

**REMOVAL OF COPPER AND CADMIUM IONS FROM
SYNTHETIC SOLUTION BY ADSORPTION USING
BAGASSE FLY ASH AS ADSORBENT**

A DISSERTATION

*Submitted in partial fulfilment of the
requirements for the award of the degree*

of

MASTER OF TECHNOLOGY

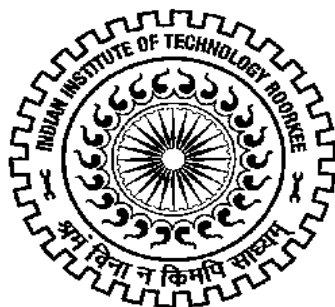
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CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2013**

DECLARATION

I hereby declare that the work being presented in the seminar report entitled “**Removal of copper and cadmium ions from synthetic solution by adsorption using bagasse fly ash as adsorbent**” in partial fulfilment of the requirements for the award of the degree of M. Tech. (with Specialization in Industrial Pollution Abatement) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee. This is an authentic record of my own work carried out during the period from June, 2012 to June, 2013 under the supervision of **Dr. Shri Chand**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The present study has been carried out on removal of copper and cadmium ions from synthetic waste water using bagasse fly ash (BFA) as an adsorbent. Study of various parameters like pH, adsorbent dose, contact time, initial metal ion concentration was done. Batch experiments were conducted for study purpose. pH = 6.0 was found to be optimum for the removal of both metal ions. Adsorbent dose = 4g/l and contact time of 90 min has been found to be optimum for copper removal, whereas adsorbent dose = 5g/l and contact time = 300 min found to be optimum for cadmium removal. Maximum removal was around 98.3% for copper ions and 98.6% for cadmium ions. Hill isotherm best fitted with experimental data for both copper and cadmium ions removal. Pseudo second order kinetics best fitted for both copper and cadmium ions removal.

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NOMENCLATURE

FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction
DTA	Differential Thermal Analysis
TGA	Thermo Gravimetric Analysis
SEM	Scanning Electron Microscope
BET	Brunauer–Emmett–Teller
C_e	Equilibrium concentration, mg/l
C_o	Initial concentration, mg/l
C_f	Final concentration, mg/l
BFA	Bagasse Fly Ash

1 INTRODUCTION

The increasing levels of heavy metals in the environment represent a serious threat to human health, living resources and ecological system. Although there are many sources of heavy metals, some industrial are at present those which contribute the most to environmental pollution with these toxic metals. Among such industrial sectors the metal finishing industry is an important one due to large number of enterprises by which is integrated as well as their geographical dispersion [Ayuso et. al., 2003]. Electroplating is also called metal finishing industry. In the electroplating process a fine layer of one metal is deposited on to another metal by electrolytic process. This process improves the properties like corrosion protection, surface hardness, colour etc. In large scale plants like automobiles electroplating operation is performed as a part of manufacturing process and in small units is performed as a job work.

The removal of toxic metals from waste water is a matter of great concern in the field of water pollution. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese etc. are known to be significantly toxic [Zheng et. al., 2008]. Metals like nickel, cadmium, platinum, gold, silver, chromium are costly which are used in electroplating industry and also these metals come out as a waste which is hazardous in nature. So it is important to control this waste as it is harmful to human as well as environment. To control these types of wastes proper technologies should be used. To achieve this government as well as private industries need to work together.

1.1 Impact of electroplating waste on environment and human health

A delicate balance exists between man and the environment. Lately this balance has been seriously disturbed by man's direct as well as indirect activities. Thousands of contaminants have found their way into the environment. The presence of metal ions in natural or industrial waste water and their potential impact has been a subject of research in environmental science for a long time. Metal ions such as cadmium, chromium, copper, lead, zinc and iron are commonly detected in both natural and industrial effluents [Singh et. al., 2005]. Various chemicals are used in electroplating industry. These chemicals include acids and alkalis (for cleaning purpose), inorganic materials like heavy metals and a few organic chemicals. Effects of these chemicals may be witnessed by following ways-

- a) When these chemicals directly react with air, water or soil.
- b) By the pathways of nonliving to living which cause toxicity to the living one.
- c) By getting in to food chain which mainly affects humans and cattle.

Due to discharge of large amounts of metal contaminated waste water, the electroplating industry is one of the most hazardous among the chemical intensive industries. Inorganic effluent from these industries contains toxic metals such as Cd, Cr, Hg, Cu, Ni, Pb and Zn which tend to accumulate in the food chain and they are usually associated with toxicity [Pereira et. al., 2010]. Heavy metals have no beneficial effects in humans. These are considered to be toxic for the human being and animals as well. Effects of these metals may include cancer, kidney damage, and even death in some cases. It is also found that once these metals are emitted in the environment, they remain for hundreds of years or more in the environment. Effect of various wastes are discussed below-

1.1.1 Cyanides

Cyanide is very toxic to human which may cause death to human. Lower concentration of cyanide to human may cause eye and skin irritation, weakness and headache. Toxic forms of cyanides are hydrogen cyanide, cyanide anion etc. Hydrogen cyanide is soluble in water and its solubility decreases with increase in the temperature.

1.1.2 Chromium

In nature chromium is found in plants, animals, rocks etc. Consumption of chromium is hazardous to human health as well as environment. Small amount of chromium may bring toxic effects to human and animals. In environment chromium is present in many forms. Most common forms of chromium are chromium metal, trivalent (III) and hexavalent (VI). Mainly Cr(III) and Cr(VI) are discharged with waste in the environment. Cr(III) is considered safe and effective nutrient for human body. Breathing in chromium to high level may create many problems with the nose. It can also create deceases like Asthma. Chromium(VI) can also develop many skin problems, damage to liver and sometimes kidney damage.

1.1.3 Cadmium

Cadmium is found in soil, rocks, earth's crust, fertilizers and also in combined with some elements like as oxygen (cadmium oxide). Cadmium enters in water and soil from electroplating industry effluent. In comparison to other metallic ions cadmium ions are easily adsorbed by plants. From roots of the plants cadmium spreads into leaves, fruits and seeds. Cadmium also transports itself into the animal milk and fatty tissues. When people consume such milk, food or plant, cadmium automatically gets inside the human body. Cadmium may cause damage to different parts of body like liver, kidney, lungs, bones, brain and nervous

system. Sometimes even moderate quantity of cadmium may create problem in stomach by bringing vomiting and diarrhea.

1.1.4 Lead

In an electroplating plant lead comes out with the wastes. It can also mix in air or contaminate with ground level drinking water and by this way it enters into the human body. Inside human body it gets distributed in blood and tissue. Long term exposure of lead in human body might result in weakness of nervous system. It may also damage the fingers, wrists and increase the blood pressure. It may also damage kidney, affect the brain or sometimes even cause death. It can also affect the sperm production.

1.1.5 Copper

Copper is one of the most common hazardous elements. Naturally copper occurs in soil, rocks, plants and animals. High concentration of copper in human body may cause many problems like liver damage. Hence it is very important to remove copper from waste.

1.1.6 Zinc

Zinc is one of the most common metals found in nature. Zinc is not very harmful to human body unless and until it's very high amount gets inside human body. If a human eats large amount of zinc then he may suffer with stomach cramps and vomiting. When high amount of zinc is taken for a long period of time then it may cause anaemia or damage the pancreas. If a person breathes fume or dust of zinc then he may suffer with short term disease called metal fume fever which affects the lungs of that person. These are the main effects of high amount consumption of zinc over a human body and hence it becomes essential to remove zinc from waste.

1.1.7 Silver

Silver plating is very common but used in a very few industries. When silver is taken in a high amount for a long period of time by a human body, it can cause discoloration of the skin and other body tissues. It can also cause breathing problem, lung and throat irritation and stomach pains. Sometimes skin contact of more quantity of silver in a human body can cause rashes or swelling.

1.1.8 Nickel

Nickel plating is one of the most common among plating operations. As a result, the amount of nickel waste is higher in industrial sector (electro plating). Although Nickel is not too dangerous for human body but a few people are found to be sensitive with nickel metal. These sensitive people may suffer with skin rashes when come into direct contact of nickel. It is found to be the most common effect of nickel on human body.

Table 1.1 Standards of electroplating industry discharge (Central Pollution Control Board, 2012)

Parameters	Limit value in mg/l (except for pH and temperature)
pH	6.0 to 9.0
Temperature	Shall not exceed 5°C above the ambient temperature of the receiving body
Oil and Grease	10
Suspended Solids	100
Total Metal	10
Trichloroethane	0.1
Trichloroethylene	0.1
Cyanides (as CN)	0.2
Aluminium	5.0
Tin	2.0
Fluorides (as F)	15
Phosphate (as P)	5.0
Cadmium (as Cd)	2.0
Nickel (as Ni)	3.0
Zinc (as Zn)	5.0
Hexavalent Chromium (as Cr)	0.1
Total Chromium (as Cr)	2.0
Copper (as Cu)	3.0
Lead (as Pb)	0.1
Iron (as Fe)	3.0
Sulphides (as S)	2
Sulphates (as SO ₄ ⁻²)	400

1.2 Objectives of the Present Work

The aim of the present work was to study the removal of copper and cadmium from synthetic waste water using Bagasse Fly Ash (BFA) as an adsorbent. The objectives of this work are given as-

1. Characterization of BFA which includes FTIR, XRD, TGA, BET surface area etc.
2. To study the utilization of BFA as an adsorbent to remove copper and cadmium from synthetic waste water.
3. To optimize the various parameters like pH, adsorbent dose during the adsorption process.
4. To select the suitable kinetic model (among the pseudo first order, pseudo second order model etc) for adsorption process based on regression analysis.
5. To select the adsorption isotherm model e.g. Langmuir, Freundlich etc. for the adsorption process by regression analysis.

2 LITERATURE REVIEW

In this section literature review on removal of copper and cadmium ions using various adsorbents is presented.

Shah et al., [2013] studied the use of synthesized zeolite sorbents and native BFA to remove the Cu(II) and Ni(II) from waste water. The characterization of adsorbents was done by XRF, FTIR, PXRD and SEM instruments. Batch column study was used to determine the sorption capacity and optimize the different sorption parameters. After calculating by Langmuir isotherm the sorption capacity for ECZBFA (Electrolyte Treated Conventional Zeolitic Bagasse Fly Ash) was found to be 93.72 mg/g for Cu ions. Best fitted isotherm was found Langmuir isotherm. Adsorption process was found to be endothermic in nature. By kinetic study it was found that second order kinetics was best fitted.

Segura et al., [2012] studied adsorption of cadmium by zeolite tuff and carbonaceous material which were obtained by pyrolysis of sewage sludge. Sodium zeolitic tuff was prepared by treating zeolitic tuff with sodium chloride and by treating it with the ferric chloride Fe-zeolitic tuff was prepared. After collecting the carbonaceous material (CM), it was treated with acid and washed with distilled water then it was used. Different parameters like pH, contact time, adsorbent dose and adsorbate concentration were studied. Langmuir adsorption isotherm was found to be best fitted. By kinetic study pseudo first order kinetic was found to best fitted. Maximum removal of cadmium ion was found to be around pH=6. Modified zeolitic tuff showed higher adsorption capacity in comparison to carbonaceous material for the removal of cadmium ion.

Zare et al., [2012] studied the removal of copper ion by activated sludge. The activated sludge was collected from pulp and paper industry. Batch process was used to study the adsorption process. Different parameters like pH, contact time, adsorbent dose were studied. DAS (Dried Activated Sludge) treated with 1 % H₂O₂ was found to be effective for the removal of copper ion. Optimum pH was found to be 5 at dose 3.5 g/l. Contact time was found to be optimized at 4 hour. Optimized copper ion concentration was 100 mg/l with maximum removal of 85%.

Jeon Choong et al., [2011] studied the removal of copper ion by using rice hulls as an adsorbent. Used rice hulls were having functional groups like hydroxyl, carboxyl and amino groups. Optimum pH was found to be 4. Langmuir isotherm was found to be best fitted with the experimental results. Maximum uptake capacity was 33% with 5 g of loading amount and it took 30 min to complete the adsorption process. NTA(organic material on copper) showed small effect in uptake capacity.

Lin et al., [2011] investigated adsorption of copper ion by HA-SMZ (Humic Acid Immobilized Surfactant Modified Zeolite) adsorbent when loading of Cetyl Pyridinium Bromide (CPB) was done on natural zeolite. SMZ (Surfactant Modified Zeolite) was prepared and by immobilization of humic acid (HA) on it HA-SMZ was prepared. Aqueous solution of copper ion was prepared for the adsorption study purpose. Adsorption of copper ion was found to be increased when pH was increased from 3 to 7. Pseudo second order Kinetics was found to be best fitted with the experimental data. Also the Langmuir isotherm was found to be best fitted with the experimental data. By the thermodynamic study it was found that adsorption process was endothermic in nature. Also by the study of removal of copper ion by HA-SMZ it was shown that adsorption process was not only chemical adsorption but it also involves in ion exchange process.

Panda et al., [2011] reported removal of cadmium and chromium ion by using dolochar as an adsorbent. Dolochar is a waste material which is obtained from iron industry. By the analysis of dolochar it was shown that it contains metallic iron, fused carbon, Ca-mg bearing phase, lots of voids and pores. Fixed carbon content of dolochar was found to be 13.8% and surface area $81.6 \text{ m}^2/\text{g}$. Batch adsorption experiments were used for the study purpose. By the experimental results it was shown that removal was higher in acidic pH in comparison to alkaline pH. Langmuir isotherm was found to be best fitted with the experimental data. Also pseudo second order kinetics was found to be fitted with the experimental results. Thermodynamic parameters like Gibb's free energy change, entropy change and enthalpy change were studied to study the removal of cadmium and copper ion by dolochar.

