adsorption capacity (mg/g), initial and equilibrium heavy metal concentration (mg/L), respectively, V is the volume of solution (L), and W is the weight of adsorbent (g).

3.7 Adsorption experiments

3.7.1 Individual metal study

The adsorption of copper, cadmium, and chromium on modified wheat bran was performed by batch techniques. In individual metal study, a known gram of adsorbent was added in 150 mL solution having copper, cadmium, and chromium of known concentration separately, and then flasks were shaken in an incubator at 180 rpm. Further, adsorbent was filtered from the solution and absorbance was measured using atomic absorption spectrophotometer by flame method. The effects of parameters such as initial concentration, pH, temperature, and adsorbent dose on the adsorption were investigated.

3.7.2 Mixed metal study

In mixed metal study, copper, chromium and cadmium containing equal volume of each solution in 250 mL flask was prepared and concentration was ranged between 15 mg/L to 100 mg/L for each metal. The multicomponent solution was prepared using salts such as cupric sulphate pentahydrate, potassium dichromate and cadmium chloride monohydrate. The adsorbent dose was varied from 0.5 gram to 5 gram and then flasks were shaked at 180 rpm at 35°C in incubator for 4 hours. The pH of the solution was maintained at 6 using hydrochloric acid (1M) and sodium hydroxide (1M) as required. Further adsorbent was separated from the solution and absorbance was measured using atomic absorption spectrophotometer. The effect of several parameters such as adsorbent dose, initial concentration of copper, initial concentration of chromium and initial concentration of cadmium were investigated using Box-Behnken design.

3.7.3 Simultaneous metal and dye removal study

In simultaneous metal study, copper, chromium, cadmium and acid black 60 dye containing equal volume of each solution in 250 mL flask was prepared. The concentration was ranged between 15 mg/L to 100 mg/L for each metal and 15 mg/L to 200 mg/L for acid black 60 dye. The multicomponent solution was prepared using salt of cupric sulphate pentahydrate, potassium dichromate and cadmium chloride monohydrate. The adsorbent dose was varied from 0.5 gram to 5 gram and then flasks were shaked at 180 rpm at 35°C in incubator for 4 hours. The pH of the solution was ranged between 2 to 10. Further adsorbent was separated from the solution and absorbance was measured using atomic absorption spectrophotometer. The effect of several parameters such as pH, temperature, adsorbent dose, initial concentration of copper, initial concentration of chromium and initial concentration of cadmium were investigated using Box-Behnken design.

3.8 Analysis of metals and dyes

3.8.1 Atomic absorption spectrophotometer

Atomic Absorption Spectrometry (AAS) was used to measure the amount of heavy metals such as copper, chromium and cadmium present in sample at MNIT, Jaipur. For all the three heavy metals acetylene flame was used in Atomic absorption spectrophotometer.

The atoms present in sample absorb ultraviolet or visible light to make transitions to higher energy levels. Atomic absorption spectrometry measures the energy in the form of photons of light absorbed by the sample. Selectivity is very important for AAS because every element has different energy level and it give rise to narrow absorption lines. Hence selection of monochromator is important to obtain a linear calibration curve. The bandwidth of element should be broader than the light source, it is not possible with ordinary monochromator. Absorbance was measured by atomic absorption spectrophotometer (AA500) as shown in Fig. 3.10. The Atomic Absorption Spectrophotometer consists of five components. Light source, burner assembly, optics, detector and signal processing. Each component is designed to minimize disturbance in the overall system and many design features are installed to minimize signal to noise ratio as low as possible.

3.8.1.1 Principle of Atomic absorption spectrophotometer

In atomic absorption spectroscopy a beam of electromagnetic radiation is passed through the sample, then the radiation is either absorbed or transmitted depending upon the wavelength of the radiation. The absorption of radiation will increase energy of the molecule. The energy gained by the molecule is directly proportional to the wavelength of radiation. The increase in the energy of the molecule leads to the electronic excitations and due to this, electrons jump to the higher energy levels. Hollow cathode lamp radiates the characteristic spectrum of the target element. The content of the measured element is calculated by measuring absorbance of spectrum.

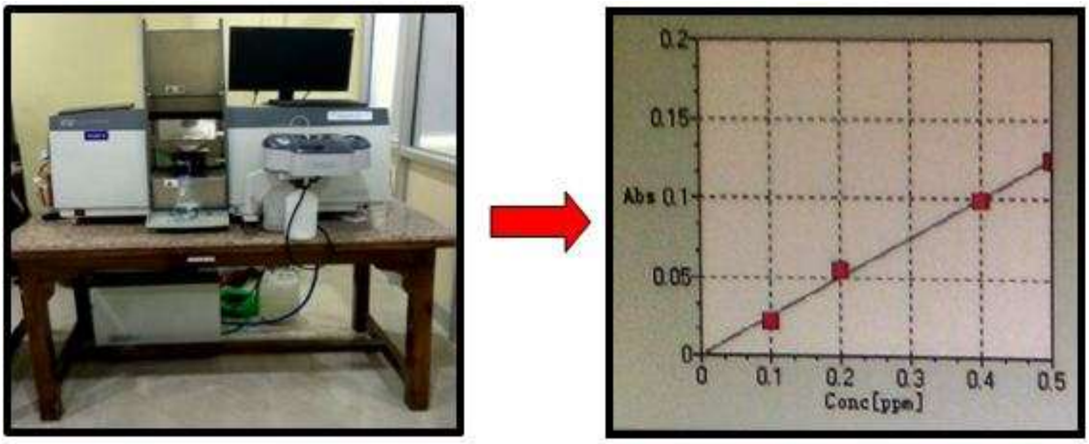


Fig. 3.10 Atomic absorption spectrophotometer model AA500

3.8.2 Ultra visible spectrophotometer

Ultra visible spectrophotometer (UV-1800 Shimadzu) was used for determining the dye intensity in samples at MNIT, Jaipur. In ultra visible spectroscopy, a substance absorbs the light and it increases energy of atoms present inside of that substance. This light may be visible light or ultravisible light. It produces a spectrum (Fig. 3.11).

3.8.2.1 Principle of ultravisible spectrophotometer

Ultravisible spectroscopy works on Beer-Lambert law. According to Beer-Lambert's law, when a monochromatic light passes through a solution containing any absorbing material. There is decrement in the radiation intensity and this is proportional to the radiation and solution concentration. The formula for Beer-Lambert's law can be written as follows,

Absorbance = log (intensity of incident light / intensity of light leaving from cell) = molar absorptivity * solute molar concentration * length of light travel

Fig. 3.11 Laboratory Ultra visible spectrophotometer (UV-1800 Shimadzu)

3.9 Factors affecting adsorption of heavy metals

There are many factors which affect heavy metal removal efficiency of adsorbents from wastewater. These factors are initial concentration, adsorbent dose, pH, temperature, contact time and stirring speed (Sahu et al., 2009). To optimize these parameters, batch adsorption experiments were carried out using design expert software.

3.10 Design of experiments

In our work, for optimization of operating conditions and removal efficiency, design of experiments was used and four parameters were included such as initial concentration, pH, temperature and adsorbent dose. 3-level, 4-factor Box Behnken design (BBD) was used to determine effect of these parameters on removal percent of copper, cadmium, chromium and dye (acid black 60). The use of Box Behnken design (BBD) has advantage that it allows few combinations of variables to determine complex response function (Muthukumar et. al., 2003). In our work, total 29 experiments were carried out for each metal ion in individual study and in mixed metal study. However, 62 experiments were carried out for simultaneous removal of heavy metal and acid black 60 dye. When effect of a parameter is positive, there is increment in the response with change in factor from low to high values. If the effects are negative, there is reduction in response for high level of the same factor (Cojocaru & Zakrzewska-Trznadel 2007). A set of experiments were performed and response variable was fitted using second order model in the form of a quadratic equation given below.

$$R = a_o + \sum a_i X + \sum a_{ii} X_{ii}^2 + \sum a_{ij} X_i \ldots\ldots (3.3)$$

The quality of fitness of experimental data in model is determined using R^2 values. R^2 values tell that how well a model fits to the data points. The range of R^2 value is from 0 to 1 and 1 indicates the ideal value. R is predicted response (Removal efficiency of heavy metal) where X_i = 1, 2, 3 are independent factors. While a_o, a_i (i=1,2,3), a_{ii} (i=1,2,3), a_{ij} (i=1,2,3; j=1,2,3) are model coefficients.

3.11 Adsorbent regeneration and reusability study

In batch study, the saturated adsorbent containing copper, cadmium and chromium separately was regenerated using 2N HCl for copper and cadmium, however 2N NaOH was used for chromium in 250 mL flask. Then flask was kept on stirring at 250 rpm for 1 h and then adsorbent was washed thoroughly by De-ionized water. Further, the regenerated adsorbent was used till five cycles to evaluate adsorbent efficiency.

3.12 Continuous fixed bed column

3.12.1 Design and fabrication of experimental setup

The experimental set up for continuous study is shown is Fig. 3.12. The column study was performed in a glass column of 63 cm height and 2.5 cm internal diameter and connected with a peristaltic pump to control flow rate. The column was filled with the adsorbent pellets and a fine sieve was placed at the bottom for support of the adsorbent. The heavy metal solution was fed at the bottom of the glass column to increase the contact time through a peristaltic pump. The effluent samples were collected at specified time interval until the outlet concentration reaches to 95% of the feed concentration. In this work, column experiments were performed for each metal ion i.e. copper, cadmium and chromium individually.

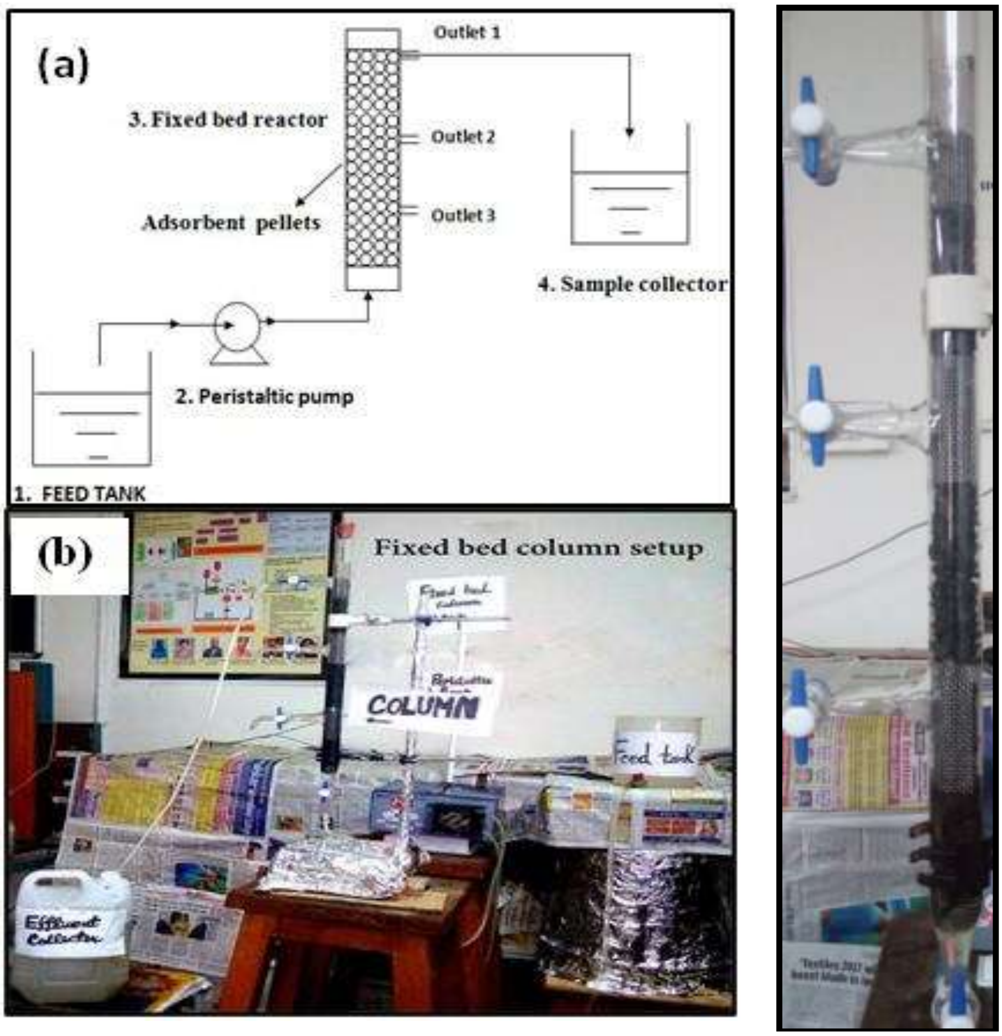


Fig. 3.12: Experimental setup (a) Schematic diagram (b) in laboratory, for continuous operation

3.12.2 Mathematical modelling

A dynamic adsorption model was developed to determine the breakthrough curves at different conditions. The developed model includes mass transfer resistance and dispersion phenomena. To formulate the mathematical model, following assumptions were taken into consideration:

1. The system is operating in isothermal conditions.
2. The adsorption process was characterized by Langmuir isotherm.
3. Mass transfer across the boundary layer was included by using the external-film mass transfer coefficient.
4. The adsorbent particles were homogeneous in size and density.
5. The flow pattern in the bed can be described by an axial dispersion plug flow model.

By using law of conservation of mass for heavy metals in the liquid phase, following equation is obtained.

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} - D_L\frac{\partial^2 C}{\partial Z^2} + \left(\frac{\rho_b}{\varepsilon}\right)\frac{\partial q}{\partial t} = 0 \qquad ..... (3.4)$$

The uptake model is assumed to be governed by mass transfer resistance,

$$\frac{\partial q}{\partial t} = k_c\,(C - C_e) \qquad ..... (3.5)$$

From Langmuir isotherm,

$$q = \frac{K_L q_m C_e}{1+K_L C_e} \qquad .....(3.6)$$

or,

$$C_e = \frac{q}{K_L\,(q_m - q)}$$

The above equation can be written as $C_e = f(q)$

Therefore, eq (3.4) becomes,

$$\frac{\partial q}{\partial t} = k_c\,(C - f(q))$$

Following are the conditions,

Initial condition:

$$\text{at } t = 0, C = 0\ [0 \le z \le L] \ldots\ldots (3.7)$$

Boundary condition:

$$\text{At outlet: } \frac{\partial C}{\partial z} = 0, z = L \ldots\ldots (3.8)$$

$$\text{At inlet: } (uC)_{z=0^-} = \left(uC - D_L \frac{\partial C}{\partial z}\right)_{z=0^+}, \quad z = 0 \ \ldots\ldots (3.9)$$

Eq. (3.8) and (3.9) are Danckwert's boundary conditions. The model Eq. (3.5) and the adsorption isotherm Eq. (3.5) form a coupled system of differential equations. In this study, this set of differential equation was solved by finite difference technique using MATLAB software after discretizing the equations.

3.12.3 Breakthrough curve analysis

The shape of the breakthrough curve and the breakthrough time are the main factors to determine the dynamics of fixed bed column. The breakthrough curves provide the information about the breakthrough time and saturation time. The breakthrough time is the time when C/C_0 value reaches to 0.05 where C is adsorbate concentration in outlet stream and C_0 is adsorbate concentration in feed stream. Similarly the saturation time is when C/C_0 value reaches to 1 or the time when no more adsorption occur.

3.12.4 Calculation of parameters

Model parameters were calculated using following correlation:

3.12.4.1 Calculation of Bed porosity (ε): Bed porosity is that fraction of total volume which is void. It is defined as,

$$\text{porosity } (\varepsilon) = \frac{\text{Void volume}}{\text{Total volume}} \qquad \ldots\ldots (3.10)$$

Bed porosity depends on the particle size, shape and how they are packed.

3.12.4.2 Calculation of bed density (ρ_b): Bed density is calculated by dividing the mass of adsorbent filled in the entire column to the volume of the column.

$$\text{Bed density } (\rho_b) = \frac{\text{mass of adsorbent}}{\text{volume of column}} \qquad \ldots\ldots (3.11)$$

3.12.4.3 Calculation of particle density (ρ_p): Particle density is calculated by dividing the weight of individual particle to per unit volume.

$$\text{Particle density}\left(\rho_b\right)=\frac{\text{Weight of individual particle}}{\text{volume of particle}} \qquad \ldots.(3.12)$$

3.12.4.4 Calculation of axial dispersion coefficient (D_m): Axial dispersion coefficient was calculated using the following correlation:

$$D_b=0.7D_m+\frac{2R_P v\varepsilon_b}{0.18+0.008\,R_e^{0.59}} \qquad \ldots.(3.13)$$

For $M_B < 1000$, molecular diffusion can be calculated using Wilke-Chang correlation as follows:

$$D_m=1.173\ \times 10^{-16}(\Psi M_B)^{1/2}\frac{T}{\mu_B v_A^{0.6}} \qquad \ldots.(3.14)$$

3.12.4.5 Calculation of external mass transfer coefficient: External mass transfer coefficient is calculated using the following correlation (Green & Perry 2007).

$$Sh=\frac{1.09}{\varepsilon}R_e^{0.33}Sc^{0.33}\text{ for }0.0015<R_e<55 \qquad \ldots..(3.15)$$

Where,

$$R_e=\frac{vd_p}{v}$$

$$Sc=\frac{v}{D}$$

$$Sh=\frac{k_f D_b}{D_m}$$

3.13 Comparison of model and experimental results

Model and experimental results were compared using R^2, Chi- square and MAPE value.

3.13.1 R^2 value: – Closeness between model and experimental value was measured by R^2 value.

$$R^2=1-\frac{\text{Regression sum of square}}{\text{Total sum of square}} \qquad \ldots\ldots(3.16)$$

3.13.2 Chi- square value – Chi- square value was measured by using following formula.

$$\chi^2 = \sum \frac{(\text{Model value} - \text{Experimental value})^2}{\text{Experimental value}} \qquad \ldots.(3.17)$$

3.13.3 MAPE value (The mean absolute percentage error) – MAPE value was calculated using following formula.

$$\text{MAPE} = \frac{100}{\text{N}} \times \sum_{\text{i}=1}^{\text{N}} \left| \frac{\text{Model value} - \text{Experimental value}}{\text{Model value}} \right| \qquad \ldots.(3.18)$$

3.14 Industrial wastewater treatment

3.14.1 Collection of wastewater samples:

In our work, without treated wastewater samples were collected from textile, dye, tannery and electroplating industry for heavy metal removal in continuous process. Textile and dye industry wastewater samples were collected from Bhilwara Industrial Area, Rajasthan and Saganer, Jaipur, Rajasthan respectively. Further, Tannery industry wastewater sample was collected from industrial area of Kanpur, Uttar Pradesh. Electroplating industry wastewater sample was collected from Vishwakarma Industrial Area of Jaipur, Rajasthan (Fig. 3.13).

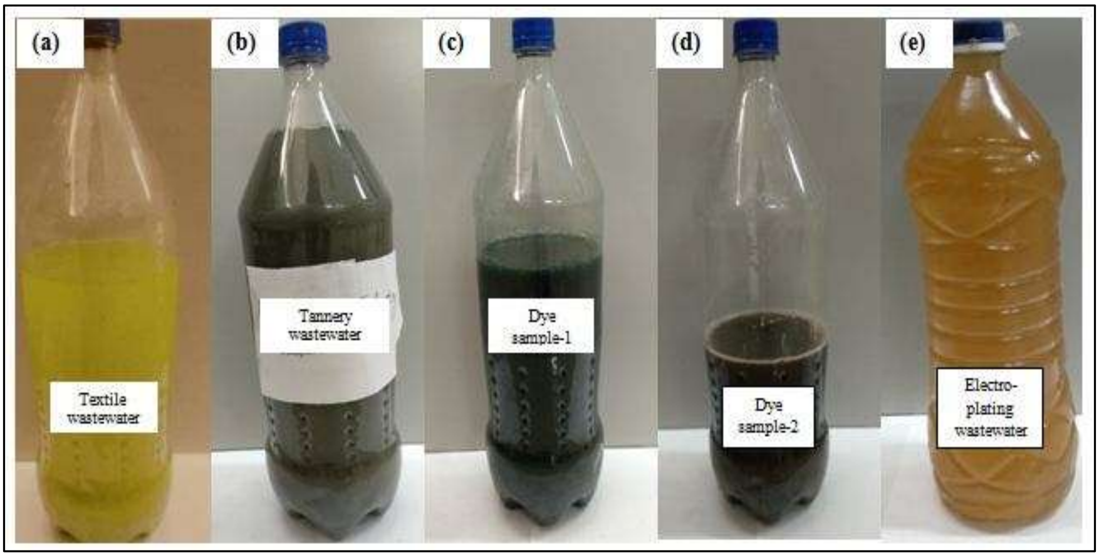


Fig. 3.13 Wastewater samples collected from (a) Textile industry (b) Tannery industry (c) Dye industry (sample-1) (d) Dye industry (sample-2) (e) Electroplating industry

3.14.2 TOC and TDS analysis of industrial effluents

3.14.2.1 Total organic carbon analyser (TOC)

Total organic carbon analyser (Sievers InnovOx) was used to determine the amount of organic carbon present in industrial effluents at MNIT, Jaipur (Fig. 3.14).

Principle of total organic carbon analyser

Total organic carbon analyser measures total organic carbon on the basis of differential conductivity. First of all, the sample water enters the analyzer and then passes through a pressure regulator to control sample pressure. Further, sample is divided into two flow paths. One flow path measures resistivity/conductivity and temperature. The remaining of the sample is directed through a second conductivity sensor to measure the sample conductivity before oxidation. This conductivity measurement is for background ions and inorganic carbon (CO_2) in the water stream. After that sample enters into oxidation chamber. In the oxidation chamber sample is subjected to the high intensity ultraviolet radiation. After oxidation, the sample is passed through a third conductivity sensor to measure the conductivity and temperature again to determine the level of Total Organic Carbon (TOC).

Fig. 3.14: Laboratory TOC analyser (Sievers InnovOx)

3.14.2.2 Total dissolved solids analyser (TDS)

Total dissolved solids analyser (HANNA, HI 5522) was used to analyse concentration of dissolved solids in industrial effluents. TDS analyser measures the TDS value in mg/L. Dissolved solids such as salt and minerals increases electrical conductivity of water. Higher TDS value causes undesirable taste in water. Similarly for aquatic life, constant level of TDS is required otherwise it harms aquatic life (Fig. 3.15).

Principle of total dissolved solids analyser

TDS analyser works on the basis of electrical conductivity of water. Pure water has zero conductivity. Dissolved ionized solids such as salt and minerals increases electrical conductivity of solution. TDS is calculated by converting electrical conductivity into TDS by a factor of 0.5 to 1.0 times. Higher the value of electrical conductivity, higher the conversion factor to determine TDS.

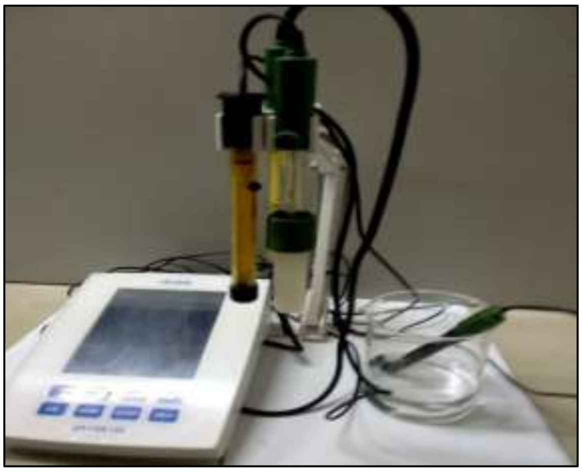


Fig. 3.15 Laboratory TDS analyser (HANNA, HI 5522)

CHAPTER - 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, an adsorbent was selected based on removal efficiency for copper, chromium, cadmium and then characterisation analysis of the developed adsorbent was discussed in detail. The study was done for individual metal ions, mixed metal ions and for simultaneous removal of metal ions and dye using hydrochloric acid-treated wheat bran as an adsorbent in batch and continuous mode was performed. In batch study, Box–Behnken design of response surface methodology was used to determine the effect of initial metal concentration, pH, temperature, and adsorbent dose on removal efficiency of copper, cadmium, and chromium. However, adsorption isotherms and rate kinetics were also investigated. Adsorption regeneration study was also carried out in batch mode for five cycles because disposal of saturated adsorbent is harmful for environment. Further, in continuous study, a model was developed using MATLAB software. Column experiments were performed for various parameters and then experimental data were validated with the model data. Also, industrial wastewater was collected from textile, dye, tannery and electroplating industries. Their physico-chemical characterisation was done and continuous experiments were performed.

4.2 Characterisation of adsorbents

4.2.1 SEM analysis coupled with EDS

Fig 4.1(a) and 4.2(b) shows SEM analysis of the activated carbon. SEM analysis is performed on electron microscope to determine the surface morphology of the adsorbent. It shows that the surface of activated carbon has irregular and porous surface, it indicates high surface area of the adsorbent, which makes this as highly efficient adsorbent. Fig. 4.1(c, e) and 4.1(d, f) show the SEM analysis of egg shell and calcined egg shell, respectively. From Fig. 4.1(c, e), it was observed that eggshell granules possess a homogenous and porous surface. But after calcination at 700°C, pore structure has been developed. Thus the removal efficiency of egg shell powder has been increased after calcination. Fig. 4.2(a—c) shows EDS analysis of activated carbon, egg shell and calcined egg shell respectively. Fig. 4.2(a) shows 85.89% carbon and 14.11% oxygen is present in activated carbon. However, egg shell shows 31.07% carbon, 45.14% oxygen and 23.79% calcium. But after calcination of egg shell, carbon and oxygen decreased to 28.37%, 43.03% respectively, however calcium increased to 28.60% due to formation of CaO and loss of CO_2 (Table 4.1).

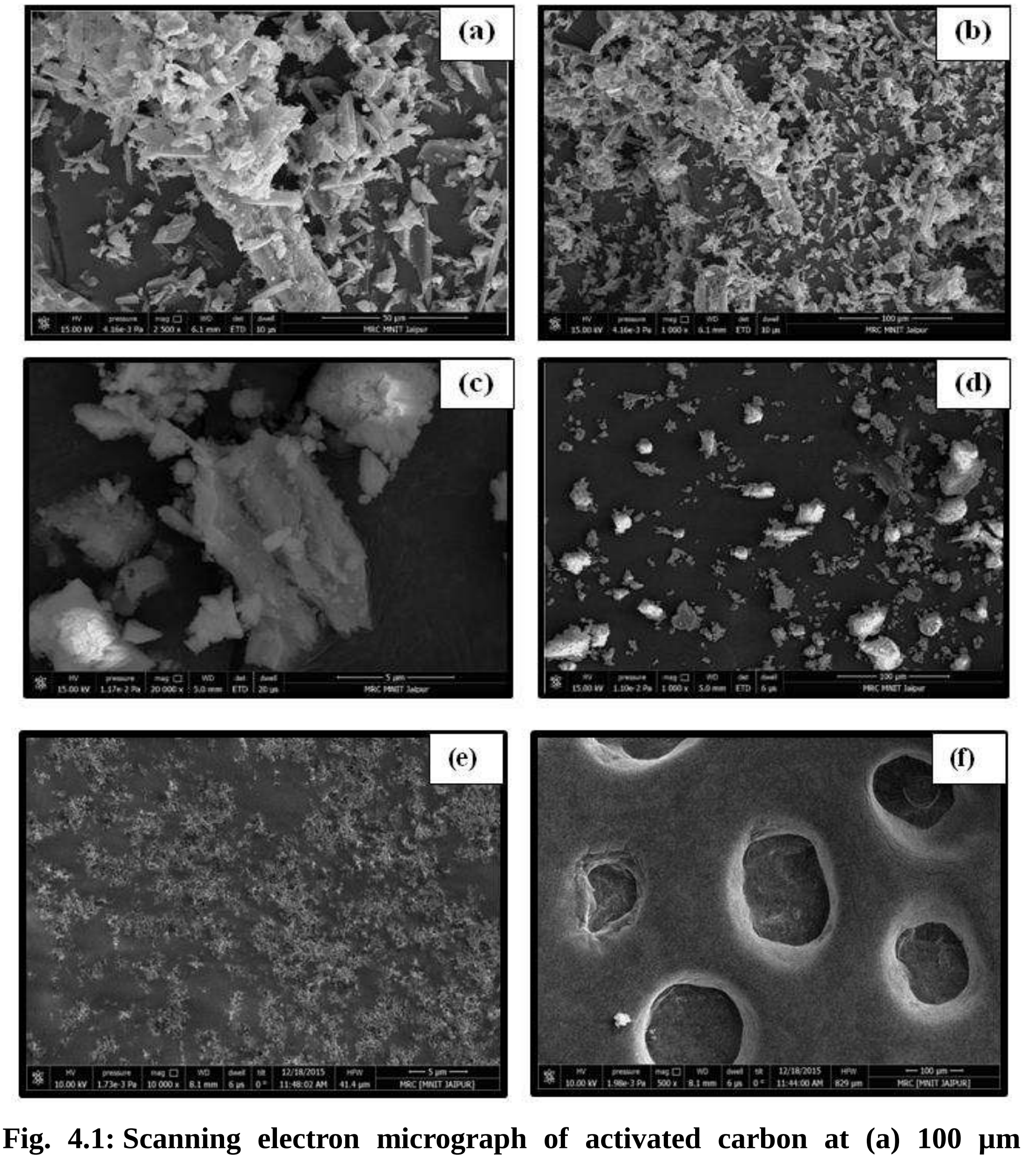
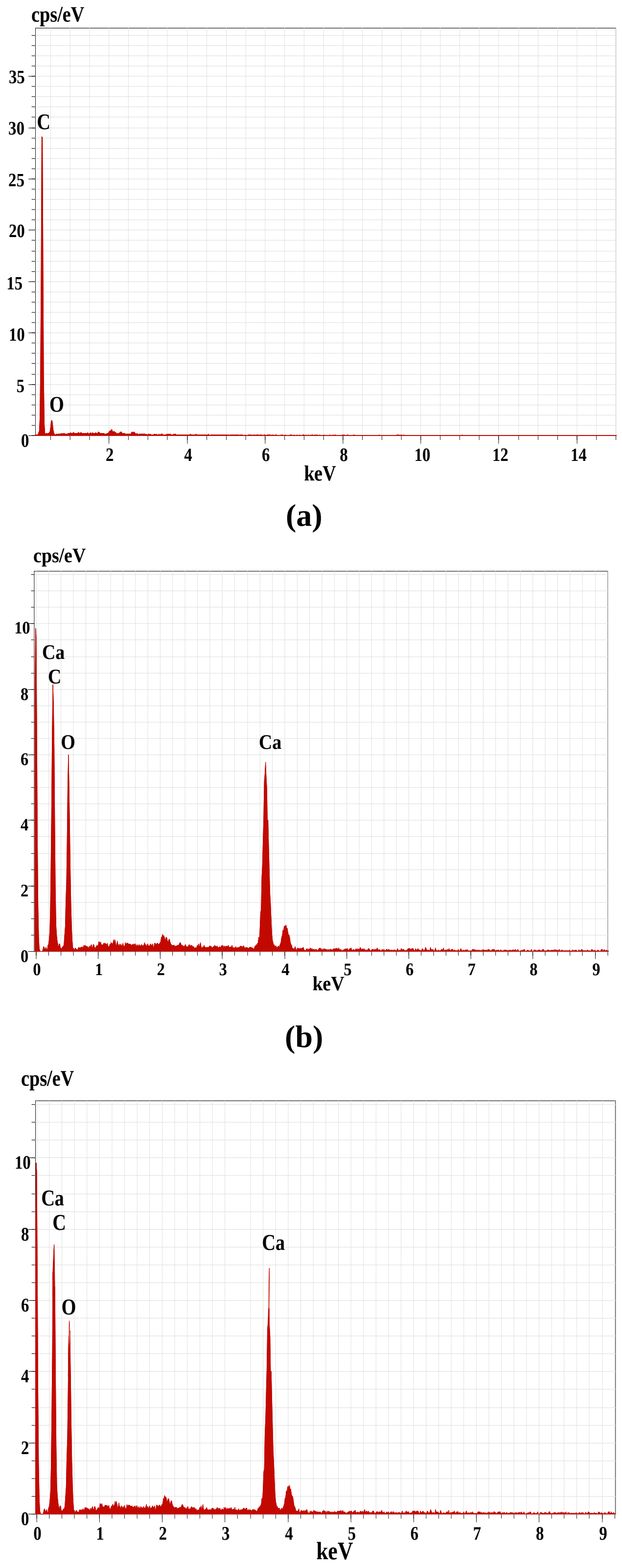


Fig. 4.1: Scanning electron micrograph of activated carbon at (a) 100 µm resolution (b) at 300 µm resolution; egg shell at (c) 5 µm resolution (d) 100 µm resolution; calcined egg shell (e) 5 µm resolution (f) 100 µm resolution



(a)

(b)

(c)

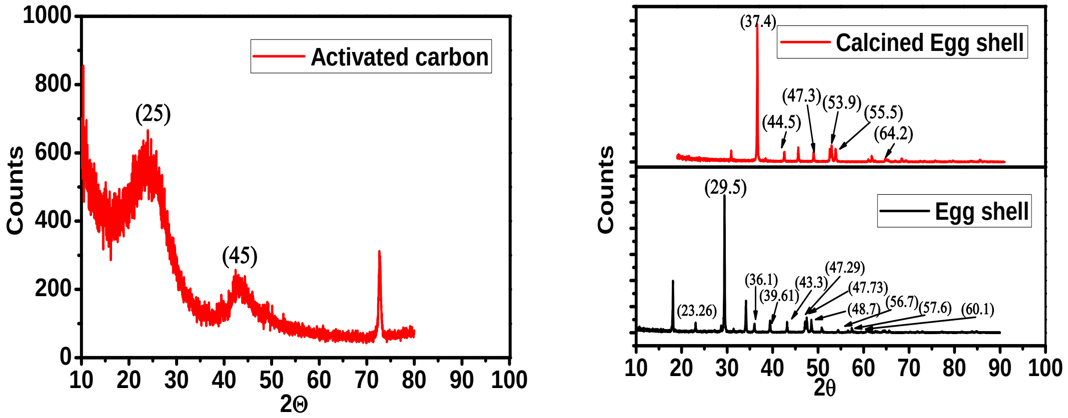
Fig. 4.2: EDS spectra of the adsorbent (a) Activated carbon (b) Egg shell (c) Calcined egg shell

Table 4.1 Elemental analysis of activated carbon and egg shell

Element (wt%)	Activated carbon	Egg shell	Calcined egg shell
C	85.89	31.07	28.37
O	14.11	45.14	43.03
Ca	-	23.79	28.60

4.2.2 X-Ray diffraction analysis

The X-Ray diffraction pattern of adsorbents has shown in Fig 4.3. Fig 4.3(a—b), shows the XRD pattern of activated carbon, egg shell and calcined egg shell. The two broad peaks were observed near 2θ = 25° and 2θ = 45°. The occurrence of broad diffraction peaks at these 2θ is an indicator of crystallinity. In XRD pattern of natural egg shell the main peak appeared at 2θ = 29.5. In addition, spectrum shows various peaks at 2θ = 23.26, 29.5, 36.1, 39.61, 43.3, 47.29, 47.73, 48.7, 56.7, 57.6, 60.1. It indicates presence of $CaCO_3$ in egg shell. But after calcination of egg shell at 700 °C, the main peak appears at 2θ = 37.4. Several peaks appear at 2θ = 44.5, 47.3, 53.9, 55.5, 64.2. These peaks show the presence of CaO in calcined egg shell. It was observed that the peak of Ca (2θ = 29.5) was absent in calcined egg shell. This is due to the conversion limestone ($CaCO_3$) into lime (CaO) during calcination.



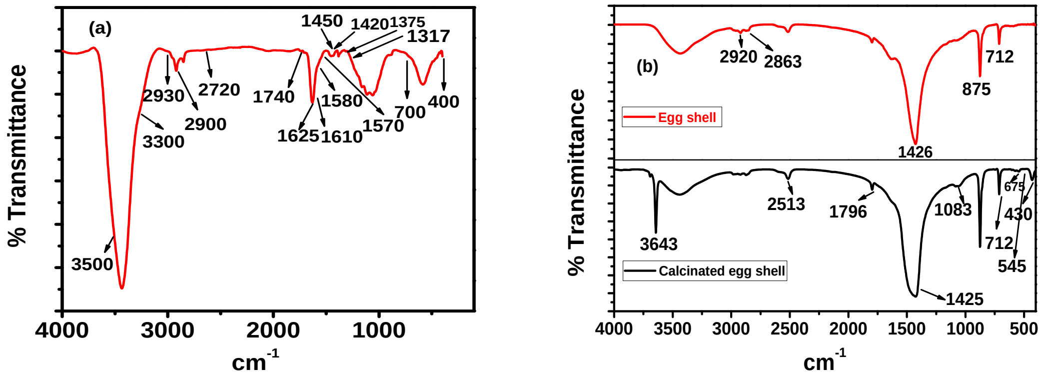
(a) (b)

Fig. 4.3 XRD pattern of (a) activated carbon (b) egg shell/Calcined egg shell

4.2.3 FTIR analysis

Fig. 4.4(a—b) shows FTIR spectra of activated carbon, natural egg shell and calcined egg shell. For activated carbon, wavelength of 3500-3300 cm^{-1} shows O-H stretching, 2930-2900 cm^{-1} is attributed to C-H asymmetric stretching, 2720 cm^{-1} is due to C-H bond present in aldehyde, 1740 cm^{-1} is attributed to C=O bonds from esters, 1625-1610 cm^{-1} is due to C=C aromatic skeletal stretching and 1580-1570 is C=C stretching band, 1450-1420 is C-H asymmetric bending, 1375-1317 is C-H asymmetric and symmetric bending, 700-400 is C-C stretching.

In natural egg shell, Broad transmission band at around 2863 cm^{-1} can be attributed to OH stretching vibration of the waste of residual and the weak band at 2920 cm^{-1} is attributed to C=O bonds from carbonate. Infrared bands at 1426 cm^{-1} and 875 cm^{-1} shows the C–O stretching and bending of $CaCO_3$, meanwhile the sharp band at 712 cm^{-1} represents a Ca–O bond. While after calcination, calcined eggshell shows the existence of OH in $Ca(OH)_2$ in the peak of around 3643 cm^{-1} and 2513 cm^{-1}. It was formed during adsorption of water by CaO. Another band existence at 430 cm^{-1} is due to Ca–O band. The functional group of 1796 cm^{-1} , 1425 cm^{-1} , 1083 cm^{-1}, 712 cm^{-1}, 675 and 545 cm^{-1} represent the stretching vibration of the CO_3^{2-} group present in the eggshell. Here Infrared results show that $CaCO_3$ had completely converted to CaO because of Ca–O bond in the calcined eggshell.



(a) **(b)**

Fig. 4.4: FTIR pattern of (a) activated carbon (b) Egg shell/ Calcined egg shell

After characterisation of adsorbents, the batch studies for removal of heavy metals have been carried out to select the adsorbent for further study. The results obtained are shown in Table 4.2.

4.3 Selection of adsorbent

Firstly, different adsorbents such as activated carbon, activated alumina balls, egg shell, calcined egg shell, wheat bran, hydrochloric acid-treated wheat bran were used for removal of copper, chromium and cadmium. The adsorbents were characterised and their removal efficiencies were compared in order to select one efficient adsorbent on the basis of cost, easy availability and percent removal. From Table 4.2, it was observed that the percent removal of hydrochloric acid-treated wheat bran has reached nearly up to the removal percent of activated carbon. Thus hydrochloric acid-treated wheat bran was selected as an adsorbent for removal of copper, chromium and cadmium because it has low cost and easy availability as compared to the activated carbon.

Table 4.2 Removal of copper, chromium and cadmium using different adsorbents

Removal (%)					
Contact time					
Adsorbent	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**
FOR COPPER (pH=5)					
Activated Carbon	98.10%	98.31%	99.79%	99.85%	99.90%
Activated alumina balls	63.31%	65.63%	69.83%	70.36%	73.69%
Egg shell	60.67%	63%	65.76%	67.45%	69.10%
Calcined eggshell	65.31%	67.95%	69.39%	70%	73.29%
Wheat bran	67.90%	69%	70.69%	73.70%	78.29%
Hydrochloric acid-treated wheat bran	95.66%	96.48%	97.87%	98.39%	99.56%
FOR CHROMIUM (pH=2)					
Activated Carbon	97.80%	97.93%	98.27%	98.64%	98.75%
Activated alumina balls	58.60%	58.86%	59.03%	59.33%	60.60%
Egg shell	59.46%	60%	60.43%	61.20%	64%
Calcined egg shell	60.83%	62.95%	65.80%	66.74%	70.19%
Wheat bran	65.20%	66.66%	74.64%	75.61%	75.89%
Hydrochloric acid-treated wheat bran	90.46%	92.98%	94.19%	96.37%	96.96%

FOR CADMIUM (pH=6)					
Activated Carbon	90%	92.73%	94.97%	96.55%	97.67%
Activated alumina balls	55.80%	57%	58.03%	59.13%	60%
Egg shell	54.60%	55%	56.31%	60%	63.37%
Calcined egg shell	55.39%	57%	58.87%	60.30%	63%
Wheat bran	60%	62.27%	64.32%	65.61%	67.89%
Hydrochloric acid treated wheat bran	80.46%	81.47%	84.19%	86%	90.40%

*Operating conditions: Initial concentration -10 mg/L; rpm-180; Temperature-35°C

4.4 Detailed characterisation of wheat bran (Selected adsorbent)

4.4.1 SEM analysis coupled with EDS

The SEM (Scanning electron microscopy) analysis of raw wheat bran and hydrochloric acid-treated wheat bran was performed on electron microscope to determine the surface morphology of the adsorbent. Fig. 4.5 (a—d) shows the SEM image of raw wheat bran and chemically MWB. It was observed that raw wheat bran has a coarse surface, but after acid treatment the surface becomes homogeneous and porous. Aggregation of particles has been broken and particles become evenly distributed, providing higher surface area for adsorption. Further elemental analysis of the raw wheat bran and chemically modified wheat bran (MWB) was done using EDS (Energy dispersive spectroscopy) to determine its chemical composition as shown in Fig. 4.6(a—b), respectively. It was observed that there is the presence of carbon and oxygen elements in cellulose, having a weight percent of 54.65% and 65.85%, respectively.

But after acid treatment of wheat bran, the carbon wt% increases to 65.85% because charring of the wheat bran leads to increase in the carbon content (Table 4.3) and development of active sites for metal adsorption. Further, oxygen wt% decreases to 31.82% due to loss of water molecules. This improves the extraction behaviour of wheat bran (Özer & Pirincci 2006; Özer & Özer 2004; Krishnani et al., 2004).

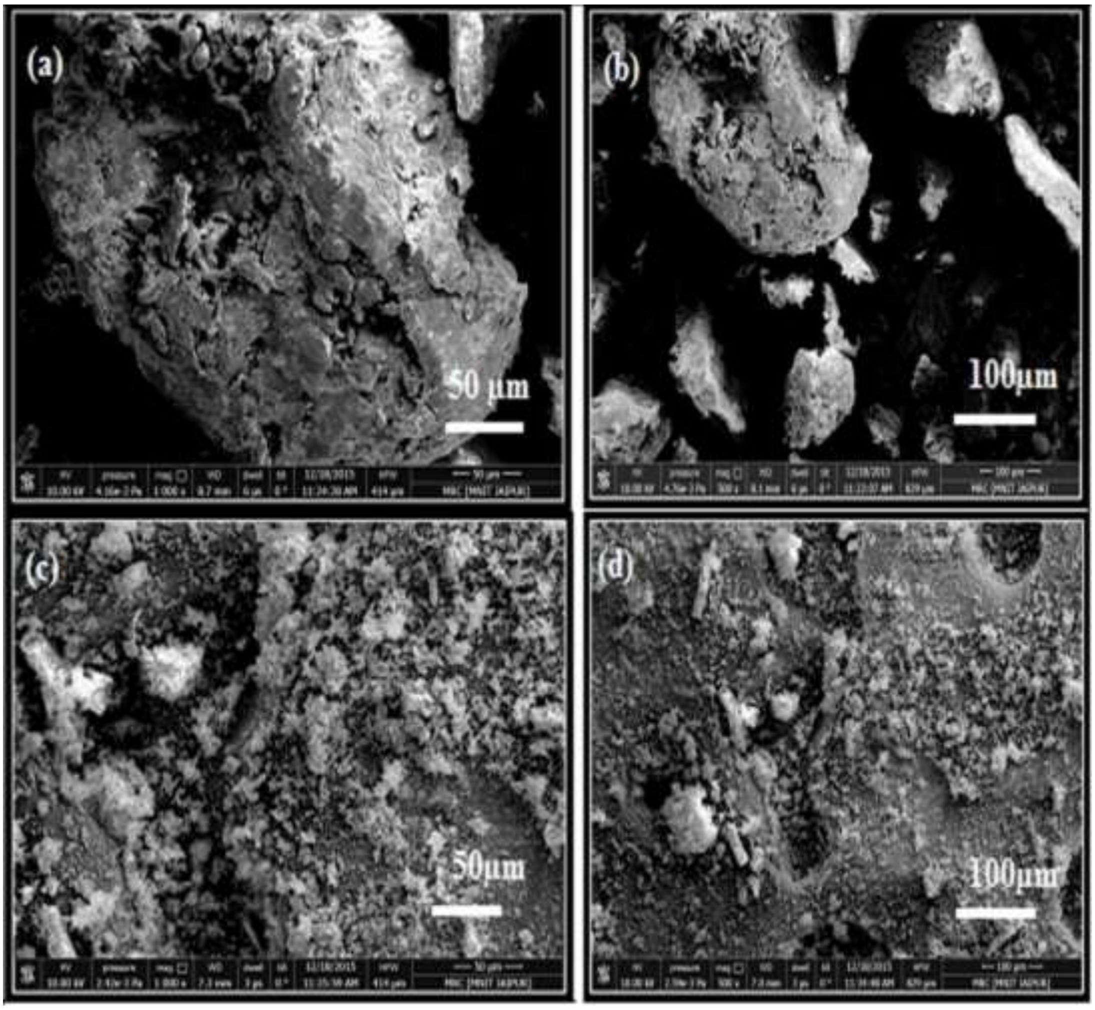


Fig. 4.5: **Scanning electron micrograph of (a) Raw wheat bran at 50 µm resolution (b) Raw wheat bran at 100 µm resolution (c) Hydrochloric acid-treated wheat bran at 50 µm resolution (d) Hydrochloric acid-treated wheat bran at 100 µm resolution**

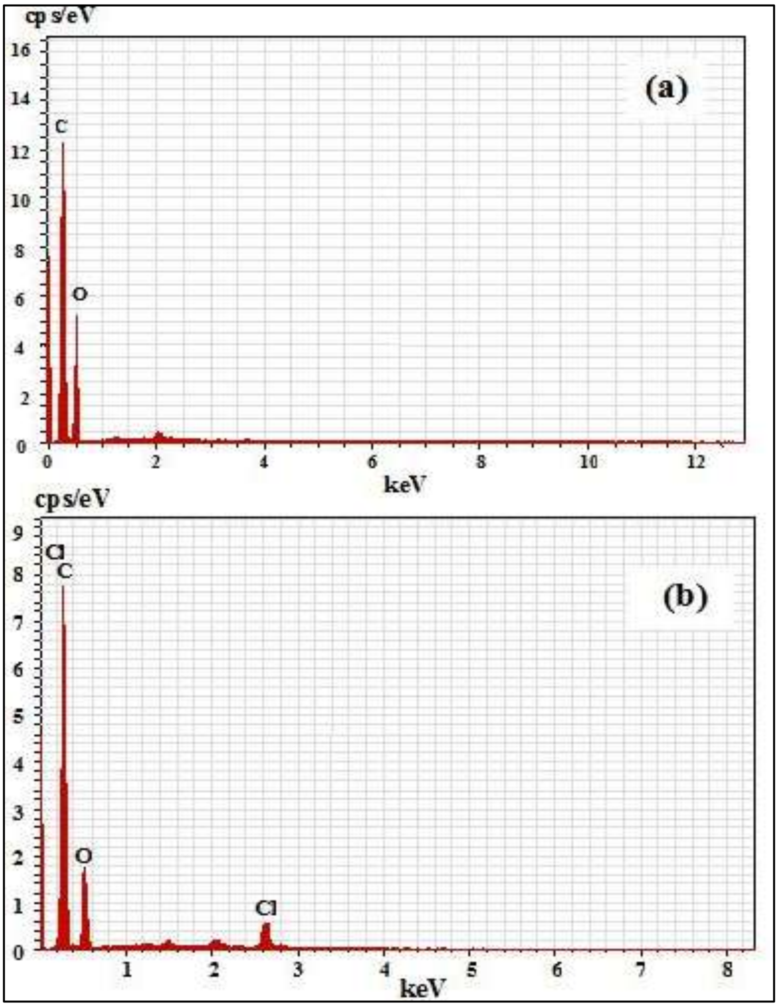


Fig. 4.6 EDS spectra of the adsorbent (a) Wheat bran (b) Hydrochloric acid-treated wheat bran

Table 4.3 Elemental analysis of raw wheat bran and chemically modified wheat bran

Element	**Raw wheat bran**		**Modified wheat bran**	
C	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
	54.65	61.92	65.85	72.86
O	44.66	37.98	31.82	26.43
Cl	×	×	1.62	0.61

4.4.2 XPS, FTIR, and XRD

Fig. 4.7(a–c) show XPS (X-ray photoelectron spectroscopy), FTIR (Fourier transform infrared spectroscopy), and XRD (X- ray diffraction analysis) analysis of raw wheat bran and MWB, respectively. XPS analysis of raw wheat bran was performed to confirm the presence of cellulose in the wheat bran. Fig. 4.7(a) shows the XPS spectra of wheat bran, and it indicates a peak at a binding energy of 285 eV, confirming the presence of carbon in the wheat bran. Another peak is at a binding energy of 533 eV because of the presence of oxygen. Thus, the presence of C and O in the wheat bran confirms the presence of cellulose, which helps in heavy metal binding.

Further, FTIR spectroscopy determines the presence of surface functional groups in the adsorbent (Fig. 4.7(b)). The spectrum was measured and recorded (500–4000 cm^{-1}) on a spectrometer with a resolution of 2.0 cm^{-1}. From FTIR spectra, it was observed that both wheat bran and MWB have the same profiles, but intensities of absorption bands are different. In raw wheat bran, peaks at 3400 cm^{-1} show –OH stretching vibration, which indicates the presence of cellulose (Kaya et al., 2014). After further treatment with hydrochloric acid, this broad stretching vibration has been reduced because partial hydrogen bond present in cellulose has been destroyed. Similarly, adsorption band of carboxyl group at 1538 cm^{-1} has been destructed in acid-treated wheat bran. Peaks at 1241, 1157, 1076, and 1024 cm^{-1} show the presence of C-O-C group in raw wheat bran, and these peaks have been reduced and destroyed in MWB. Further, peaks at 860, 766, and 723 cm^{-1} have also disappeared in MWB. There is a peak at 1657 cm^{-1} in raw wheat bran due to C = O group. There is a shift and intensity decrease in this peak from 1657 cm^{-1} to 1712 cm^{-1}, which confirms the amorphous nature of raw wheat bran. Further, the X-ray diffraction pattern of wheat bran and chemically modified bran is shown in Fig. 4.7(c). Wheat bran scanning was done between 10^o and 90^o angles. It was observed that MWB becomes more amorphous as compared to the raw wheat bran because crystallinity of the raw wheat bran gets disrupted after acid addition; therefore sharp peaks have been converted into diffused peaks.

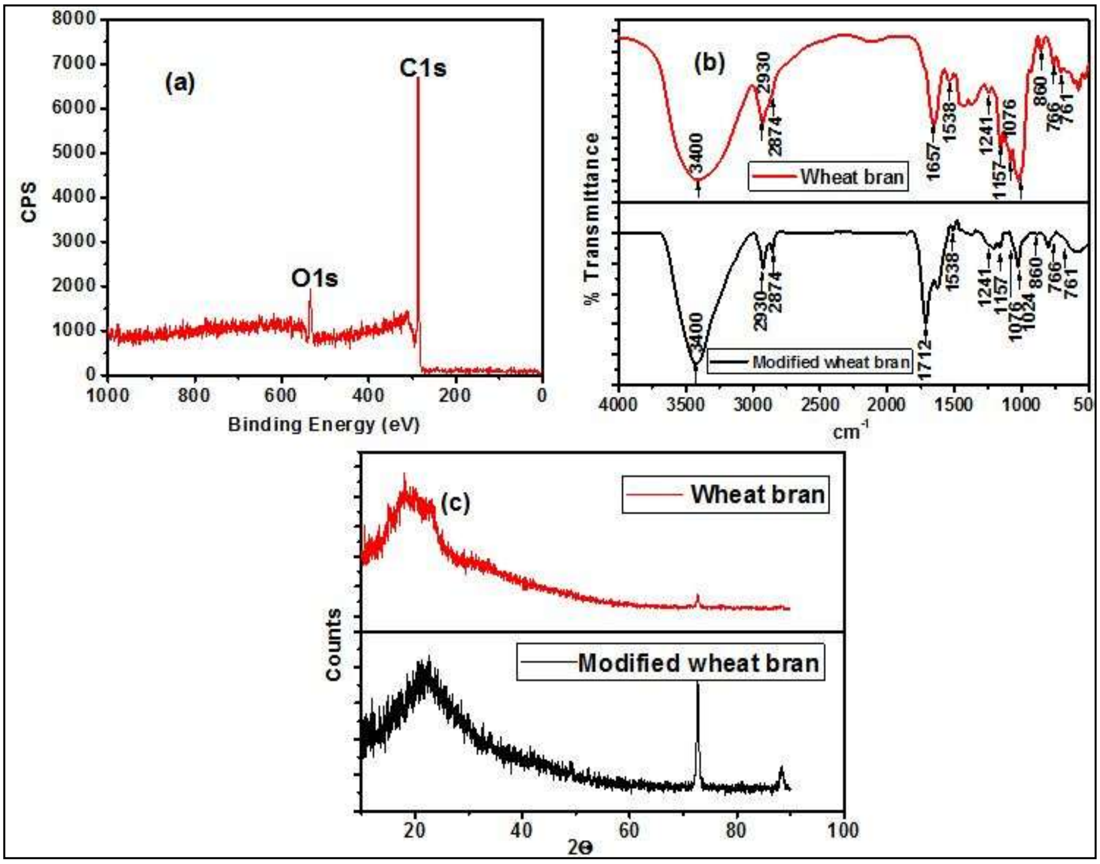


Fig. 4.7 (a) The high-resolution XPS spectra of raw wheat bran, (b) FTIR analysis of wheat bran and hydrochloric acid-treated wheat bran, and (c) XRD pattern of wheat bran and hydrochloric acid-treated wheat bran.

4.4.3 Point of zero charge

The pH is very important factor in adsorption. pH controls adsorption of the ion on the adsorbent surface. In Fig. 4.8, point of zero charge for hydrochloric acid-treated wheat bran is 4. It is clear from this figure that when pH of the solution is higher than point of Zero Charge, the negative charge on the adsorbent surface provides electrostatic interactions, which are helpful in adsorption of positive ions such as copper and cadmium. However, when pH decreases, the adsorbent surface is positively charged and it is helpful in adsorption of negative ion such as chromium.

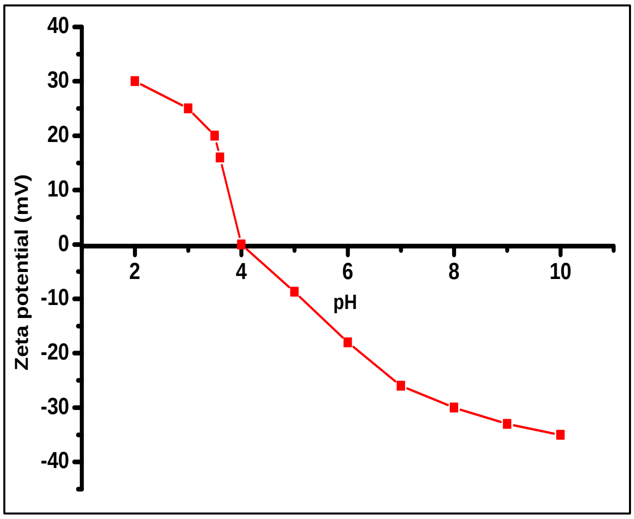


Fig. 4.8 Zeta potential vs. pH curve for hydrochloric acid-treated wheat bran

4.5 Batch Experiments

Batch experiments were performed for individual metal ions, mixed metal ions and for simultaneous removal of metal ions and dye using selected adsorbent based on design of experiments to optimise operating parameters such as initial concentration, pH, temperature and adsorbent dose for maximum removal of copper, chromium and cadmium.

4.5.1 Individual metal study

4.5.1.1 Design of experiment

In this work, for optimization of operating conditions and removal efficiency, design of experiments was used and four parameters were included such as initial concentration (15-100 mg/L), pH (2-10), temperature (17°C-55°C), and adsorbent dose (0.5-5g) (Table 4.4). Three-level, four-factor BBD was used to determine the effect of these parameters on removal percent of copper, cadmium, and chromium. The use of BBD has the advantage that it allows few combinations of variables to determine complex response function (Muthukumar et al., 2003). In this work, a total of 29 experiments were carried out for each metal ion (Table 4.5).

Table 4.4 Process factors and their levels

Factor Coded values	**-1**	**0**	**1**
Initial concentration (mg/L)	15	57.5	100
pH	2	6	10
Temperature (°C)	17	36	55
Adsorbent dose (gram)	0.5	2.75	5

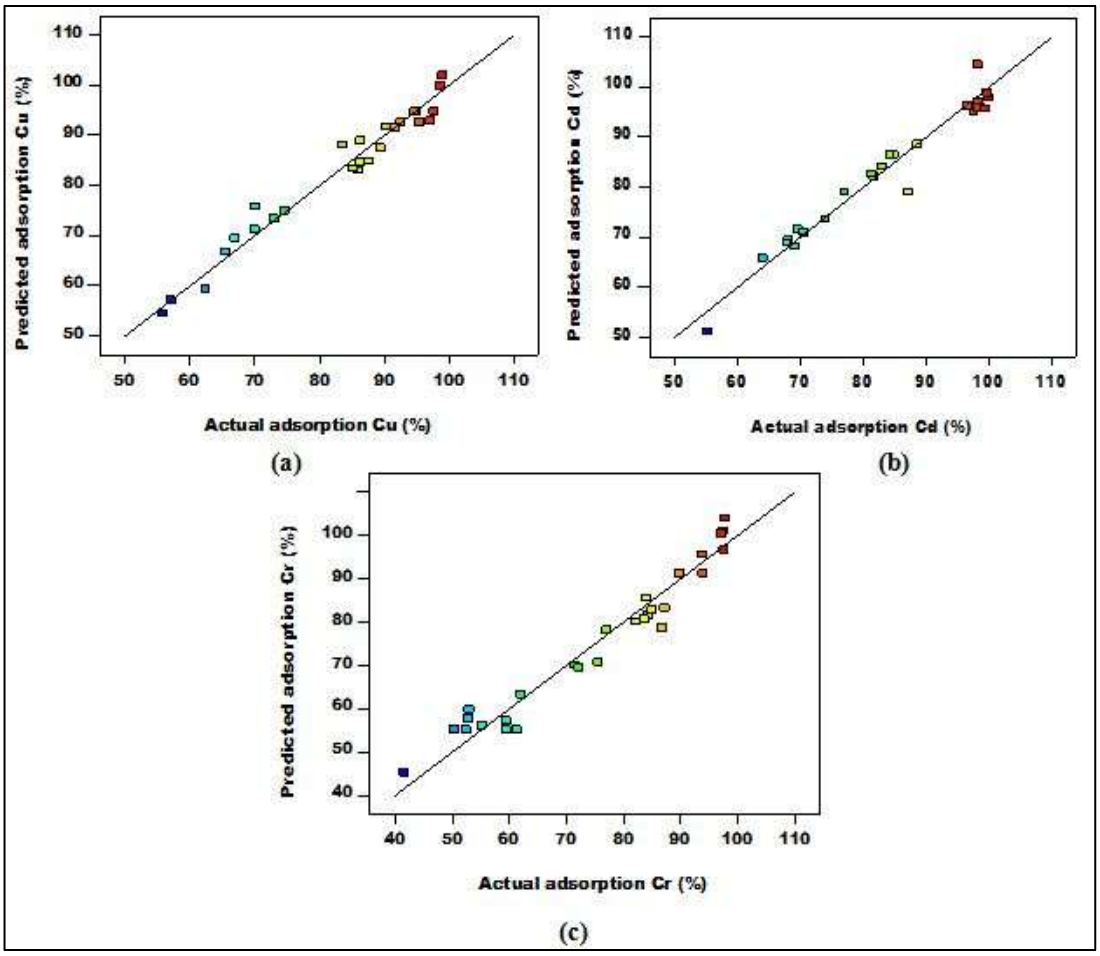
Table 4.5 Box–Behnken Design matrix for four variables and response values

Run	**Initial metal conc. (A)**	**pH (B)**	**Adsorbent dose (C)**	**Temp. (D)**	**Response (R)**		
					Copper removal (%)	**Cadmium removal (%)**	**Chromium removal (%)**
1	57.5	6	2.75	36	94.599	77.041	78.336
2	100	6	5	36	98.990	67.885	72.238
3	57.5	10	5	36	98.607	62.059	88.094
4	57.5	6	2.75	36	94.596	52.220	87.433
5	57.5	2	2.75	55	83.414	69.650	97.857
6	100	10	2.75	36	90.188	52.045	64.955
7	100	6	0.5	36	86.276	69.061	41.609
8	15	6	0.5	36	57.003	98.568	52.743
9	100	6	2.75	17	97.093	81.627	83.643
10	57.5	6	2.75	36	94.596	61.041	77.237
11	57.5	2	0.5	36	85.864	81.420	59.465
12	15	6	5	36	72.956	99.635	71.475
13	57.5	10	2.75	55	87.615	70.494	97.636
14	57.5	6	5	55	95.382	73.998	85.064
15	57.5	6	2.75	36	94.967	77.041	52.433
16	15	2	2.75	36	62.368	97.557	86.769
17	15	10	2.75	36	65.497	84.913	99.105
18	57.5	10	0.5	36	74.543	84.240	75.598
19	57.5	2	2.75	17	70.000	98.125	97.182
20	57.5	6	2.75	36	94.967	77.041	59.441
21	100	2	2.75	36	97.691	68.062	93.976
22	57.5	10	2.75	17	85.098	99.275	87.238
23	15	6	2.75	17	55.798	77.125	98.015
24	15	6	2.75	55	66.909	84.825	93.845
25	57.5	6	5	17	92.455	89.125	98.855
26	100	6	2.75	55	91.692	55.319	82.319
27	57.5	6	0.5	55	86.337	70.661	84.329
28	57.5	6	0.5	17	70.001	96.562	55.176
29	57.5	2	5	36	89.460	88.521	97.416

4.5.1.2 Statistical analysis

To optimize response surface, an adequate fit of model should be obtained. There is requirement of an adequate model because it avoids poor results (Myers et al., 2009; Sahu et al., 2009). The actual and predicted adsorption plots for copper, cadmium, and chromium removal are shown in Fig. 4.9(a–c), respectively. In Fig. 4.9(a–c), the actual R^2 value and adjusted R^2 value were found to be 0.97 and 0.94 for copper, 0.96 and 0.92 for cadmium, and 0.95 and 0.91 for chromium, respectively. Further, R^2 value determines the goodness of fit of the model. In our work, R^2 value shows that there is good fitness of regression models for obtaining the results.

Fig. 4.10(a–c) shows the plot between % normal probability and externally studentized residuals. It indicates that how well model satisfies ANOVA assumption where studentized residual is the measure of number of standard deviation. They also show that neither response transformation was needed nor there was any problem with normality. Fig. 4.11 (a–c) shows the plot between studentized residuals and predicted removal percent for copper, cadmium and chromium. These plots are randomly scattered suggesting the variance of original observation to be constant for all values of the response. Fig. 4.12(a–c) shows the plot between studentized residuals and runs. The residual values should lie in the range of ± 3.50 and any value outside this range is unused. In Fig. 4.12(a–c) the value of studentized residuals lies in the interval of ± 3.50.

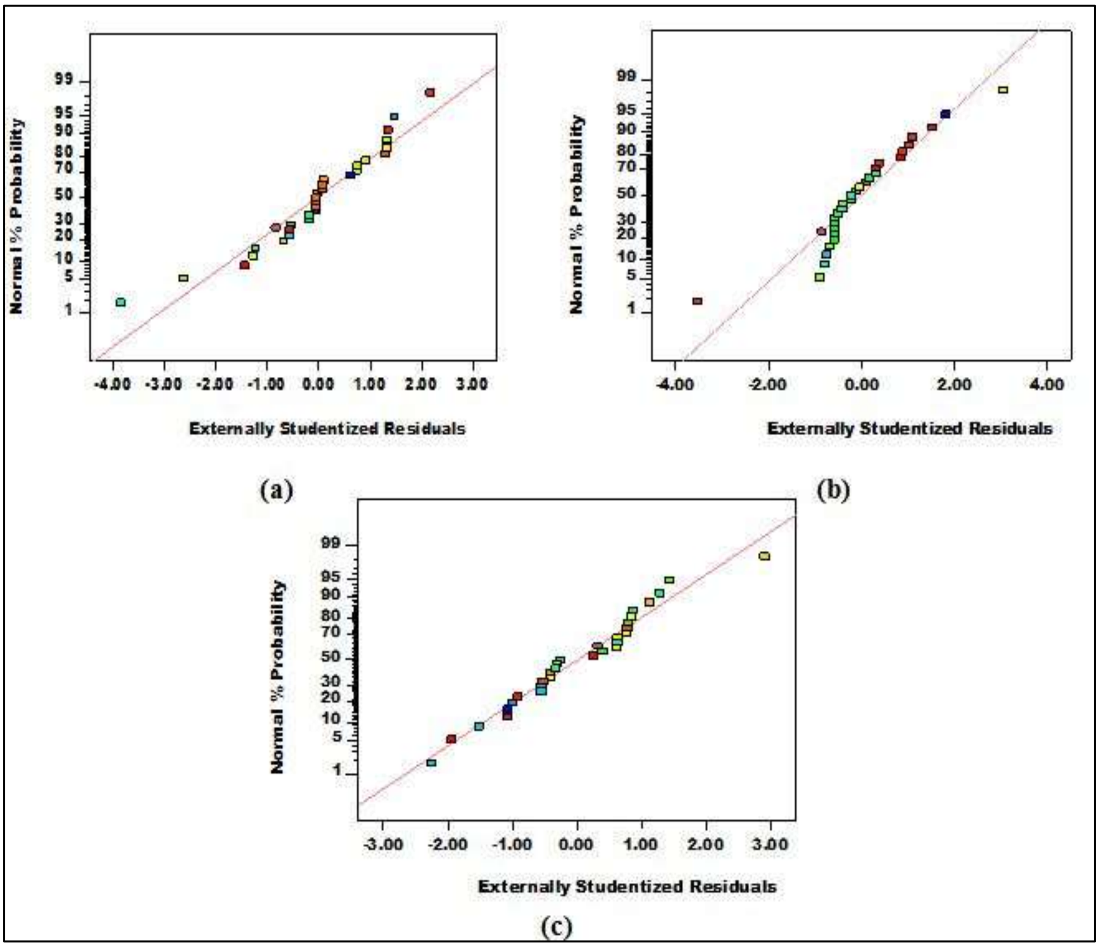


(a)

(b)

(c)

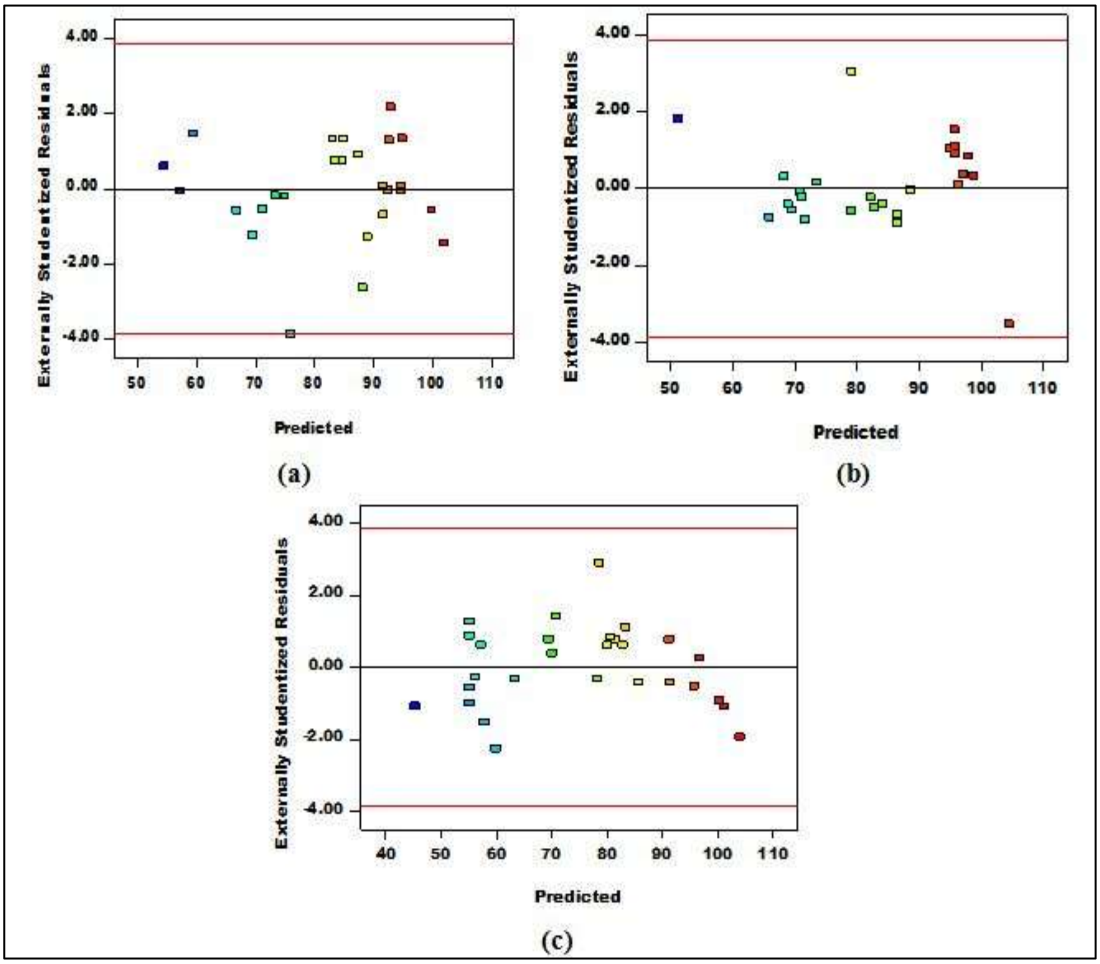
Fig. 4.9 The actual and predicted plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent.