Senthikumar et. al., [2011] studied the removal of copper (II) ions by using Cashew nut shell as an adsorbent. Batch experiments were conducted to know the effect of pH, contact time, initial copper ion concentration and adsorbent dose. Optimum pH was found to be around 5.0. Results showed that removal of copper ion decreased when temperature was increased.

Equilibrium time was found about 30 min. Experimental data were fitted to Langmuir adsorption isotherm and Freundlich isotherm. Pseudo second order kinetics was found to be fitted with experimental data. By the thermodynamic study it was shown that adsorption process was exothermic in nature.

Huang et al., [2010] studied the removal of copper ions by modified activated carbon cloths. Characterization of ACF (Activated Carbon Fibre) was done by Fourier Transform Infrared Spectroscopy (FTIR), X-ray photo electron spectroscopy (XPS), Zeta potential. The initial pH of copper ion solution was set to 4 in the experiment. The equilibrium adsorption capacity was found to be 0.389 m mol/g which was double then that of open circuit. Maximum electro sorption capacity of copper ion on the impregnated ACF cloths was found to be 0.0854m mol/g which was 2.2 times then that of pristine cloths.

Chen et al., [2009] studied the removal of copper and lead ion by CM-BC (Carboxyl Methylated-Bacterial Cellulose). CMBC was synthesized by using acetobacter xylinum by the addition of CMC which is done in the culture medium. Effect of various parameters like pH, adsorbent dose and contact time were also studied. Optimum pH was found to be 4.5. Adsorption capacity for CM-BC found to be 12.63 mg/g (copper) and 60.42 mg/g (lead) while that in case of BC these values found to be 9.67 mg/g (copper) and 22.56 mg/g (lead). Hence CMBC showed better adsorption capacity than that of BC. Pseudo second order kinetics and Langmuir adsorption isotherm were found to be best fitted with the experimental data.

Kyzas et al., [2009] investigated the removal of copper and cadmium ion by chitosan derivatives. Chitosan sorbents were prepared by grafting with amide or Carboxyl groups. Equilibrium data was found to be best fitted to Langmuir isotherm. Optimized pH for carboxyl grafted chistosan was 6.0 while in case of amide grafted chitosan it was 4. Maximum adsorption capacity in case of carboxyl grafted chitosan was found to be 318 mg/g and in case of amide grafted chitosan maximum adsorption capacity was found to be 935 mg/g.

Tajar et al., [2009] reported removal of cadmium by sulfurized activated carbon. Used activated carbon was obtained from nut shell. Sulfurization of activated carbon was done by SO₂ gas at the ambient temperature. Effect of various parameters like pH, adsorbent dose and

contact time were also studied during adsorption process. It was found that removal increased with increase in pH. Maximum removal was found in case of SPAC (Sulfurized Prepared Activated Carbon) and it was about 92.4%. The adsorption was found suitable to both Langmuir and Freundlich adsorption isotherm and it was more fitted to Langmuir in comparison to Freundlich adsorption isotherm. The adsorption capacity was found 90.09 mg/g for CAC (Commercial Activated Carbon), 104.17 mg/g for PAC (Prepared Activated Carbon), 126.58 mg/g for SCAC (Sulfurized Commercial Activated Carbon) and 142.86 mg/g for SPAC (Sulfurized Prepared Activated Carbon).

Amber et al., [2008] studied adsorption of cadmium ions by olive cake. Batch adsorption experiments were conducted for the removal. Parameters like pH, adsorbent dose, contact time were also studied. Optimum pH was found to be 6 for the removal. At optimized pH the obtained removal efficiency was 66% at 30°C temperature. Experimental data fitted both Langmuir and Freundlich adsorption isotherm. By the study of thermodynamic parameters it was found that adsorption process was exothermic in nature. Pseudo Second order Kinetics was found to be best fitted with correlation coefficient value of 0.99.

Benhima et al., [2008] studied the removal of lead and cadmium ions by micro particles of dry plants. Different parameters like pH, adsorbent dose and contact time were studied. Optimum dose was found to be 25 g/l. For both metal ions maximum removal was obtained with particle size <50 micrometers. It was observed that removal increase with initial metal ion concentration in case of both metal ions. Removal of more than 90% was found in case of both metal ions.

Garg et al., [2008] studied removal of cadmium(II) by agricultural waste biomass. Used adsorbent were S.C.B. (Sugar Cane Bagasse), M.C.C. (Maize Corn Cob) and JOC (Jatropha Oil Cake). Batch experiments were carried out at pH range from 2 to 7, adsorbent doses 250 to 2000 mg and cadmium ion concentration from 5 to 500 mg/l and at contact time of 60 min. Maximum cadmium ion removal was found in case of JOC (99.5%). Optimum pH was found to be 6.0 at string speed of 250 rpm. Optimum adsorbent dose was 20 g/l. Removal in case of JOC, MCC and SCB were 99.5%, 99% and 85% respectively.

Liu et al., [2008] studied the removal of copper and lead ions by DETA (Di Ethyl Tri Amines). The adsorbent (P-DETA) was prepared by amination of micro beads which were

prepared by glycidyl methacrylate and trimethylolpropane trimethacrylate co-polymerization. It was found that P-DETA was having a slightly higher adsorption uptake capacity for lead ions than copper ions. P-DETA showed excellent selectivity to adsorb copper ions over lead ions. During competitive adsorption in binary metal system P-DETA selectively adsorbed copper ions over lead ions, this shows greater electro negativity of copper ions over lead ions.

Y.C. Sharma [2008] studied removal of cadmium by adsorption on china clay. By the study of thermodynamic parameter it was found that adsorption process was exothermic in nature. When temperature was increased from 30 to 50°C, the removal decreased from 80.3% to 51.3% at initial concentration of 5.1×10^{-5} M of cadmium. Experiments were performed at pH 6.5. Reaction rate constant value at 30°C was found to be $5.1 \times 10^{-2} \text{ min}^{-1}$. Thermodynamic parameters like change in free energy, change in enthalpy and change in entropy were also determined.

Zheng et al., [2008] studied removal of copper and cadmium by areca waste. Optimum pH was found to be 5.6. Optimum contact time for adsorptive removal of copper and cadmium ions was 1h. Equilibrium value showed that process was following both Langmuir as well as Freundlich adsorption isotherm. It was also found that adsorption process might involve both surface adsorption and ion-exchange. It was also reported that copper and cadmium ion can be easily desorbed by adjusting pH values.

Marin et al., [2007] studied removal of cadmium by adsorption using orange waste as an adsorbent. FTIR was used for the characterization of adsorbent and batch experiments were conducted to study the adsorption process. During the experiments pH value range was from 4 to 6 and optimum adsorptive capacity were found to be 0.40, 0.41, 0.43 mmol/g at pH value range from 4 to 6.

Papandreou et al., [2007] studied removal of copper and cadmium by coal fly ash. Main source of coal fly ash is power plants. After collecting from power plants coal fly ash was converted to pallet form and then used for adsorption purpose. Optimum contact time was found to be 72h. Pseudo second order kinetics was found to be best fitted with experimental data. Adsorption capacity for copper and cadmium were found to be 20.92 and 18.98 mg/g respectively. Langmuir isotherm was found to be best fitted with experimental data.

Srivastava et al., [2007] studied adsorption of toxic metal ions by baggage fly ash (BFA) and rice husk ash (RHA) as an adsorbent. Cd(II), Ni(II) and Zn(II) metal ions were removed using BFA and RHA as an adsorbent. It was found that with increase in temperature adsorption rate increases. It was also shown that BFA had greater surface heterogeneity in comparison to RHA. Heat of adsorption was found to be in range of 26-44 kJ/molK and change in entropy was found to be in the range of 127-194 kJ/molK.

Srivastava et al., [2006] studied adsorption of cadmium and Nickel ions by baggage fly ash (BFA) as an adsorbent. Optimum pH value of the removal was found to be 6.0. Experimental conditions and parameters were including as contact time of 5h, temperature of 30°C, BFA dosage of 10 mg/l, initial concentration ranging from 10 to 100 mg/l at pH 6.0. Adsorption capacity of Ni(II) was found to be higher to Cd(II). Hydrochloric acid was found to be the best solvent for desorption. Maximum elution was noted 65% for Cd(II) and 42% for Ni(II).

Larous et al., [2005] studied removal of copper by using wood saw dust as an adsorbent. Batch experiment was conducted to study the adsorption process. Maximum removal was found at pH range from 2 to 8. Langmuir and Freundlich were found to be fitted with experimental data. Sodium chloride proved to be best extractant for the desorption process.

Yu et al., [2000] studied removal of copper by sawdust as an adsorbent. Optimum pH for removal was found to be 7.0. Adsorption capacity of sawdust for copper was found to be 1.7 mg/g. Linear Freundlich and Langmuir isotherms fitted the experimental data. Ion exchange was indicated to be one of the major mechanisms for adsorptive removal of copper by saw dust adsorbent.

3 TREATMENT METHODS FOR REMOVING COPPER AND CADMIUM

3.1 Treatment methods

Different treatment techniques for waste water taken with heavy metals have been developed in recent years both to decrease the amount of waste water produced and to improve the quality of the treated effluent. Although various treatments such as chemical precipitation, coagulation -flocculation, flotation, ion exchange and membrane filtration can be employed to remove heavy metals from contaminated waste water, they have their inherent advantages and limitations in application [Kurniawan et. al., 2006]. There are many methods to remove copper and cadmium from waste. Main methods of treatment are given below –

3.1.1 Chemical Precipitation

The method is very useful to remove heavy metals from the waste. At basic pH dissolved metal ions react with alkali and get precipitated, which can be easily removed. Reaction can be presented as –



where, M^{2+} = dissolved metal ions

$M(OH)_2$ = Precipitated metal hydroxide

Main heavy metals which are removed by this method are Zn(II), Cd(II) and Mn(II). Essential condition for chemical precipitation is basic medium which is generally completed by using lime or calcium hydroxide. Main advantages of chemical precipitation method are its simplicity, inexpensive, safe operation. There are also disadvantages associated with this method. One of them is requirement of large amount of chemicals. Also large amount of sludge is produced by this method and also it is a slow reaction with poor settling.

3.1.2 Coagulation-Flocculation

In the coagulation process some coagulating agents are added, as a result colloidal particles destabilize and get sedimented. Later on flocculating agent is added into it so that particle size increases and bulky floccules are formed which can be easily removed away. Generally ferric alum is used as coagulant and pH adjustment is essential parameter for this reaction. To remove heavy metal pH range from 11 to 11.5 is found to be effective. Main

advantage of this method over chemical precipitation includes improved sludge settling and sludge stability. Except these advantages there are few disadvantages also which are high operational cost, large amount of sludge production. These disadvantages can be overcome by using electro coagulation which produces small amount of sludge and removes even smallest colloidal particles. However further purification is still a problem associated with this method.

3.1.3 Flotation

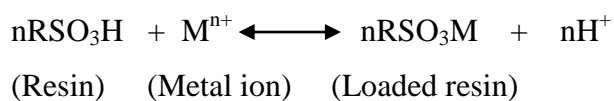
Flotation is used to remove solid or liquid from liquid phase. It removes heavy metals from waste by bubble attachment. Flotation can be of many types like dispersed air flotation dissolved air flotation, vacuum air flotation, electro flotation and biological flotation. But mostly used method for removing heavy metals is dissolved air flotation. Flotation provides better removal of small particles, less retention time and low cost. Flotation is a physical separation process but still it is found useful to remove heavy metals from waste water.

3.1.4 Membrane Filtration

This method is useful not only in case of suspended solid but also in case of organic compounds and inorganic contaminants like heavy metals as well. To remove heavy metals from waste water different membrane filtration processes like ultra filtration, reverse osmosis and nano filtration are used. Out of these methods which method is useful it will be decided by particle size to be removed. Other parameters which are helpful to decide the best method to be used are pH, temperature, waste water characteristics and compatibility of membrane with solution. Overall this method is useful to remove heavy metals from waste water.

3.1.5 Ion exchange

In comparison to other techniques discussed so far ion exchange is most useful to remove heavy metals from waste water. In ion exchange method resins are added and then inter change of charge takes place without any structural change of resin and loaded resin is removed. The equation can be given as –



If we compare chemical precipitation with ion exchange method then we find that there is no sludge disposal problem which reduces the operational cost of the process. Other advantages of ion exchange method are reliability and portability of this method. But there are some

disadvantages also associated with this method which are selection of suitable resin and removal of sludge.

3.1.6. Adsorption

In adsorption process mass transfer takes place from liquid to solid phase. In the adsorption process solid phase is introduced inside liquid phase and solute particle which were present in liquid phase, get transferred to solid phase. Hence adsorption is a separation process which involves fluid solid operation. The solid surface on which adsorption takes place is called adsorbent and solute which gets adsorbed on adsorbent is called adsorbate. Usually adsorbent is solid and adsorbate may be gas or liquid or solid. Dissolved heavy metal ions are adsorbed on the surface of adsorbent by using adsorption method.

Accumulation of heavy metals in the food chain and their persistence in nature, once they are discharged by numerous industrial activities, are well known phenomenon. There are many treatment process that can be used for the removal of metal ions from waste water and, certainly the cost plays an important, if not crucial, role for determining which one is to be applied consequently, in the last few decades alternative sorbents for the treatment of heavy metal contamination have been investigated [sciban et al., 2007].