(a) (b)

(c)

Fig. 4.10 Normal % probability and studentized residual plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent



(a)

(b)

(c)

Fig. 4.11 The studentized residuals and predicted response plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

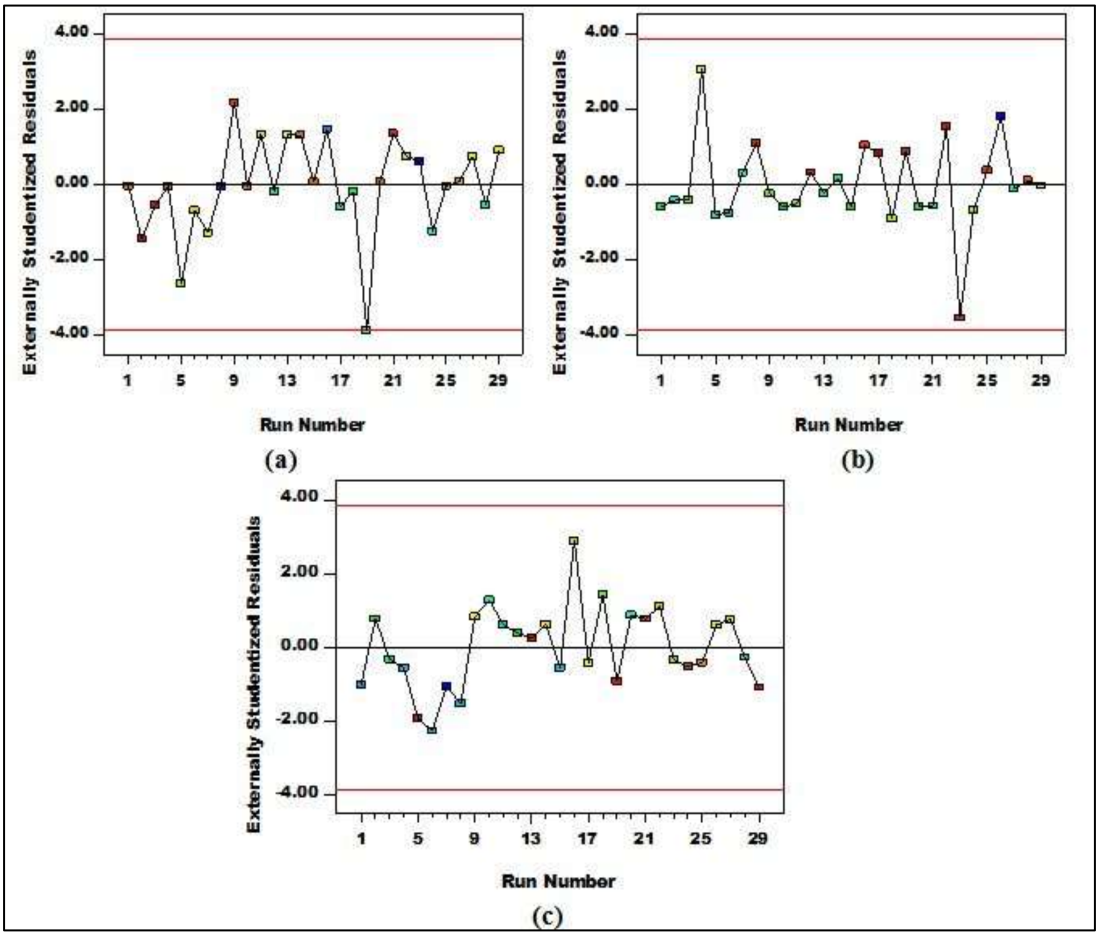


Fig. 4.12 Studentized residuals and and run number plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

4.5.1.3 Analysis of variance

The following second-order polynomial model equations (Mohan et al., 2006; Gopalakrishnan et al., 2015) are obtained from experimental data, which demonstrate the relationship between copper, cadmium, and chromium removal efficiency (R_{Cu}, R_{Cd}, R_{Cr}) and independent variables (A, B, C, D). These model equations (4.1 — 4.3) are applicable for A=B=C=D≠0.

$$\begin{aligned} R_{Cu} = 94.74 + 15.12 * A + 1.06 * B + 7.32 * C + 3.41 * D - 2.66 * AB - 0.81 \\ * AC - 4.13 * AD + 5.12 * BC - 2.72 * BD - 3.35 * CD - 11.28 \\ * A^2 - 5.30 * \ B^2 - 3.11\ C^2 - 6.37 * \ D^2 \qquad \ldots\ldots (4.1) \end{aligned}$$

$$\begin{aligned} R_{Cd} = +79.08 - 14.39 * A - 0.19 * B + 0.89 * C - 12.24 * D - 1.59 * AB - 0.56 \\ * AC - 3.25 * AD - 2.07 * BC - 0.076 * BD + 0.44 * CD + 0.26 \\ * A^2 + 2.73 * \ B^2 + 3.65\ C^2 + 1.78 * \ D^2 \qquad \ldots\ldots (4.2) \end{aligned}$$

$$\begin{aligned} R_{Cr} = 55.18 - 3.27 * A - 6.09 * B + 9.10 * C + 4.25 * D - 9.59 * AB + 2.97 * AC \\ - 4.54 * AD - 12.86 * BC + 2.43 * BD - 8.49 * CD + 5.60 \ * A^2 \\ + 18.05 * \ B^2 - 0.11\ C^2 - 22.91 * \ D^2 \qquad \ldots (4.3) \end{aligned}$$

Table 4.6 shows ANOVA for response surface quadratic model. The model F value is 30.80, 22.55, and 20.10 for copper, cadmium, and chromium, and this value measures how well factors describe the variation in the data about its mean. Probability value (P) is a measurement of effects in a model that should be less than 0.05 for being significant, and in this work probability values are less than 0.05 for parameters A, C, D, AD, BC, A^2, B^2, C^2, and D^2 for copper; A, C, D, AD, BC, A^2, B^2, C^2, and D^2 for cadmium; and B, C, D, AB, BC, CD, A^2, B^2, and D^2 for chromium. It means that only these parameters are significant for copper, cadmium, and chromium removal. Adequate precision ratio is 19.802 for copper removal, 19.643 for cadmium removal, and 15.107 for chromium removal, which is much higher than the minimum desirable value of 4 and it indicates that there is a presence of adequate signal to noise ratio for this model (Ahmadi et al., 2014; Srinivasan & Viraraghavan 2010).

Table 4.6 Analysis of variance (ANOVA) of copper, cadmium and chromium removal

R-Square = 0.9686, Adj R-Square = 0.9371 (Cu); R-Square = 0.9575, Adj R-Square = 0.9151 (Cd); R-Square = 0.9526, Adj R-Square = 0.9052 (Cr)

Source	Sum of squares			*df	F value			
	Cu	Cd	Cr		Cu	Cd	Cr	Remarks
Model	4805.16	4486.37	8213.73	14	30.80	22.55	20.10	Significant/ Significant/ Significant
A-Initial metal concentration	2742.06	2483.22	128.12	1	246.08	174.76	4.39	
B-Ph	13.55	0.44	444.55	1	1.22	0.03	15.23	
C-Dose	642.77	9.56	994.10	1	57.68	0.67	34.05	
D-Temperature	139.42	1798.08	216.26	1	12.51	126.55	7.41	
AB	28.26	10.15	367.82	1	2.54	0.71	12.60	
AC	2.62	1.26	35.38	1	0.24	0.09	1.21	
AD	68.16	42.30	82.38	1	6.12	2.98	2.82	
BC	104.73	17.15	661.88	1	9.40	1.21	22.67	
BD	29.69	0.02	23.63	1	2.66	1.644 E-003	0.81	
CD		0.79	288.05	1	4.03	0.05	9.87	
A^2		0.43	203.30	1	74.10	0.03	6.96	
B^2		48.17	2112.90	1	16.33	3.39	72.37	
C^2		86.28	0.07	1	5.62	6.07	2.466 E-003	
D^2		20.52	3403.60	1	23.59	1.44	116.58	
Residual		198.93	408.74	14				
Lack of Fit		116.04	315.34	10	376.97			Significant/ Significant/ Not Significant
Pure Error		82.88	93.39	4				
Cor Total		4685.29	8622.40	28				

4.5.1.4 Effect of process variables

The effects of process variables on removal of copper, cadmium, and chromium have been described with the help of three-dimensional plots, Fig. 4.13(a–f), Fig. 4.14(a)–(f), and Fig. 4.15(a)–(f).

(i) Effect of temperature

From Fig. 4.13(c, e, f), it is clear that removal efficiency of copper increases with increase in temperature from 17ºC to 39.8ºC, which is due to the increase in diffusion rate of the metal ion, but after 39.8ºC removal percent decreases, which is due to the deactivation of the adsorbent surface or destruction of the active sites because of bond rupture. Similarly, in the case of chromium, removal percent increases on increasing temperature from 17°C to 55°C. This is also because of increase in diffusion rate of the metal ion (Nouri et al., 2007; Wu et al., 2011) and endothermic nature of the adsorption operation. The coefficient of temperature in Eq. (4.2) for cadmium has a negative sign, and also from Fig. 4.15(c,e,f), it is clear that removal efficiency of cadmium decreases with increase in temperature from 17°C to 55°C, which may be due to the desorption of metal from adsorbent surface at higher temperature (Nouri et al., 2007; Wu et al., 2011). This is also due to the deactivation of the adsorbent surface or destruction of the active sites because of bond rupture (Ertugay & Bayhan 2010) Lower adsorption at high temperature shows the exothermic behaviour of cadmium adsorption.

(ii) Effect of initial metal concentration

As shown in Fig. 4.13 (a, d, e), it is clear that removal efficiency of copper increases with increase in initial concentration from 15 mg/L to 100 mg/L. But from Fig. 4.13 (g), it is clear that after 100 mg/L removal efficiency of copper decreases due to the decreased number of available sites for adsorption of larger number of molecules (Olgun & Atar 2011). Initial metal ion concentration has the highest effect on removal of copper among various studied variables in ANOVA results. Further, the coefficient of metal concentration in Eq. (4.2) and in Eq. (4.3) is negative; thus the removal percent of cadmium and chromium falls with increase in metal concentration from 15 mg/L to 100 mg/L. This is due to the decreased number of available sites for adsorption of larger number of molecules (Olgun & Atar 2011).

(iii) Effect of adsorbent dose

Adsorbent surface provides the sites for adsorption of metal ions. The effect of adsorbent doses on removal of metal ions has been studied by varying adsorbent doses from 0.5 g to 5 g. From Fig. 4.13 (b,d,f), Fig. 4.14(b,d,f), and Fig. 4.15(b,d,f), it is obvious that the copper, chromium, and cadmium removal percent increases with increase in adsorbent dose from 0.5 g to 5 g. For adsorbent dose of 0.5 g, less adsorption sites are available for adsorption of metal ions but on increasing the adsorbent dose, available surface area of the adsorbent increases and as a result a large number of active sites are available for metal ion adsorption. Thus, the removal percent increases with increase in adsorbent dose from 0.5g to 5g (Dakiky et al., 2002; Özer and Özer 2004; Sayen et al., 2006).

(iv) Effect of pH

Effects of pH on removal of copper, cadmium, and chromium give information of adsorption mechanism. From Fig. 4.13 (a,b, c), it can be observed that the removal percent of copper increases with increase in pH from 2 to 5 but beyond pH 5, the removal percent decreases. At low pH, modified wheat bran (MWB) surface is surrounded by hydronium ions and it decreases the interaction between copper and MWB sites. Further increase in pH increases copper removal because the surface of MWB becomes negative and causes attraction between copper and MWB sites. Beyond pH of 5, copper exists in the form of hydroxide. As a result, copper hydroxide starts precipitating and reduces adsorption process (Özer and Özer 2004; Sayen et al., 2006). The possible mechanism for copper removal is written as follows:

$$2(MWB)\text{-}H + Cu^{2+} \rightarrow (MWB)_2\,Cu + 2H^+ \text{ ....(4.4)}$$

$$(MWB)\text{-}H + Cu(OH)^+ \rightarrow MWB\text{-}Cu(OH) + H^+ \text{ ....(4.5)}$$

However, Chromium is present in the form of $Cr_2O_7^-$, $HCrO_4^-$ at pH 2-6 in the solution and $HCrO_4^-$ predominates. However at high pH, chromium is present in the form of CrO_4^{2-} and $Cr_2O_7^{2-}$. The equilibrium equations for chromium (VI) are given below (Ni et al., 2017; Garg et al., 2008).

(1) $HCr_2O_7^- \leftrightarrows Cr_2O_7^{2}\text{-}+H^+$..(4.6)

(2) $Cr_2O_7^{2}-+H_2O \leftrightarrows 2HCrO_4^{-}$ ....(4.7)

(3) $HCrO_4- \leftrightarrows CrO_4^{2-}+H^{+}$ ....(4.8)

(4) $HCrO_4 \leftrightarrows HCrO_4^{-}+H^{+}$ ....(4.9)

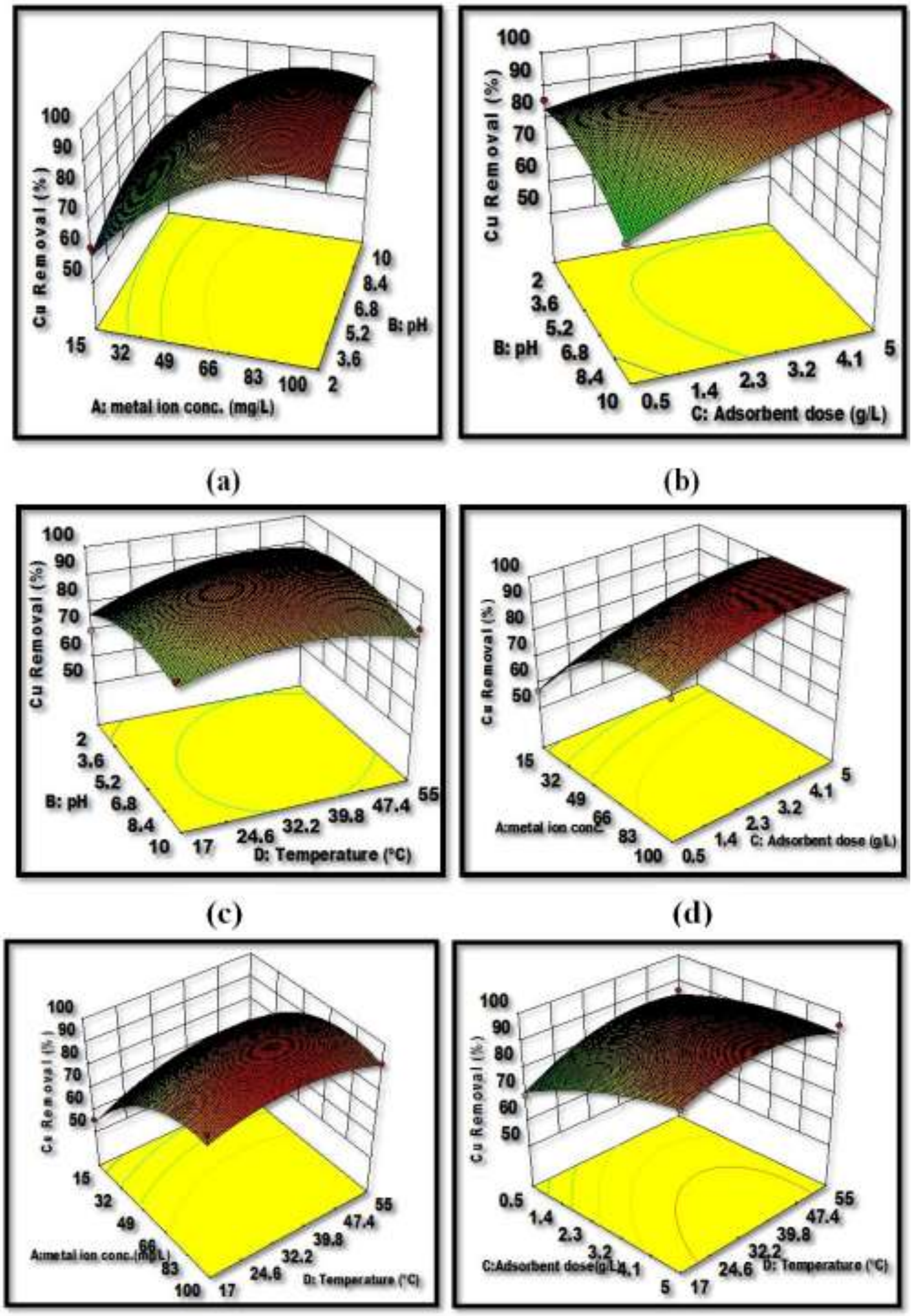
For chromium ion, removal is low at high pH and it is the highest at 98.92% for pH value of 2. (Fig. 4.14 a, b, c). At low pH, functional groups present in modified wheat bran becomes protonated and as a result strong attraction force is produced between negatively charged chromate and protonated surface of modified wheat bran (Özer et al., 2004). However on increasing pH, functional groups present in modified wheat bran become deprotonated and repel negatively charged chromate and removal decreases (Özer and Özer 2004, Özer et al., 2004).

Further, Cadmium removal increases with pH from 6-10 (Fig. 4.15 a, b, c) because at lower pH adsorbent surface becomes protonated and it causes repulsive force between cadmium ion and modified wheat bran sites, but at pH range of 6-10, adsorbent surface become negatively charged and it causes attraction force between cadmium ions and modified wheat bran sites. Beyond pH of 10, cadmium removal starts decreasing due to the cadmium hydroxide precipitation (Özer and Pirincci 2006; Sayen et al., 2006).

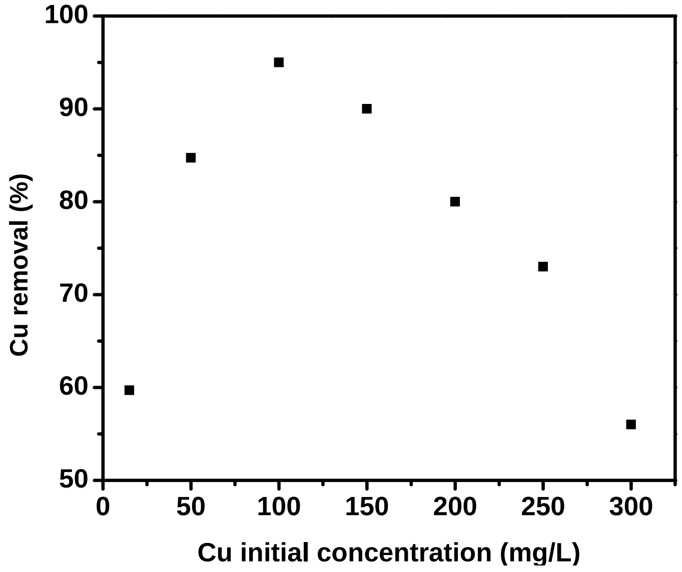
The possible chemical reactions for cadmium removal using modified wheat bran can be given as follows:

$2(MWB)\text{-}H + Cd^{2+} \rightarrow (MWB)_2Cd + 2H^{+}$ ....(4.10)

$(MWB)\text{-}H + Cd(OH)^{+} \rightarrow MWB\text{-}Cd(OH) + H^{+}$ ....(4.11)


Cu Removal (%)
100
90
80
70
60
50
15
32
49
66
83
100
A: metal ion conc. (mg/L)
2
3.6
5.2
6.8
8.4
10
B: pH
0.5
1.4
2.3
3.2
4.1
5
C: Adsorbent dose (g/L)
17
24.6
32.2
39.8
47.4
55
D: Temperature (°C)

(a) (b) (c) (d) (e) (f)



(g)

Fig. 4.13 Response surface plots for combined effect of (a) metal ion concentration and pH, (b) pH and adsorbent dose, (c) pH and temperature, (d) metal ion concentration and adsorbent dose, (e) metal ion concentration and temperature and (f) adsorbent dose and temperature (g) Initial metal concentration (from 15-300 mg/L) on removal efficiency of copper

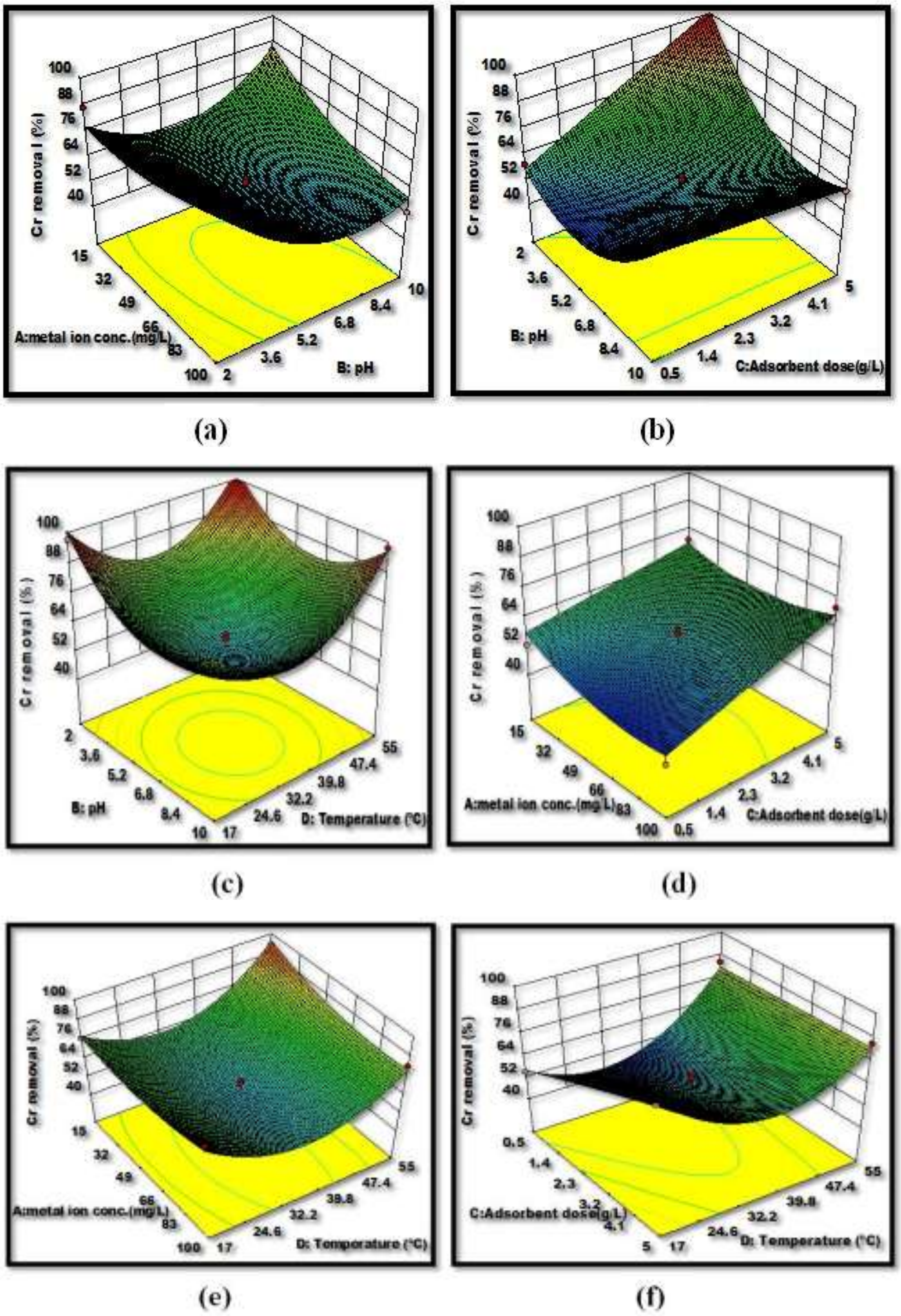
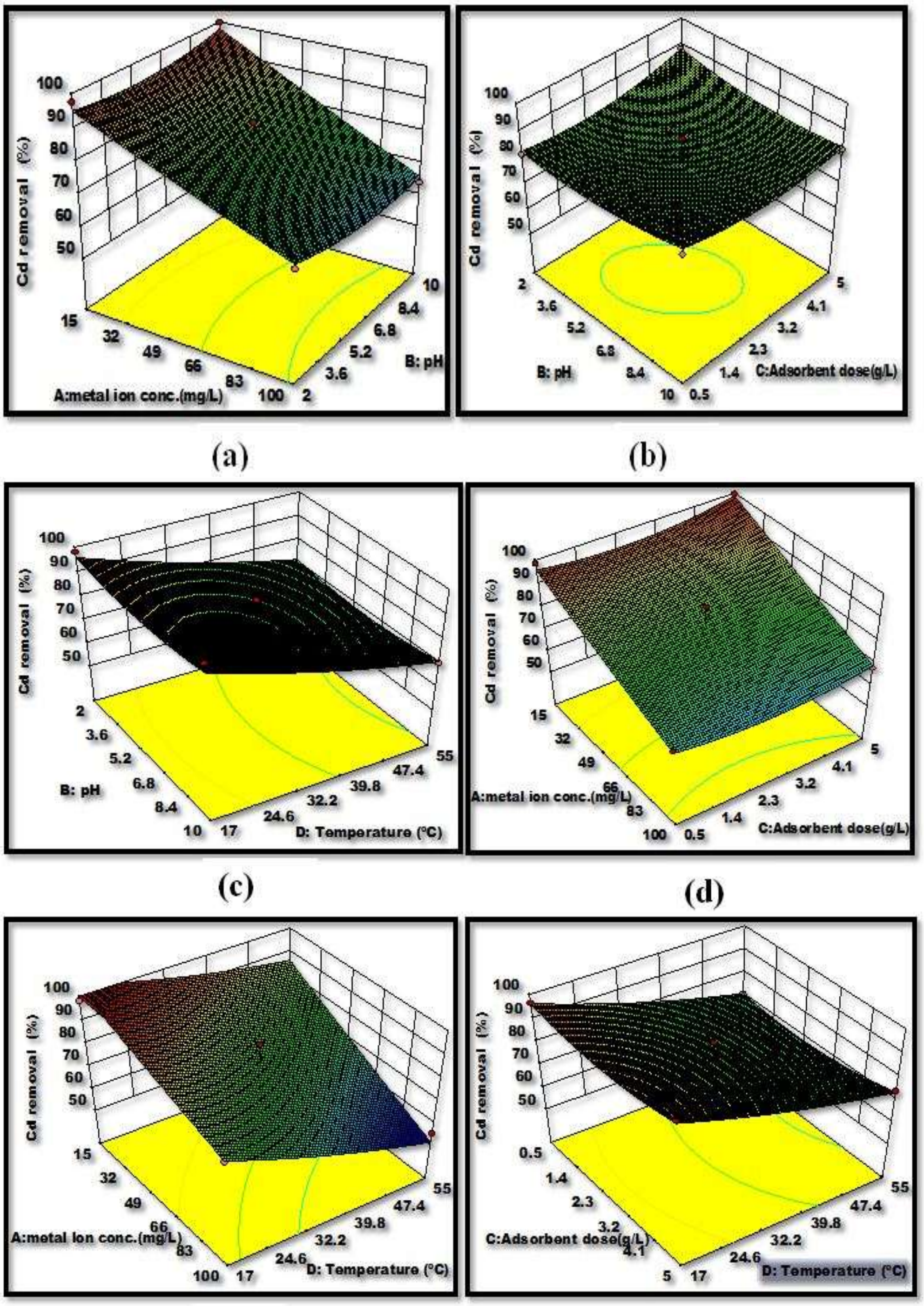


Fig. 4.14 Response surface plots for combined effect of (a) metal ion concentration and pH, (b) pH and adsorbent dose, (c) pH and temperature, (d) metal ion concentration and adsorbent dose, (e) metal ion concentration and temperature, (f) adsorbent dose and temperature on removal efficiency of chromium.



(a) (b) (c) (d) (e) (f)

Fig. 4.15 Response surface plots for combined effect of (a) metal ion concentration and pH, (b) pH and adsorbent dose, (c) pH and temperature, (d) metal ion concentration and adsorbent dose, (e) metal ion concentration and temperature, (f) adsorbent dose and temperature on removal efficiency of cadmium.

4.5.1.5 Optimization

Further optimization was performed by numerical analysis. The best local maximum value is found is at pH of 6, initial metal concentration 90.58 mg/L, temperature 35.9°C and adsorbent dose 2.39 gram. Removal efficiency obtained at these conditions is 98.54% for copper, 54.19% for cadmium and for 68.04% for chromium; the desirability for these heavy metals is 0.919 (Fig. 4.16). Further, the removal efficiency was verified with experimental results, which showed removal efficiency of 98%, 54% and 68% for copper, cadmium and chromium, respectively conforming the agreement in those obtained using Box-Behnken design. Thus it shows that Box-Behnken design can be used effectively.

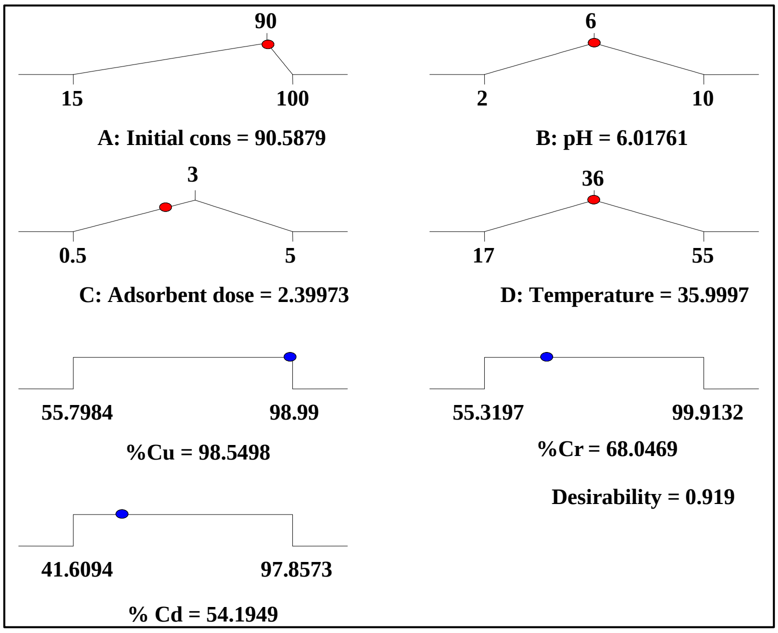


Fig. 4.16 Desirability ramp for numerical optimization obtained by software Design Expert®

4.5.1.6 Equilibrium modelling

The value of adsorption energy further provides information as to whether adsorption process is physical or chemical in nature and Fig. 4.17(a–d), Fig. 4.18(a–d) and Fig. 4.19(a–d) show the equilibrium data for fitting Freundlich, Langmuir, D-R (Dubinin-Radushkevitch), and Temkin isotherms for copper, cadmium and chromium removal. The values of isotherm parameters, R^2 and RMSE (root mean square error) are shown in Table 4.7. It is concluded that for copper, chromium and cadmium removal, Langmuir and Temkin isotherms are the best suitable.

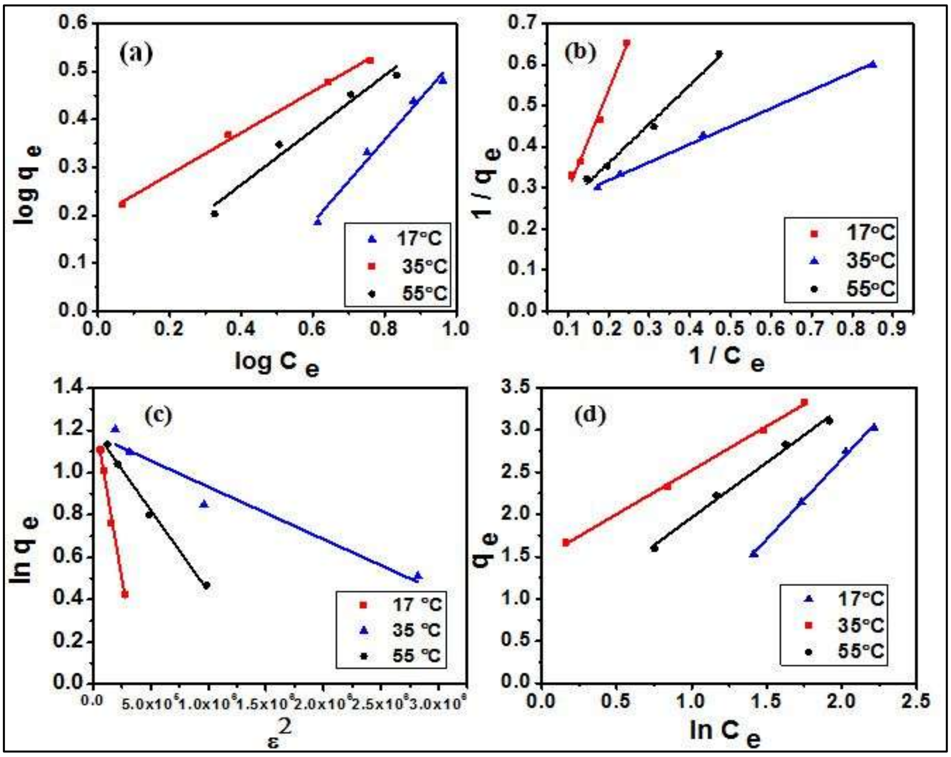


Fig. 4.17 Isotherm plots (a) Freundlich (b) Langmuir (c) D-R (d) Temkin for adsorption of copper

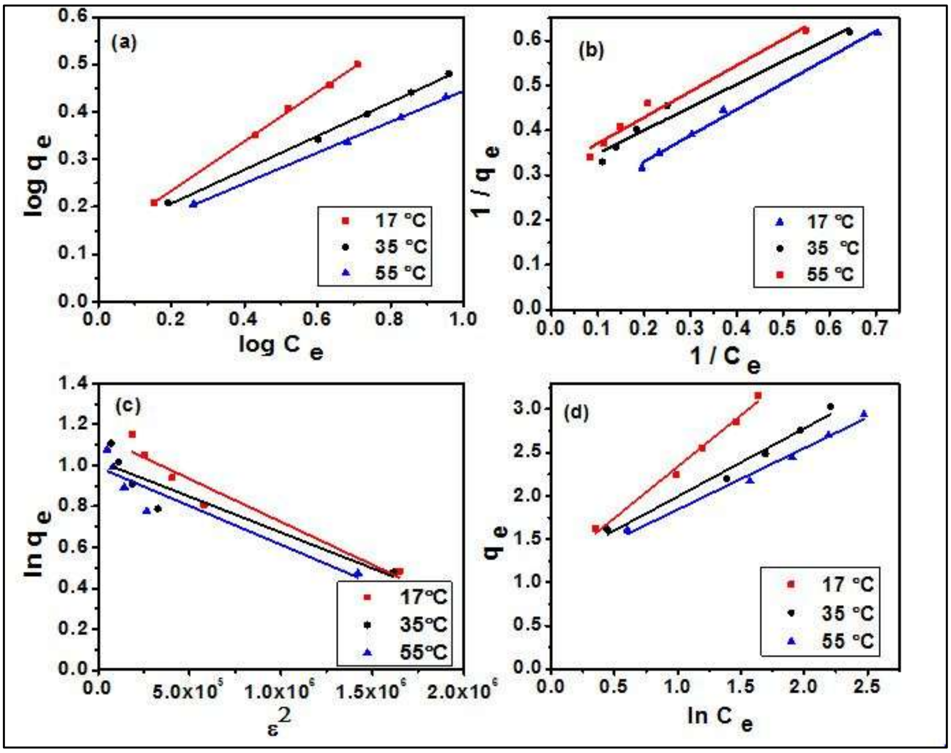


Fig. 4.18: Isotherm plots (a) Freundlich (b) Langmuir (c) D-R (d) Temkin for the adsorption of cadmium

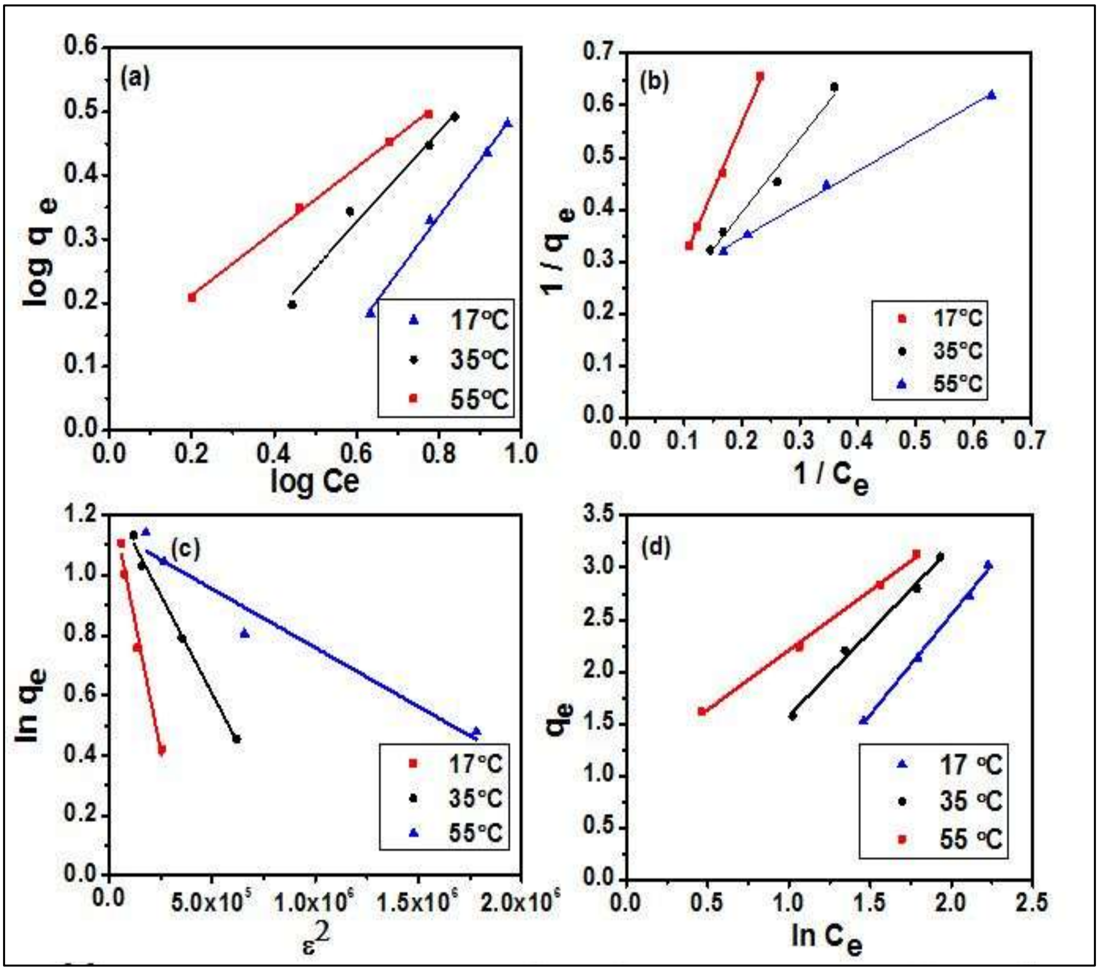


Fig. 4.19 Isotherm plots (a) Freundlich (b) Langmuir (c) D-R (d) Temkin for adsorption of chromium

Table 4.7 Kinetic parameters for adsorption on modified wheat bran

Isotherm	**T=17°C**			**T=35°C**			**T=55°C**		
	Cu	**Cr**	**Cd**	**Cu**	**Cr**	**Cd**	**Cu**	**Cr**	**Cd**
Freundlich									
k_f	0.718	0.691	1.137	1.219	0.902	1.146	1.035	1.117	1.126
1/n	0.860	0.882	0.521	0.434	0.716	0.355	0.570	0.501	0.325
R^2	0.984	0.996	0.998	0.971	0.997	0.976	0.996	0.999	0.998
RMSE	1.010	1.000	1.084	1.180	1.054	1.023	1.070	1.078	0.983
Langmuir									
q_m	20.40	20.83	4.673	4.330	9.000	3.367	5.850	4.629	3.205
k_L	0.020	0.018	0.368	0.529	0.078	0.578	0.182	0.335	0.538
R^2	0.990	0.997	0.992	0.990	0.982	0.968	0.990	0.998	0.971
RMSE	0.082	0.033	0.062	0.045	0.079	0.118	0.075	0.032	0.104
D-R									
B	3×10^{-6}	3×10^{-6}	4×10^{-7}	2×10^{-7}	1×10^{-6}	3×10^{-7}	8×10^{-7}	4×10^{-7}	4×10^{-7}
q_m	3.636	3.589	3.136	3.254	3.532	2.778	3.336	3.158	2.694
R^2	0.994	0.985	0.932	0.947	0.994	0.872	0.992	0.952	0.874
RMSE	0.578	1.513	0.164	0.667	1.522	1.371	0.827	0.588	0.187
Temkin									
B	1.895	1.925	1.187	1.042	1.621	0.786	1.303	1.144	0.707
k_T	0.549	1.925	2.637	4.142	1.621	4.644	1.661	1.144	4.979
b_T	1272	1252	2031	2457	1579	3257	2092	2383	3857
R^2	0.997	0.997	0.988	0.998	0.993	0.980	0.992	0.997	0.988
RMSE	0.027	0.029	0.093	0.021	0.048	0.068	0.049	0.028	0.049

4.5.1.7 Kinetic modelling

Pseudo-first order and pseudo-second order kinetic parameters were used to describe the adsorption kinetics (Table 4.8).