Hence if we compare other removal methods with adsorption we find adsorption as the best method to remove heavy metals from waste water.

3.1.6.1 Adsorbents

Many adsorbents have been researched to remove heavy metals. General properties of an adsorbent should be that it should have a large surface area with high porosity. It should be free flowing for easy handling. It should be specific in properties for a particular adsorbate. Many adsorbents have been investigated so far, few of them are activated carbon, activated alumina, bone char, activated clays, silica gel, bagasse fly ash, rice husk ash, fuller's earth, zeolite etc. Adsorption process takes place on the wall of pores inside the adsorbent. When these pores of adsorbent are completely filled then capacity of adsorbent is decreased. In this situation no adsorption takes on the surface of adsorbent. To increase the capacity of adsorbent we use desorption process so that porosity of adsorbent is increased.

When we remove adsorbate by desorption and increase the adsorption capacity of adsorbent, this is called regeneration of adsorbent. For the last few decades different agricultural wastes have been investigated to remove heavy metals. These different adsorbent are saw dust,

sugarcane dust, Peanut, rice husk, orange peel, banana peel and many more. This work is mainly focused on study of adsorption behaviour of bagasse fly ash.

Table 3.1 Physical adsorption vs chemisorption

Physical Adsorption	Chemisorption
Adsorbed quantity by same amount of adsorbent is high.	Adsorbed quantity by same amount of adsorbent is low.
Energy of activation is low.	Energy of activation is high.
Adsorption rate decreases with temperature rise.	Adsorption rate increases with temperature rise.
Mass transfer controls the adsorption rate.	Surface reaction controls the adsorption rate.
Whole surface is used for physical adsorption.	Adsorption takes place on active sites of surface.
If partial pressure is low adsorption rate will also be slow and as partial pressure is high adsorption rate will also be high.	If partial pressure is low adsorption rate is high and at high partial pressure adsorption rate slightly increases.
Weak forces are used.	Stronger forces are used.
Heat of adsorption is low.	Heat of adsorption is high.
Its nature is non specific and whole surface is used in adsorption.	Specific in nature and only active sites are used in adsorption.
Reversible process	Irreversible process
Complete surface is covered and it can be extended to multilayer.	Complete surface is not covered and it is limited to unimolecular layer

3.1.6.2 Characteristics of adsorption by solids

The adsorption by solids has following characteristics

1. Adsorption depends on surface area, if surface area is large then adsorption rate will be high.
2. Adsorption rate depends on characteristics of both adsorbent and adsorbate. This is where selection of appropriate adsorbent plays the role in adsorption process.
3. It is a reversible process.
4. It is an exothermic process.

5. Amount of adsorbate adsorbed by adsorbent depends on concentration of adsorbate and temperature.

3.2 Copper and cadmium

Cadmium may enter into soil, water or human body by different sources like waste water of an industry. Cadmium is a metallic element which is soft, silvery white in colour. Cadmium is highly soluble in nitric acid, relatively lower soluble in HCl and slightly soluble in water. Atomic number of cadmium is 48 and atomic weight is 112.41 and density of cadmium is 8.642 g/cm^3 at 20°C . Melting point and boiling point of cadmium are 320.9°C and 765°C respectively. Cadmium is not an essential metal for human body and its exposure may show negative effects on human body. If contact is made with dust or fume of cadmium then it may cause irritation but it will not damage tissues. If fumes of cadmium are inhaled then it may damage the lungs. It may also create problems like headache, diarrhea and vomiting. Prolong exposure of cadmium may bring even kidney failure.

Copper metal is red in colour and crystalline in structure. It is ductile in nature. Atomic number and atomic mass of copper are 29 and 63.5 respectively. Density of copper is 8.9 g/cm^3 at 20°C . Melting and boiling points of copper are 1083°C and 25.95°C respectively. Although copper is not a toxic element and is essential for human body, still large quantity of copper brings many troubles for human body. These effects include irritation in different parts of body like mouth, nose and eyes. Sometimes it may also produce headache, stomach pain or diarrhoea. Too much amount of copper may bring liver or kidney damage or even death some times.

4 MATERIAL AND METHODS

In this work bagasse fly ash (BFA) is used for the removal of copper ion from synthetic sample and cadmium ion from another synthetic sample. Experimental details of study are presented in this Chapter.

4.1 Adsorbate

Synthetic waste water of copper ion having initial concentration of 100 mg/l and cadmium ion having initial concentration also of 100 mg/l were prepared for present study. Copper sulphate pentahydrate was obtained from R.F.C.L. Ltd. (Batch No. J022CI), New Delhi and Calcium Chloride monohydrate was obtained from Sisco Research Laboratories Pvt. Ltd. (Batch No. T- 8341323), Mumbai. Stock Solutions were prepared by adding 1g of copper sulphate in 1 litre distilled water (DW) and 1g of cadmium chloride in 1 litre distilled water separately.

4.2 Adsorbent

Bagasse fly ash (BFA) was collected from Uttam Sugar Mill, Manglaur (Dist. Haridwar), India. It was washed and dried and then used for adsorption purpose.

4.3 Characterization of Adsorbent

Characterization of BFA was done using standard procedures as described below.

4.3.1 Proximate Analysis

It involves measurement of moisture content, volatile content and ash content. In this process known amount of sample is taken in a crucible which is heated inside a furnace. By measuring the weight loss we measure the moisture, volatile and ash content. To know moisture content we put known amount of sample in an oven at 105-110°C for 1h. For volatile content we put known amount of sample in a crucible and then put it inside a furnace at 925±20°C for 7 min with lid closed. For ash content we put crucible with known amount of sample inside furnace at 700 to 750°C for 30 min with lid open.

4.3.2 Surface area

Brunauer–Emmett-Teller (BET) method provides the value of surface area of adsorbent. Principle of this method is based on adsorption of a gas on a surface. By knowing

the amount of gas adsorbed at given pressure we determine the surface area. BET (Micromeritics 2720, USA) available in our department was used to determine the surface area of the adsorbent.

4.3.3 XRD

XRD (X-ray diffraction) analysis provides information about degree of crystalline, deviation from ideal compositions, structure and degree of hydration. In a mixture sample XRD determines proportion of different minerals. XRD analysis of BFA was carried out by Phillips diffraction unit, in which copper target was used with nickel as filter media and k radiation was maintained at 1.542Å.

4.3.4 TGA

Thermo Gravimetric Analysis (TGA, Perkin Elmer, Japan) measure the rate of change of mass with respect to temperature or time in a controlled atmosphere. It describes the thermal stability of the material. TGA of bagasse fly ash was carried at 25 to 1000°C.

4.3.5 FTIR

Fourier Transform Infrared (FTIR, Nicolet 6700, USA) was used to identify the composition of the sample. Pallet technique is used for this purpose. Information provided by FTIR is a molecular finger print for organic, polymeric and in some cases inorganic material.

4.3.6 SEM

With the help of SEM (Scanning Electron Microscope) morphology of loaded and unloaded bagasse fly ash was studied. For this purpose coating of sample was done by gold so that conductivity was enhanced, then SEM spectra was recorded.

4.4 Analytical measurement

Concentrations of metallic solutions were determined by AAS (Atomic Absorption Spectrophotometer, Avanta, Australia). AAS works on the principle that neutral or ground state atoms of an element absorb electromagnetic radiation over a series of a very narrow range of detection wavelength. Concentration range of detection in AAS for Copper is 1 to 5 ppm and for Cadmium is 0.2 to 1.8 ppm. The calibration curve is shown in figures 4.1 and 4.2.

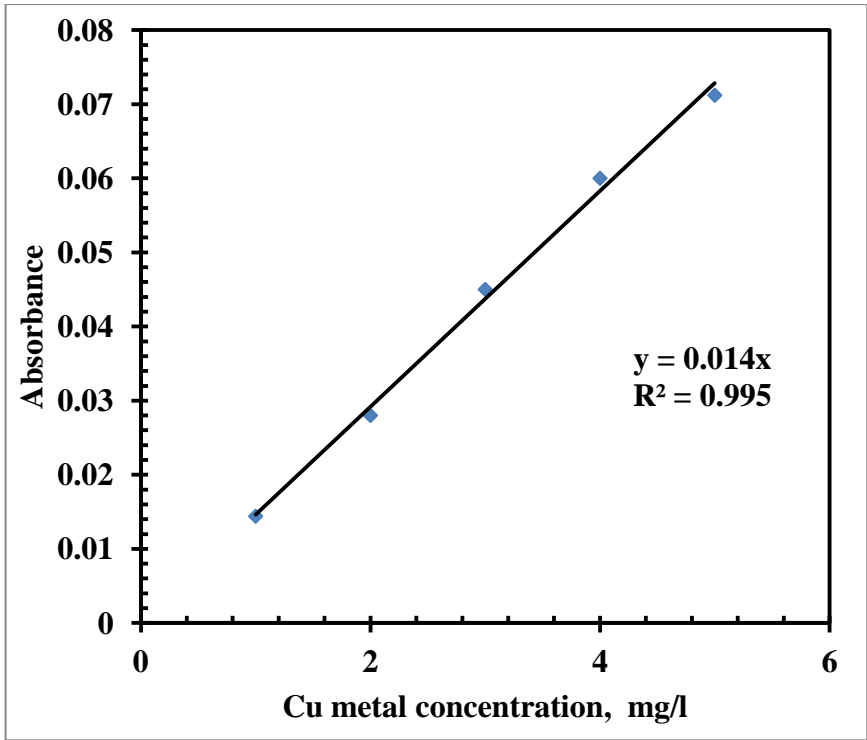


Figure 4.1 Calibration curve between concentration of copper ion and absorbance

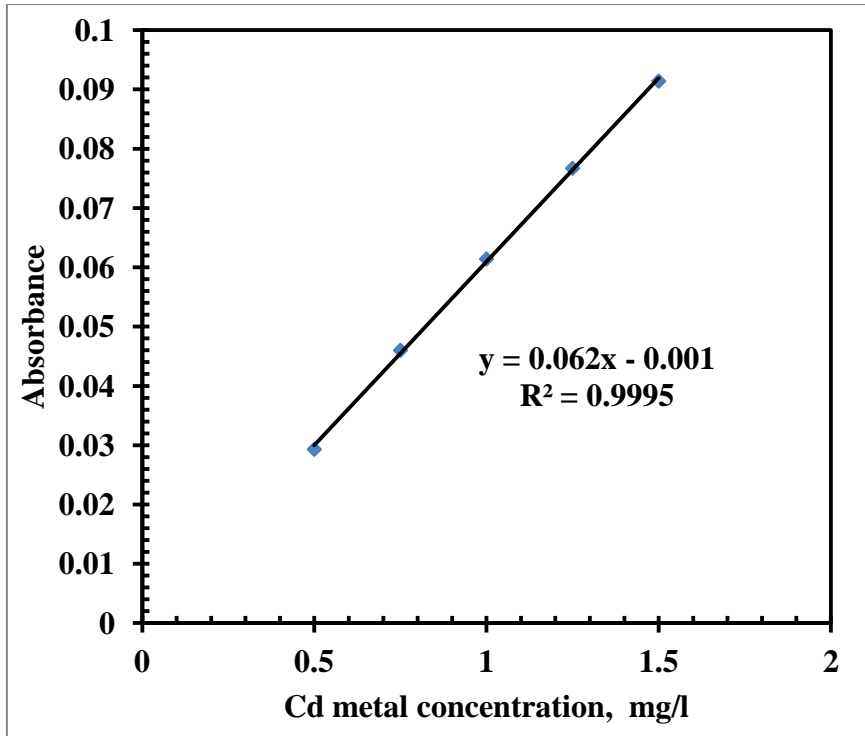


Figure 4.2 Calibration curve between concentration of cadmium ion and absorbance

4.5 Experimental programme

In this work removal of copper and cadmium by BFA adsorbent is studied. In the study effect of various parameters like pH, adsorbent dose, contact time were studied. To study these parameters batch experiments were conducted at the temperature of $30\pm 1^\circ\text{C}$. To conduct each experiment we took 100 ml of metallic solution in 250 ml conical flask. These samples were taken of known concentration; known pH and known amount of adsorbent were added in to it. These samples were put inside shaker at agitation speed of 150 rpm and temperature $30\pm 1^\circ\text{C}$. After that the samples were taken out after the appropriate time intervals. If BFA particles do not settle down easily then we centrifuged the samples at 6400 rpm for 5 min. After the experiment concentration of samples were known by AAS.

Study of effect of pH on the removal of copper and cadmium was done at pH range of 2 to 10. pH of samples were adjusted by using HCl and NaOH solution. To study effect of adsorbent dose we added different amount of adsorbent in each sample of 100 ml and while performing it we maintained the pH optimum for each and every sample and put the samples inside shaker till the equilibrium was attained. To study the kinetics same amount and same concentration of samples as above were put inside shaker for different time intervals. pH and adsorbent dose were kept fixed at optimum for all samples. To study adsorption isotherms metallic solutions of different concentrations were used and they were kept under different temperatures.

Batch experiments were conducted during all experiments. Also blank experiments were conducted simultaneously. In the blank experiment adsorbent was added in 100 ml of double distilled water at similar conditions. The percentage metallic removal and equilibrium adsorption uptake q_e (mg/g) was calculated by following equation

$$\% \text{ removal} = 100 \times (C_o - C_e) / C_o$$

$$\text{Adsorbed amount, } q_e = (C_o - C_e) V / m$$

where, C_e = equilibrium adsorbate concentration (mg/l)

4.6 Modeling studies

Before optimizing the design of adsorption of copper and cadmium by BFA, it is important to establish the correlation for equilibrium curves. Freundlich, Langmuir and Temkin isotherms were used to describe the adsorption of copper and cadmium by BFA.

4.6.1 Freundlich isotherm

The Freundlich expression is an empirical equation based sorption on a heterogeneous surface [Garg et al., 2008]. Freundlich equation is-

$$q_e = K_F C_e^{1/n}$$

or

$$\log q_e = \log K_F + 1/n \log C_e$$

where, C_e = equilibrium concentration of metal ion in the solution (mg/l)

K_F and n = Freundlich model constants

q_e = amount of metal ion adsorbed at equilibrium per gram of adsorbent (mg/g).

4.6.2 Langmuir isotherm

The Langmuir model assumes that the uptake of metal ions on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions [Anber et al., 2008]. Equation of Langmuir modal is given by –

$$q_e = q_{\max} bC_e / (1+bC_e)$$

Where, q_e = amount of metal ion at equilibrium per gram of adsorbent (mg/g)

q_{\max} =maximum metal up take per unit mass of adsorbent (mg/g)

This equation can be rearranged as –

$$C_e/q_e = 1/q_{\max}b + C_e/q_{\max}$$

Hence, if we plot C_e/q_e versus C_e , it will give straight line with slope $1/q_{\max}$ and intercept $1/q_{\max}b$.

4.6.3 Temkin isotherm

Assumptions of Temkin isotherm are –

- (a) Because of interactions between adsorbate heat of adsorption decreases linearly.
- (b) The characterisation of adsorption is done with help of distribution of binding energy.

Equation of Temkin isotherm is –

$$q_e = RT/b \ln(K_T C_e)$$

OR

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where, $B_1 = RT/B$

b = Tempkin energy constant (j/mole)

K_T = Explicitly which takes into account interaction between adsorbate and adsorbent.

4.6.4 Redlich-Peterson isotherm model

This isotherm is combination of both Freundlich and Langmuir isotherm. It is useful in wide range of concentration for homogeneous as well as heterogeneous system.

4.7 Kinetic and diffusion study

The kinetic study is done to determine the order of the reaction, which is described as follows:

4.7.1 Pseudo first order

Pseudo first order can be expressed as –

$$dq_t/dt = K_f (q_e - q_t)$$

Where, q_t = adsorbed amount at 't' time (mg/g)

q_e = equilibrium adsorption capacity (mg/g)

K_f = pseudo first order rate constant

t = contact time (min.)

Integrating the above equation and using, $q_t = 0$ at $t = 0$ we get –

$$\log (q_e - q_t) = \log q_e - k_f t / 2.303$$

With the help of plot between $\log (q_e - q_t)$ versus t we get value of adsorption rate constant k_f .

4.7.2 Pseudo second order

Equation of second order can be given as –

$$dq_t/dt = K_s (q_e - q_t)^2$$

Integrating above equation and using the relation, $q_t = 0$ at $t = 0$, we get

$$q_t = t K_s q_e^2 / (1 + t K_s q_e)$$

Where, K_s = pseudo second order rate constant (g/mg min).

4.7.3 Intra Particle Diffusion study

Adsorption process takes place in many steps. Basically film diffusion, pore diffusion, surface diffusion, adsorption on pore surface or combination of these steps. Intra particle diffusion equation can be given as –

$$q_t = K_{id} t^{1/2} + I$$

Where , K_{id} = Diffusion rate content.

5 RESULTS AND DISCUSSION

Detailed discussion of the experimental results is given in this chapter:

5.1 Characterization of BFA

Characterization of bagasse fly ash (BFA) includes proximate analysis, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA) etc.

5.1.1 Proximate Analysis

The proximate analysis is as shown in table 5.1.

Table 5.1 Proximate Analysis of BFA

Contents	Percentage
Moisture Content	12.16
Volatile Content	15.59
Ash Content	28.97
Fixed Carbon	43.28

5.1.2 BET Surface area

BET surface area of bagasse fly ash is given in table 5.2

Table 5.2 BET Analysis of BFA

Adsorbent	Mass of BFA used(g)	BET Surface Area (m ² /g)	Total Pore Volume (m ² /g)
BFA	0.0213	230.0687	0.1158

5.1.3 Bulk density

Bulk density of BFA was found by using bulk density meter in which a measuring cylinder was used to fill BFA up to the mark of 50 ml. Bulk density of BFA was found to be 0.081 g/ml and tapped density came out to be 0.088 g/ml.

5.1.4 Ultimate Analysis of BFA

The ultimate analysis is used to measure the quantity of components carbon, hydrogen, nitrogen, oxygen and sulphur present in sample. Result of ultimate analysis of bagasse fly ash is given in table 5.3.

Table 5.3 Ultimate Analysis of BFA

Elements %	Blank BFA	Cu Loaded BFA	Cd Loaded BFA
C	73.65	75.10	76.2
H	0.186	0.235	0.238
N	0.548	0.689	0.691
S	0.150	0	0
O	25.46	23.97	22.871
Weight used (mg)	3.290	3.237	3.242

5.1.5 X-ray diffraction analysis (XRD)

The XRD analysis of blank, copper (Cu) loaded and cadmium (Cd) loaded BFA shows the absence of any peak in the curve, which confirms the amorphous nature of the adsorbent or absence of crystalline structure (figures 5.1, 5.2 and 5.3).

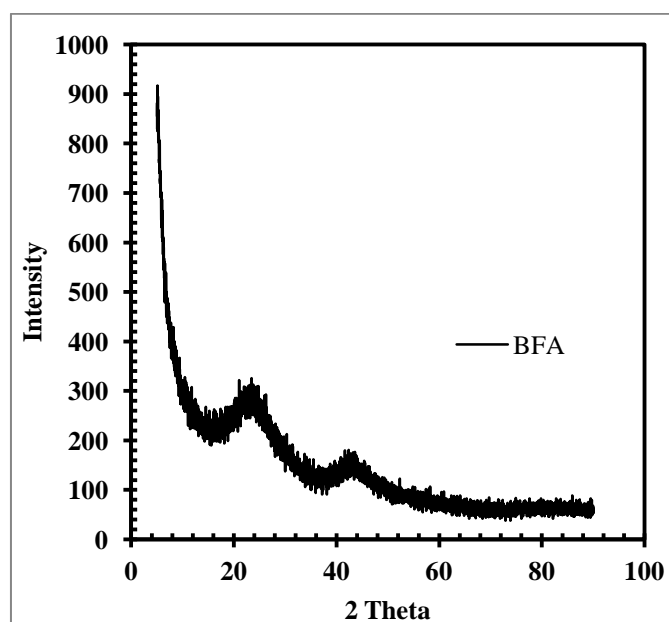


Figure 5.1 XRD of Blank BFA

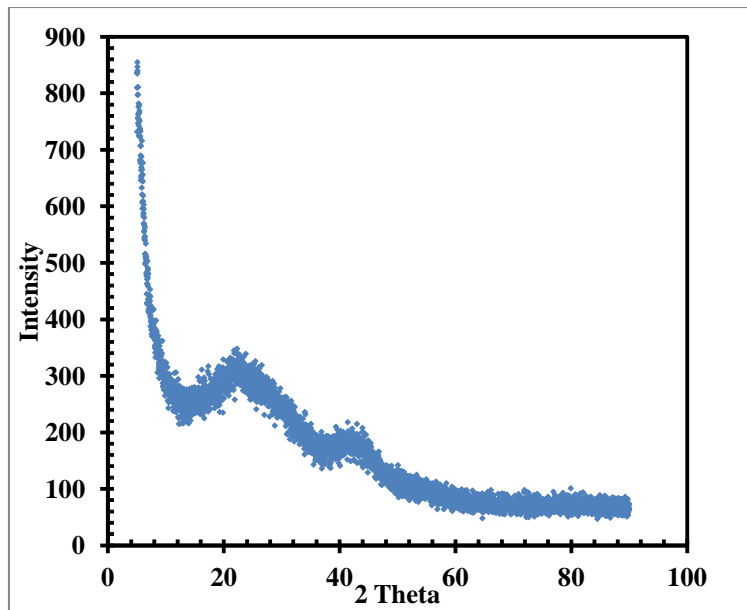


Figure 5.2 XRD of copper loaded BFA

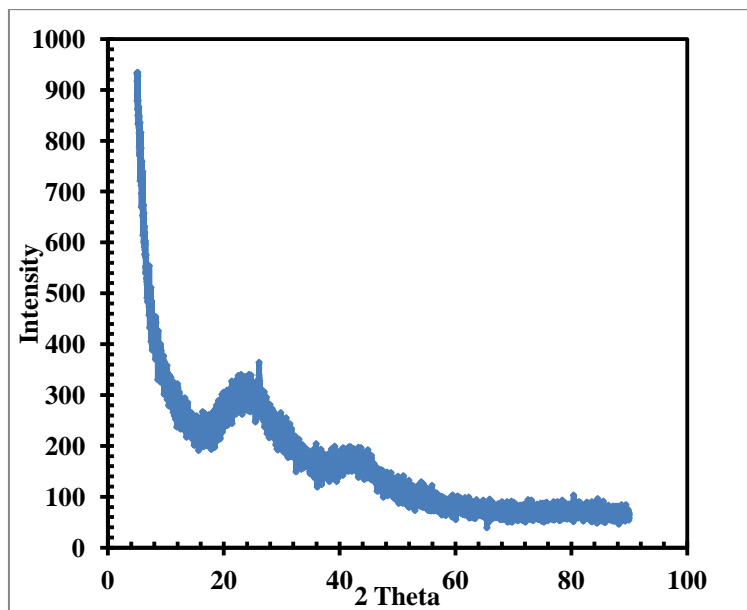


Figure 5.3 XRD of cadmium loaded BFA

5.1.6 Fe-SEM of the adsorbent and EDX of adsorbent

5.1.6.1 Fe-SEM of the adsorbents

The Scanning Electron Microscopy of the blank, Cu loaded and Cd loaded BFA was studied. The result was analyzed at three different magnifications, i.e. 50, 100 and 500X. The blank BFA showed the presence of pores while that for Cu and Cd loaded BFA, there was presence of these metals as shown in figures 5.4 and 5.5.