From Table 4.8, it is clear that pseudo-second order kinetic model has high value of R^2 as compared to that for pseudo-first order kinetic model. Theoretical value of q_e for copper, chromium and cadmium removal are found to be closer to experimental value ($q_{e\ (exp)}$) for the case of pseudo-second order rate kinetics (Fig. 4.20(a—c); Fig. 4.21 (a—c); Fig. 4.22(a—c); Fig. 4.23 (a—c); ; Fig 4.24(a—c); Fig. 4.25 (a—c)).

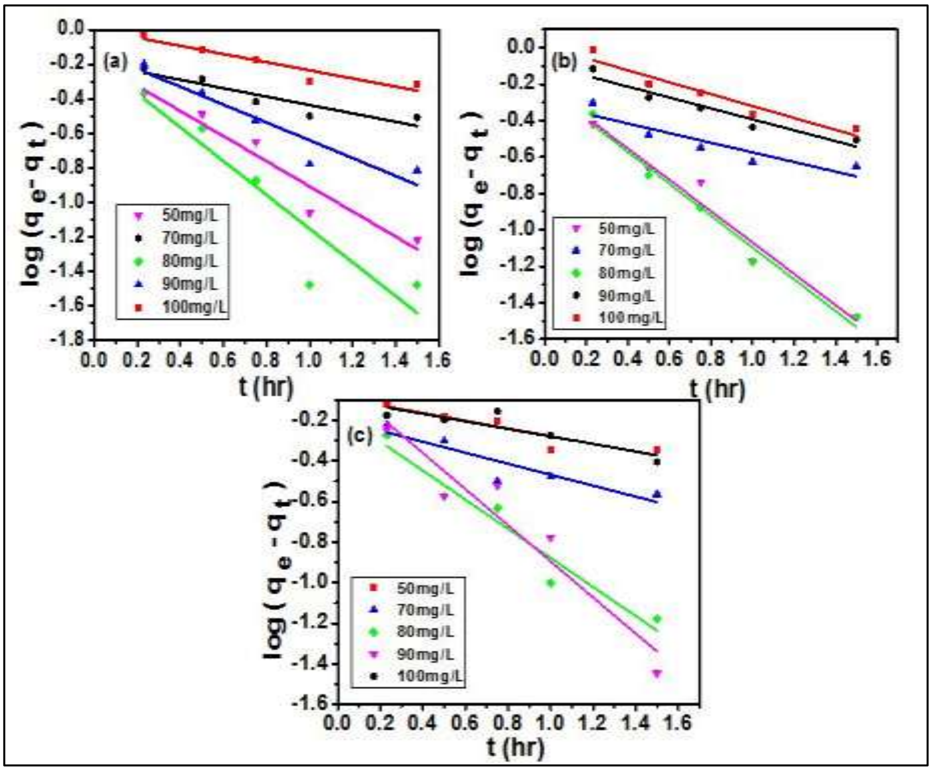


Fig. 4.20 Pseudo-first order kinetic plots for adsorption of Copper at (a) 17 °C (b) 35 °C (c) 55 °C

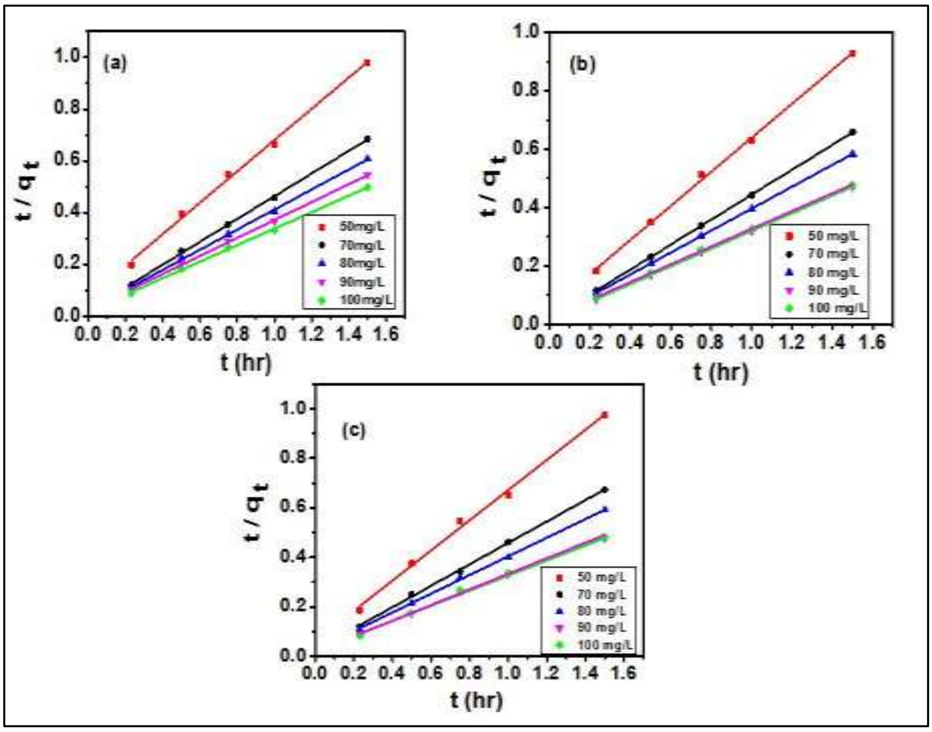


Fig. 4.21 Pseudo-second order kinetic plots for adsorption of Copper at (a) 17 °C (e) 35 °C (f) 55 °C

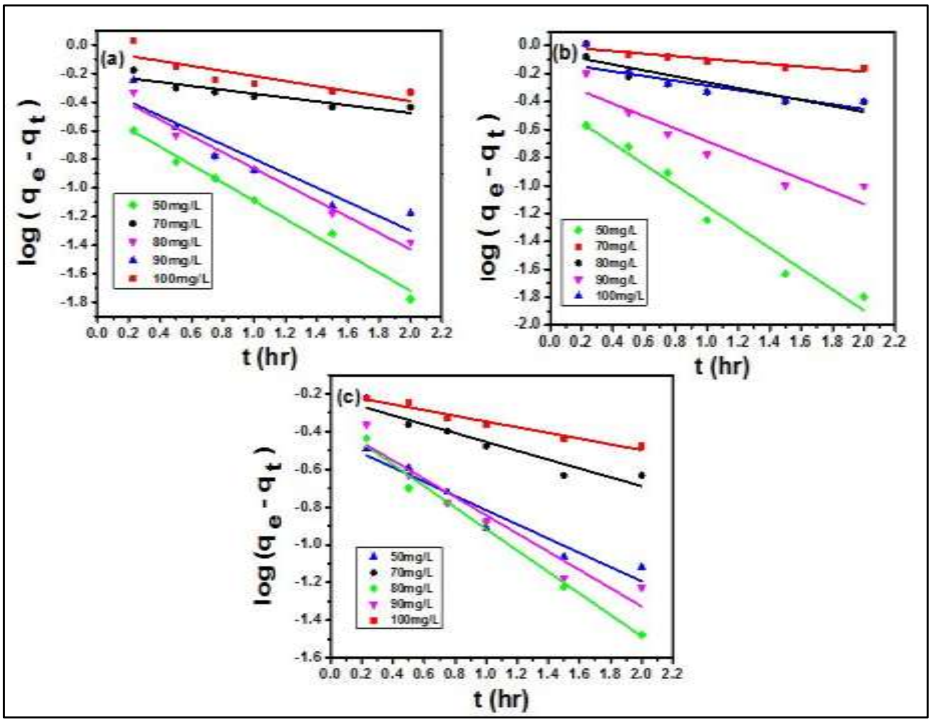


Fig. 4.22 Pseudo-first order kinetic plots for adsorption of Chromium at (g) 17 °C (h) 35 °C (i) 55 °C

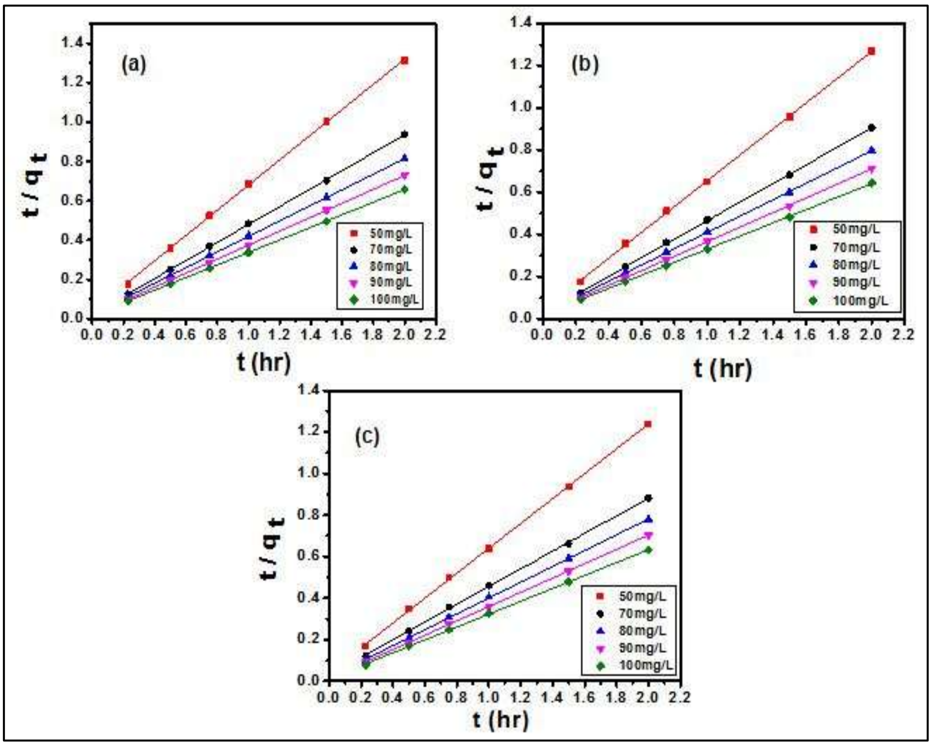


Fig. 4.23 Pseudo-second order kinetic plots for adsorption of Chromium at (a) 17 °C (b) 35 °C (c) 55 °C

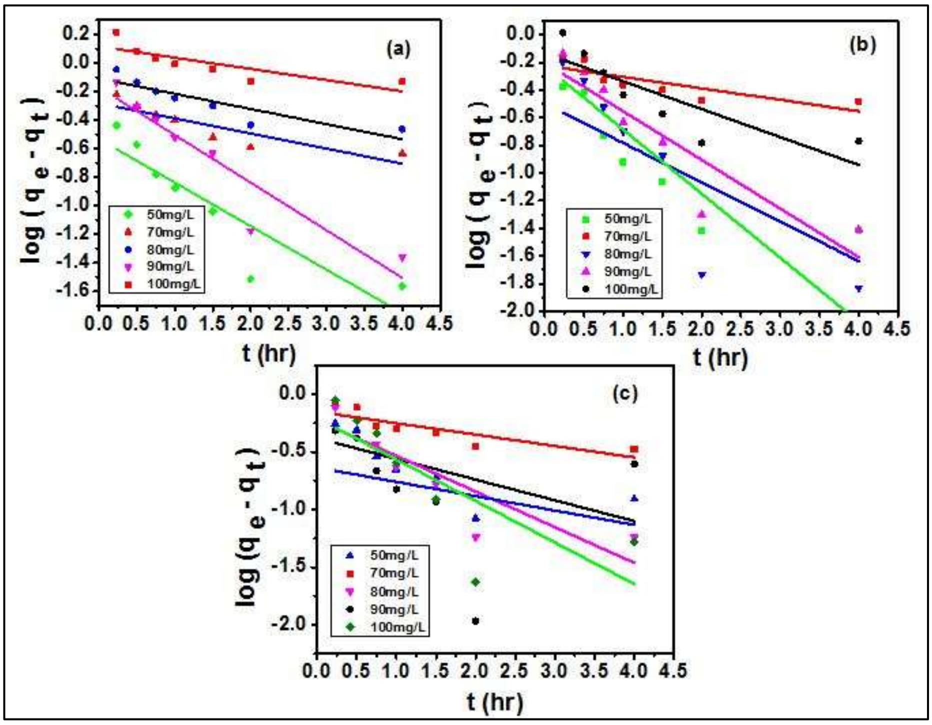


Fig. 4.24 Pseudo-first order kinetic plots for adsorption of Cadmium at (a) 17 °C (b) 35 °C (c) 55 °C

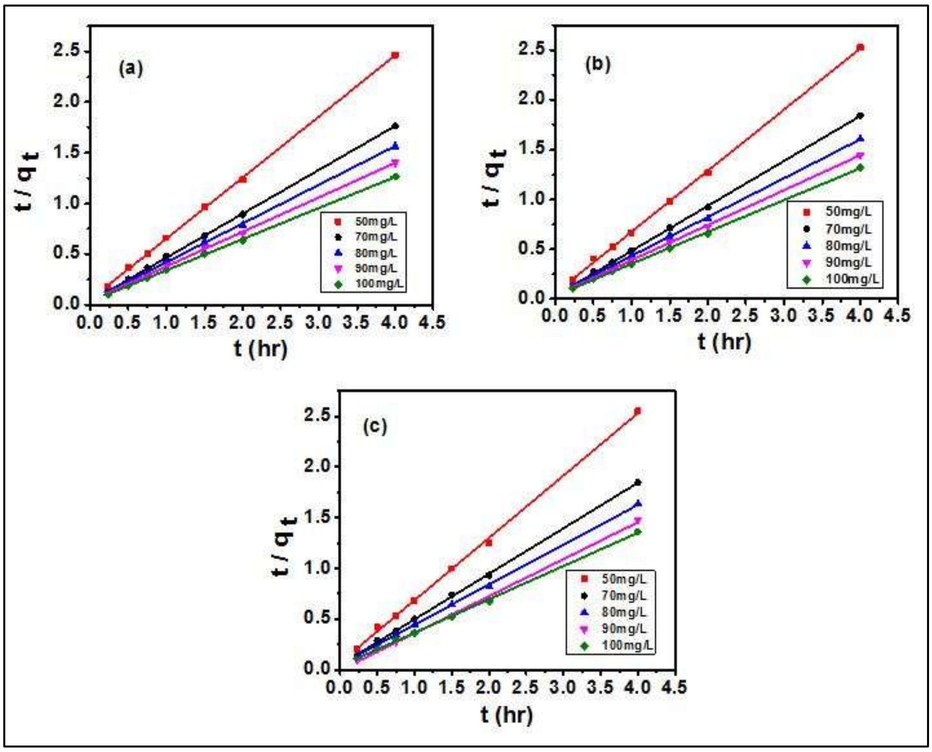


Fig. 4.25 Pseudo-second order kinetic plots for adsorption of Cadmium at (a) 17 °C (b) 35 °C (c) 55 °C

4.5.1.8 Thermodynamic modelling

In Table 4.8, positive values of ΔH for copper and chromium shows that adsorption is endothermic, however negative value of ΔH for cadmium shows that adsorption is exothermic reaction. For physical adsorption, ΔH is in the range of 20×10^3 – 40×10^3 J/mol thus in our work, physical adsorption is prevalent. The negative values of ΔG indicate spontaneous nature of adsorption. The positive values of ΔS indicate that randomness increases at the solid/liquid interface during the adsorption process.

Table 4.8 Kinetic and Thermodynamic parameters for adsorption of Cd(II), Cr(VI) and Cu(II) on modified wheat bran at optimum temperature (308 K)

		Cu	**Cr**	**Cd**
	$q_{e\ (exp)}$	3.241	3.167	3.030
Pseudo first order Kinetics	k_1 (1/min)	0.751	0.486	0.463
	q_e (mg/g)	1.098	0.952	0.874
	R^2	0.926	0.771	0.708
Pseudo second order kinetics	k_2 (1/min)	3.992	4.837	2.994
	q_e (mg/g)	3.300	3.215	3.134
	R^2	0.999	0.999	0.999
Thermodynamic Parameter	ΔG (J/mol)	-9543.700	-7253.850	-8806.170
	ΔH (J/mol)	13,159	22,080	-5413
	ΔS (J/mol K)	68.400	95.590	10.800

4.5.1.9 Comparison of adsorption capacity of other adsorbents used for heavy metal removal

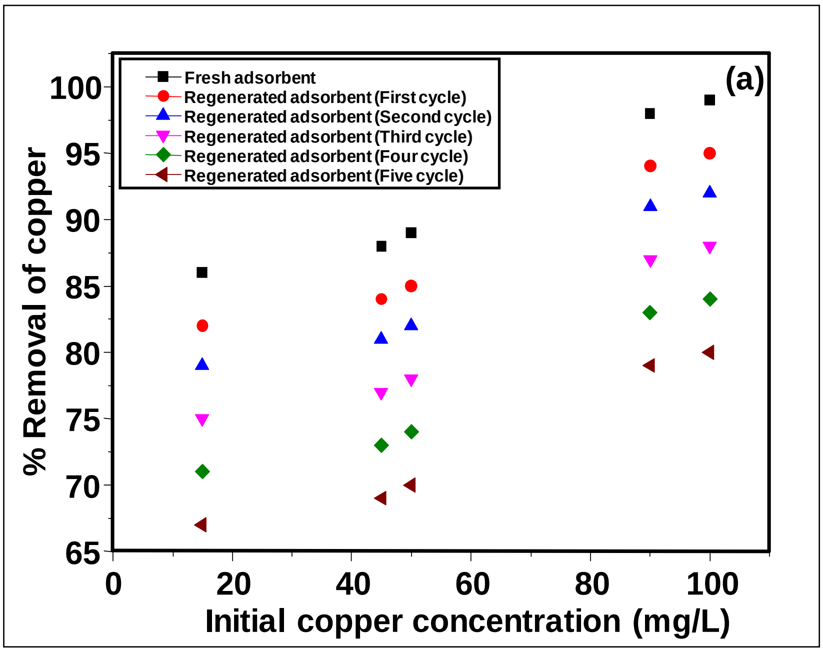
Table 4.9 shows adsorption capacities of various adsorbents for copper, chromium and cadmium removal from literature. It can be observed from this table that modified wheat bran has highest adsorption capacity for chromium and then for copper and cadmium removal.

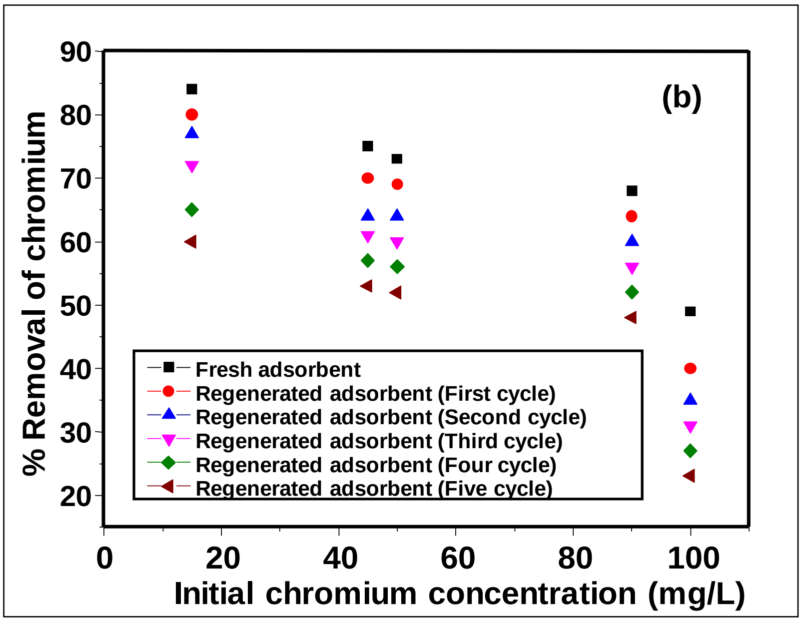
Table 4.9 Adsorption capacities of various biosorbents for Cu(II), Cr(VI) and Cd(II)

Heavy metal	Bio-adsorbent	Adsorption capacity (mg/g)	Percent removal (%)	Reference
Copper	Sugarcane bagasse	3.65	84.58%	Putra et al., 2014
	Maize corncob	3.70	80.80%	Duru and Duru., 2017
	Papaya wood	1.62	97.80%	Saeed et al., 2005
	Modified wheat bran	4.33	98.55%	Present study
Chromium	Dust coal	4.40	50.40%	Selomulya et al., 1999
	Cactus	7.08	55.20%	Dakiky et al., 2002
	Rice straw	3.15	68.00%	Gao et al., 2008
	Rice husk	8.50	40.00%	Bansal et al., 2009
	Modified wheat bran	9.00	68.04%	Present study
Cadmium	Rice husk ash	3.04	29.80%	Srivastava et al., 2008
	Sponge iron sphere	1.86	40.00%	Li et al., 2011
	Modified wheat bran	3.37	54.19%	Present study

4.5.1.10 Regeneration studies

The disposal of saturated adsorbent containing copper, cadmium and chromium is harmful for the environment and it is also against the environmental constraints. Thus the saturated adsorbent is regenerated and used for removal of copper, cadmium and chromium at different initial concentration from 15-100 mg/L. Fig. 4.26 (a)—(c) shows comparison of percent removal of copper, cadmium and chromium using fresh adsorbent and regenerated adsorbent in five cycles. The percent removal of cadmium and chromium decreases from 82% to 40%, 84% to 49% and increases from 86% to 99% for copper on increasing metal concentration from 15 mg/L to 100 mg/L using fresh adsorbent i.e. modified wheat bran. However after regeneration of adsorbent, percent removal decreases for cadmium from 79% to 37%, 75% to 34%, 71% to 32%, 67% to 25% and 61% to 20% for first, second, third, fourth and fifth cycle on increasing metal concentration from 15 mg/L to 100 mg/L. Similarly, for chromium percent removal decreases from 80% to 40%, 77% to 35%, 72% to 31%, 65% to 27% and 60% to 23% for first, second, third, fourth and fifth cycle respectively. However, for copper percent removal increases 82% to 95%, 79% to 92%, 75% to 88%, 71% to 84%, 67% to 80% for first, second, third, fourth and fifth cycle on increasing metal concentration from 15 mg/L to 100 mg/L respectively. These results shows that good desorption efficiency is obtained using regenerated wheat bran.





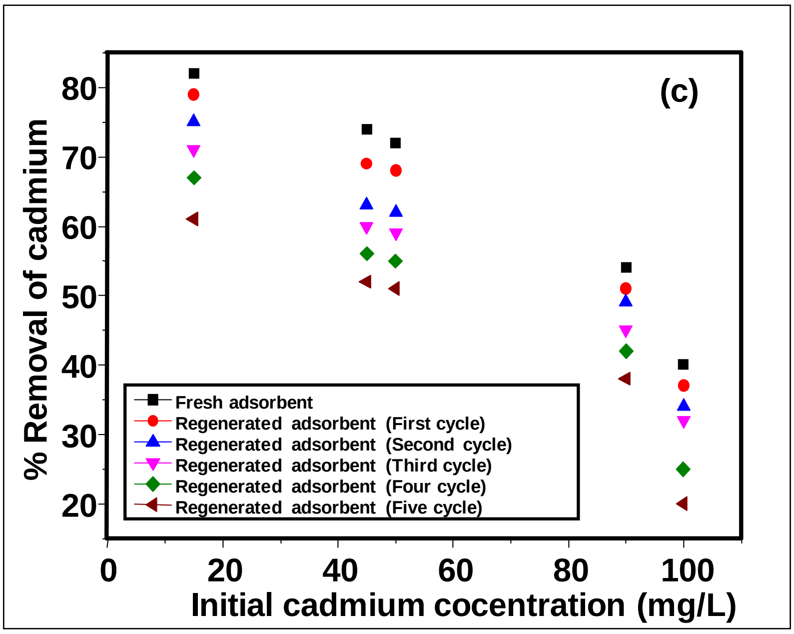


Fig. 4.26 Percentage removal of (a) Copper (b) Chromium (c) Cadmium using fresh and regenerated adsorbent

4.5.2 Mixed metal study

4.5.2.1 Design of experiments

In this study all three metals such as copper, cadmium and chromium were mixed together as a ternary system. The effect of several parameters such as adsorbent dose, initial concentration of copper, initial concentration of chromium and initial concentration of cadmium were investigated at optimum pH of 6 and temperature of 35.99 °C using response surface methodology (Table 4.10). The experimental design was generated using Design expert 9.0.6. A total of 29 experiments were performed (Table 4.11).

Table 4.10 Process factors and their levels

Factor Coded values	**-1**	**0**	**1**
Initial concentration of copper (mg/L)	15	57.5	100
Initial concentration of cadmium (mg/L)	15	57.5	100
Initial concentration of chromium (mg/L)	15	57.5	100
Adsorbent dose (gram)	0.5	2.75	5

Table 4.11: Box–Behnken design matrix for four variables and response values

Run	**Initial metal conc. of Cu (A)**	**Initial metal conc. of Cd (B)**	**Initial metal conc. of Cr (C)**	**Adsorbent dose (D)**	**Response(R)**		
					Cu removal (%)	**Cd removal (%)**	**Cr removal (%)**
1	57.5	57.5	57.5	2.75	87.042	97.141	94.170
2	15	57.5	57.5	0.5	93.480	97.141	73.319
3	57.5	15	100	2.75	87.751	88.339	95.854
4	100	57.5	100	2.75	90.871	90.173	99.331
5	57.5	57.5	57.5	2.75	89.788	97.141	98.210
6	100	57.5	57.5	0.5	80.654	92.510	78.092
7	57.5	100	100	2.75	97.897	95.648	87.484
8	57.5	57.5	100	0.5	100.000	88.235	70.276
9	100	15	57.5	2.75	60.302	90.742	99.836
10	15	57.5	100	2.75	85.080	92.369	96.469
11	57.5	57.5	57.5	2.75	85.364	97.141	98.210
12	57.5	57.5	57.5	2.75	93.364	97.141	97.170
13	57.5	15	15	2.75	89.005	98.460	96.902
14	57.5	100	15	2.75	81.861	100.000	98.933
15	100	57.5	15	2.75	97.726	99.315	96.920
16	100	57.5	57.5	5	100.000	94.995	85.589
17	15	57.5	57.5	5	77.860	99.223	94.000
18	15	15	57.5	2.75	95.632	96.920	98.444
19	57.5	57.5	100	5	100.000	93.157	90.062
20	57.5	15	57.5	5	98.429	93.683	92.548
21	57.5	57.5	15	0.5	97.376	96.384	82.218
22	57.5	100	57.5	5	75.176	99.061	86.888
23	57.5	100	57.5	0.5	95.080	96.448	77.669
24	57.5	57.5	57.5	2.75	86.846	97.141	98.786
25	57.5	57.5	15	5	100.000	99.482	85.163
26	15	100	57.5	2.75	52.670	99.497	96.894
27	100	100	57.5	2.75	94.116	98.300	92.697
28	57.5	15	57.5	0.5	76.522	92.660	78.833
29	15	57.5	15	2.75	73.738	100.000	99.920

4.5.2.2 Statistical analysis

The residual plots were analysed for model adequacy in Fig. 4.27 (a—c), Fig. 4.28 (a—c), Fig. 4.29 (a—c), Fig. 4.30 (a—c). Fig. 4.27 (a—c) Shows plot between actual and predicted removal percent for copper, cadmium and chromium. In Fig. 4.27 (a—c) the actual value of R^2 and predicted value of R^2 were found to be 0.95 and 0.91 for copper, 0.97 and 0.94 for cadmium and 0.97 and 0.94 for chromium respectively. Actual values are measured response data for a particular run, however predicted values are calculated from model and generated using approximating functions (Sahu et al., 2009). Further R^2 value determines goodness of fit of the model. In our work R^2 value shows that there is good fitness of regression models for obtaining the results. In our work R^2 value shows that there is good fitness of regression models for obtaining the results. Fig. 4.28 (a—c) are plot between % normal probability and externally studentized residuals and shows that how well model satisfies ANOVA assumption where studentized residual is the measure of number of standard deviation. They also show that neither response transformation was needed nor there was any problem with normality. Fig. 4.29 (a—c) shows plot between studentized residuals and predicted removal percent for copper, cadmium and chromium. These plots should be random scatter and suggesting the variance of original observation to be constant for all values of the response. Fig. 4.30 (a—c) shows plot between studentized residuals and runs. The residual values should lie in the range of ± 3.50 and any value outside this range is unused. In Fig. 4.30 (a—c) the value of studentized residuals lies in the interval of ± 3.50.

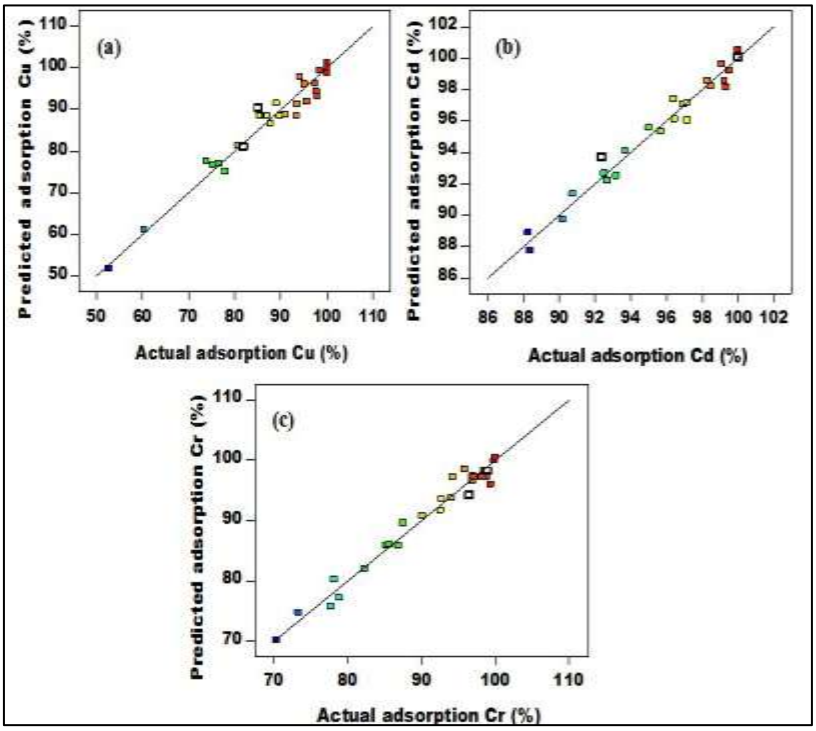


Fig. 4.27 The actual and predicted plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

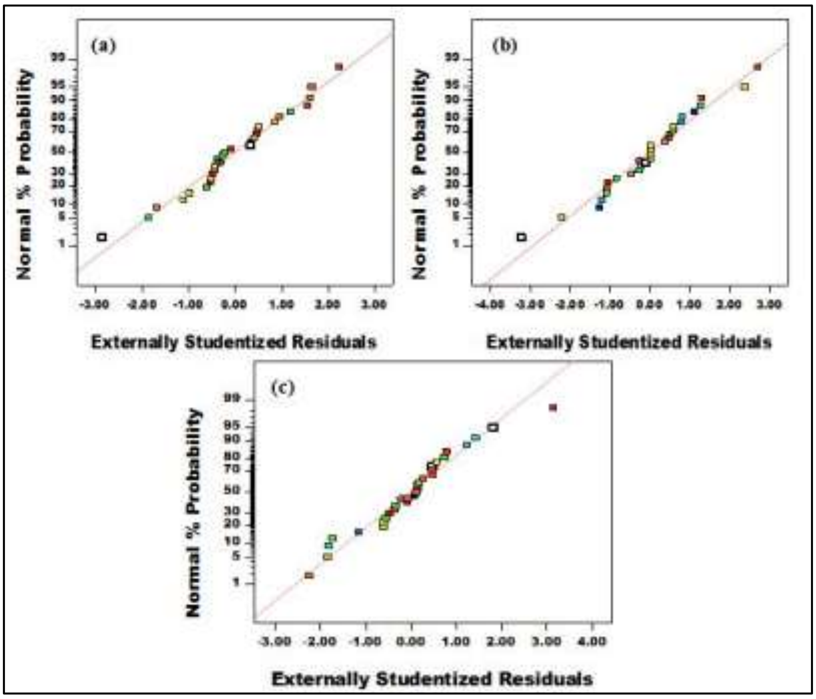


Fig. 4.28 Normal % probability and studentized residual plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

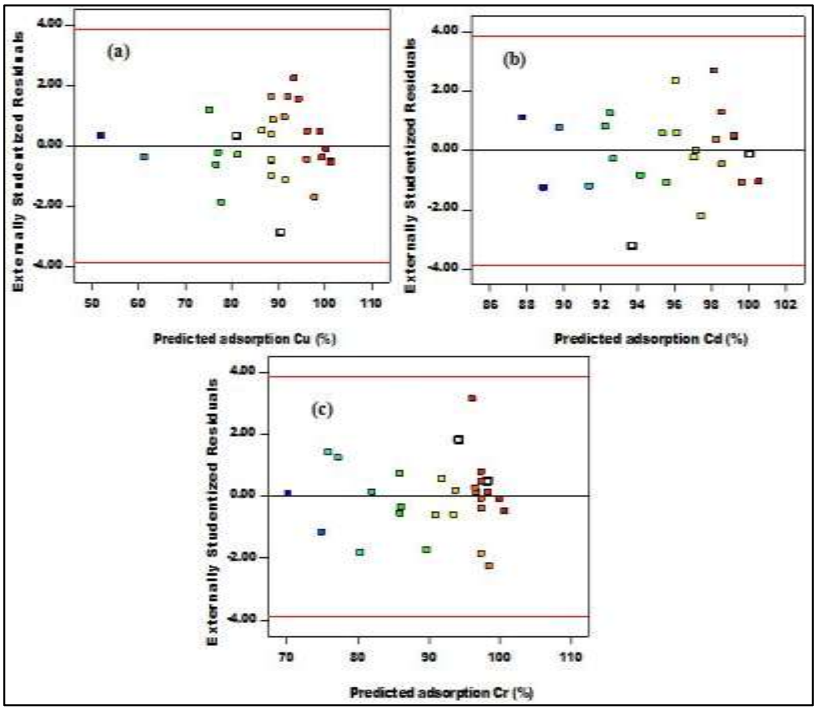


Fig. 4.29 The studentized residuals and predicted response plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

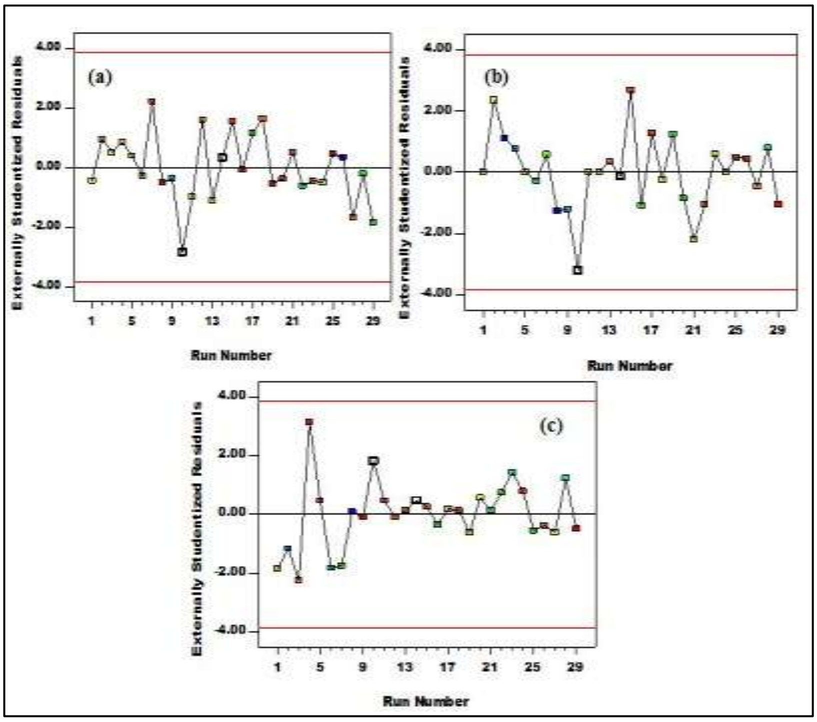


Fig. 4.30 Studentized residuals and and run number plot for (a) copper (b) Cadmium (c) Chromium uptake capacity of biosorbent

4.5.2.3 Analysis of variance

The following second-order polynomial model eqns. (4.12–4.13) are obtained from experimental data, and it demonstrates the relationship between copper, cadmium, and chromium removal efficiency (R_{Cu}, R_{Cd}, R_{Cr}) and independent variables (A, B, C, D). These polynomial model eqns. (4.12–4.13) are applicable for $A=B=C=D\neq0$.

$$R_{Cu}\,(\%) = +88.48 + 3.77 * A - 0.90 * B + 1.82 * C + 0.70 * D + 19.19 * AB - 4.55 * AC + 8.74 * AD + 4.32 * BC -10.45 * BD - 0.66 * CD - 6.53 * A^2 - 6.24 * B^2 + 5.87 * C^2 + 5.03 * D^2 \qquad \text{…..(4.12)}$$

$$R_{Cd}\,(\%) = +97.14 – 1.59*A + 2.35*B - 3.81* C + 1.35 * D + 1.25\, A*B - 0.38\, A*C + 0.10\, A*D + 1.44\, B*C + 0.40\, B*D + 0.46\, C*D - 0.20*A^2 - 0.38*B^2 - 1.41*C^2 - 1.23*D^2 \qquad \text{…..(4.13)}$$

$$R_{Cr}\,(\%) = +97.31 – 0.55*A -1.82*B – 1.71* C + 6.15 * D -1.40\, A*B +1.47\, A*C – 3.30\, A*D -2.60\, B*C -1.12\, B*D + 4.21\, C*D + 0.52*A^2 - 0.55*B^2 – 0.98*C^2 – 14.09*D^2 \qquad \text{…..(4.14)}$$

Table 4.12 shows ANOVA for response surface quadratic model. The model F value is 20.84, 34.66, and 34.79 for copper, cadmium, and chromium, and this value measures how well factors describe the variation in the data about its mean. Probability value (P) is a measurement of effects in a model that should be less than 0.05 for being significant, and in our work probability values are less than 0.05 for parameters A, AB, AC, AD, BC, BD, A^2, B^2, C^2 and D^2 for copper; A, B, C, D, AB, BC, C^2, D^2 for cadmium; and B, C, D, AD, BC, CD, D^2 for chromium. It means that only these parameters are significant for copper, cadmium, and chromium removal. Adequate precision ratio is 19.211 for copper removal, 21.629 for cadmium removal, and 20.484 for chromium removal, which is much higher than the minimum desirable amount 4 and it indicates that there is the presence of adequate signal to noise ratio for this model (Ahmadi et al., 2014; Srinivasan & Viraraghavan 2010).

Table 4.12 ANOVA results for the response surface quadratic model for copper, chromium and cadmium

For copper

R-Squared = 0.9542; Adj R-Squared = 0.9084

Source	Sum of squares	Degree of freedom	Mean square	F-Value	P-Value	
Model	3728.11	14	266.29	20.84	< 0.0001	Significant
A- Cu	170.31	1	170.31	13.33	0.003	
B-Cd	9.79	1	9.79	0.77	0.39	
C-Cr	39.94	1	39.94	3.13	0.09	
D-dose	5.82	1	5.82	0.46	0.51	
AB	1473.62	1	1473.62	115.30	< 0.0001	
AC	82.78	1	82.78	6.48	0.02	
AD	305.66	1	305.66	23.92	0.0002	
BC	74.74	1	74.74	5.85	0.03	
BD	437.05	1	437.05	34.20	< 0.0001	
CD	1.72	1	1.72	0.13	0.72	
A^2	276.17	1	276.17	21.61	0.0004	
B^2	252.24	1	252.24	19.74	0.001	
C^2	223.64	1	223.64	17.50	0.001	
D^2	164.16	1	164.16	12.84	0.003	
Residual	178.92	14	12.78			
Lack of Fit	138.91	10	13.89	1.39	0.40	Not significant
Pure Error	40.01	4	10.00			
Cor Total	3907.03	28				

For Cadmium

R-Squared = 0.9720; Adj R-Squared = 0.9439

Source	Sum of squares	Degree of freedom	Mean square	F-Value	P-Value	
A- Cu	328.57	14	23.47	34.66	< 0.0001	Significant
B-Cd	30.44	1	30.44	44.95	< 0.0001	
C-Cr	66.03	1	66.03	97.51	< 0.0001	
D-dose	174.19	1	174.19	257.22	< 0.0001	
AB	21.93	1	21.93	32.38	< 0.0001	
AC	6.20	1	6.20	9.16	0.01	
AD	0.57	1	0.57	0.84	0.37	
BC	0.04	1	0.04	0.06	0.81	
BD	8.32	1	8.32	12.28	0.004	
CD	0.63	1	0.63	0.93	0.35	
A^2	0.83	1	0.83	1.23	0.28	
B^2	0.27	1	0.27	0.40	0.54	
C^2	0.94	1	0.94	1.39	0.26	
D^2	12.82	1	12.82	18.93	0.001	
Residual	9.48	14	0.68			
Lack of Fit	9.48	10	0.95			
Pure Error	0.00	4	0.00			
Cor Total	338.05	28				

For Chromium

R-Squared = 0.9721; Adj R-Squared = 0.9439

Source	Sum of squares	Degree of freedom	Mean square	F-Value	P-Value	
Model	2075.74	14	148.27	34.79	< 0.0001	Significant
A- Cu	3.61	1	3.61	0.85	0.37	
B-Cd	39.79	1	39.79	9.34	0.01	
C-Cr	35.29	1	35.29	8.28	0.01	
D-dose	454.38	1	454.38	106.61	< 0.0001	

AB	7.81	1	7.81	1.83	0.19	
AC	8.59	1	8.59	2.02	0.17	
AD	43.45	1	43.45	10.19	0.01	
BC	27.05	1	27.05	6.35	0.02	
BD	5.05	1	5.05	1.19	0.29	
CD	70.90	1	70.90	16.64	0.001	
A^2	1.75	1	1.75	0.41	0.53	
B^2	1.93	1	1.93	0.45	0.51	
C^2	6.20	1	6.20	1.45	0.25	
D^2	1287.16	1	1287.16	302.00	< 0.0001	
Residual	59.67	14	4.26			
Lack of Fit	45.99	10	4.60	1.35	0.42	not significant
Pure Error	13.68	4	3.42			
Cor Total	2135.41	28				

4.5.2.4 Effect of process variables

The effects of process variables on removal of mixed copper, cadmium, and chromium have been described with the help of three-dimensional Fig. 4.31(a–f), Fig. 4.32(a)–(f), and Fig. 4.33(a)–(f).

(i) Effect of adsorbent dose

From Fig. 4.31(a, d), 4.32(a, d), 4.33(a, d), it is clear that copper, cadmium and chromium removal increases from 77% to 100%, 96% to 98% and 70% to 91% respectively with increase in adsorbent dose from 0.5 gram to 5 gram. This may be due to the availability of large surface area with more functional group at higher mass of adsorbent.

(ii) Effect of copper initial concentration

From Fig. 4.31(b, e), 4.33(a, d) it is clear that copper and chromium removal increases from 77% to 91% and 74% to 80% respectively with increase in copper concentration from 15 mg/L to 100 mg/L. This shows that presence of copper has synergistic effect on removal of copper and chromium. The magnitude of this synergistic effect increases with increase in copper concentration in the solution.

However, cadmium removal decreases from 96% to 92% with increase in copper concentration from 15 mg/L to 100 mg/L (Fig. 4.32(b, e)).This shows that presence of copper has antagonistic effect on removal of cadmium. The magnitude of this antagonistic effect increases with increase in copper concentration in the solution.

(iii) Effect of cadmium initial concentration

From Fig. 4.31 (c, f), 4.33 (b), it is clear that copper and chromium removal decreases from 91% to 53% and 77% to 75% with increase in cadmium concentration from 15 mg/L to 100 mg/L. This shows that presence of cadmium has antagonistic effect on removal of copper and chromium. The magnitude of this antagonistic effect increases with increase in cadmium concentration in the solution. However, from Fig. 4.25 (b, c, e, f), it is clear that cadmium removal increases form 87% to 95% with increase in cadmium concentration from 15 mg/L to 100 mg/L.

(iv) Effect of chromium initial concentration

From Fig. 4.31(b, e) it is clear that copper removal increases from 78% to 90% with increase in chromium concentration from 15 mg/L to 100 mg/L. This shows that presence of chromium has synergistic effect on removal of copper. The magnitude of this synergistic effect increases with increase in chromium concentration in the solution. From Fig. 4.32(c, f) and 4.33(c, f), it is clear that cadmium and chromium removal decreases from 98% to 87% and 82% to 70% with increase in chromium concentration from 15 mg/L to 100 mg/L respectively. This shows that presence of chromium has antagonistic effect on removal of cadmium and chromium. The magnitude of this antagonistic effect increases with increase in chromium concentration.

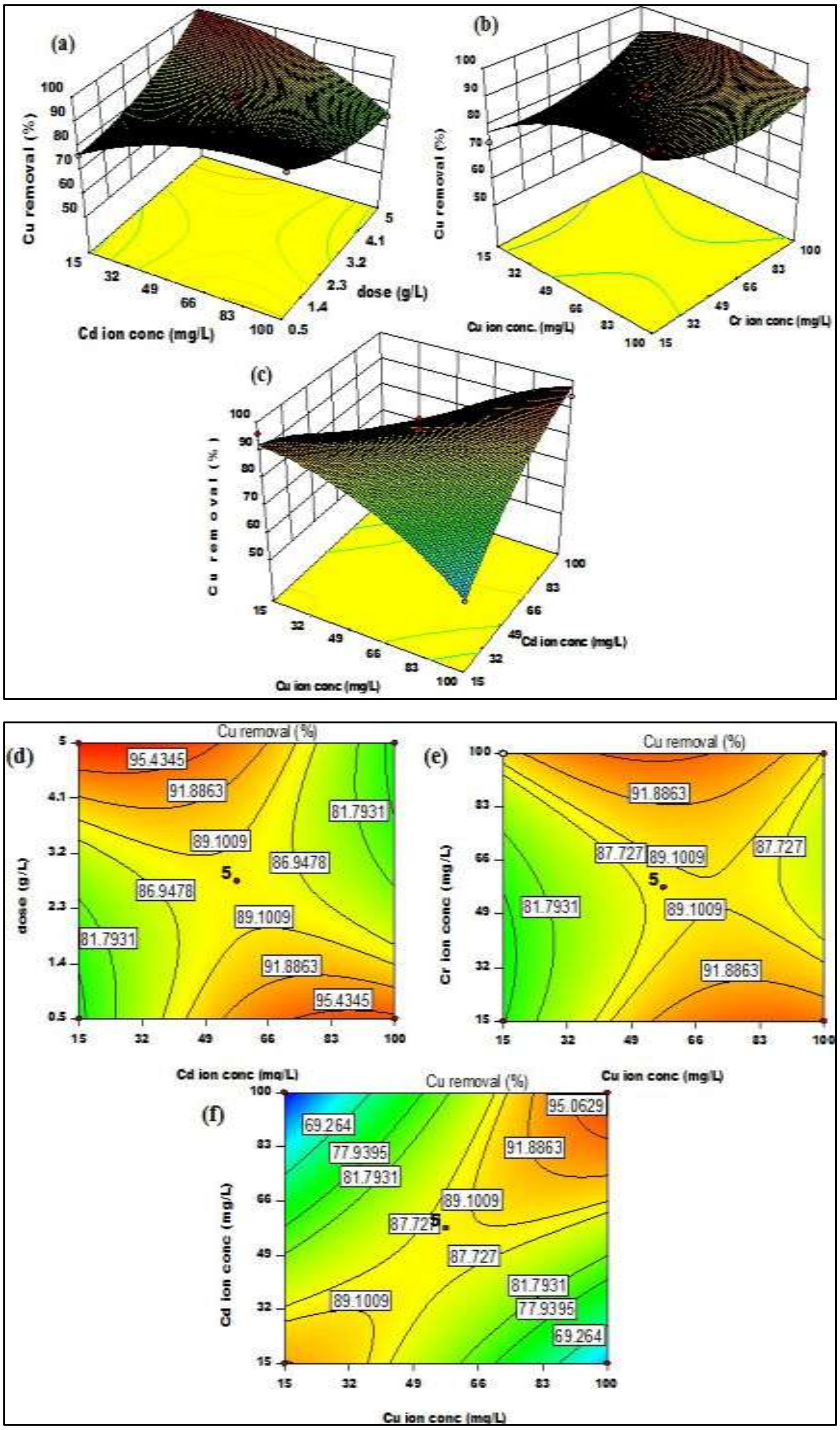


Fig. 4.31 Response surface 3-D plots for combined effect of (a) cadmium ion concentration and dose, (b) copper ion concentration and chromium ion concentration (c) copper ion concentration and cadmium ion concentration on removal efficiency of copper and response surface 2-D plots for combined effect of (d) cadmium ion concentration and dose, (e) copper ion concentration and chromium ion concentration (f) copper ion concentration and cadmium ion concentration on removal efficiency of copper

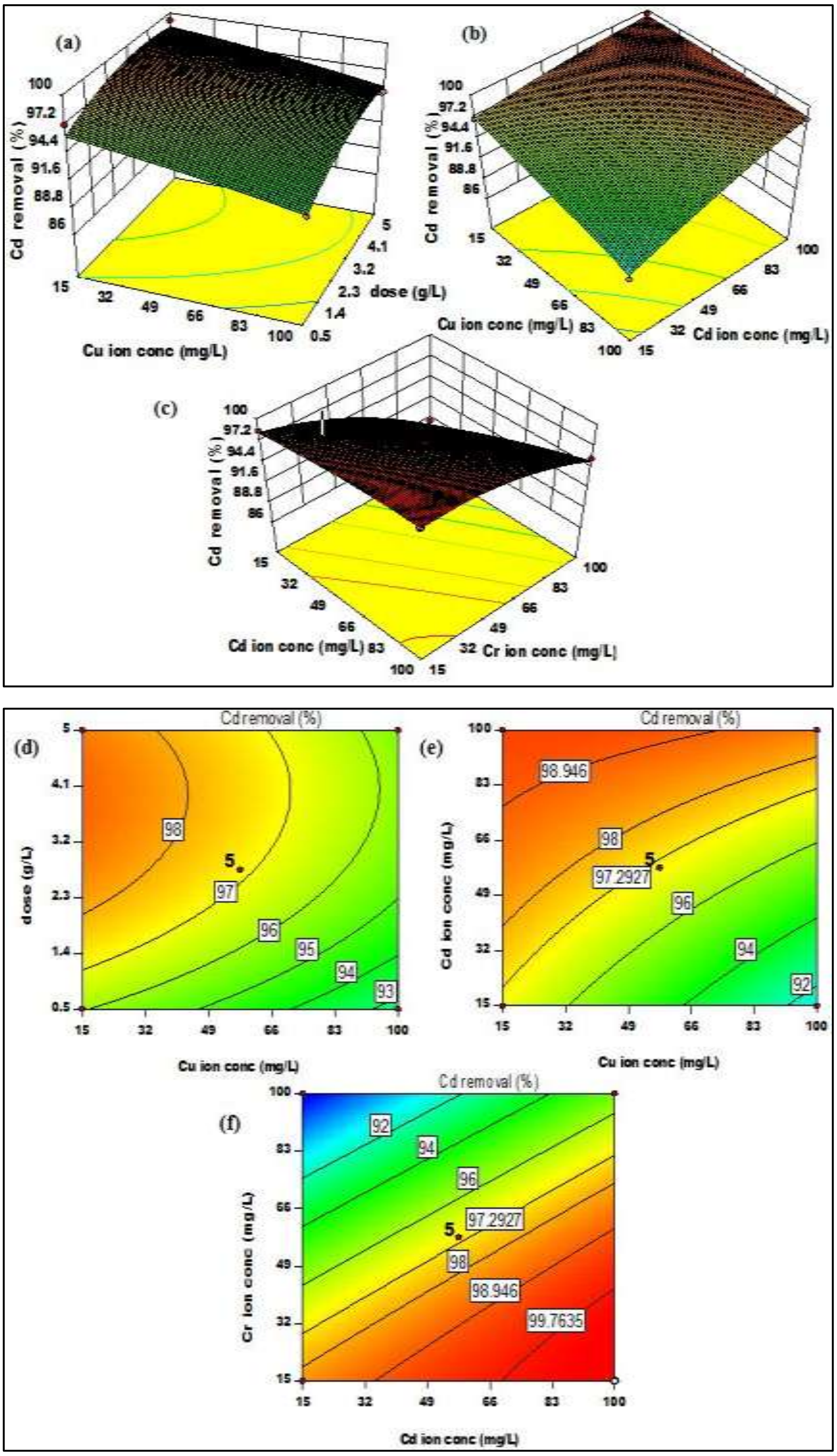


Fig. 4.32 Response surface 3-D plots for combined effect of (a) copper ion concentration and dose, (b) copper ion concentration and cadmium ion concentration, (c) cadmium ion concentration and chromium ion concentration and response surface 2-D plots for combined effect of (d) copper ion concentration and dose, (e) copper ion concentration and cadmium ion concentration, (f) cadmium ion concentration and chromium ion concentration on removal efficiency of cadmium.

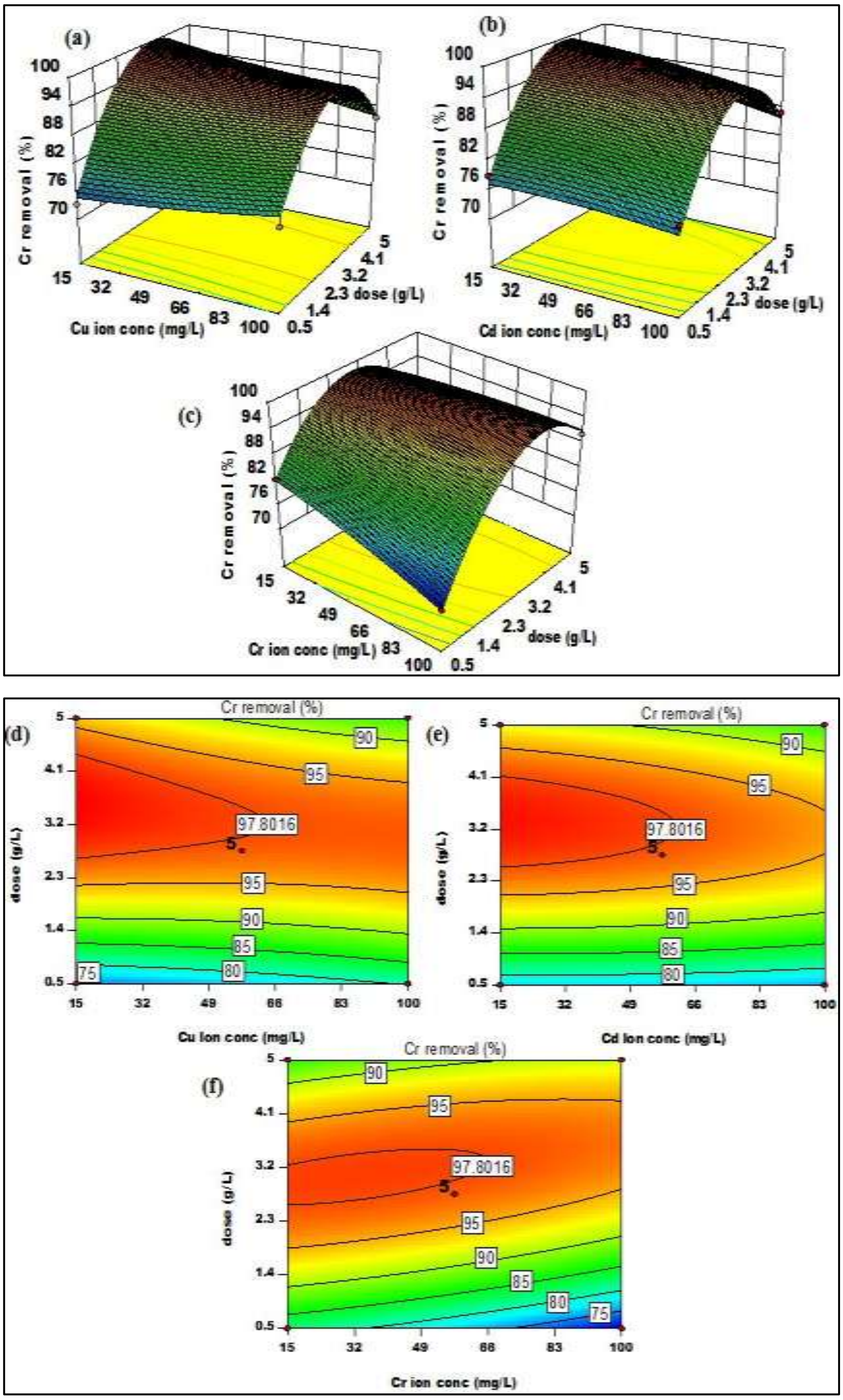


Fig. 4.33 **Response surface 3-D plots for combined effect of (a) copper ion concentration and dose (b) cadmium ion concentration and dose (c) chromium ion concentration and dose on removal efficiency of chromium and response surface 2-D plots for combined effect of (d) copper ion concentration and dose (e) cadmium ion concentration and dose (f) chromium ion concentration and dose on removal efficiency of chromium**

4.5.2.5 Antagonistic and synergistic effects in ternary system

Table 4.13 shows antagonistic and synergistic effects in ternary system. The parameters are copper, cadmium and chromium concentration for 15-100 mg/L and adsorbent dose 0.5-5 g.

Table 4.13 Antagonistic and synergistic effects in ternary system

Parameters	Variation	%Removal of chromium	%Removal of cadmium	%Removal of copper
Copper concentration	15-100 mg/L	Increases	Decreases (Antagonistic)	Increases
Cadmium concentration	15-100 mg/L	Decreases (Antagonistic)	Increases	Increases (Synergistic)
Chromium concentration	15-100 mg/L	Decreases (Antagonistic)	Decreases (Antagonistic)	Increases (Synergistic)
Adsorbent dose	0.5-5 g	Increases	Increases	Increases

4.5.3 Simultaneous removal of heavy metals and dye

4.5.3.1 Design of experiments

In this study all three metals such as copper, cadmium and chromium were mixed together with dye (acid black 60). The effect of several parameters such as pH, adsorbent dose, temperature, initial concentration of metals i.e. copper, chromium and cadmium and of dye were investigated using response surface methodology (Table 4.14). The experimental design was generated using Design expert 9.0.6. A total of 62 experiments were run was performed (Table 4.15).

Table 4.14: Process factors and their levels

Factor Coded values	-1	0	1
Initial concentration of copper (mg/L)	15	57.5	100
Initial concentration of cadmium (mg/L)	15	57.5	100
Initial concentration of chromium (mg/L)	15	57.5	100
Initial concentration of dye	15	107.5	200
Adsorbent dose (gram)	0.5	2.75	5
Temperature (°C)	17	36	55
pH	2	6	10

Table 4.15 Box–Behnken design matrix for four variables and response values

Run	Metal ion conc.				pH (B)	Dose (C)	Temp (D)	Response (R)			
								Removal (%)			
	Cu (A_1)	Cd (A_2)	Cr (A_3)	Dye (A_4)				Cu	Cd	Cr	Dye
1	15	57.5	57.5	200	2	2.75	36	18.00	13.77	66.92	14.00
2	57.5	57.5	57.5	15	6	0.5	17	65.00	96.56	45.17	25.00
3	57.5	15	100	15	6	2.75	36	97.34	100.00	100.00	91.90
4	57.5	57.5	100	107.5	10	5	36	96.82	44.76	38.00	36.20
5	100	15	57.5	107.5	6	0.5	36	100.00	16.00	58.00	97.31
6	15	57.5	100	107.5	6	2.75	17	45.00	100.00	20.00	40.00
7	15	100	57.5	107.5	6	0.5	36	96.67	100.00	16.00	13.12
8	57.5	57.5	57.5	107.5	6	2.75	36	85.53	99.33	60.80	76.00
9	57.5	57.5	57.5	107.5	6	2.75	36	74.36	98.81	67.58	70.00
10	57.5	15	100	200	6	2.75	36	35.00	50.80	37.00	16.11
11	100	100	57.5	107.5	6	5	36	100.00	18.79	90.00	17.56
12	57.5	15	57.5	107.5	10	2.75	55	35.00	74.00	77.00	95.00
13	57.5	15	15	200	6	2.75	36	20.00	13.33	82.00	98.29
14	57.5	57.5	57.5	15	6	5	55	85.00	100.00	65.00	52.18
15	57.5	57.5	15	107.5	2	0.5	36	35.86	81.42	95.00	30.79
16	57.5	57.5	57.5	200	6	0.5	55	76.00	20.00	74.33	49.00
17	57.5	57.5	57.5	200	6	5	55	68.00	21.00	58.00	50.00
18	15	15	57.5	107.5	6	0.5	36	96.66	100.00	45.00	96.91
19	15	15	57.5	107.5	6	5	36	96.67	99.81	58.00	99.00
20	57.5	57.5	57.5	15	6	0.5	55	92.01	100.00	64.00	15.00
21	100	57.5	57.5	15	2	2.75	36	87.00	18.53	90.00	90.68
22	57.5	100	57.5	107.5	10	2.75	17	46.00	99.27	15.00	45.00
23	57.5	100	57.5	107.5	10	2.75	55	99.00	55.31	77.63	21.00
24	100	57.5	15	107.5	6	2.75	17	20.00	55.00	98.00	55.00
25	57.5	57.5	57.5	107.5	6	2.75	36	79.82	87.46	75.75	88.89
26	100	15	57.5	107.5	6	5	36	90.00	16.00	59.00	74.00
27	57.5	57.5	15	107.5	10	0.5	36	35.00	51.37	95.00	94.69
28	100	57.5	100	107.5	6	2.75	17	87.00	17.04	70.00	14.50
29	100	100	57.5	107.5	6	0.5	36	91.00	16.05	56.00	18.00
30	57.5	100	15	200	6	2.75	36	33.00	30.00	91.00	16.59
31	100	57.5	100	107.5	6	2.75	55	87.00	70.49	35.00	20.00
32	57.5	100	57.5	107.5	2	2.75	17	67.00	17.55	69.00	55.52
33	57.5	57.5	100	107.5	2	0.5	36	95.65	41.20	42.00	25.23
34	15	57.5	57.5	15	2	2.75	36	37.60	100.00	79.16	80.32

35	57.5	15	57.5	107.5	2	2.75	17	20.00	55.31	90.00	30.00
36	57.5	57.5	57.5	107.5	6	2.75	36	82.68	98.01	64.00	75.14
37	57.5	15	57.5	107.5	2	2.75	55	14.00	84.82	61.00	67.00
38	57.5	100	100	15	6	2.75	36	100.00	15.00	90.00	20.23
39	57.5	57.5	57.5	200	6	0.5	17	60.00	25.00	10.00	38.99
40	57.5	57.5	57.5	15	6	5	17	82.45	55.00	72.00	77.77
41	57.5	57.5	100	107.5	2	5	36	96.81	10.00	69.62	26.20
42	15	57.5	57.5	15	10	2.75	36	28.53	83.96	90.00	91.27
43	57.5	100	57.5	107.5	2	2.75	55	96.00	90.50	10.00	52.86
44	57.5	57.5	57.5	200	6	5	17	82.45	18.00	15.00	59.14
45	15	57.5	57.5	200	10	2.75	36	28.03	62.78	20.00	92.79
46	100	57.5	57.5	200	2	2.75	36	39.00	16.00	64.86	33.00
47	57.5	57.5	57.5	107.5	6	2.75	36	74.36	95.47	63.51	91.13
48	15	57.5	15	107.5	6	2.75	55	25.00	90.00	92.00	96.00
49	57.5	57.5	15	107.5	2	5	36	20.34	98.00	98.00	99.75
50	15	100	57.5	107.5	6	5	36	50.00	69.68	50.00	53.12
51	15	57.5	100	107.5	6	2.75	55	99.00	20.00	15.00	66.00
52	57.5	57.5	15	107.5	10	5	36	40.30	93.68	98.00	99.75
53	57.5	57.5	100	107.5	10	0.5	36	33.32	45.70	41.00	92.00
54	57.5	100	100	200	6	2.75	36	51.23	33.98	63.74	35.00
55	100	57.5	57.5	200	10	2.75	36	43.28	52.17	55.00	62.40
56	57.5	57.5	57.5	107.5	6	2.75	36	75.00	95.47	63.51	97.24
57	57.5	15	57.5	107.5	10	2.75	17	95.09	98.12	51.00	87.00
58	100	57.5	15	107.5	6	2.75	55	44.00	90.00	98.00	45.00
59	100	57.5	57.5	15	10	2.75	36	53.00	95.00	90.00	66.12
60	15	57.5	15	107.5	6	2.75	17	45.79	89.27	95.00	85.56
61	57.5	100	15	15	6	2.75	36	94.48	97.02	92.00	83.12
62	57.5	15	15	15	6	2.75	36	21.00	94.95	90.00	82.77

4.5.3.2 Statistical analysis

The residual plots were analysed for model adequacy in Fig 4.34-4.37. Fig. 4.34(a—d) shows plot between actual and predicted removal percent for copper, cadmium, chromium and dye. In Fig. 4.34(a—d) the actual value of R^2 were found to be 0.80 for copper, 0.82 for cadmium, 0.82 for chromium and 0.80 for dye. Actual values are measured response data for a particular run, however predicted values are calculated from model and generated using approximating functions (Sahu et al., 2009). Further R^2 value determines goodness of fit of the model. In our work R^2 value shows that there is good fitness of regression models for obtaining the results. Fig. 4.35 (a—d) shows plot between % normal probability and externally studentized residuals. Fig. 4.35 (a—d) shows that how well model satisfies ANOVA assumption where studentized residual is the measure of number of standard deviation. They also show that neither response transformation was needed nor there was any problem with normality. Fig. 4.36(a—d) shows plot between studentized residuals and predicted removal percent for copper, cadmium, chromium and dye. These plots should be random scatter and suggesting the variance of original observation to be constant for all values of the response. Fig.4.37 (a—d) shows plot between studentized residuals and runs. The residual values should lie in the range of ± 3.50 and any value outside this range is unused. In Fig.4.37 (a—d), the value of studentized residuals lies in the interval of ± 3.50.