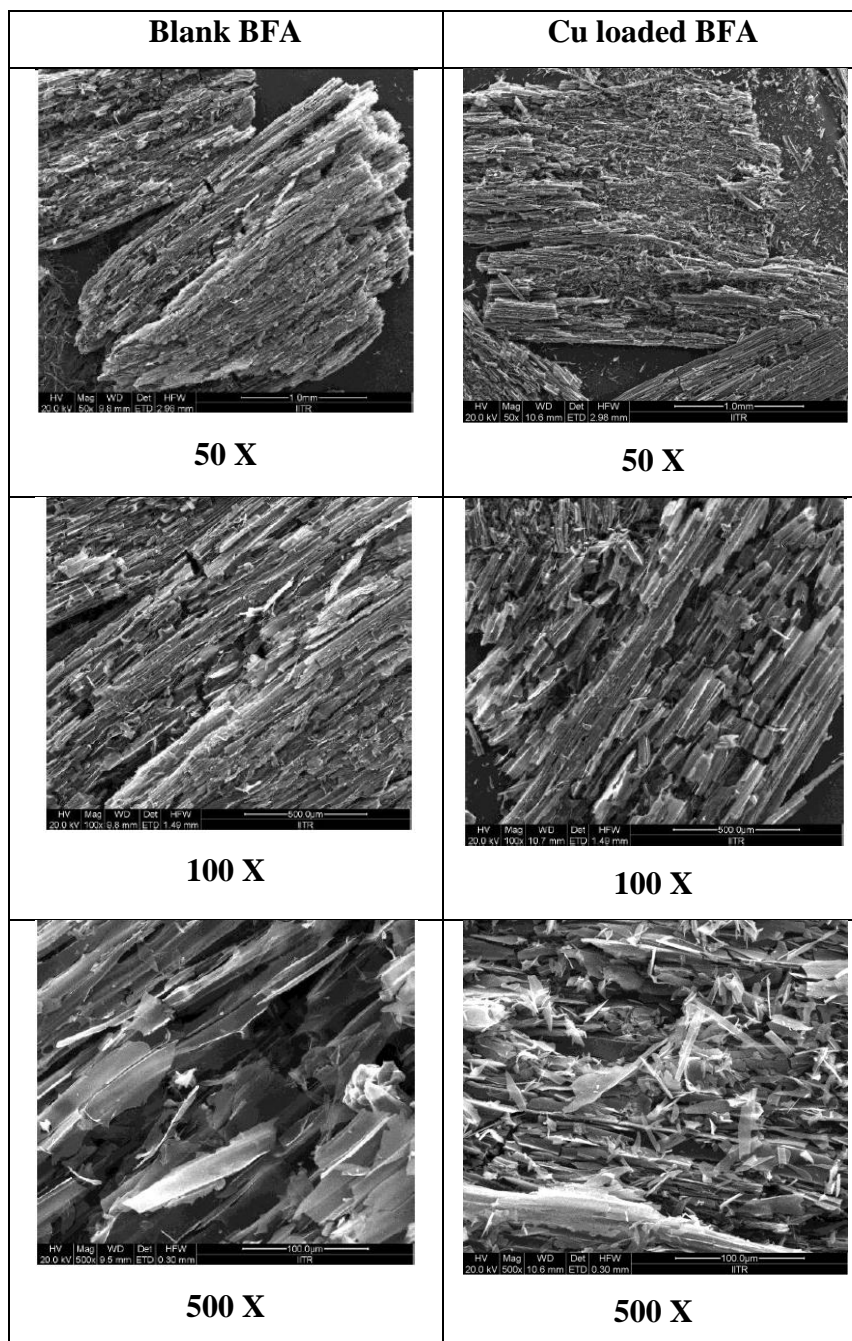


Figure 5.4 Fe-SEM of blank and copper loaded BFA

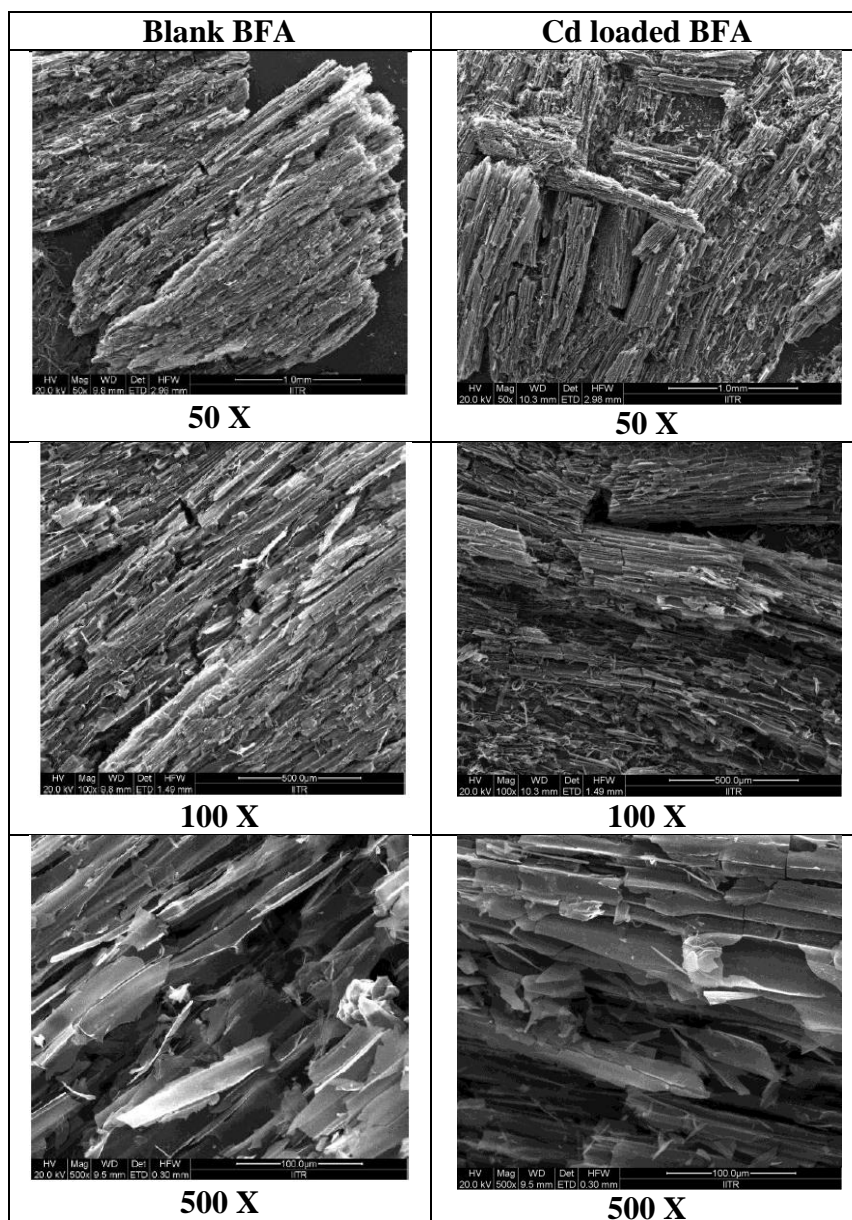


Figure 5.5 Fe-SEM of blank and cadmium loaded BFA

5.1.6.2 EDX of adsorbent

With the help of EDX various elements present in sample are analysed, few of them are given in table 5.4.

Table 5.4 EDX of the adsorbent

Elements (%)	Blank BFA	Cu loaded BFA	Cd loaded BFA
C	81.5	90.10	86.93
O	15.46	9.59	9.85
Si	1.08	0.16	0.16

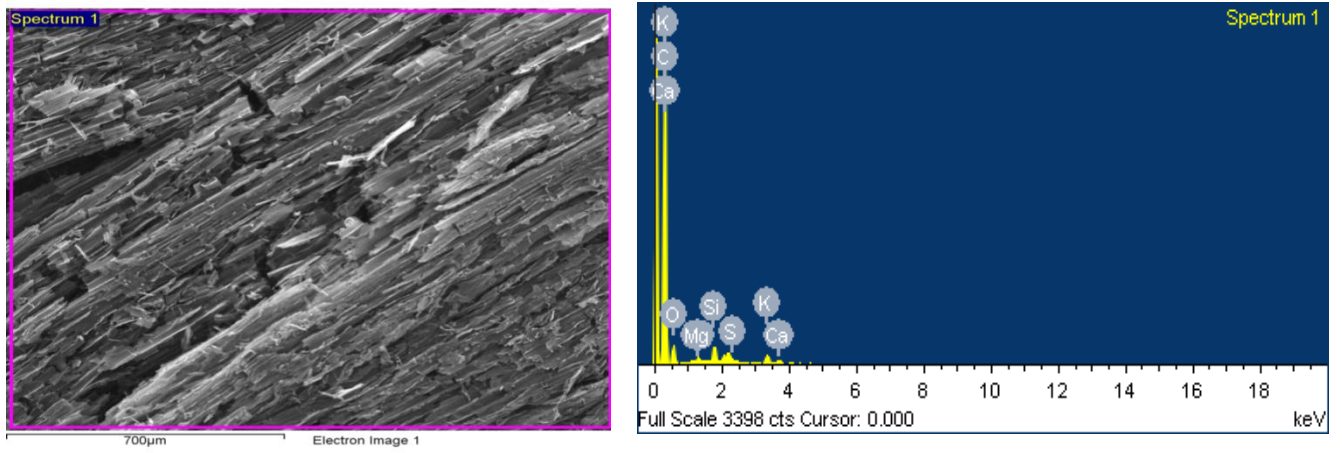


Figure 5.6 EDX of blank BFA

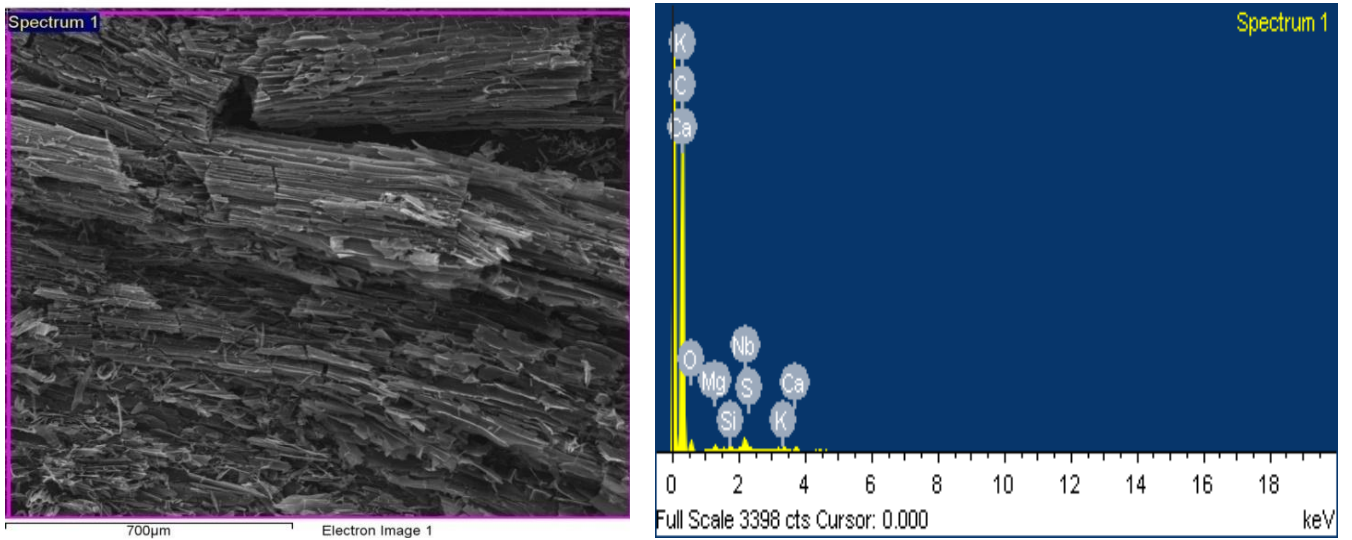


Figure 5.7 EDX of Cd loaded BFA

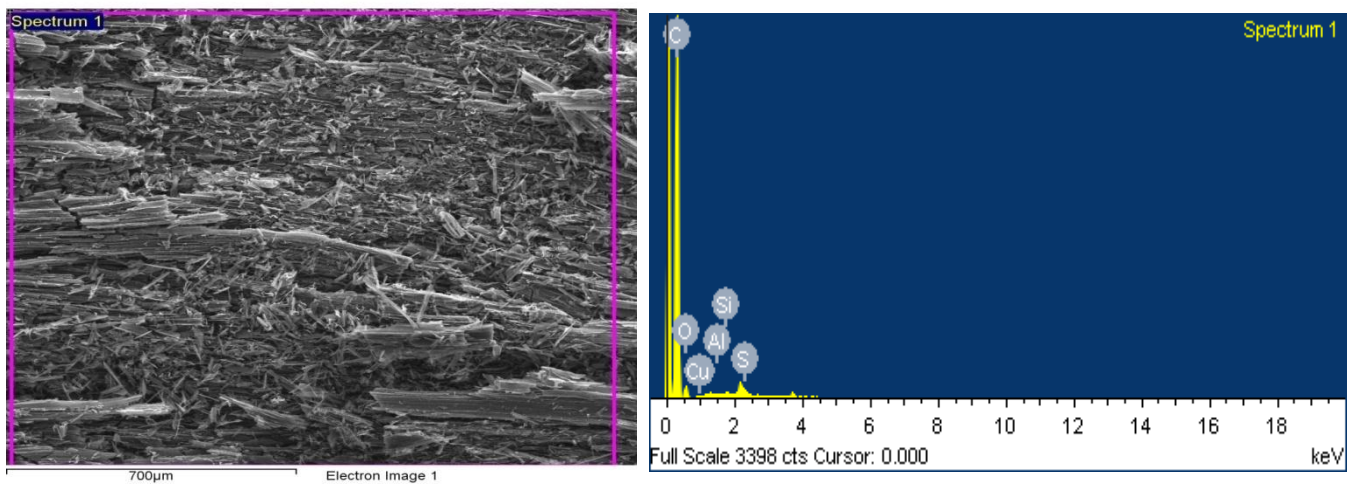


Figure 5.8 EDX of Cu loaded BFA

5.1.7 TGA/DTA/DTG curve of blank and loaded BFA

Figures 5.9, 5.10 and 5.11 represent the TGA/DTA/DTG analysis of blank BFA, copper loaded BFA and cadmium loaded BFA, respectively. Heating rate used was 10°C/min. It is basically a study of degradation of adsorbent in air atmosphere with respect to temperature.

Total weight loss in blank BFA from 15.1°C to 500°C was found to be 17.75%, in copper loaded BFA between 25°C to 450°C was found to be 25% and in cadmium loaded from 27°C to 470°C was found to be 21.4%. Also in case of blank BFA maximum weight loss of around 83.7% took place from 500°C to 630°C, in copper loaded it was 69.8% from 450°C to 550°C and in case of cadmium loaded 72% from 470°C to 560°C.

In DTA analysis a peak is clearly showing that it is an exothermic reaction. Energy of reaction is -25j/mg for blank BFA, -5.67j/mg for copper loaded BFA and -3.61j/mg for cadmium loaded BFA. Most of weight loss is taking place around 600°C in case of blank BFA, around 500°C in case of copper loaded BFA and 520°C for cadmium loaded BFA.

DTG graph gives us information about rate of weight loss with respect to time. Maximum weight loss is taking place around 570°C for blank BFA, around 480°C for copper loaded BFA and 500°C for cadmium loaded BFA. Rate of weight loss is found to be 1.01 mg/min for blank BFA, 3 mg/min for copper loaded BFA and 3.15 mg/min for cadmium loaded BFA.

5.1.8 FTIR analysis of blank and loaded BFA

The FTIR analysis shows the bond responsible for the adsorption process. The pallet-KBR method was used for the process. An adsorbent mainly consists of various bonds and the bonds responsible for the process show stretch after adsorption. Figure 5.12 shows FTIR analysis of blank and copper loaded BFA. Figure 5.13 shows FTIR analysis of blank and cadmium loaded BFA. From both curves, following conclusions can be drawn. 3429 cm⁻¹ shows the alkyne C-H stretch as well as O-H stretch. 2916 cm⁻¹ bond shows the methylene C-H stretch. The wavenumber 2358 cm⁻¹ shows the medial alkyne group stretch. The carboxylic acid band stretch is represented by 1746 cm⁻¹. 1446 cm⁻¹ is represented by methylene C-H band. The skeletal alkane vibrations are shown by 1235 cm⁻¹. 1055 cm⁻¹ is characterized by skeltel C-H vibrations. 610 cm⁻¹ is shown by aliphatic compound. Moreover, the curves are similar for both Cu and Cd metals.