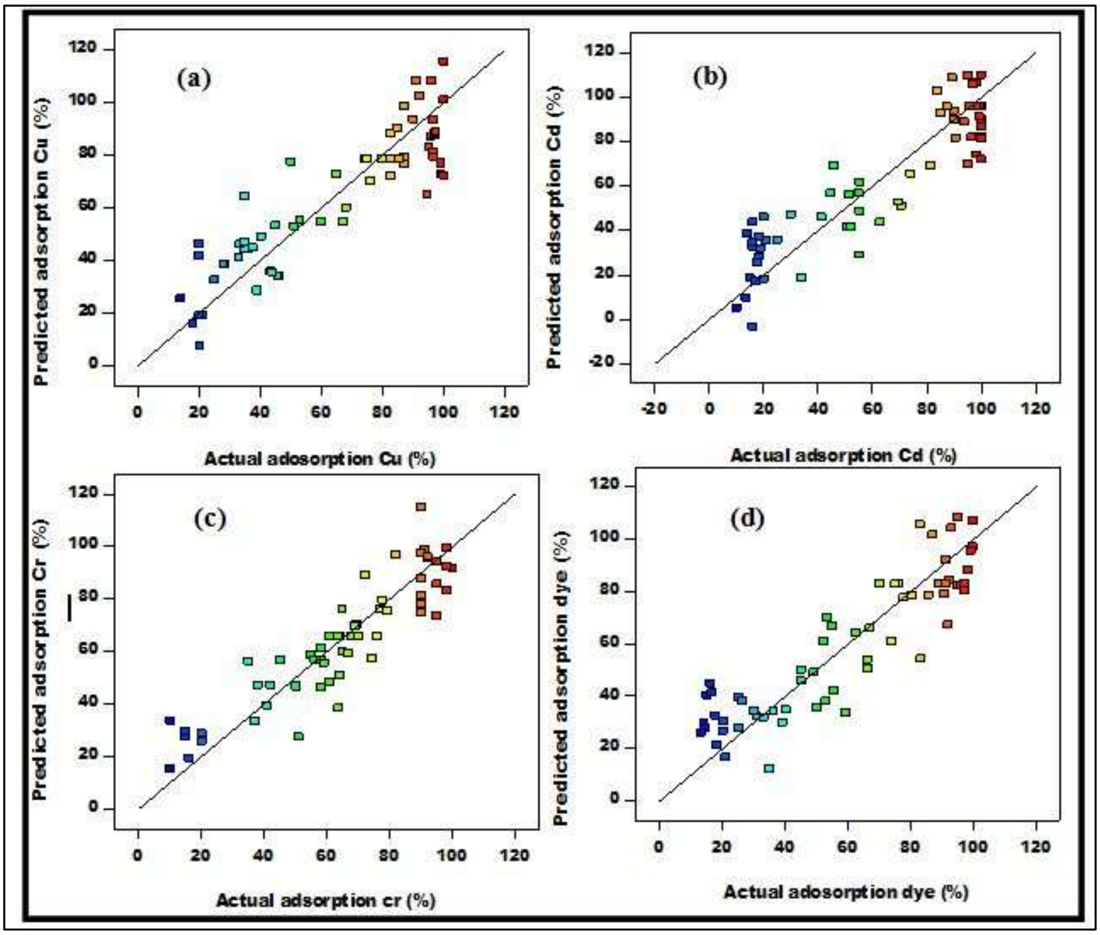


Fig. 4.34 The actual and predicted plot for (a) copper (b) Cadmium (c) Chromium (d) Acid black 60 dye uptake capacity of biosorbent

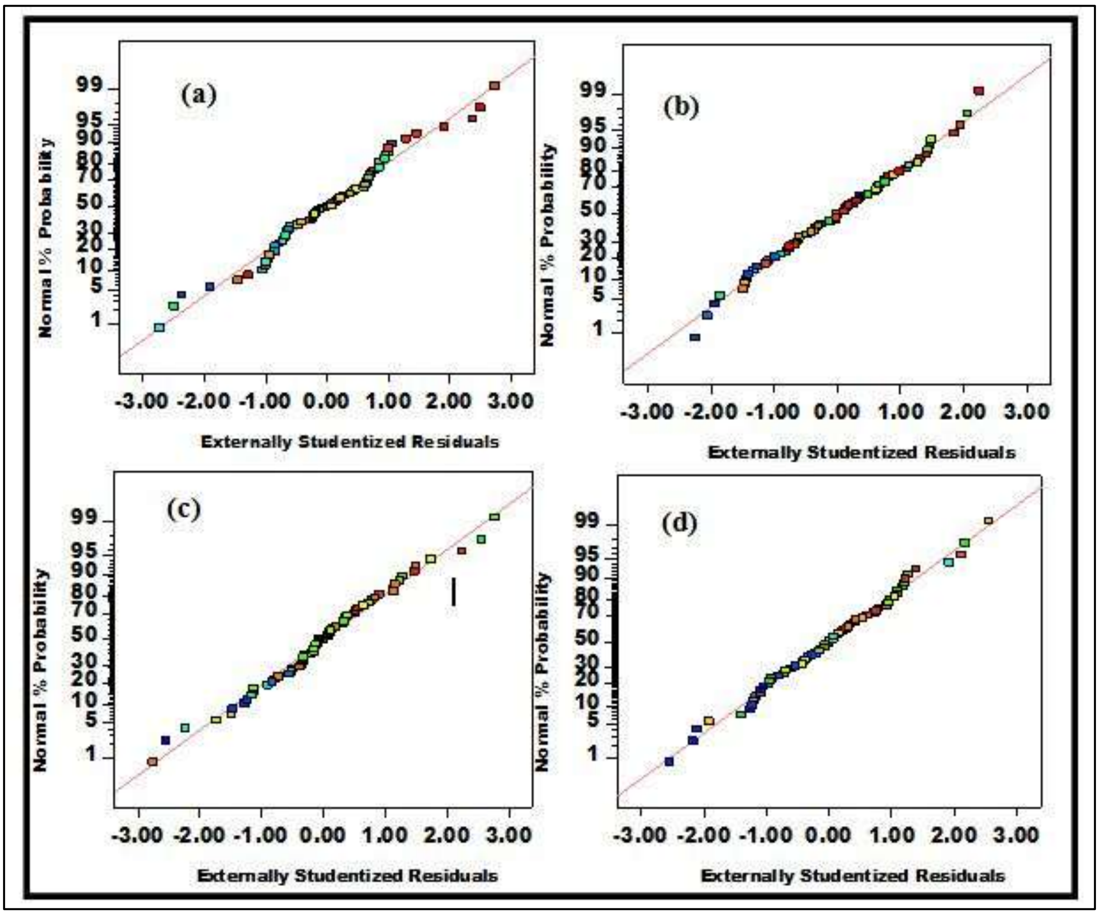


Fig. 4.35 Normal % probability and studentized residual plot for (a) copper (b) Cadmium (c) Chromium (d) acid black 60 dye, uptake capacity of biosorbent

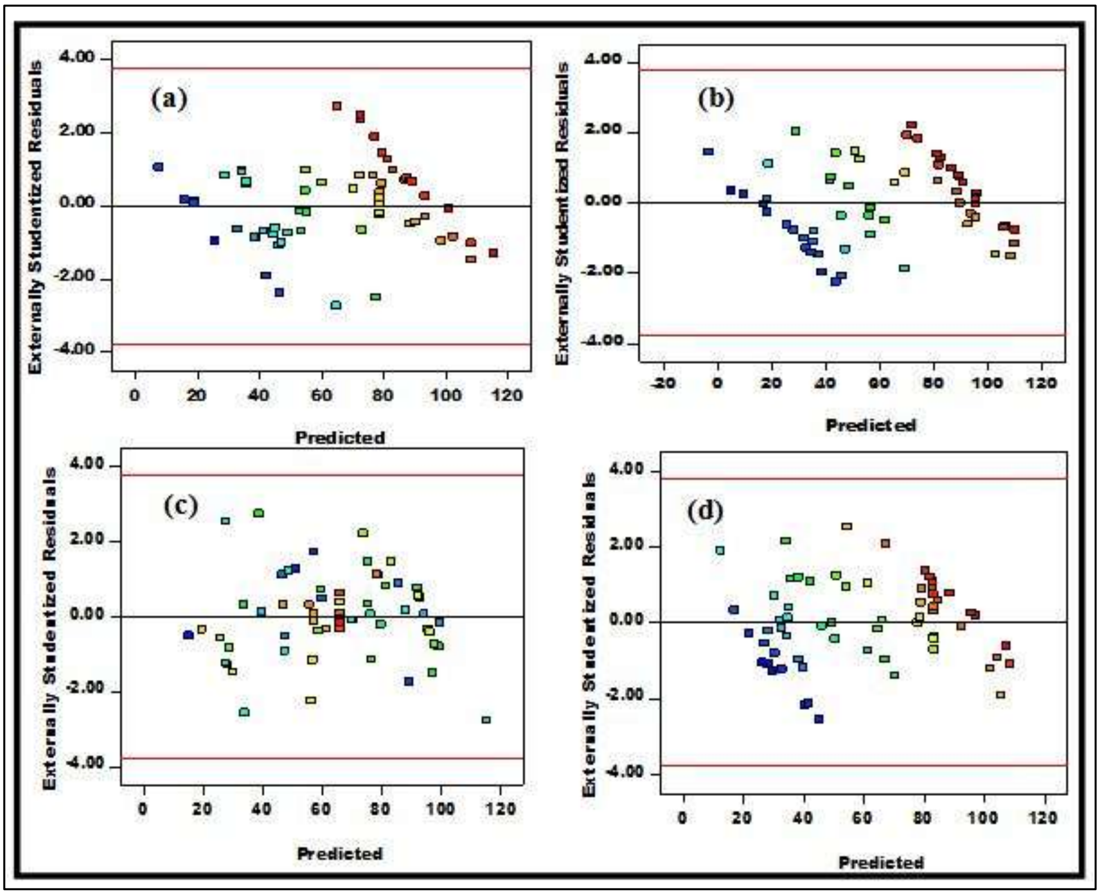


Fig. 4.36 The studentized residuals and predicted response plot for (a) copper (b) Cadmium (c) Chromium (d) acid black 60 dye, uptake capacity of biosorbent

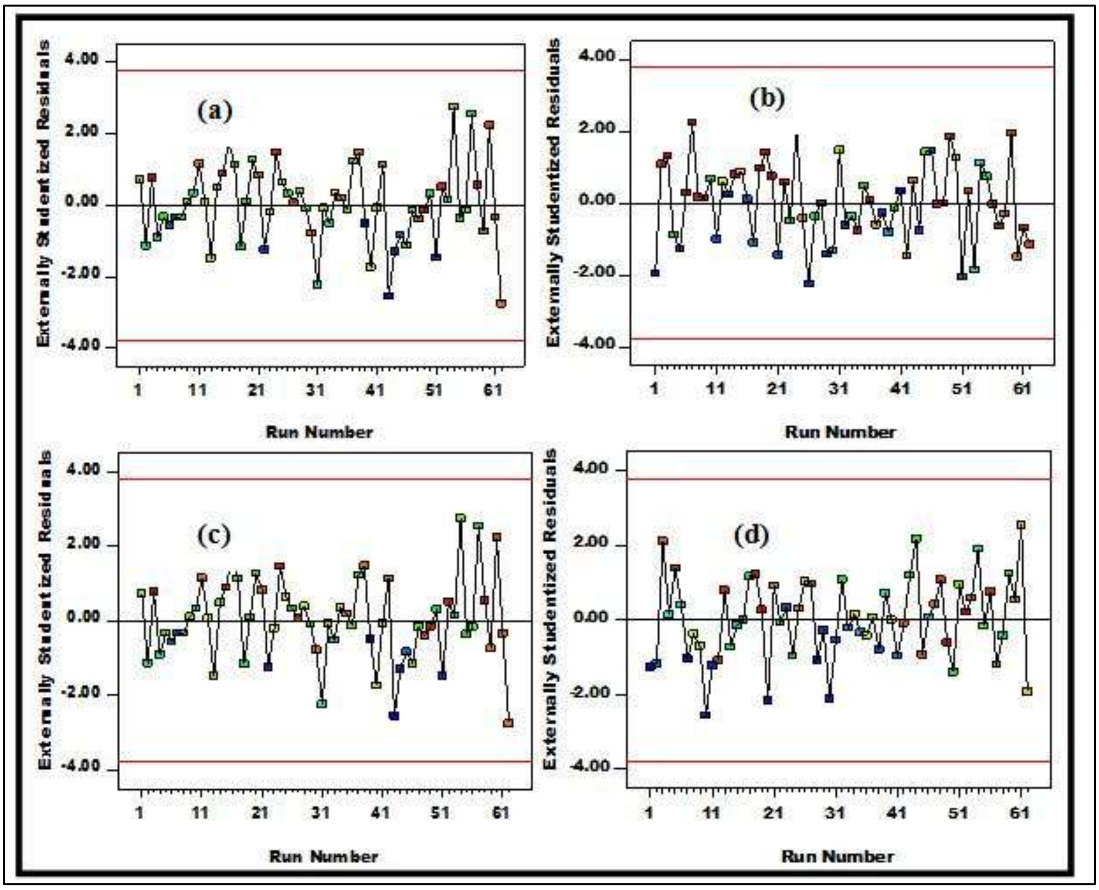


Fig. 4.37 Studentized residuals and and run number plot for (a) copper (b) Cadmium (c) Chromium (d) acid black 60 dye, uptake capacity of biosorbent

4.5.3.3 Analysis of variance

In this study, A Box-Behnken design of response surface methodology was applied to predict the effect of initial concentration of copper (mg/L), initial concentration of cadmium (mg/L), initial concentration of chromium (mg/L), initial concentration of dye (mg/L), adsorbent dose (gram), temperature (ºC) and pH on removal efficiency of copper, cadmium, chromium and dye (Table). The following second-order polynomial model equations-(4.15–4.18) are obtained from experimental data, and are applicable when $A_1=A_2=A_3=A_4=B=C=D=E=F=G\neq0$ and they demonstrates the relationship between copper, cadmium, chromium and dye removal efficiency (R_{Cu}, R_{Cd}, R_{Cr}, R_{dye}) and independent variables (A_1, A_2, $A_{3,}$ A_4, B, C, D, E, F, G).

$$R_{Cr}= +65.86 - 20.94\,A_3 - 3.65\,A_2 + 9.03\,A_1 - 13.73\,A_4 + 3.20D + 5.38C - 3.66B + 0.71A_3A_2 + 7.63\,A_3A_1 - 10.03\,A_3A_4 - 4.63\,A_3D + 2.33\,A_3C - 4.08\,A_3B + 8.25\,A_2A_1 + 5.47A_2E + 0.83\,A_2D + 6.75\,A_2C + 4.58\,A_2B + 2.76\,A_1A_4 - 3.38\,A_1D - 1.50\,A_1C + 3.28\,A_1B + 11.94\,A_4D - 4.89\,A_1C - 8.45\,A_1B - 5.89DC + 22.08DB - 3.83CB + 12.39A_3^2 - 1.17A_2^2 - 2.26A_1^2 + 3.63A_4^2 - 10.62D^2 - 8.43C^2 + 2.26B^2 \quad \ldots\ldots(4.15)$$

$$R_{Cd}= +95.77 - 13.96\,A_3 - 6.67\,A_2 + 18.67\,A_1 - 24.97\,A_4 + 3.75D - 2.02C + 9.54B - 15.07\,A_3A_2 + 0.23\,A_3A_1 - 14.80\,A_3A_4 - 7.78\,A_3D - 11.38\,A_3C + 9.20\,A_3B + 4.12\,A_2A_1 + 10.35\,A_2E + 2.95\,A_2D - 3.43\,A_2C + 1.82\,A_2B + 7.76\,A_1A_4 + 20.97 + 4.15 + 9.96 - 6.30 + 4.45 + 3.09 + 6.20 - - 21.32 + 7.00 - 11.57 - 10.74 - 12.98 - 19.08 - 4.74 - 17.50 - 8.43 \quad \ldots\ldots(4.16)$$

$$R_{Cu}= +78.63 + 20.39\,A + 9.23B + 8.01C - 12.06D + 4.34E + 2.07F + 0.25G - 8.45AB + 4.60\,AC - 6.08\,AD + 6.35\,AE + 9.36AF - 10.18AG + 8.21BC - 5.86BD + 18.51BE - 1.21BF - 14.26BG - 4.70CD - 1.15CE + 7.96CF - 3.84CG - 3.50DE + 0.50DF + 7.17DG - 6.87EF - 3.76EG + 10.40FG - 14.51A^2 + 4.50B^2 - 4.06C^2 - 12.11D^2 - 3.46E^2 + 13.31F^2 - 20.66G^2 \quad \ldots\ldots(4.17)$$

$$R_{dye}= +83.07 - 16.83\,A - 21.01B - 9.77C - 8.79D + 0.65E + 6.19F + 11.58G + 3.57AB + 1.26\,AC - 1.25\,AD + 3.88\,AE - 16.11\,AF + 1.61AG - 0.76\,BC + 1.06\,BD - 8.96\,BE + 7.60\,BF - 15.92BG + 0.42\,CD - 5.12\,CE - 8.23CF - 10.61CG + 4.56DE - 8.60DF + 15.23DG - 4.34EF - 6.29EG - 15.08FG - 8.49A^2 - 8.76B^2 -$$

$5.31C^2 - 10.31D^2 - 16.51E^2 - 10.37F^2 - 1.13G^2$ …..(4.18)

Table 4.16 shows ANOVA for response surface quadratic model. The model F value is 2.97, 3.47, 3.46, 3 for copper, cadmium, chromium and dye and this value measures how well factors describe the variation in the data about its mean. Probability value (P) is a measurement of effects in a model that should be less than 0.05 for being significant, and in our work probability values are less than 0.05 for parameters A_3, A_2, A_4, A_2D, A_3^2, A_4^2, C^2, B^2 for copper; A_3, A_1, A_4, B, A_1D, DB, A_1^2, A_4^2, C^2 for cadmium; A_3, A_1, A_4, DB, A_3^2, D^2 for chromium and A_3, A_2, A_1, A_4, B, A_3C, A_2B, A_4B, CB, D_2 for dye. It means that only these parameters are significant for copper, cadmium, and chromium removal. Adequate precision ratio is 7.158 for copper removal, 6.807 for cadmium removal, 7.860 for chromium removal, and 6.201 for dye removal which is much higher than the minimum desirable amount 4 and it indicates that there is the presence of adequate signal to noise ratio for this model (Ahmadi et al., 2014; Srinivasan & Viraraghavan 2010).

Table 4.16: ANOVA results for the response surface quadratic model for copper, chromium, cadmium and dye

For copper and dye

(R_{Cu} - Squared = 0.8001 and R_{dye} -Squared = 0.8016)

Source	Sum of squares		Df	Mean square		F-Value		P-Value		Cu	Dye
	Cu	Dye		Cu	Dye	Cu Dye		Cu	Dye		
Model	42762.49	43580.68	35	1221.79	1245.16	3.26	3.00	0.001	0.01	Significant	Significant
A_3-Cr conc.	9979.09	6798.29	1	9979.09	6798.29	26.64	16.39	< 0.0001	0.0004		
A_2-Cd conc.	2046.37	10591.87	1	2046.37	10591.87	5.46	25.53	0.03	< 0.0001		
A_1-Cu conc.	1541.01	2291.18	1	1541.01	2291.18	4.11	5.52	0.05	0.03		
A_4-dye conc.	3490.31	1855.82	1	3490.31	1855.82	9.32	4.47	0.005	0.04		
D-temp	452.45	10.08	1	452.45	10.08	1.21	0.02	0.28	0.87		
C-dose	102.76	920.41	1	102.76	920.41	0.27	2.22	0.60	0.14		
B-pH	1.56	3217.37	1	1.56	3217.37	4.161E-003	7.76	0.95	0.01		
A_3A_2	571.07	102.08	1	571.07	102.08	1.52	0.25	0.23	0.62		
A_3A_1	169.27	12.67	1	169.27	12.67	0.45	0.03	0.51	0.86		
A_3A_4	295.46	12.55	1	295.46	12.55	0.79	0.03	0.38	0.86		
A_3D	322.56	120.48	1	322.56	120.48	0.86	0.29	0.36	0.59		
A_3C	700.84	2074.97	1	700.84	2074.97	1.87	5.00	0.18	0.03		
A_3B	828.62	20.70	1	828.62	20.70	2.21	0.05	0.15	0.82		
A_2A_1	539.07	4.62	1	539.07	4.62	1.44	0.01	0.24	0.92		
A_2E	275.11	9.07	1	275.11	9.07	0.73	0.02	0.39	0.88		
A_2D	2741.65	642.01	1	2741.65	642.01	7.32	1.55	0.01	0.22		
A_2C	11.69	461.89	1	11.69	461.89	0.03	1.11	0.86	0.30		

A_2B	1627.31	2028.24	1	1627.31	2028.24	4.34	4.89	0.05	0.04		
A_1A_4	176.90	1.43	1	176.90	1.43	0.47	3.445E-003	0.49	0.95		
A_1D	10.58	209.65	1	10.58	209.65	0.03	0.51	0.86	0.48		
A_1C	506.63	541.81	1	506.63	541.81	1.35	1.31	0.25	0.26		
A_1B	117.70	900.90	1	117.70	900.90	0.31	2.17	0.58	0.15		
A_4D	98.11	166.19	1	98.11	166.19	0.26	0.40	0.61	0.53		
A_1C	2.01	591.61	1	2.01	591.61	5.374E-003	1.43	0.94	0.24		
A_1B	411.54	1854.60	1	411.54	1854.60	1.10	4.47	0.30	0.04		
DC	377.08	150.84	1	377.08	150.84	1.01	0.36	0.33	0.55		
DB	113.24	316.68	1	113.24	316.68	0.30	0.76	0.59	0.39		
CB	864.50	1820.26	1	864.50	1820.26	2.31	4.39	0.14	0.05		
A_3^2	2842.89	974.19	1	2842.89	974.19	7.59	2.35	0.01	0.14		
A_2^2	273.48	1036.36	1	273.48	1036.36	0.73	2.50	0.40	0.13		
A_1^2	222.13	380.42	1	222.13	380.42	0.59	0.92	0.45	0.35		
A_4^2	1978.92	1434.57	1	1978.92	1434.57	5.28	3.46	0.04	0.07		
D^2	161.42	3678.49	1	161.42	3678.49	0.43	8.87	0.52	0.01		
C^2	2389.95	1451.52	1	2389.95	1451.52	6.38	3.50	0.02	0.07		
B^2	5760.18	17.15	1	5760.18	17.15	15.38	0.04	0.001	0.84		
Residual	9739.86	10785.12	26	374.61	414.81	19.91	4.16	0.001	0.06		
Lack of Fit	9624.77	10201.68	21	458.32	485.79	3.26	3.00	0.001	0.002	Significant	not significant
Pure Error	115.09	583.43	5	23.02	116.69	26.64	16.39	< 0.0001	0.001		
Cor Total	52502.34	54365.79	61	1221.79	1245.16	5.46	25.53	0.03	< 0.0001		

For chromium and cadmium

R_{Cr} - Squared = 0.8233 and R_{Cd} -Squared = 0.8237

Source	**Sum of squares**		**Df**	**Mean square**		**F-Value**		**P-Value**		
	Cr	**Cd**		**Cr**	**Cd**	**Cr**	**Cd**	**Cr**	**Cd**	
Model	33762.71	58035.07	35	964.65	1658.14	3.46	3.47	0.001	0.001	Significant
A_3-Cr conc.	10526.96	4678.06	1	10526.96	4678.06	37.76	9.79	< 0.0001	0.004	
A_2-Cd conc.	319.91	1066.52	1	319.91	1066.52	1.15	2.23	0.29	0.15	
A_1-Cu conc.	1958.11	8369.93	1	1958.11	8369.93	7.02	17.52	0.01	0.0003	
A_4-dye conc.	4523.24	14959.93	1	4523.24	14959.93	16.23	31.31	0.0004	< 0.0001	
D-temp	245.69	337.41	1	245.69	337.41	0.88	0.71	0.36	0.41	
C-dose	694.61	98.35	1	694.61	98.35	2.49	0.21	0.13	0.65	
B-pH	322.23	2185.55	1	322.23	2185.55	1.16	4.57	0.29	0.04	
A_3A_2	4.12	1816.54	1	4.12	1816.54	0.02	3.80	0.90	0.06	
A_3A_1	465.13	0.41	1	465.13	0.41	1.67	8.575E-004	0.21	0.98	
A_3A_4	805.21	1753.01	1	805.21	1753.01	2.89	3.67	0.10	0.06	
A_3D	171.13	484.73	1	171.13	484.73	0.61	1.01	0.44	0.32	
A_3C	43.34	1035.76	1	43.34	1035.76	0.16	2.17	0.69	0.15	
A_3B	133.01	677.73	1	133.01	677.73	0.48	1.42	0.49	0.24	
A_2A_1	544.50	135.99	1	544.50	135.99	1.95	0.28	0.17	0.59	
A_2E	239.15	856.64	1	239.15	856.64	0.86	1.79	0.36	0.19	
A_2D	5.51	69.69	1	5.51	69.69	0.02	0.15	0.88	0.71	
A_2C	364.50	93.85	1	364.50	93.85	1.31	0.20	0.26	0.66	
A_2B	167.78	26.48	1	167.78	26.48	0.60	0.05	0.44	0.82	

A_1A_4	61.12	481.17	1	61.12	481.17	0.22	1.01	0.64	0.32	
A_1D	91.13	3516.58	1	91.13	3516.58	0.33	7.36	0.57	0.01	
A_1C	18.00	138.11	1	18.00	138.11	0.06	0.29	0.80	0.59	
A_1B	85.92	793.23	1	85.92	793.23	0.31	1.66	0.58	0.20	
A_4D	1140.15	317.99	1	1140.15	317.99	4.09	0.67	0.05	0.42	
A_1C	191.62	158.09	1	191.62	158.09	0.69	0.33	0.41	0.57	
A_1B	571.66	76.61	1	571.66	76.61	2.05	0.16	0.16	0.69	
DC	277.93	307.06	1	277.93	307.06	1.00	0.64	0.32	0.43	
DB	3900.06	3635.17	1	3900.06	3635.17	13.99	7.61	0.001	0.01	
CB	117.20	391.85	1	117.20	391.85	0.42	0.82	0.52	0.37	
A_3^2	2073.31	1806.25	1	2073.31	1806.25	7.44	3.78	0.01	0.06	
A_2^2	18.44	1555.74	1	18.44	1555.74	0.06	3.26	0.79	0.08	
A_1^2	68.80	2275.57	1	68.80	2275.57	0.25	4.76	0.62	0.03	
A_4^2	178.16	4913.08	1	178.16	4913.08	0.64	10.28	0.43	0.01	
D^2	1522.87	303.16	1	1522.87	303.16	5.46	0.63	0.02	0.43	
C^2	960.41	4136.34	1	960.41	4136.34	3.45	8.66	0.07	0.01	
B^2	68.86	958.43	1	68.86	958.43	0.25	2.01	0.62	0.17	
Residual	7247.52	12424.56	26	278.75	477.87		30.49	0.02	0.001	
Lack of Fit	7106.54	12328.28	21	338.41	587.06	12.00	3.47	0.001	0.001	Significant
Pure Error	140.99	96.28	5	28.20	19.26		9.79	< 0.0001	0.01	
Cor Total	41010.23	70459.63	61	964.65	1658.14	3.46	2.23	0.29	0.15	

4.5.3.4 Effect of process variables

The effects of process variables on simultaneous removal of copper, cadmium, chromium and dye has been described with the help of three-dimensional Fig. 4.38(a–b), Fig. 4.39(a–b), and Fig. 4.40(a–b).

(i) Effect of copper initial concentration

As it is clear from Table 4.13, that increase of copper concentration has synergistic effect on chromium removal and antagonistic effect on cadmium removal. It can also be seen in Fig. 4.40(b), 4.39(a). Thus when mixed metals are present removal percent of chromium increases and of cadmium decreases.

(ii) Effect of cadmium initial concentration

As it is clear from Table 4.13, that increase in cadmium concentration has synergistic effect on copper removal and antagonistic effect on chromium removal. It can also be seen in Fig. 4.38(a), 4.40(a). Thus when mixed metals are present removal percent of copper increases and of chromium decreases.

(iii) Effect of chromium initial concentration

As it is clear from Table 4.13, that increase in copper concentration has synergistic effect on copper removal and antagonistic effect on cadmium removal. It can also be seen in Fig. 4.38(a), 4.39(a). Thus when mixed metals are present removal percent of copper increases and of cadmium decreases.

(iv) Effect of dye initial concentration

In simultaneous removal of heavy metals and dye, dye is also added with the heavy metals. It is clear from Fig. 4.39 (b), 4.38 (b) that, when dye is added in ternary mixture of copper, cadmium and chromium; copper, cadmium and chromium removal decreases.

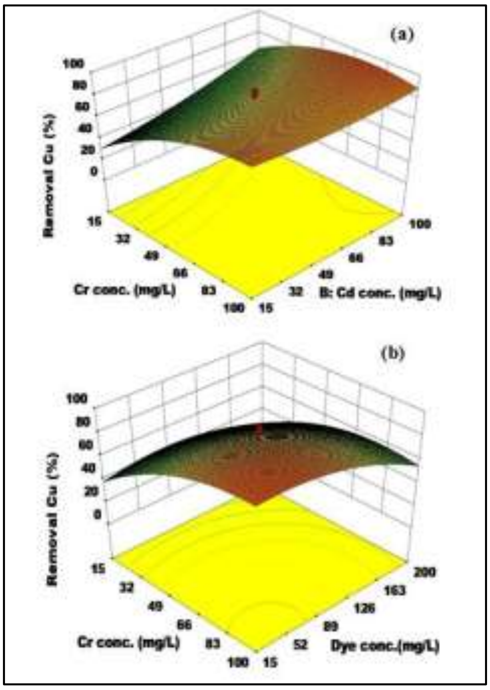


Fig. 4.38 Response surface 3-D plots for combined effect of (a) chromium ion concentration and cadmium ion concentration, (b) chromium ion concentration and dye ,on removal efficiency of copper.

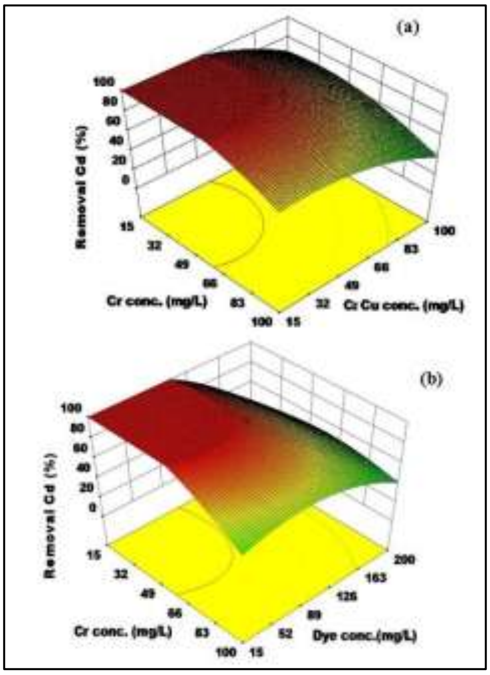


Fig. 4.39 Response surface 3-D plots for combined effect of (a) chromium ion concentration and copper ion concentration, (b) chromium ion concentration and dye on removal efficiency of cadmium

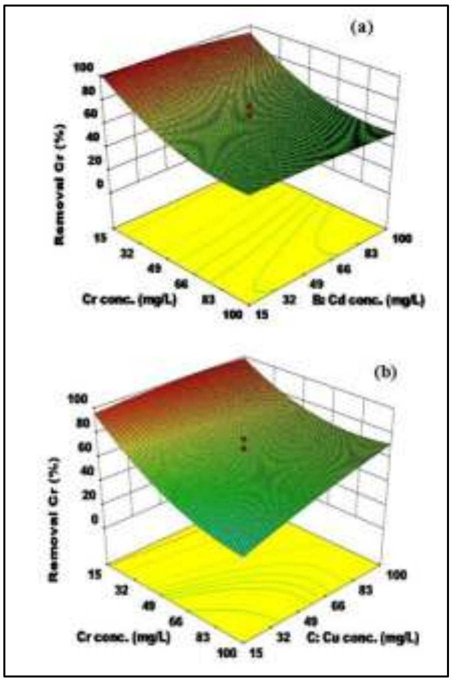


Fig. 4.40 Response surface 3-D plots for combined effect of (a) chromium ion concentration and cadmium ion concentration, (b) chromium ion concentration and copper ion concentration on removal efficiency of chromium

4.5.3.5 Equilibrium modelling

In Table 4.17, Freundlich and Langmuir models were used to analyse the adsorption data (Fig. 4.41). Then these data were compared with the monometal data. Table 4.18, shows kinetic study. It was concluded from isotherm and kinetic study that after addition of dye in ternary metal system, metal removal percent decreases.

Table 4.17 Adsorption isotherm for copper, cadmium, chromium and dye in quaternary system

Metals	**System**	**k_f**	**1/n**	**R^2**	**q_m**	**k_L**	**R^2**
Copper		**Freundlich isotherm**			**Langmuir isotherm**		
	Monometal (Cu)	1.22	0.43	0.99	4.33	0.53	0.99
	Multimetal (Cu-Cr-Cd)	1.29	0.45	0.97	4.71	0.62	0.99
	(Cu-Cr-Cd-dye)	1.05	0.45	0.99	3.98	0.26	0.98
Cadmium	Monometal (Cd)	1.15	0.35	0.99	3.37	0.58	0.97
	Multimetal (Cd-Cr-Cu-dye)	1.12	0.29	0.98	3.00	0.56	0.97
Chromium	Monometal (Cr)	0.90	0.72	0.97	9.00	0.08	0.98
	Multimetal (Cd-Cr-dye)	0.86	0.62	0.96	6.28	0.09	0.98
	(Cd-Cr-dye-Cu)	0.94	0.67	0.99	7.04	0.12	0.99

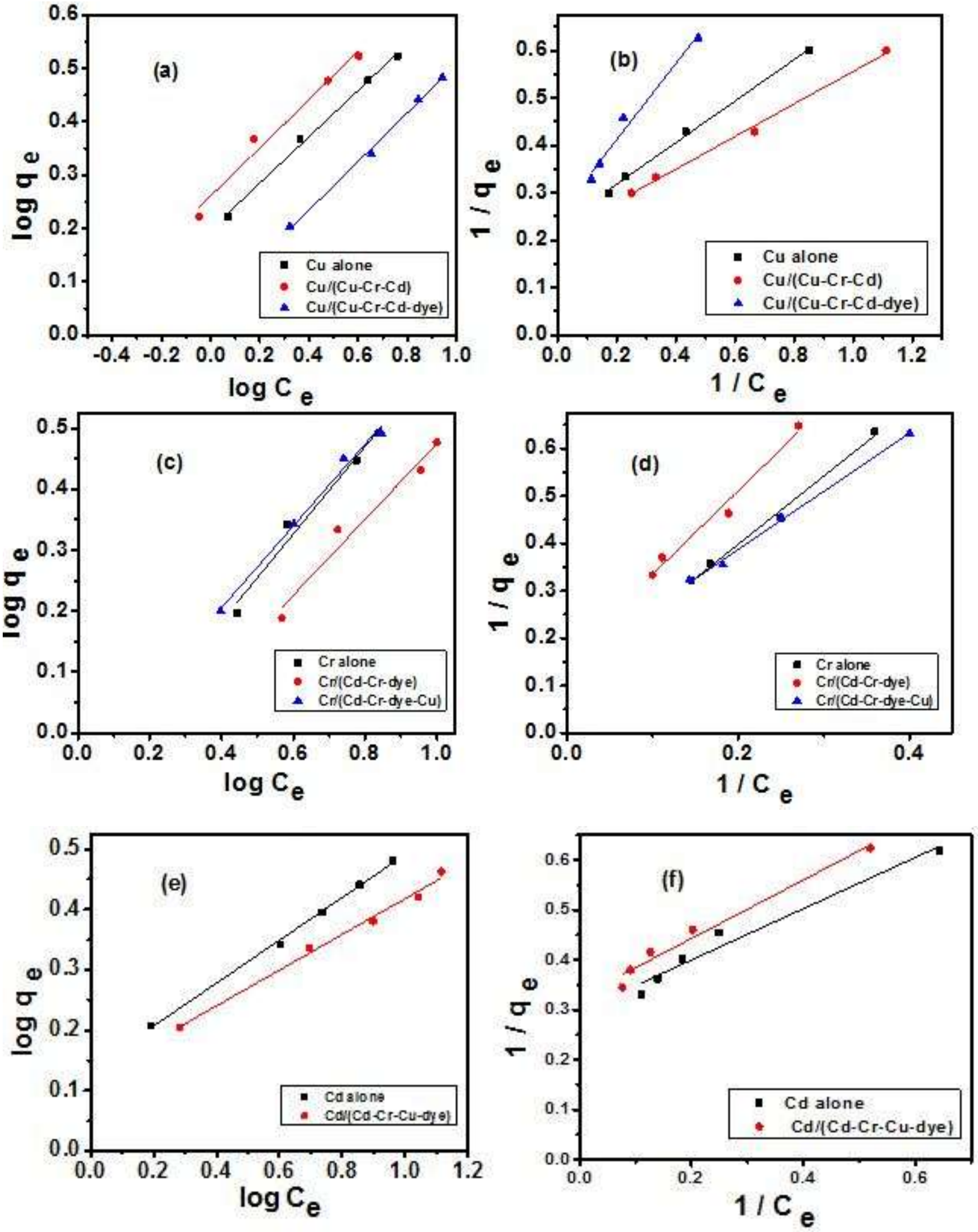


Fig. 4.41 Isotherm plots for adsorption of copper (a) Freundlich (b) Langmuir; for chromium (c) Freundlich (d) Langmuir; for cadmium (e) Freundlich (f) Langmuir at optimum conditions

Table 4.18 Kinetic parameters for Langmuir isotherm for simultaneous adsorption of copper, cadmium, copper and dye on hydrochloric acid-treated wheat bran

Solution	Conc.(mg/L)	q_m (mg/g)	k(g/mg.min)	R^2
Cd alone	50	1.63	5.33	0.99
Cr alone	50	1.62	5.36	0.99
Cu alone	50	1.75	2.82	0.99
Dye	50	1.63	8.95	0.99
Cd alone	100	3.12	2.94	0.99
Cr alone	100	3.18	2.50	0.99
Cu alone	100	3.26	2.03	0.99
Dye alone	100	3.22	4.84	0.99
FOR CADMIUM				
Cd-Cr-Cu	50-100-100	Cd-1.52	0.55	0.93
		Cr-2.93	1.01	0.99
		Cu-2.39	0.76	0.96
Cd-Cr-Cu-dye	50-100-100-100	Cd-1.47	8.62	0.99
		Cr-1.52	3.68	0.92
		Cu-1.63	5.33	0.90
		Dye-3.13	2.94	0.99
FOR CHROMIUM				
Cr-Cd-dye	50-100-100	Cr-1.61	5.00	0.99
		Cd-3.10	3.19	0.99
		Dye-3.17	0.54	0.97
Cr-Cd-Cu-dye	50-100-100-100	Cr-1.76	2.68	0.99
		Cd-3.48	3.90	0.99
		Cu-3.42	1.99	0.99
		Dye-3.06	6.07	0.99
FOR COPPER				
Cu-Cr-Cd	50-100-100	Cu-2.17	1.53	0.99
		Cr-3.53	1.35	0.99
		Cd-3.47	1.27	0.99
Cu-Cr-Cd-dye	50-100-100-100	Cu-1.94	2.00	0.99
		Cr-2.65	1.73	0.99
		Cd-3.13	2.87	0.99
		Dye-3.13	2.93	0.99

4.6 Removal of heavy metals using adsorption process combined with oxidation process

In this study, metal complex dyes of chromium such as acid black 60, acid black 52 and acid violet 90 respectively, were oxidised. Metal complex dyes were oxidised with hydrogen peroxide and in the presence of iron sulphate as a catalyst. It was observed that metal has been released after oxidation and then released metal was removed using adsorbent. Following results were obtained when adsorption process was combined with the oxidation process.