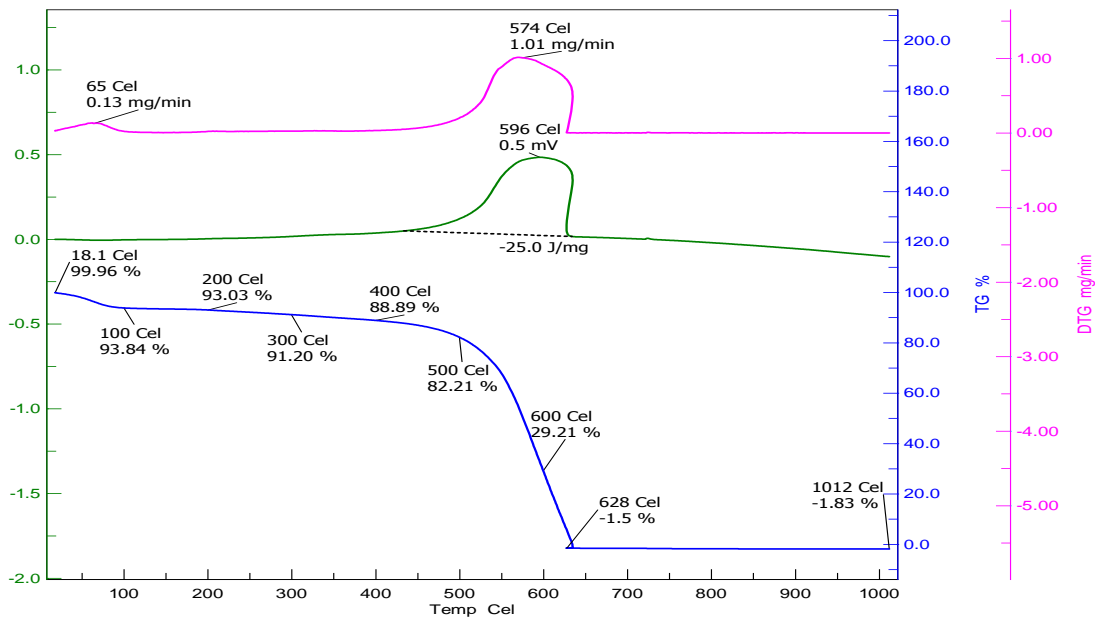


Figure 5.9 TGA/DTA/DTG curve of blank BFA

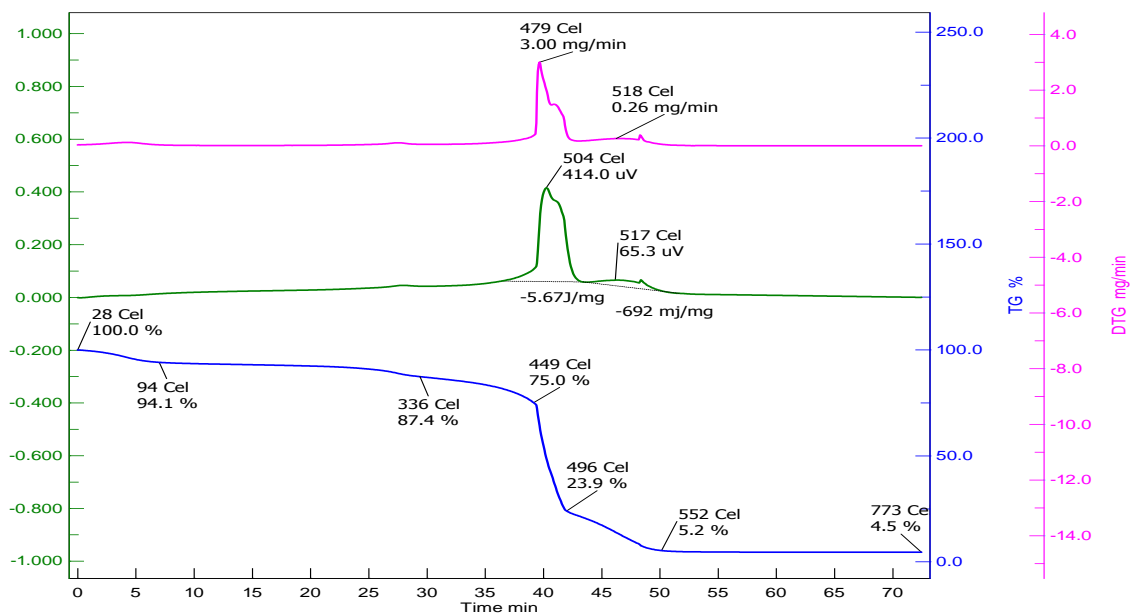


Figure 5.10 TGA/DTA/DTG curve of Cu loaded BFA

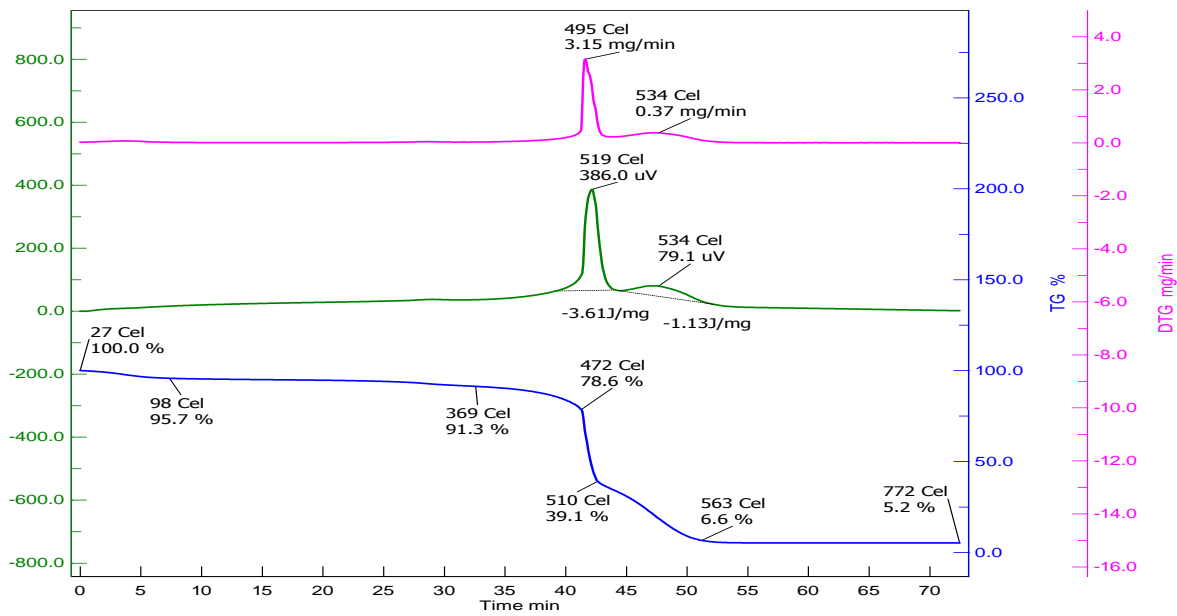


Figure 5.11 TGA/DTA/DTG curve of Cd loaded BFA

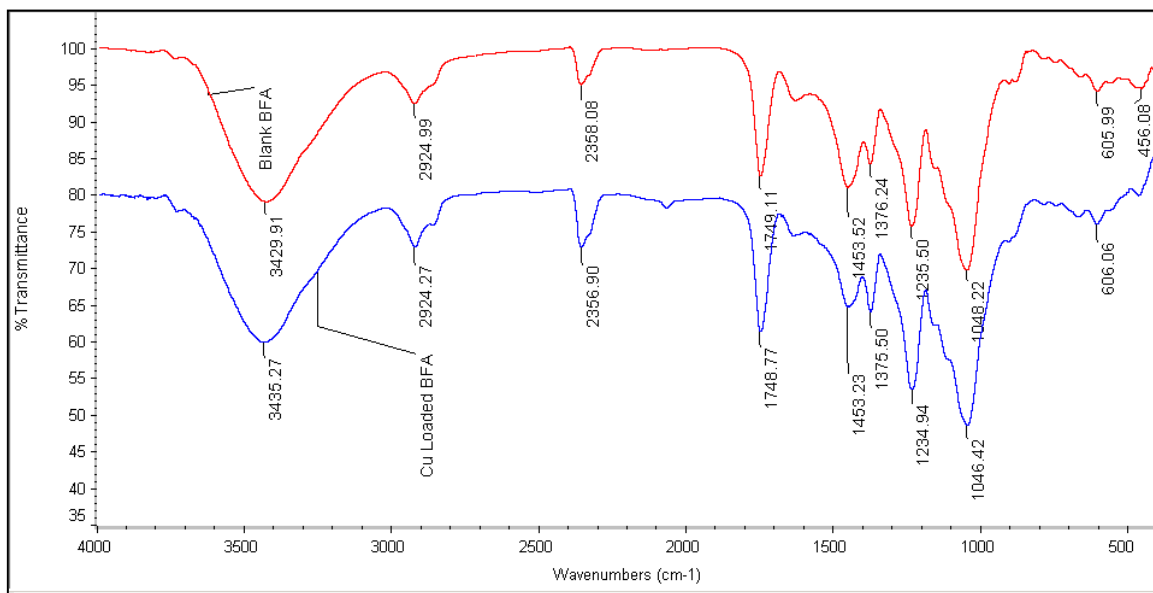


Figure 5.12 FTIR curve of blank and Cu loaded BFA

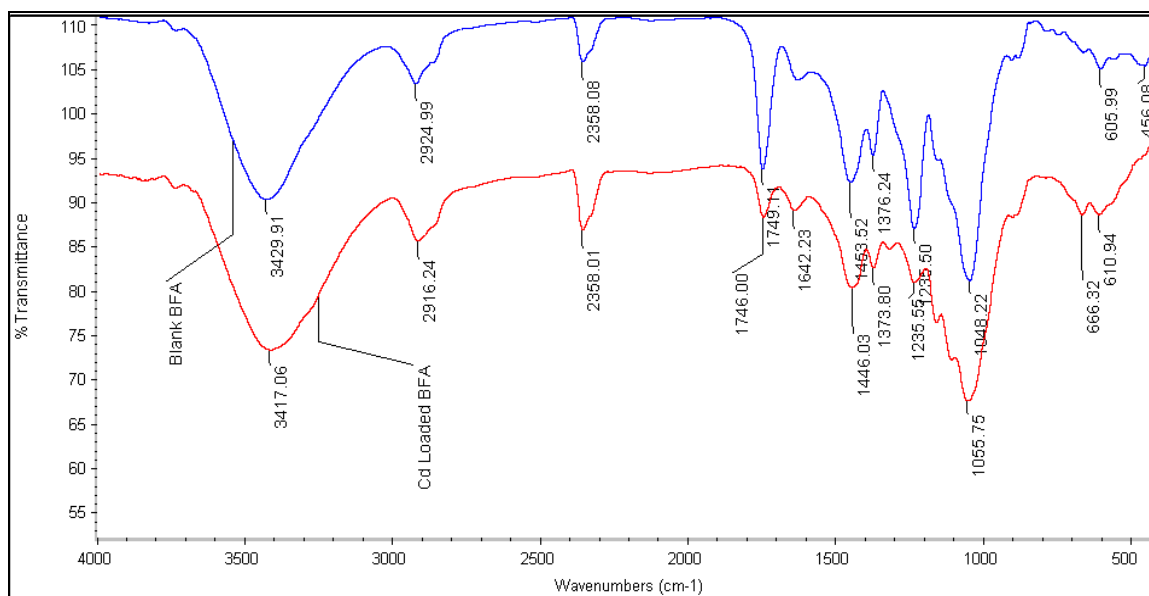


Figure 5.13 FTIR curve of blank and Cd loaded BFA

5.2 BATCH EXPERIMENTAL RESULTS

Study of various parameters like pH, adsorbent dose, contact time is done in this section. The results are shown below.

5.2.1 Effect of pH

Things which are affected by pH of a solution are degree of ionization and surface charge on adsorbent. Since hydrogen and hydroxyl ions also get adsorbed by the adsorbent so adsorption process for other ions gets affected by this. As dissociation of functional group in adsorbent takes place by change in pH, the adsorption process also gets affected.

Figures 5.14 and 5.15 present the effect of pH on adsorption of copper and cadmium. To study the effect of pH experiments were conducted with pH range from 2 to 10. It is found that as pH increases, removal also increases. It is clear from figure that removal is high at normal or low acidic situation and at high acidic situation removal is low. At high acidic situation hydrogen cations are present in high amount which compete with the negative charge present in adsorbent. As pH gets increased hydrogen cations concentration is reduced, so removal is increased. Also at high pH or alkaline situation removal takes place by precipitation. From the pH study it is clear that optimum pH for the removal is 6.0 for both metal ions. Hence pH 6.0 was used for further study.

5.2.2 Effect of adsorbent dose

Figures 5.16 and 5.17 present the effect of adsorbent dose on removal of copper and cadmium respectively. Initial concentration used for present study is 100 mg/l. From both figure it is clear that removal increases with increase in adsorbent dose and after a limit removal becomes constant with respect to adsorbent dose. When the adsorbent dose is increased, it increases the surface area of adsorbent, increasing active sites present in adsorbent and hence adsorption also getting increased.

Optimum dose of BFA for copper removal was found to be 4 g/l after which removal becomes constant. Optimum dose of BFA for cadmium removal is found to be 5g/l and removal becomes constant even we increased the adsorbent dose after it.