Table 4.19 Metal concentration in metal complex dyes before and after oxidation.

Metal complex dye	Initial conc. of Cr solution	Chromium present in solution (mg/L)		
		Before oxidation	After oxidation	After adsorption
Acid Black 60	100 mg/L	0.96	1.51	1.02
	200 mg/L	4.00	6.16	5.66
Acid Black 52	100 mg/L	0.85	1.02	0.95
	200 mg/L	3.44	4.88	3.44
Acid violet 90	100 mg/L	0.76	1.64	1.48
	200 mg/L	3.13	4.59	3.88

4.7 Continuous fixed bed column study

In this study, heavy metals such as copper, chromium and cadmium were removed using adsorbent pellets. These adsorbent pellets were prepared using 3:1:1 of modified wheat bran, clay and chitosan respectively. Fixed bed column study was performed for individual metals, mixed metals and simultaneous removal of metals and dye. A mathematical model was developed using MATLAB software to present a fixed bed column. Further, breakthrough curve analysis was done to determine the effect of various parameters such as bed height (0.15-0.45 m), flow rate (5-15 mg/L) and initial metal concentration (100-500 mg/L) on breakthrough time for three metals such as copper, cadmium and chromium. Further, model was also validated by comparing of model data with experimental data.

4.7.1 Characterisation of Adsorbent pellet and adsorption mechanism

4.7.1.1 SEM with EDS

The SEM analysis of adsorbent pellet before and after adsorption are shown in Fig. 4.42(a–d). SEM analysis was performed on electron microscope to determine the surface morphology of the adsorbent. It was observed that the structure and morphology of adsorbent has been changed after loading with heavy metals such as copper, cadmium and chromium. The pores of adsorbent have filled with the metal and the surface has become puffy due to the heterogeneity. Further elemental analysis of the adsorbent pellets was done before and after adsorption using EDS to determine their chemical composition as shown in Fig. 4.43(a) (b). It was observed that there is the presence of carbon, oxygen, silica, aluminium, iron, magnesium, barium, sodium, potassium, calcium and chlorine. However, after adsorption heavy metals such as copper, cadmium and chromium were also observed (Table 4.20). It confirms presence of cellulose, clay and chitosan in the adsorbent. However, presence of heavy metals after adsorption confirms adsorption of metals on the surface of adsorbent.

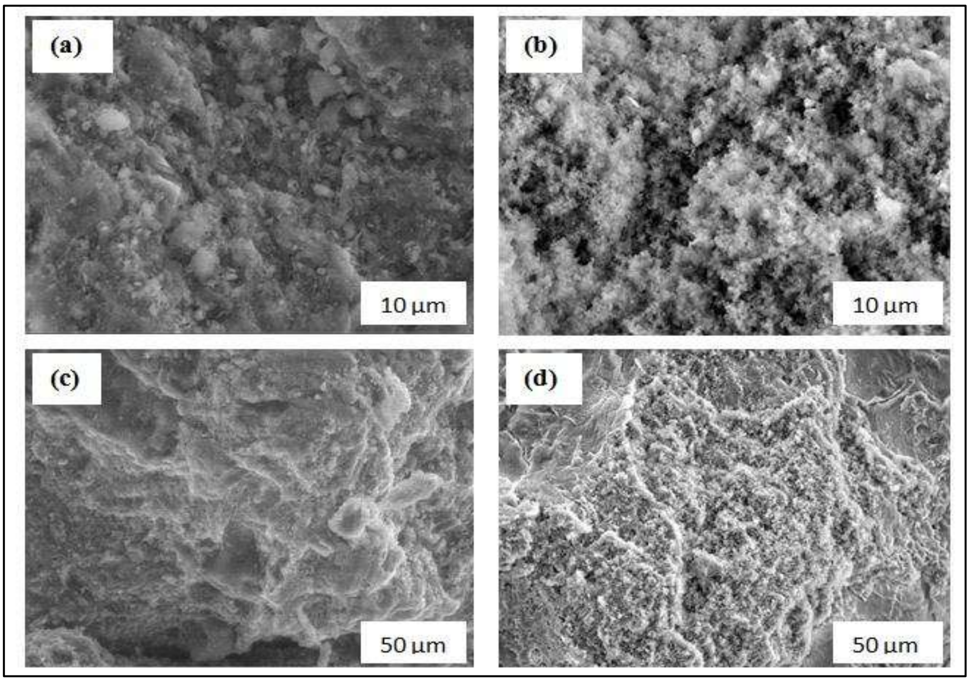
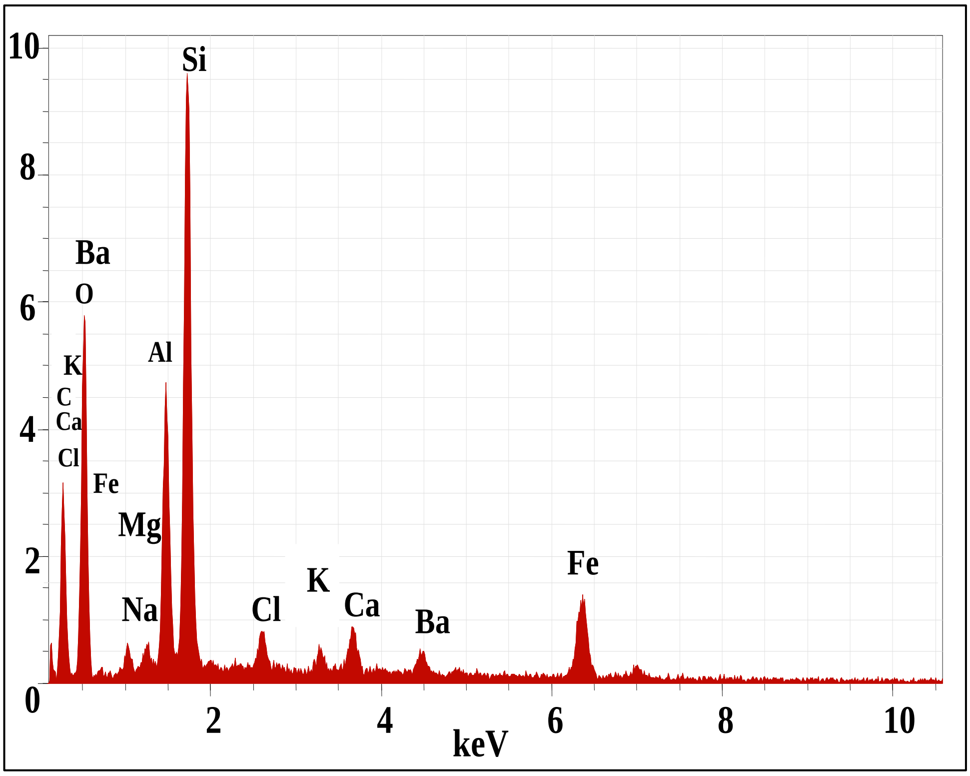
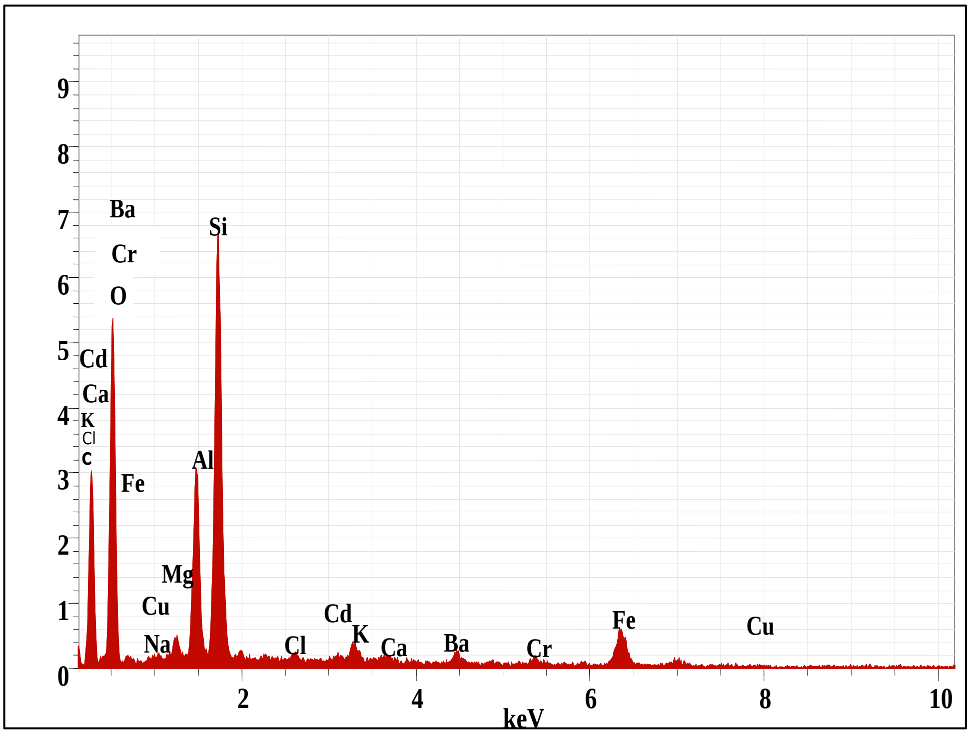


Fig. 4.42: Scanning electron micrograph of adsorbent pellet (a) before adsorption at 10 µm resolution, (b) after adsorption at 10 µm resolution, (c) before adsorption at 50 µm resolution (d) after adsorption at 50 µm resolution



(a)



(b)

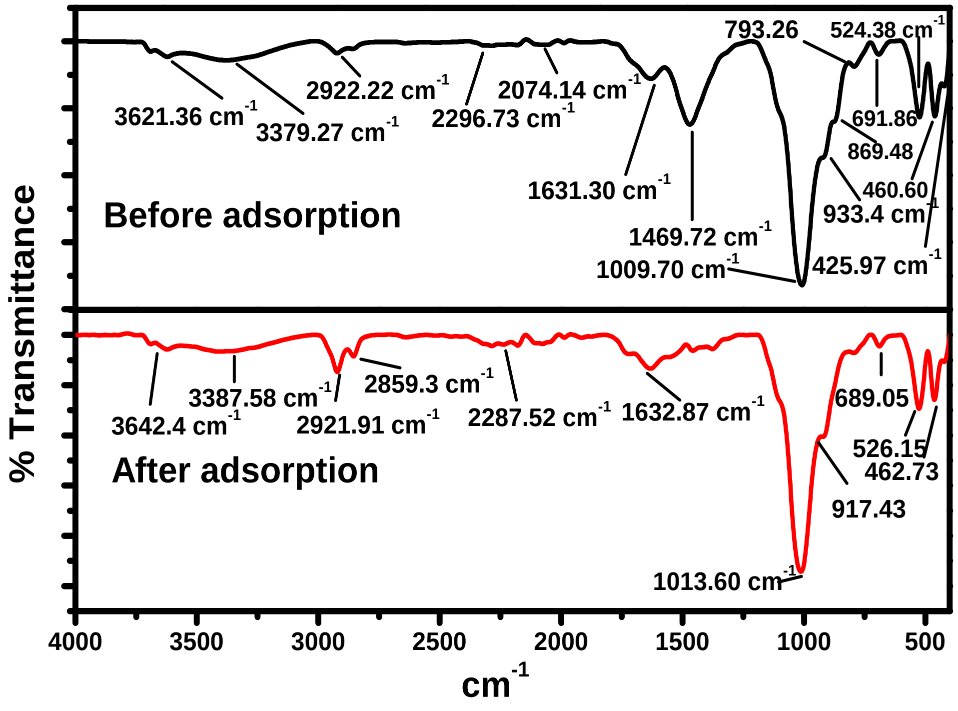
Fig. 4.43 EDS spectra of the adsorbent pellet (a) before adsorption (b) after adsorption

Table 4.20: Elemental analysis of raw wheat bran and chemically modified wheat bran

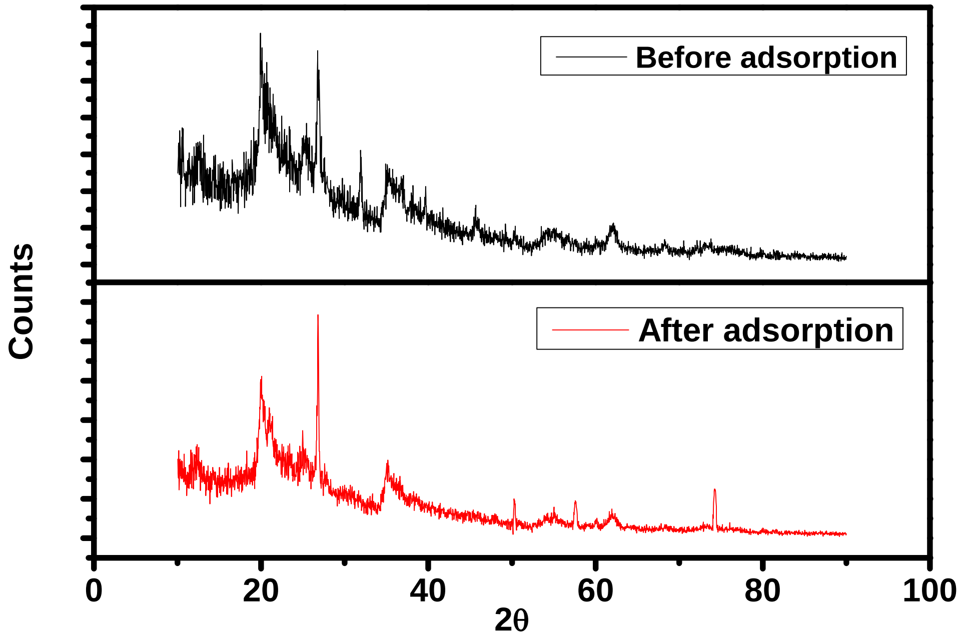
Element	Weight%	
	Before adsorption	After adsorption
Cl	0.54	0.33
Ca	0.75	0.60
C	33.11	33.00
K	1.45	0.91
O	44.54	44.00
Ba	0.89	0.85
Fe	3.08	2.48
Mg	0.70	0.69
Na	1.12	0.49
Al	4.64	4.45
Si	9.18	8.72
Cu	-	1.44
Cr	-	0.89
Cd	-	1.15

4.7.1.2 FTIR and XRD

Fig. 4.44(a) shows the X-Ray diffraction pattern (XRD) of adsorbent before and after adsorption. In Fig. 4.44(a), before adsorption, various peaks were observed. The peak at $2\theta=20^o$ is due to chitosan. Further at $2\theta=22^o$ a broad peak was observed and it indicates the presence of amorphous silica present in wheat bran. Peaks observed at $2\theta=25.32^o$, 26.83^o, 31.90^o, 35.11^o, 45.68^o, 62.12^o, 68.26^o are due to bentonite clay. After adsorption the peaks have been shifted towards the low diffraction and 2θ value has changed to $2\theta=19.99^o$, $25.17\ ^o$, 26.81^o, $35.03\ ^o$ and $62.11\ ^o$. This shift in 2θ value is due to increase in d-spacing caused by intercalation of the metals in the interlayer. However new peaks were observed at $2\theta=74.20^o$, 51^o, 57.5^o, it indicates the adsorption of copper, chromium and cadmium on the adsorbent surface respectively. Further, in Fig. 4.44 (b), Fourier transform infrared spectroscopy (FTIR) determines the presence of surface functional groups in the adsorbent. It was observed that before adsorption, peak at 1469 cm^{-1} shows bending vibrations of amine group (–NH$_2$) present in chitosan. After adsorption 1469 cm^{-1} peak diminishes, it shows that the adsorbent is loaded with metals. Further, 1631 cm^{-1} peak shows N–H bending vibrations in N–H, 1009 cm^{-1} is due to –CO stretching vibration in –COH. However, peak at 3621 cm^{-1} is due to the asymmetric stretching of Al–OH–Al, 3379 cm^{-1} peak is due to vibrations of water molecules, the peak at 793 cm^{-1} shows stretching vibration of Al-O-Si present in clay, Further, 933 cm^{-1}, 869 cm^{-1}, 691 cm^{-1}, 524 cm^{-1}, and 425 cm^{-1} peak shows Al–Al–OH deformation, Al-Mg-OH deformation, coupled Al-O and Si-O, Al-O-Si deformation and Si-O-Si bending vibrations. Peaks at 2922 cm^{-1}, 2296 cm^{-1} and 2074 cm^{-1} is due to the –C–H stretching in cellulose present in wheat bran.



(a)



(b)

Fig. 4.44 (a) XRD pattern of adsorbent pellet before and after adsorption process (b) FTIR analysis of adsorbent pellet before and after adsorption process

4.7.1.3 Adsorption mechanism

The adsorption mechanism for heavy metals removal using adsorbent pellet is evident by comparing XRD and FTIR of adsorbent pellet before and after adsorption. After adsorption of heavy metals on adsorbent pellet, all XRD peaks shift toward the low diffraction (Fig. 4.44(a)). It is clear that peaks at 2θ=25.32°, 26.83°, 35.11° and 62.12° shift to 25.17 °, 26.81°, 35.03 ° and 62.11° due to expansion in *d*-spacing caused by intercalation of the metals in the interlayer of adsorbent pellets.

Similarly, in Fig. 4.44(b), FTIR of adsorbent pellets shows heavy metals adsorption on adsorbent pellets because after adsorption, peak at 1469 cm^{-1} of an amine group ($-NH_2$) diminishes due to the adsorbent loading with heavy metals. Thus it is clear that adsorption is taking place by surface modification and ion exchange.

4.7.2 Fixed bed column adsorption study

4.7.2.1 Calculation of parameters

Following model parameters were calculated using appropriate correlations (Table 4.21).

Table 4.21 Model parameters value in present study

Parameter	**Value**
Bed porosity, ε	0.59
Bed diameter, d	0.025 meter
Bed height, L	0.45 meter
Bed density	651.52 kg/m^3
Particle density	1954 kg/m^3
Particle radii, a_p	0.002 meter
Axial dispersion coefficient, D_L	4.0259×10^{-6} m^2/s
External mass transfer coefficient, k_f	0.3217×10^{-4} m/s
Flow rate	5, 10, 15 mL/min
Initial metal concentration	100, 300, 500 mg/L

4.7.2.2 Individual metal study

In individual metal study, the column experiments were performed by varying flow rate from 5 mL/min to 15 mL/min, initial metal concentration from 100 mg/L to 500 mg/L and bed height from 0.15 meter to 0.45 meter for copper, chromium and cadmium individually.

(i) Effect of flow rate

The effect of flow rate on adsorption of copper, cadmium and chromium is shown in Fig. 4.45(a)—(c), by varying the flow rate from 5 mL/min to 15 mL/min at initial metal concentration of 100 mg/L and bed height of 0.15 cm. The breakthrough time varies from 9431 to 776 s for chromium, from 4390 to 445 s for copper and from 4052 to 382 s for cadmium on increasing the flow rate from 5 mL/min to 15 mL/min. However, the bed exhaustion time varies from 25000 to 22000 s for chromium, 20000-18000 s for copper and 18000-15621 s for cadmium on increasing the flow rate from 5 mL/min to 15 mL/min, the details of which are given in Table 4.22. At high flow rate, the contact time is low hence the breakthrough time and exhaustion time reach earlier, because at high flow rate, the adsorbate solution leaves the column before equilibrium achieves. Further, at low flow rate the contact time is large, hence the breakthrough and exhaustion reach later. As per results from Fig. 4.45(a)—(c), 5 mL/min has been choosen as an optimum flow rate. Fig. 4.45(a)—(c), show that the removal is in the order of Cr > Cu > Cd. Chromium metal has the highest removal than copper and cadmium due to the longest breakthrough time. Calero et al. 2018 has performed similar study for removal of copper using olive stone with pinion shell and reported that 2 mL/min of flow rate as an optimum for efficient metal removal. However, Akhigbe et al. 2016 has performed the continuous study for removal of lead, cadmium, zinc using silver-modified zeolite and reported that 1 mL/min of flow rate as an optimum for efficient metal removal.

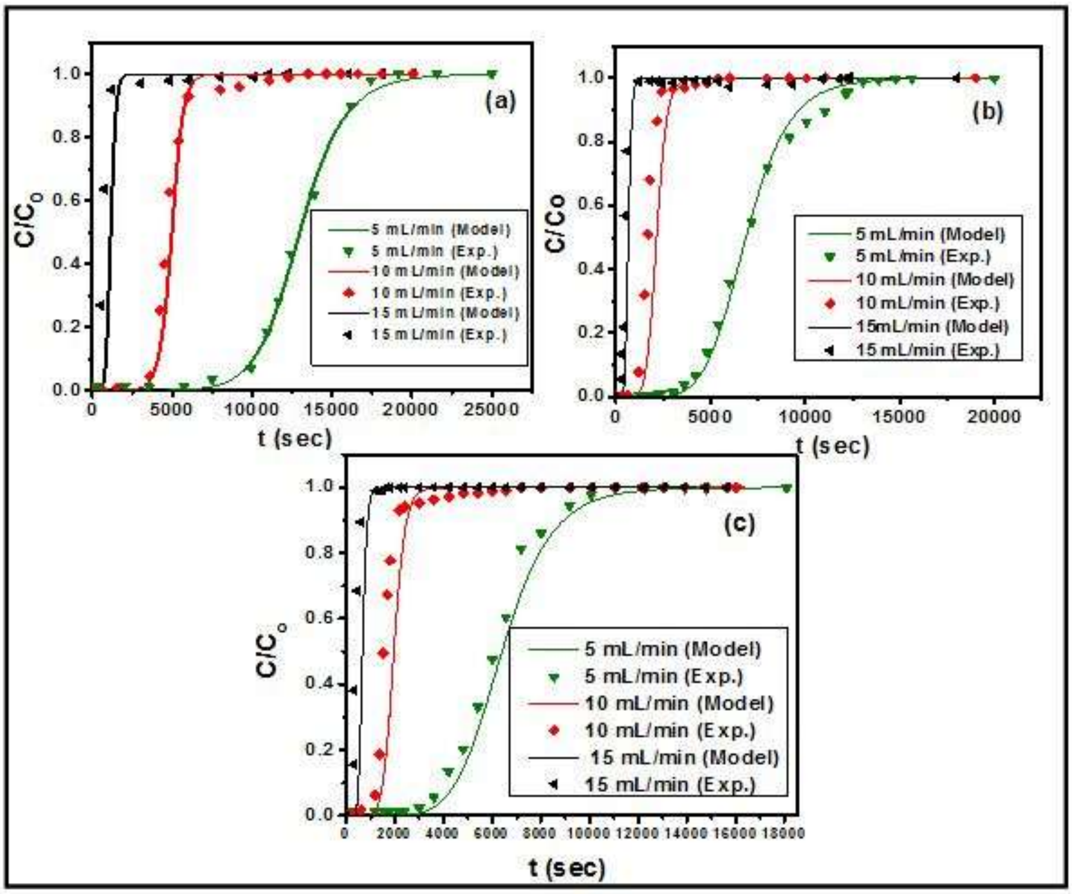


Fig. 4.45 Effect of flow rate on breakthrough curve for (a) chromium (b) copper (c) cadmium

(ii) Effect of initial metal concentration

Fig. 4.46(a)—(c), shows the effect of initial metal concentration on adsorption of copper, cadmium and chromium by varying the initial metal concentration from 100 mg/L to 500 mg/L at bed height of 0.15 m and flow rate of 5 mg/L. The breakthrough time varies 3803-859 s for chromium, 2343-708 s for copper, 1852-702 s for cadmium on increasing the initial metal concentration from 100 mg/L to 500 mg/L. However, the bed exhaustion time varies 25000-21000 s for chromium, 20000-17000 s for copper, 18000-15263 s for cadmium on increasing the initial metal concentration from 100 mg/L to 500 mg/L, the details of which are given in Table 4.22. At high initial metal concentration breakthrough and exhaustion time reach earlier because the binding sites become saturated in the column. But as the initial metal concentration is decreased the breakthrough and exhaustion time become large because transport is slow due to decrease in diffusion coefficient. As per results from Fig. 4.46(a)—(c), 100 mg/L has been choosen as an optimum initial metal concentration. Fig. 4.46(a)—(c), shows that the removal order is as follows Cr > Cu > Cd. Chromium metal has the highest removal than copper and cadmium due to the highest breakthrough time. Sukumar et al. 2016 has performed continuous study for removal of chromium using co-immobilized activated carbon with bacillus subtilis and reported that 100 mL/min of flow rate as an optimum for efficient metal removal.

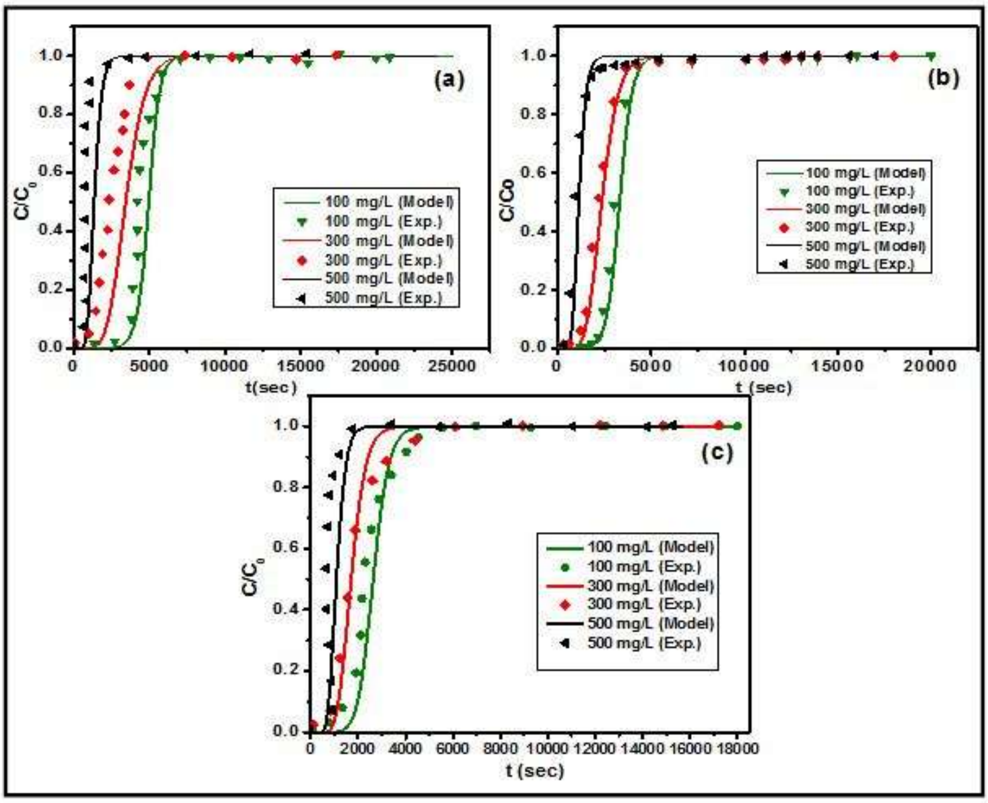


Fig. 4.46 Effect of initial metal concentration on breakthrough curve for (a) chromium (b) copper (c) cadmium

(iii) Effect of bed height

Fig. 4.47(a)—(c) shows breakthrough curves obtained for adsorption of copper, cadmium and chromium separately at various bed height of 0.15, 0.30 and 0.45 m, at flow rate of 5 mL/min and initial metal concentration of 100 mg/L. Breakthrough time increases from 1192-8245 s for chromium, 457-3000 s for copper and 448-2712 s for cadmium on increasing bed height from 0.15 m to 0.45 m. However, exhaustion time varies 17000-20000 s for chromium, 8000-10000 s for copper and 6000-9000 s for cadmium on increasing the bed height from 0.15 m to

0.45 m, the details of which are given in Table 4.22. Higher bed height means large amount of adsorbent and also large mass transfer zone. It will also take large time to reach the mass transfer zone to the exit, thus higher bed height will increase the breakthrough and exhaustion time. As per results from Fig. 4.47(a)—(c), 0.30 m has been choosen as an optimum bed height. Fig. 4.47(a)—(c) shows that the removal order is Cr > Cu > Cd and chromium metal has highest removal than copper and cadmium due to the highest breakthrough time.

Sukumar et al., 2016 has performed continuous study for removal of chromium using co-immobilized activated carbon with bacillus subtilis and reported that 0.10 m of bed height as an optimum for efficient metal removal. Ronda et al., 2018 has performed continuous study for removal of lead using olive tree pruning and reported that 0.057 m of bed height as an optimum for efficient metal removal. However, Calero et al., 2018 has performed continuous study for removal of copper using olive stone and pinion shell and reported that 0.044 m of bed height as an optimum for efficient metal removal.

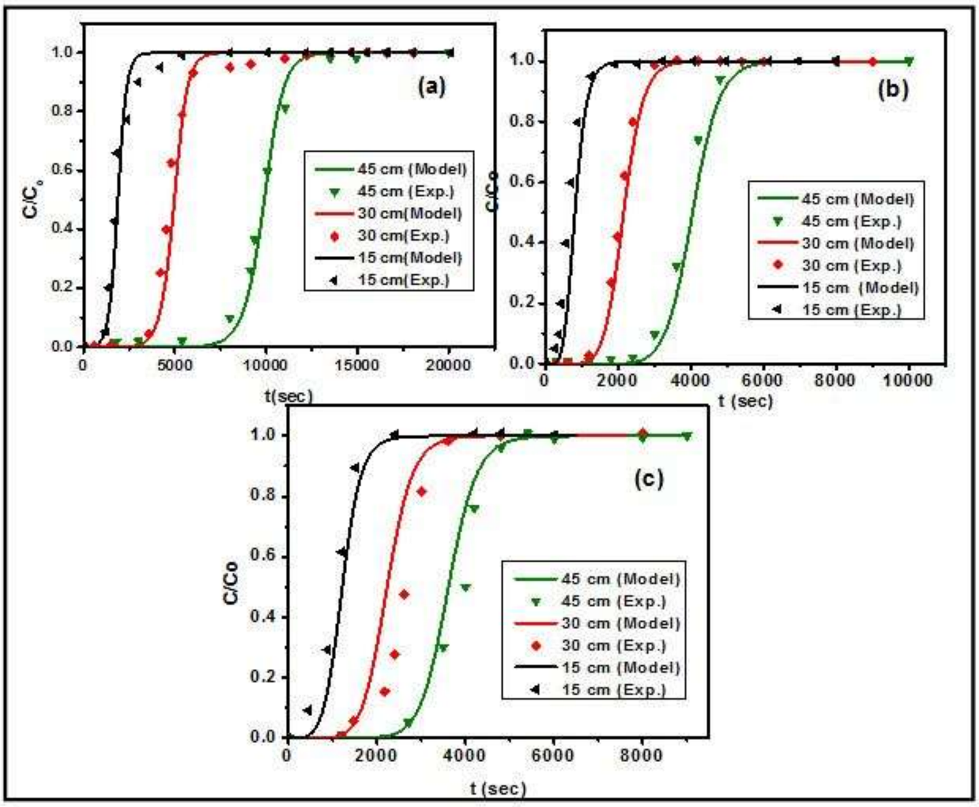


Fig. 4.47 Effect of bed height on breakthrough curve for (a) chromium (b) copper (c) cadmium

Table 4.22: Breakthrough and exhaustion time for copper, cadmium and chromium at various parameters in individual metal study

Parameters	**Breakthrough time (s)**		
	Cd	**Cr**	**Cu**
Bed height (0.15 cm – 0.30cm - 0.45 cm)	448-1471-2712	1192-3803-8245	457-2000-3000
Overall removal efficiency (mg/g)	0.893-1.785	1.790-5.050	0.990-2.380
Flow rate (5-10-15 mL/min)	4052-1404-382	9431-3803-776	4390-1480-445
Overall removal efficiency (mg/g)	5.370-4.640	7.360-5.950	5.950-5.000
Initial metal concentration (100-300-500 mg/L)	1852-1089-702	3803-2029-859	2343-1415-708
Overall removal efficiency (mg/g)	1.780-0.890	10.410-6.200	8.320-5.960
	Exhaustion time (s)		
	Cd	**Cr**	**Cu**
Bed height (0.15 cm – 0.30cm - 0.45 cm)	6000-8000-9000	17000-17500-20000	8000-9000-10000
Flow rate (5-10-15 mL/min)	18000-16000-15621	25000-22000-20000	20000-19000-18000
Initial metal concentration (100-300-500 mg/L)	18000-17000-15263	25000-22000-21000	20000-18000-17000

(iv) Model validation

The breakthrough curves obtained from experimental data and model data are shown in Fig. 4.45—4.47. In Fig. 4.45(a)—(c), The *R*-square value for chromium is 0.99, 0.97, 0.91, for copper 0.95, 0.99, 0.99 and for cadmium is 0.99, 0.91, 0.99, respectively for flow rate of 5 mL/min, 10 mL/min and 15 mL/min. The chi-square value for chromium is 0.002, 0.084, 0.116, for copper 0.008, 0.450, 0.025 and for cadmium is 0.025, 0.497, 0.660, respectively for flow rate of 5 mL/min, 10 mL/min and 15 mL/min. The MAPE (Mean absolute percentage error) value for chromium is 1.900%, 2.610%, 1.820%, for copper 7.234%, 1.253%, 1.527% and for cadmium is 1.010%, 3.190%, 0.378% respectively for flow rate of 5 mL/min, 10 mL/min and 15 mL/min. In Fig. 4.46(a)—(c), The *R*-square value for chromium is

0.91, 0.91, 0.92, for copper 0.98, 0,98, 0.96 and for cadmium is 0.95, 0.98, 0.92 respectively for initial metal concentration of 100 mg/L, 300 mg/L and 500 mg/L respectively. The Chi-square value for chromium is 0.264, 0.178, 0.174, for copper 0.066, 0.045, 0.097 and for cadmium is 0.163, 0.036, 0.141 respectively for initial metal concentration of 100 mg/L, 300 mg/L and 500 mg/L respectively. The MAPE (Mean absolute percentage error) value for chromium is 2.460%, 8.050%, 8.180%, for copper 1.520%, 1.860%, 2.980% and for cadmium is 4.680%, 3.170%, 1.790%, respectively for initial metal concentration of 100 mg/L, 300 mg/L and 500 mg/L. In Fig. 4.47(a)—(c), The *R*-square value for chromium is 0.96, 0.98, 0.99, for copper is 0.95, 0.99, 0.99 and for cadmium is 0.96, 0.95, 0.96 for bed height 0.15 m, 0.30 m and 0.45 m respectively. The chi-square value for chromium is 0.105, 0.054, 0.016, for copper is 0.113, 0.014, 0.017 and for cadmium is 0.021, 0.183, 0.080 for bed height 0.15 m, 0.30 m and 0.45 m respectively. The MAPE (Mean absolute percentage error) value for chromium is 2.334%, 1.690%, 2.582%, for copper 1.406%, 3.818%, 5.969% and for cadmium is 1.170%, 3.170%, 4.260% for bed height 0.15 m, 0.30 m and 0.45 m, respectively.