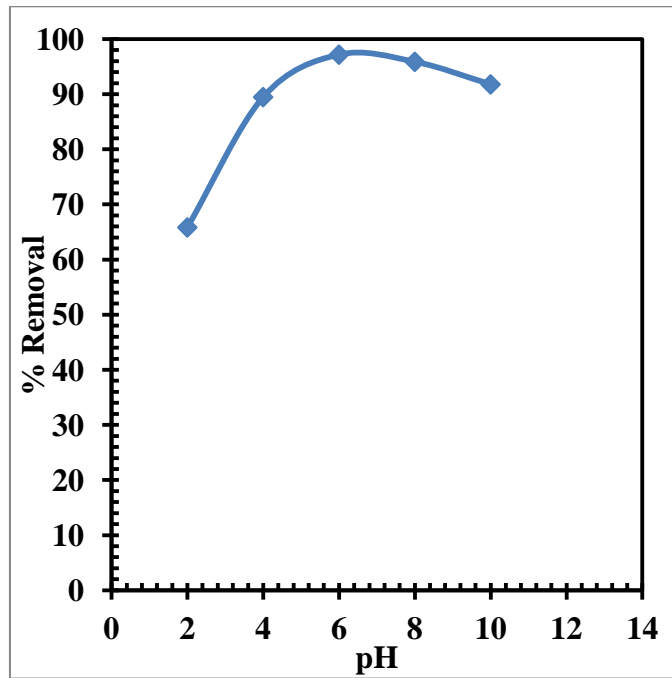


Figure 5.14 Effect of pH on Cu removal by BFA ($T = 30^{\circ}\text{C}$, $m = 10 \text{ g/l}$, $C_o = 100 \text{ mg/l}$)

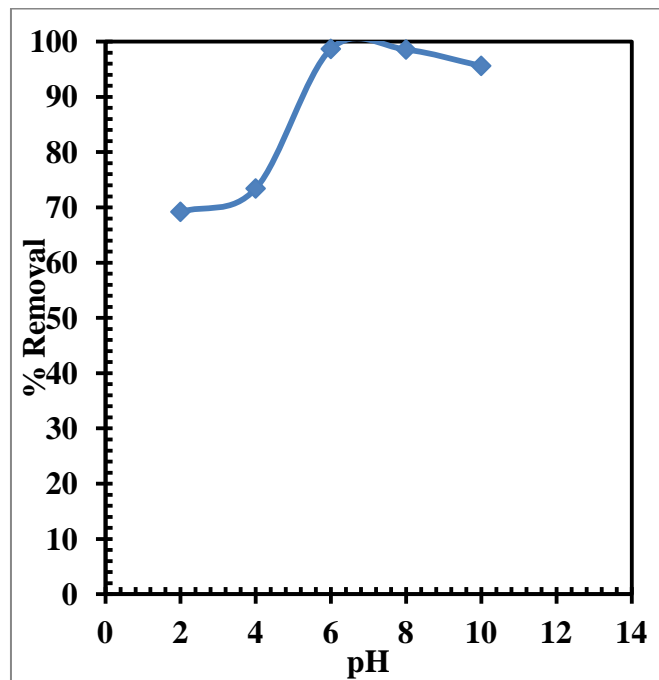


Figure 5.15 Effect of pH on Cd removal by BFA ($T = 30^{\circ}\text{C}$, $m = 10 \text{ g/l}$, $C_o = 100 \text{ mg/l}$)

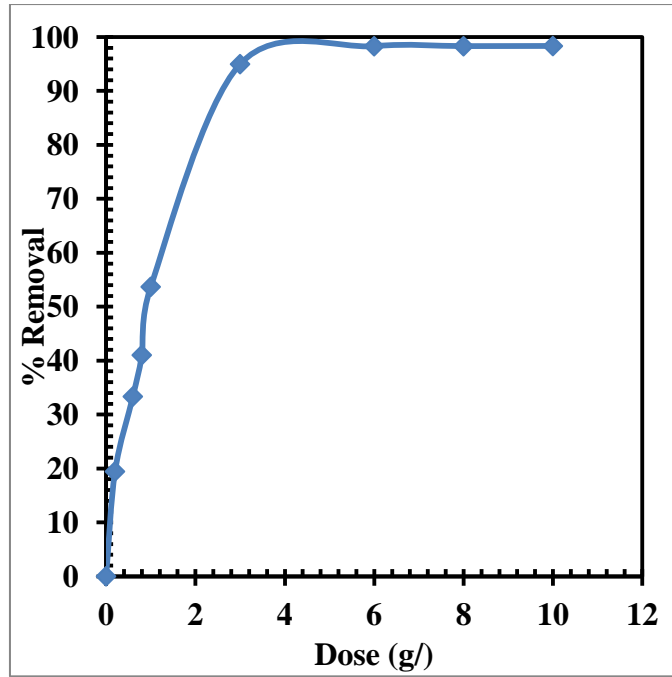


Figure 5.16 Effect of dose on Cu removal by BFA (pH = 6, T = 30°C, C₀ = 100 mg/l)

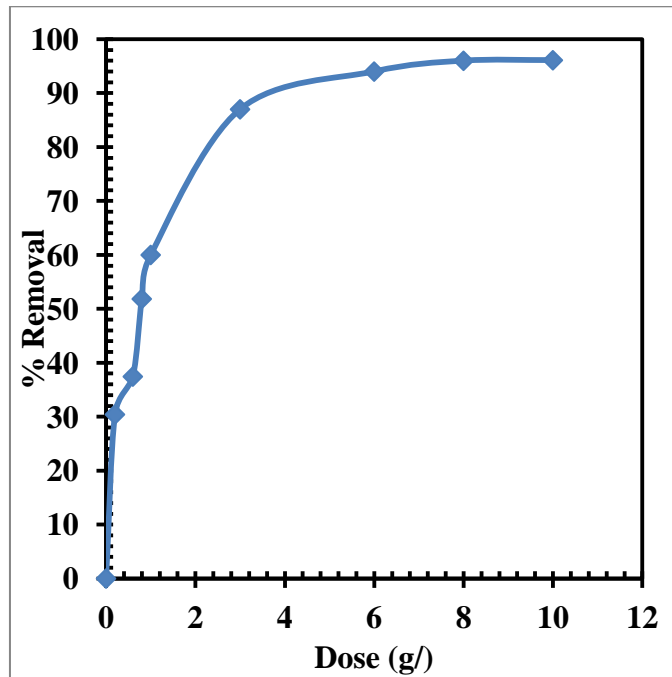


Figure 5.17 Effect of dose on Cd removal by BFA (pH = 6, T = 30°C, C₀ = 100 mg/l)

5.2.3 Effect of initial metal concentration

Figures 5.18 and 5.19 represent the effect of initial metal concentration on removal of copper and cadmium ion respectively. Used experimental conditions for copper are pH = 6.0, adsorbent dose = 4g/l and for cadmium are pH = 6.0, adsorbent dose = 5g/l. It is clear from figure that percentage removal decreases with increase in initial metal concentration in case of both metals i.e. copper and cadmium.

5.2.4 Effect of contact time on percent removal

Contact time of adsorption is very important parameter in removal of metal ions. Significance of lower contact time is that adsorbent is highly efficient for the adsorption process. Generally contact time is lower in physical adsorption.

Figures 5.20 Fig 5.21 presents the effect of contact time on removal of copper and cadmium respectively. Experimental conditions used for copper are pH = 6.0 and dose = 4 g/l and for cadmium are pH = 6.0 and dose = 5 g/l. From figure it is clear that adsorption rate is high at initial stage and later on it gets slow. This is because number of vacant sites present in adsorbent is high initially, and as time passes these vacant sites get filled and repulsive force acts between the solute molecules. Optimum time for removal of copper is 90 min and for cadmium it is found to be 300 min.

5.2.6 Kinetic study

Experiments for the removal of copper and cadmium by BFA were conducted at optimized conditions which include optimum pH, optimum adsorbent dose etc. Figures 5.22 and 5.23 shows the kinetic study of copper and cadmium ions removal. With the help of various kinetic models value of q_t was calculated. Value of correlation coefficient was taken in to account to select the best fitting model for adsorption process. Value of kinetic parameters for copper removal and cadmium removal are presented in Tables 5.5 and 5.6 respectively. In case of copper the value correlation coefficient is closer to 1 for second order kinetics in comparison to first order kinetics, hence removal of copper follows second order kinetics. In case of cadmium value of correlation coefficient for second order kinetics is closer to 1 in comparison to first order kinetics. Hence pseudo second order kinetics is found to be best fitted for copper and cadmium removal by BFA.

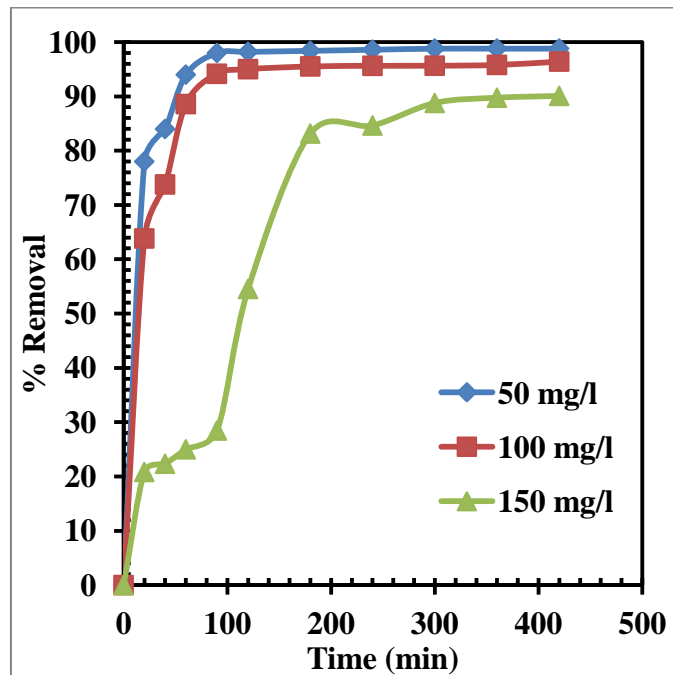


Figure 5.18 Effect of initial concentration on Cu removal by BFA (pH = 6, T = 30°C, m = 4 g/l, C_o = 100 mg/l)

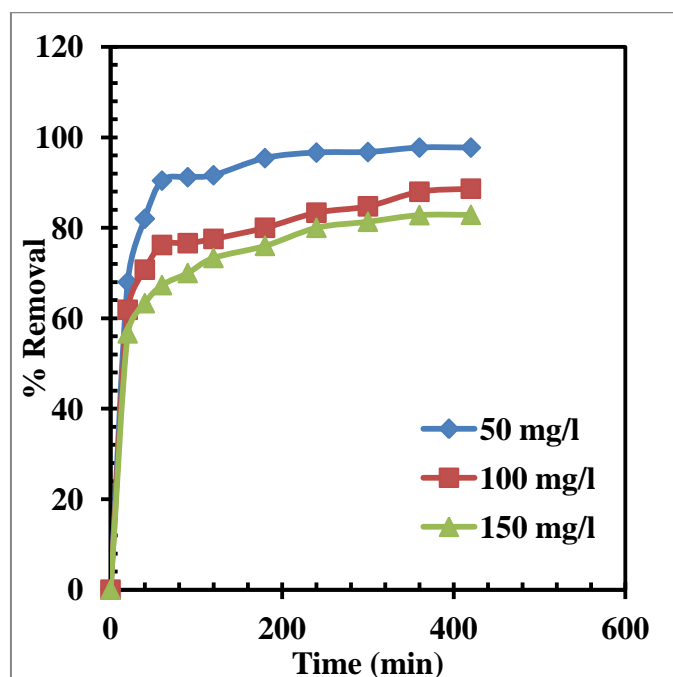


Figure 5.19 Effect of initial concentration on Cd removal by BFA (pH = 6, T = 30°C, m = 5 g/l, C_o = 100 mg/l)

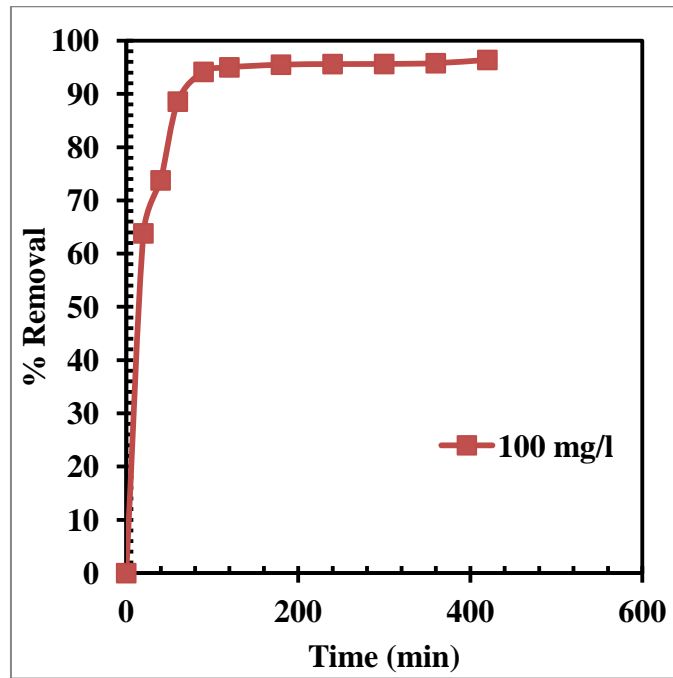


Figure 5.20 Effect of contact time on Cu removal by BFA (pH = 6, T = 30°C, m = 4 g/l, C₀ = 100 mg/l)

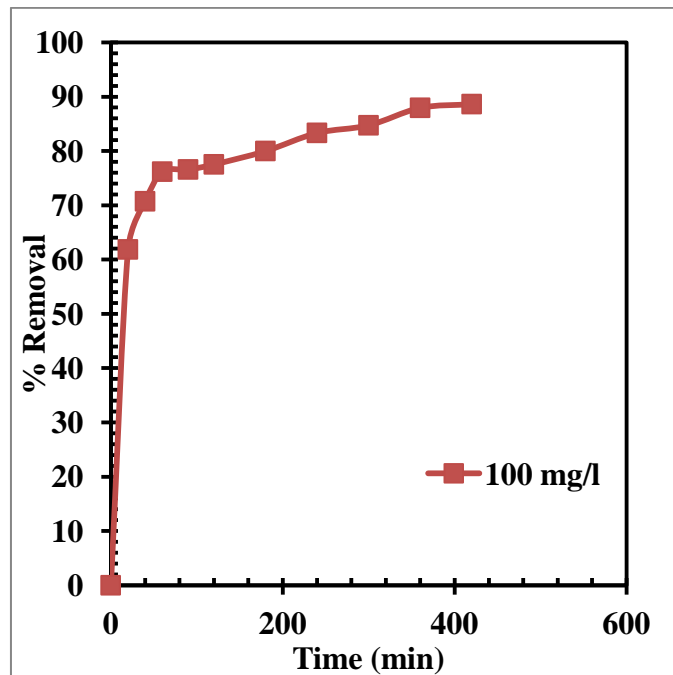


Figure 5.21 Effect of contact time on Cd removal by BFA (pH = 6, T = 30°C, m = 5 g/l, C₀ = 100 mg/l)

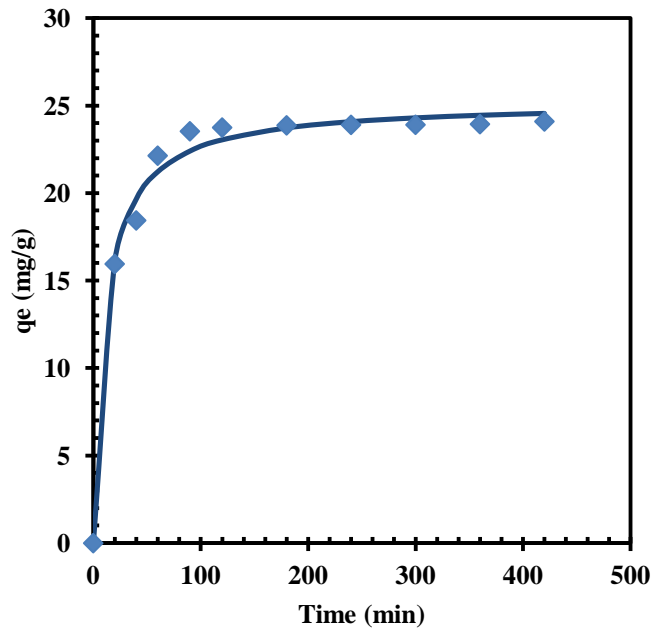


Figure 5.22 Study of kinetics on Cu removal by BFA (pH = 6, T = 30°C, m = 4 g/l, C_o = 100 mg/l)

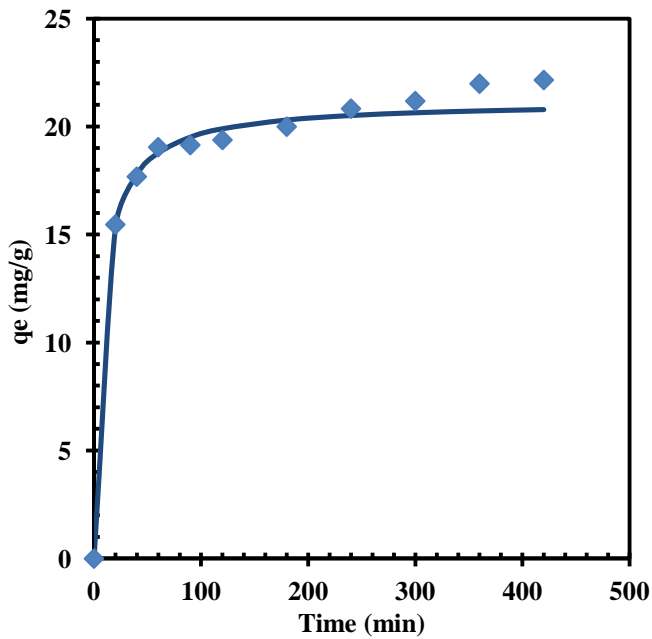


Figure 5.23 Figure 5.19 Study of kinetics on Cd removal by BFA (pH = 6, T = 30°C, m = 5 g/l, C_o = 100 mg/l)

Table 5.5 Kinetic parameters for removal of Cu by BFA

Pseudo first order			
Adsorbent	$q_{e,cal}$ (mg g ⁻¹)	K_f (min ⁻¹)	R^2
BFA	22.35	0.995	0.867

Pseudo second order			
Adsorbent	$q_{e,cal}$ (mg g ⁻¹)	K_S (g mg ⁻¹ min ⁻¹)	R^2
BFA	25.22	.0035	0.991

Table 5.6 Kinetic parameters for removal of Cd by BFA

Pseudo first order			
Adsorbent	$q_{e,cal}$ (mg g ⁻¹)	K_f (min ⁻¹)	R^2
BFA	19.69	0.999	0.932

Pseudo second order			
Adsorbent	$q_{e,cal}$ (mg g ⁻¹)	K_S (g mg ⁻¹ min ⁻¹)	R^2
BFA	21.16	0.0061	0.997

5.2.7 Isotherm study

The isotherm modelling for copper and cadmium removal experiments were conducted at different temperatures i.e. 15°C, 30°C and 45°C. Other conditions which were used were pH =6.0, adsorbent dose = 4 g/l for copper and pH = 6.0, adsorbent dose = 5 g/l for cadmium. Analysis of equilibrium data for copper and cadmium removal was done by regression analysis using Microsoft Office Excel. Srivastava et al., 2007 described various isotherm models for the isotherm fitting like Freundlich, Langmuir etc. A curve was plotted between extent of adsorption and equilibrium concentration. The curve fitting showed that Hill isotherm best fitted the experimental data for cadmium and copper removal. Figures 5.24 and 5.25 show adsorption isotherm of copper and cadmium removal. Tables 5.7 and 5.8 show values of isotherm parameters for different models like Freundlich, Langmuir etc.

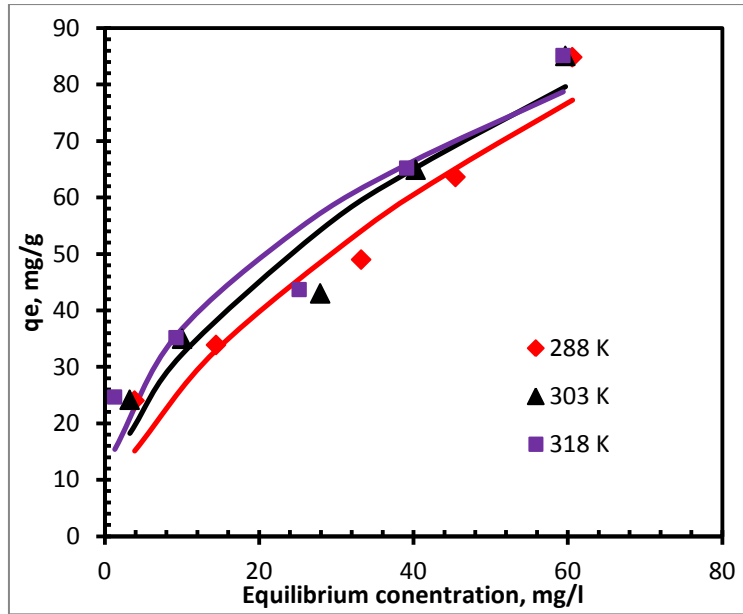


Figure 5.24 Isotherm study of adsorption of copper on BFA (pH = 6, T = 30°C, m = 4 g/l, C₀ = 100 mg/l). Experimental and theoretical values are denoted by points and line, respectively

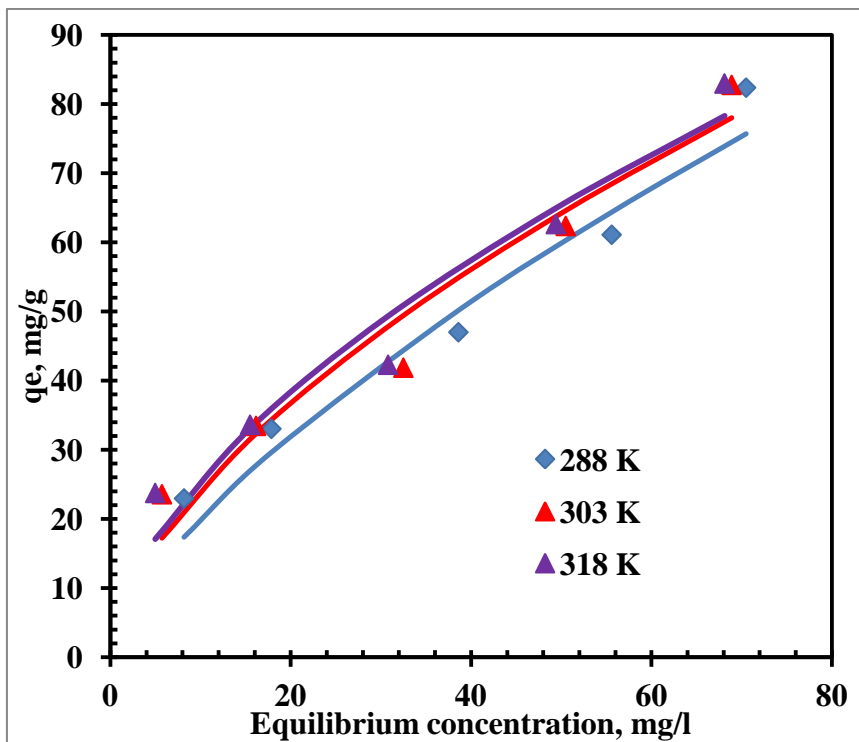


Figure 5.25 Isotherm study of adsorption of cadmium on BFA (pH = 6, T = 30°C, m = 5 g/l, C₀ = 100 mg/l). Experimental and theoretical values are denoted by points and line, respectively

Table 5.7 Isotherm parameters for removal of Cu by BFA

Isotherms	Parameters	BFA		
		Temperature (K)		
		288	303	318
Langmuir $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q _o	184.42	115.73	116.01
	b	0.012	0.034	0.035
	R ²	0.875	0.863	0.867
Freundlich $q_e = K_F C_e^{1/n}$	K _F	6.631	6.631	13.66
	1/n	0.598	0.598	0.428
	R ²	0.885	0.934	0.903
Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a _R	198.93	134.92	2970.45
	K _R	1347.8	1358.5	40823.94
	g	0.4069	0.4341	0.572
	R ²	0.884	0.920	0.903
Hill $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	k _D	4410.8	4405.2	4405.2
	q	4312.4	4317.9	4317.8
	n	1.008	1.008	1.008
	R ²	0.943	0.970	0.983
Tempkin $q_e = B_1 \ln K_T + B_1 \ln C_e$	K _T	2779.3	0.793	2.613
	B ₁	4.509	18.753	13.892
	R ²	0.742	0.813	0.755

Table 5.8 Isotherm parameters for removal of Cd by BFA

Isotherms	Parameters	BFA		
		Temperature (K)		
		288	303	318
Langmuir $q_e = \frac{Q_0 b C_e}{1 + b C_e}$	Q ₀	195.61	151.52	142.3
	B	0.008	0.015	0.017
	R ²	0.899	0.919	0.918
Freundlich $q_e = K_F C_e^{1/n}$	K _F	4.136	5.961	6.715
	1/n	0.683	0.607	0.581
	R ²	0.917	0.947	0.949
Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a _R	9749.29	6881.3	6126.9
	K _R	40330.11	41023	41150
	G	0.316	0.332	0.418
	R ²	0.917	0.947	0.949
Hill $q_e = \frac{Q_{sH} C_e^{nH}}{k_D + C_e^{nH}}$	k _D	4414.69	4414.7	4414.7
	Q	4308.46	4308.5	4308.5
	N	1.009	1.009	1.009
	R ²	0.949	0.983	0.988
Tempkin $q_e = B_1 \ln K_T + B_1 \ln C_e$	K _T	0.245	0.371	0.441
	B ₁	24.227	21.778	20.768
	R ²	0.811	0.829	0.827

6 CONCLUSIONS

From the present study it is shown that bagasse fly ash (BFA) is an effective adsorbent for the removal of both copper and cadmium ions from synthetic waste water. The conclusions of work done are as follows-

- i. Removal of metal was found to be higher when initial metal concentration was lower.
- ii. Optimum pH of the removal was found to be around 6.0 in case of copper and also 6.0 in case of cadmium removal.
- iii. Optimum dose of maximum removal was found to be 4 g/l in case of copper and 5 g/l in case of cadmium ion.
- iv. Contact time of maximum removal was found to be 90 min for copper and 300 min for cadmium.
- v. Maximum removal of around was found to be around 98.3% in case of copper ion and 98.6% in case of cadmium ion.
- vi. Hill isotherm was found to be best fit for copper and cadmium removal.
- vii. It was also shown that removal of both copper and cadmium ions followed pseudo second order kinetics.

From the present study it is clear that BFA is more efficient for the removal of copper in comparison to cadmium under optimized conditions.

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