It indicates that there is good agreement between model and experimental data. The high value of R-square, low value of chi-square and MAPE for all the parameters concludes that our model can predict the column behaviour with accuracy.

4.7.2.3 Mixed metal study

In mixed metal study three metals copper, cadmium and chromium were mixed together and passed through the continuous column. Mixed metal study was performed in fixed bed column for flow rate of 10 mL/min, initial metal concentration of 300 mg/L and bed height of 0.30 meter (Table 4.23). Fig. 4.48 shows effect of parameters on breakthrough curve for mixed metal study with error bars.

(i) Effect of flow rate

Fig. 4.48 (a), shows the breakthrough curve for copper, cadmium and chromium in mixed system at initial metal concentration of 100 mg/L, flow rate of 10 mg/L and bed height of 0.15 meter. It was observed that the breakthrough time in mixed metal study has been reached 1480 to 2929 s for copper, 1404 to 968 s for cadmium and 3803 to 2200 s for chromium. However, the exhaustion time reaches from 19000 to 24000 for copper, 16000 to 14000 for cadmium and 22000 to 20000 for chromium. In mixed metal study, breakthrough and exhaustion time has been decreased for chromium and cadmium due to the antagonistic effect, however for copper breakthrough time has been increased due to the synergistic effect as compared to the breakthrough time obtained for individual metal study.

(ii) Effect of initial metal concentration

Fig. 4.48 (b), shows the breakthrough curve for copper, cadmium and chromium in mixed system at initial metal concentration of 300 mg/L, flow rate of 5 mg/L and bed height of 0.15 meter. It was observed that the breakthrough time in mixed metal study for copper, cadmium and chromium has been reached from 1480 to 2037 s for copper, 1404 to 825 s cadmium and 3803 to 1514 s chromium. However, the exhaustion time reaches from 18000 to 22500 s for copper, 17000 to 14000 s for cadmium and 22000 to 17500 s for chromium.

For mixed metal, breakthrough time and exhaustion time has been decreased for chromium and cadmium due to antagonistic effect, however for copper breakthrough time has been increased due to synergistic effect as compared to the breakthrough time obtained for individual metal study.

(iii) Effect of bed height

Fig. 4.48 (c), shows the breakthrough curve for copper, cadmium and chromium in mixed system at initial metal concentration of 100 mg/L, flow rate of 5 mg/L and bed height of 0.30 meter. It was observed that the breakthrough time in mixed metal study for copper, cadmium and chromium has been reached from 2000 to 2783 s for copper, 1471 to 1436 s for cadmium and 3803 to 966 s for chromium.

However, the exhaustion time reaches from 9000 to 12000 s for copper, 8000 to 7000 s for cadmium and 17500 to 14656 s for chromium. In mixed metal study, breakthrough and exhaustion time has been decreased for chromium and cadmium due to antagonistic effect, however for copper breakthrough time has been increased due to synergistic effect as compared to the breakthrough time obtained for individual metal study.

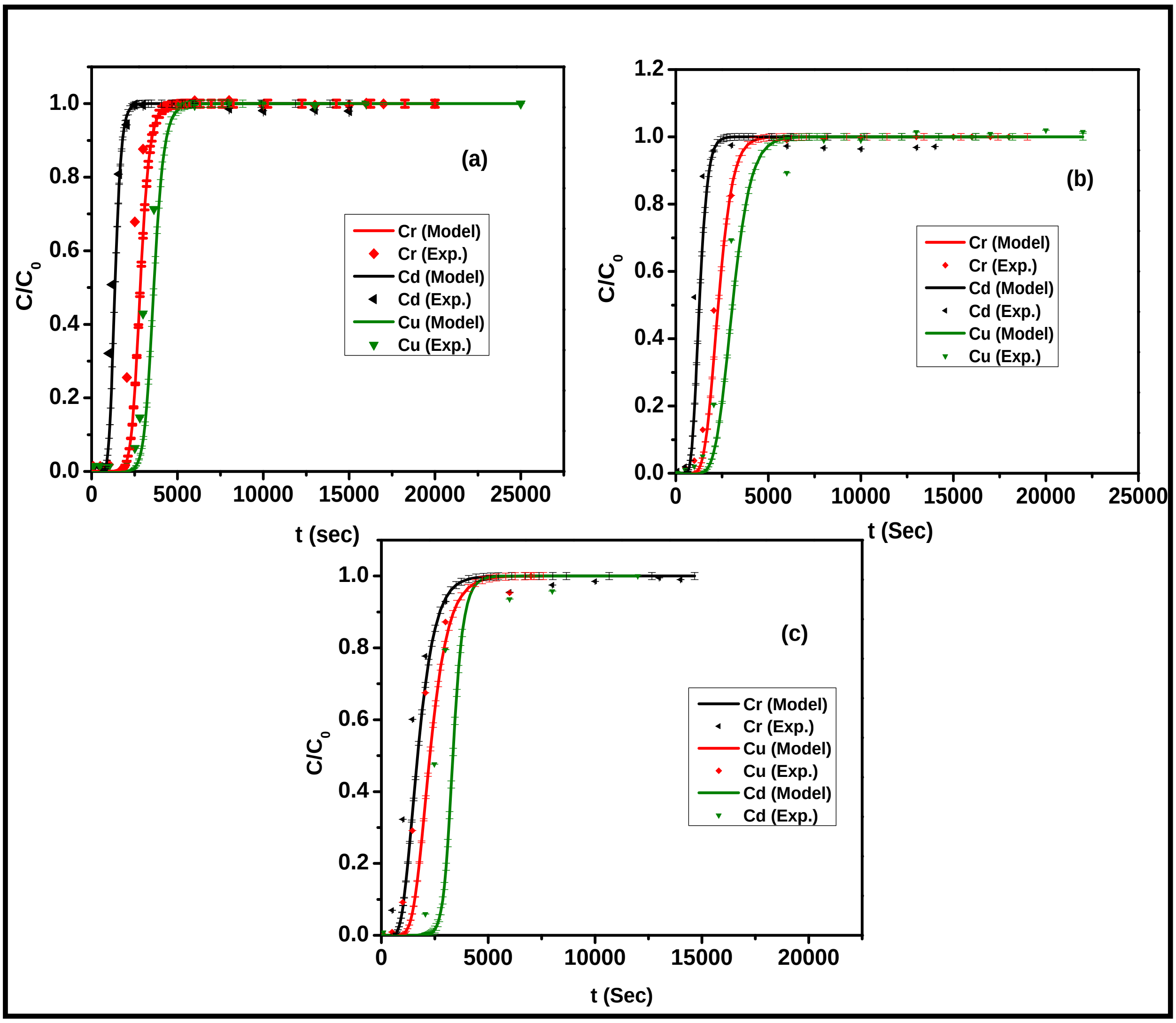


Fig. 4.48 Effect of parameters (a) flow rate = 10 mL/min (b) initial metal concentration = 300 mg/L (c) bed height = 0.30 cm on breakthrough curve for mixed metal study

Table 4.23 Breakthrough and exhaustion time for copper, cadmium and chromium at various parameters in mixed metal study

	Breakthrough time (s)		
Parameters	**Cd**	**Cr**	**Cu**
Bed height (0.30 cm)	1436	966	2783
Flow rate (10 mL/min)	968	2200	2929
Initial metal concentration (300 mg/L)	825	1514	2037
	Exhaustion time (s)		
Parameters	**Cd**	**Cr**	**Cu**
Bed height (0.30cm)	7000	14656	12000
Flow rate (10 mL/min)	14000	20000	24000
Initial metal concentration (300 mg/L)	14000	17500	22500

(iv) Model validation

Fig. 4.48 (a-c), shows breakthrough curves for copper, chromium and cadmium present in mixed metal system. Fig. 4.48(a), shows breakthrough curves for copper, chromium and cadmium at 10 mL/min flow rate. The value of R-square is 0.96, 0.89 and 0.95 for copper, chromium and cadmium respectively. The chi-square value is 0.133%, 0.283%, 0.098% for copper, chromium and cadmium respectively. Further, the MAPE value is 0.071%, 0.037%, 0.145% for copper, chromium and cadmium. Fig. 4.48(b) shows breakthrough curves for copper, chromium and cadmium at 300 mg/L initial metal concentration. The value of R-square is 0.98, 0.99 and 0.93 for copper, chromium and cadmium respectively. The chi-square value is 0.061%, 0.018%, 0.114% for copper, chromium and cadmium respectively. Further, the MAPE value is 0.218%, 0.068%, 0.380% for copper, chromium and cadmium. Fig. 4.48(c), shows breakthrough curves for copper, chromium and cadmium at 0.30 cm bed height. The value of R-square is 0.93, 0.95 and 0.93 for copper, chromium and cadmium respectively. The chi-square value is 0.439%, 0.100%, 0.103% for copper, chromium and cadmium respectively. Further, the MAPE value is 0.700%, 0.332%, 1.140% for copper, chromium and cadmium. These values high value of R-square, low values of chi-square and MAPE shows that the model value and experimental value are close enough.

4.7.2.4 For simultaneous removal of heavy metal and dye

In simultaneous removal, heavy metals (copper, cadmium and chromium) and dye (acid black 60) were mixed together and passed through the continous column. Simultaneous removal of heavy metals and dye was performed for flow rate of 10 mL/min, initial metal concentration of 300 mg/L and bed height of 0.30 meter (Table 4.24).

(i) Effect of flow rate

Fig. 4.49 (a), shows the breakthrough curve for simultaneous removal of copper, cadmium, chromium and dye at initial metal concentration of 100 mg/L, flow rate of 10 mg/L and bed height of 0.15 meter. It was observed that the breakthrough time in simultaneous study has been reached to 2929 to 1946 s for copper, 968 to 769 s for cadmium and 2200 to 1092 s for chromium, 4414 to 3553 s dye. However, the exhaustion time reaches from 24000 to 13306 s for copper, 14000 to 11984 s for cadmium, 20000 to 17016 s for chromium, 20000 to 19418 s for dye. In simultaneous removal study, breakthrough and exhaustion time has been decreased for copper, cadmium, chromium and dye due to the antagonistic effect.

(ii) Effect of initial metal concentration

Fig. 4.49 (b), shows the breakthrough curve for copper, cadmium and chromium in mixed system at initial metal concentration of 300 mg/L, flow rate of 5 mg/L and bed height of 0.15 meter. It was observed that the breakthrough time in mixed metal study for copper, cadmium and chromium has been reached from 2037 to 922 s for copper, 825 to 512 s for cadmium, 1514 to 565 s for chromium and 4653 to 2870 s for dye. However, the exhaustion time reaches from 22500 to 20000 s for copper, 14000 to 11981 s for cadmium, 17500 to 16406 s for chromium and 20000 to 18393 s for dye.

In mixed metal study, breakthrough and exhaustion time has been decreased for copper, cadmium, chromium and dye due to the antagonistic effect.

(iii) Effect of bed height

Fig. 4.49 (c), shows the breakthrough curve for copper, cadmium and chromium in mixed system at initial metal concentration of 100 mg/L, flow rate of 5 mg/L and bed height of 0.30 meter. It was observed that the breakthrough time in simultaneous removal study for copper, cadmium and chromium has been reached from 2783 to 1925 s for copper, 1436 to 1034 s for cadmium, 966 to 542 s for chromium and 4826 to 3712 s for dye. However, the exhaustion time reaches from 12000 to 10184 s for copper, 7000 to 6749 s for cadmium, 14656 to 12406 s for chromium and 20000 to 17000 for dye. In mixed metal study, breakthrough and exhaustion time has been decreased for copper, cadmium, chromium and dye due to the antagonistic effect

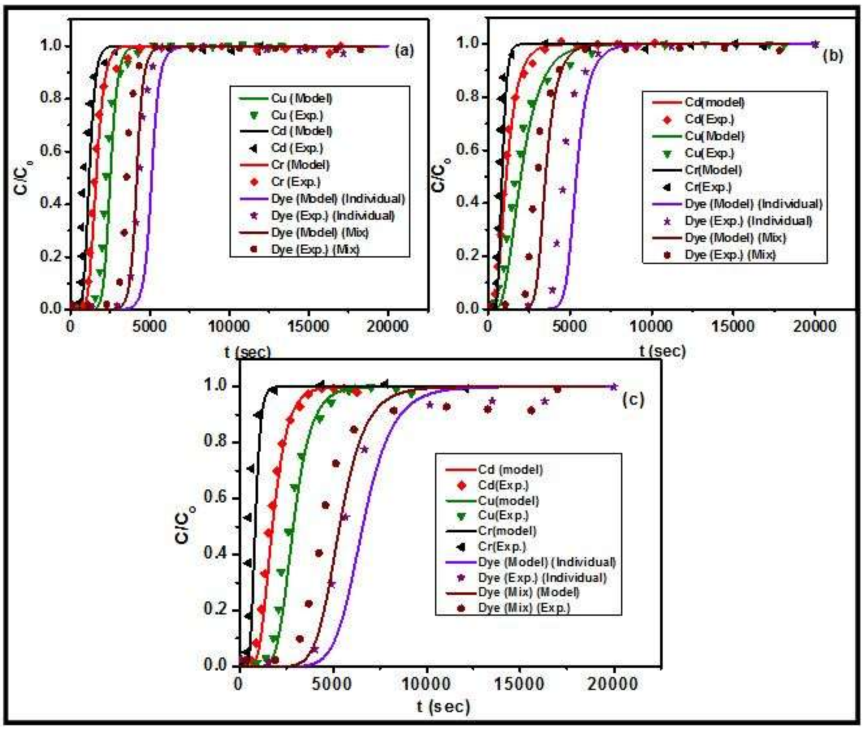


Fig. 4.49 Effect of parameters (a) flow rate = 10 mL/min (b) initial metal concentration = 300 mg/L (c) bed height = 0.30 cm on breakthrough curve for simultaneous removal study

Table 4.24 Breakthrough and exhaustion time for copper, cadmium, chromium and dye at various parameters in simultaneous removal study

Parameters	**Breakthrough time (s)**			
	Cd	**Cr**	**Cu**	**Dye**
Bed height (0.30 cm)	1034	542	1925	3712
Flow rate (10 mL/min)	769	1092	1946	3553
Initial metal concentration (300 mg/L)	512	565	922	2870
Parameters	**Exhaustion time (s)**			
	Cd	**Cr**	**Cu**	**Dye**
Bed height (0.30 cm)	6749	12406	10184	17000
Flow rate (10 mL/min)	11984	17016	13306	19418
Initial metal concentration (300 mg/L)	11981	16406	20000	18393

4.8 Industrial wastewater treatment

In this study, without treated wastewater samples were collected from textile, dye, and tannery and electroplating industry. Physico-chemical analysis was performed for collected samples and column experiments were performed at optimum conditions.

4.8.1 Textile industry wastewater

Physico-Chemical characteristics of wastewater sample are presented in Table 4.25. The column experiments were performed at optimum conditions such as flow rate of 5 mL/min, bed height of 0.45 meter and initial metal concentration of 3.91 mg/g, 3.218 mg/g and 1.23 mg/g for chromium, copper and cadmium respectively for textile industry wastewater treatment. In textile industry wastewater three metals such as copper, cadmium and chromium were present together. It was observed that the breakthrough time is 23245 s, 20496 s and 15233 s for copper, cadmium and chromium respectively and exhaustion time is 50000s, 44000 s and 38000 s for copper, cadmium and chromium respectively (Fig. 4.50).

Table 4.25: Physico-Chemical characteristics of wastewater sample collected from textile industry of Bhilwara industrial area, Jaipur

Parameter	Value
pH	6.88
TDS	6,832 mg/L
TOC	100 mg/L
Color	Yellow
Heavy metals	Cu – 3.91 mg/L
	Cr – 3.22 mg/L
	Cd – 1.23 mg/L
Removal efficiency	Cu – 4.08 mg/g
	Cr – 7.57 mg/g
	Cd – 2.10 mg/g

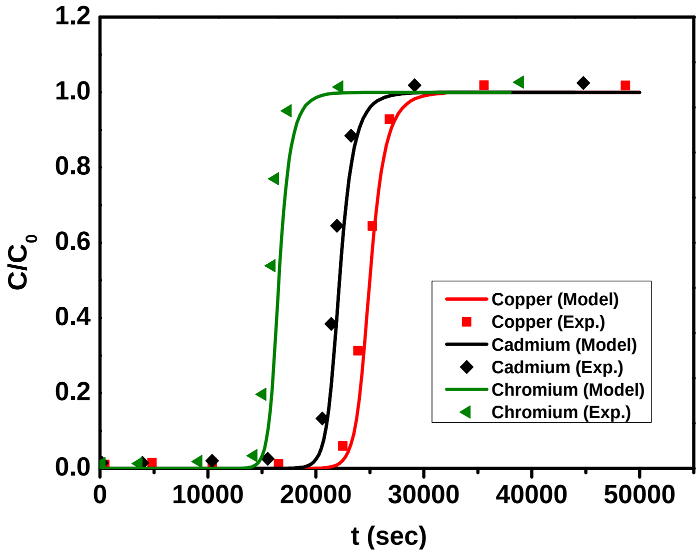


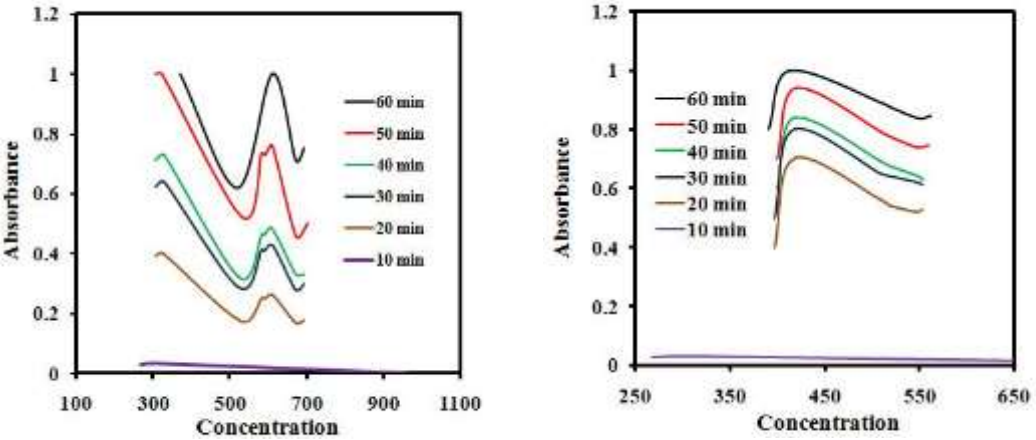
Fig. 4.50 Breakthrough curve for copper, chromium and cadmium removal from textile industry wastewater at flow rate of 5 mL/min, bed height of 0.45 meter

4.8.2 Dye industry wastewater

Dye wastewater sample was collected from bhilwara industrial area, Jaipur. Physico-Chemical characteristics of wastewater sample are presented in Table 4.26. The column experiments were performed at optimum conditions such as flow rate of 5 mL/min, bed height of 0.45 meter. Samples were collected at an interval of 10 minute and complete dye was removed after 1 hr as shown in Fig. 4.51.

Table 4.26: Physico-Chemical characteristics of dye sample collected from dye industry of Bhilwara industrial area, Jaipur

Parameter	Sample-1	Sample-2
pH	7.51	7.61
TDS	723.60 mg/L	2,055 mg/L
TOC	189 mg/L	180 mg/L
Color	Blue	Purple
λ_{max}	581 nm	519 nm
Heavy metals	Cu - 0.001 mg/g	Not present
	Cr - 0.008 mg/g	
	Cd- not present	



(a) **(b)**

Fig. 4.51 Fig: Absorption spectra for dye removal in (a) sample-1 (b) sample-2 at various time interval

4.8.3 Tannery industry wastewater

Tannery industry wastewater sample was collected from industrial area of Kanpur, U.P. Physico-Chemical characteristics of wastewater sample are presented in Table 4.27. Then column experiments were performed at optimum conditions such as flow rate of 5 mL/min, bed height of 0.45 meter and initial metal concentration of 0.575 mg/g for chromium. Samples were collected at different time interval as shown in Fig. 4.52.

Table 4.27 Physico-Chemical characteristics of wastewater sample collected from tannery industry of Kanpur, U.P.

Parameter	Value
pH	12.74
TDS	12,850 mg/L
TOC	816 mg/L
Color	Greenish brown
Heavy metals	Cr – 0.58 mg/g
	Cu – not present
	Cd – not present
Removal efficiency	0.96 mg/g

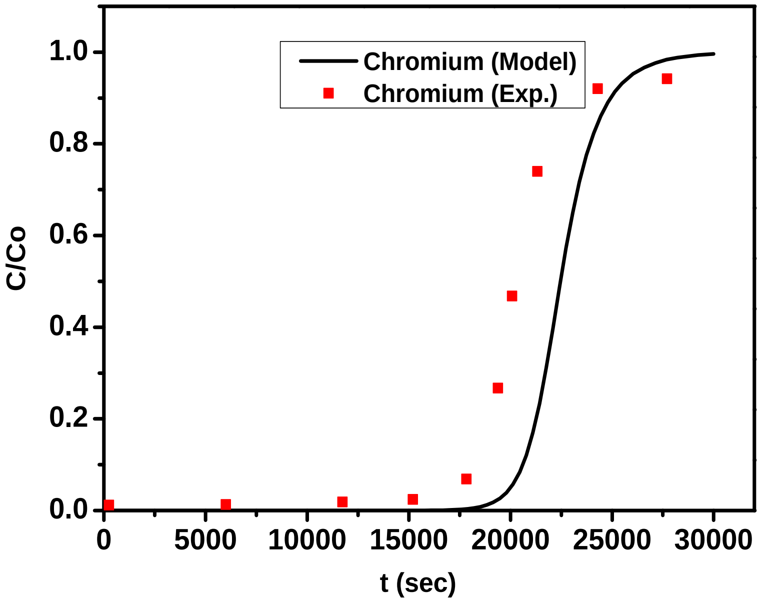


Fig. 4.52 Breakthrough curve for chromium removal from tannery industry

wastewater at flow rate of 5 mL/min, bed height of 0.45 meter

4.8.4 Electroplating industry wastewater

Electroplating industry wastewater sample was collected from industrial area of Jaipur. Physico-Chemical characteristics of wastewater sample are presented in Table 4.28. Then column experiments were performed at optimum conditions such as flow rate of 5 mL/min, bed height of 0.45 meter. Samples were collected at different time interval as shown in Fig.4.53.

Table 4.28 Physico-Chemical characteristics of wastewater sample collected from electroplating industry of, jaipur

Parameter	Value
pH	5.84
TDS	40,000 mg/L
TOC	8,320 mg/L
Color	Yellow
Heavy metals	Cu-0.97
	Cd-0.45
Removal efficiency	Cu – 0.46 mg/g
	Cd – 0.13 mg/g

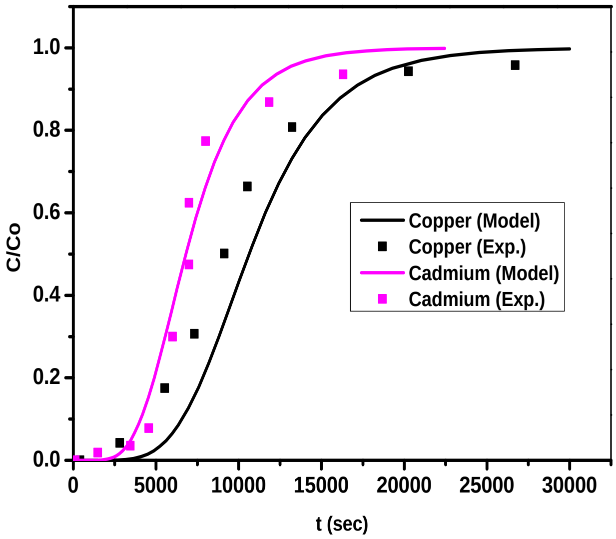


Fig. 4.53 Breakthrough curve for chromium removal from Electroplating industry wastewater at flow rate of 5 mL/min, bed height of 0.15 meter

4.9 Comparison with other related study

In Table 4.29, present work was compared with other related studies and large breakthrough curve and exhaustion time was observed.

Table 4.29 Result of present work compared with other related studies in continuous study

Heavy metals	Optimum conditions	Breakthrough time (s)	Exhaustion time (s)	References
Cadmium	flow rate 1 mL/min, bed height 2.5 cm and initial concentration 100 mg/L.	64,800	31,3200	Akhigbe et al., 2016
chromium	flow rate 3 mL/min, bed height 20 cm and initial concentration 100 mg/L.	9000	24,000	Sukumar et al., 2016
copper	flow rate 2 mL/min, bed height 13.4 cm and initial concentration 40 mg/L.	2,400	15,000	Calero et al., 2018
Copper, cadmium	flow rate 10 mL/min, bed height 12 cm and initial concentration mg/L.	3,000	12,600	Tadepalli & Srivastava., 2016
copper, chromium and cadmium	flow rate 5 mL/min, bed height 45 cm and initial concentration 100 mg/L.	4,390 9,431 4052	20,000, 25,000 and 18,000	Present study

CHAPTER - 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

The conclusions of this study are as follows:

1. An adsorbent from wheat bran was prepared and treated with HCl. The pellets of the modified adsorbent in the size 2 to 2.5 mm were prepared by using Chitosan and clay as binders.
2. The modified adsorbent was characterised for SEM, EDS, XPS, XRD, FTIR, point of zero charge, and BET.
3. The results in the present study show that modified wheat bran is an efficient adsorbent for copper, chromium, and cadmium. The optimum operating conditions for maximum adsorption were obtained by statistical analysis as given below:
    a. The optimum adsorption conditions for copper removal by modified wheat bran are initial metal concentration 76.17 mg/L, pH 4.58, temperature 41°C, and adsorbent dose 2.86 g/100 mL at which 99.55% copper removal was obtained.
    b. The optimum adsorption conditions for chromium removal by modified wheat bran are initial metal concentration 57.50 mg/L, pH 2.00, temperature 55°C, and adsorbent dose 2.75 g/100 mL at which 98.56% chromium removal was obtained.
    c. The optimum adsorption conditions for cadmium removal by modified wheat bran are initial metal concentration 15.08 mg/L, pH 9.51, temperature 37.08°C, and adsorbent dose 0.576 g/100 mL at which 98.03% cadmium removal was obtained.

    Therefore, initial metal concentration 90.58 mg/L, pH 6, temperature 35.9°C, and adsorbent dose 2.39 g has been selected as an optimum condition for heavy metal removal from mixed metal solution.

The order of maximum adsorption capacity for heavy metal removal is chromium > copper > cadmium.

4. From the results, it has been found that initial copper concentration, adsorbent dose, and temperature have the most significant effect on the removal efficiency of copper. Adsorbent dose, pH and temperature played significant effect on removal efficiency of chromium. Initial metal concentration and temperature have the most significant effect on cadmium removal.
5. The adsorption followed the pseudo-second order model for all the metals.
6. The equilibrium data fitted well to both Langmuir and Temkin isotherms with the maximum adsorption capacity of 4.33 mg/g for copper, 9.0 mg/g for chromium, and 3.37 mg/g for cadmium.
7. At optimum temperature of 35°C, the changes in Gibbs free energy (ΔG) values are −9543.70, −7253.85 and −8806.17 J/mol for copper, chromium and cadmium, respectively. The change in enthalpy values (ΔH) are 13159, 22080 and −5,413 J/mol for copper, chromium and cadmium respectively. Further, the changes in entropy value (ΔS) are 68.40, 95.59 and 10.80 J/molK for copper, chromium and cadmium, respectively. From these thermodynamic parameters, it is obvious that adsorption process is spontaneous and endothermic for copper and chromium, but exothermic for cadmium.
8. In regeneration study, the adsorbent was regenerated and reused up to five cycles and it showed good desorption efficiency up to 95% for copper, 79% for cadmium and 80% for chromium.
9. Metal complex dyes were oxidised with hydrogen peroxide and in the presence of iron sulphate as a catalyst. It was observed that metal has been released after oxidation and then released metal was removed by adsorption process using modified wheat bran.
10. In ternary metal system, presence of both copper and chromium had antagonistic effect on cadmium removal, presence of cadmium had antagonistic effect and copper had synergistic effect on chromium removal, however for copper removal, cadmium and chromium had synergistic effect.
11. In simultaneous removal of dye and heavy metals, dye acted as an interferring species in heavy metal removal.

12. For fixed bed continuous study, the optimum conditions obtained are flow rate 5 mL/min, bed height 0.45 m and initial concentration 100 mg/L. Fixed bed column works efficiently at higher bed height, low flow rate and low initial metal concentration.
13. A dynamic mathematical model was developed for continuous fixed bed adsorption column to compare the breakthrough curve with experimental results. The high value of correlation coefficient R^2 up to 0.999, low value of chi-square and mean absolute percent error (MAPE) up to 0.025 and 0.378% for all the parameters indicate that the present model can predict the column behaviour with good accuracy and there is a good agreement in experimental data and model-predicted data obtained in MATLAB software.
14. In mixed metal continuous study, cadmium and chromium have synergistic effect on copper removal. However, in simultaneous removal of heavy metal and dye, dye causes antagonistic effect for heavy metal removal, as a result breakthrough and exhaustion time decrease.

5.2 Recommendations for future work

The following work is recommended for future:

1. Detailed study of metallic dye decomposition and release of metal in water can be done.
2. Adsorbent can be further modified by attaching various functional groups such as amino groups, hydroxyl groups, etc. which can enhance adsorption efficiency.
3. The continuous adsorption and regeneration can also be studied in fixed bed column.

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APPENDIX-A

1. Model Equation and boundary condition after discretization

c_0=c(2) + 2*v*dz* (cin-c(1)) / D_L [Derived from boundary condition]

dcdz(1) = -v*(cin-c(1)) / DL [Inlet Boundary condition]

d^2cdz^2(1)=(c_0-2*c(1)+c(2)) / dz^2

dqdt(i)=3*k_f*(c(i)-cs(i))/(rhop*a_p)

dcdt(i)=D_L*d^2cdz^2(i)-v*dcdz(i)-rhop*(1-eps)*dqdt(i)/eps [Model Equation]

dc dz(i) = (c(i+1) - c(i-1)) / (2*dz) [Formula used]

d^2cdz^2(i) = (c(i+1) - 2*c(i) + c(i-1)) / (dz^2) [Formula used]

dqdt(i) = 3*kf*(c(i) - cs(i)) / (rhop*a_p)

dcdz(i) = 0 [Inlet Boundary condition]

d^2cdz^2(i) = 2*(c(i-1)-c(i)) / dz^2

dqdt(i) = 3*k_f*(c(i)-cs(i)) / (rhop*ap)

dcdt(i) = D_L*d^2cdz^2(i) - v*dcdz(i) - rhop*(1-eps)*dqdt(i) / eps [Model equation after discretization]

2. MATLAB mathematical program used in Modelling

```
function [t, c, q]=finitemethod()
global Nz dz L cin
%inputs
Nz=100; %No. of FD intervals
%Nr=50;
L =0.45; %Length of fixed bed.,m
cin = 1; %inlet conc., mg/ml
dz=L/Nz;
 %Expt data...
texpt=[x,y,z  ];
cexpt=[a, b,c];
 %Grid
z=linspace(0,L,Nz+1);%Mesh
%r=linspace(0,R,Nr+1);
```

```
yinit(1:2*Nz+2)=0;
[t, y]=ode15s(@FDE,[0,20000],yinit);
c(:,1:Nz+1)=y(:,1:Nz+1);
q(:,1:Nz+1)=y(:,Nz+2:2*Nz+2);
figure(1),plot(t,c(:,end),texpt,cexpt,'o')
count=0;sumerror=0;
for i=1:length(cexpt)
if cexpt>0
count=count+1;
error=abs(c(i,end)-cexpt(i))/cexpt(i);
sumerror=sumerror+1;
End
end
MAPE=sumerror*100/count
function f=FDE(t,y)
global Nz dz  cin
c=y(1:Nz+1);
q(1:Nz+1)=y(Nz+2:2*Nz+2);
eps=0.59;
rhop=1.954; %particle density g/ml
DL=4.0259e-6; %Axial Dispersion Coefficient m2/s
kf = 0.3217e-4; %mass tr coeff, m/s
d=0.025; %Bed Dia, m
ap=0.002; %particle radius, m
FlowRate = 5/60; %mL/s
v=FlowRate*1e-6/(3.14*d^2/4); %superficial vel, m/s
%At i=1
i=1;
c0=c(2)+2*v*dz*(cin-c(1))/DL;
dcdz(1)=-v*(cin-c(1))/DL;
d2cdz2(1)=(c0-2*c(1)+c(2))/dz^2;
cs(i)=Langmuir(q(i));
```

```
dqdt(i)=3*kf*(c(i)-cs(i))/(rhop*ap);
dcdt(i)=DL*d2cdz2(i)-v*dcdz(i)-rhop*(1-eps)*dqdt(i)/eps;
 %At interior points
for i=2:Nz %loop over z-direction, skipping Ist and last grid points
dcdz(i)=(c(i+1)-c(i-1))/(2*dz);
d2cdz2(i)=(c(i+1)-2*c(i)+c(i-1))/(dz^2);
cs(i)=Langmuir(q(i));
dqdt(i)=3*kf*(c(i)-cs(i))/(rhop*ap);
dcdt(i)=DL*d2cdz2(i)-v*dcdz(i)-rhop*(1-eps)*dqdt(i)/eps;
end
%At i=Nz+1, Boundary point
i=Nz+1;
dcdz(i)=0;
d2cdz2(i)=2*(c(Nz)-c(Nz+1))/dz^2;
cs(i)=Langmuir(q(i));
dqdt(i)=3*kf*(c(i)-cs(i))/(rhop*ap);
dcdt(i)=DL*d2cdz2(i)-v*dcdz(i)-rhop*(1-eps)*dqdt(i)/eps;
f(1:Nz+1)=dcdt(1:Nz+1);
f(Nz+2:2*Nz+2)=dqdt(1:Nz+1);
f=f';
 function cs=Langmuir(q)
qm=4.33; %mg/g
b=0.529; %mL/mg
cs=q/(b*(qm-q));
```

BIO-DATA

RENU

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Educational Qualifications:

1. **Ph.D.**, Chemical Engineering
   Malaviya National Institute of Technology, Jaipur (from July, 2014 – December 2018)
   Thesis Title: "Adsorptive removal of copper, cadmium and chromium from wastewater: Modelling and Experimental study"
   Publications: Science citation indexed Papers- 3
   Scopus indexed Paper – 1
   Other reputed international Journal papers -6
2. **M.Tech** in Chemical Engineering
   Aligarh Muslim University, 2014(Marks obtained 81.60%) (Gold Medalist)
   Thesis Title: Modelling and simulation of reaction diffusion process in a porous catalyst: Evaluation of Effectiveness factor".
   Area of Work: catalysts, diffusion, modelling and simulation,
3. **B.Tech** in Chemical Engineering from MJP Rohilkhand University, Bareilly 2012, (Marks obtained 77.62%)
4. **Secondary (10th)** from U.P Board, 2006 (Marks obtained 72.33%),
5. **Higher Secondary (12th)** from U.P Board, 2008 (Marks obtained 69.81%)

Declaration

I hereby declare that all the above information are true and correct to the best of my knowledge.

Place: Jaipur **Renu**
Data: