REMOVAL OF CADMIUM AND HUMIC ACID BY ADSORPTION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By
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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation titled **"REMOVAL OF CADMIUM AND HUMIC ACID BY ADSORPTION"**, in partial fulfillment of the requirements for the award of the degree of Master of technology in Chemical Engineering with specialization in "**Industrial Pollution Abatement**", and submitted to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of the work carried out by me during the period July 2007 to June 2008, under the guidance of **Dr. SHRI CHAND**. The matter embodied in this work has not been submitted for the award of any other degree.

Date: 30|06|08
Place: IIT, Roorkee

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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

With the rapid increase in population and growth of industrialization in the country, quality of both surface and ground water is deteriorating day by day. Land disposal of municipal, leachate from municipal solid waste, industrial wastes and utilization of fertilizers and pesticides in agriculture all contribute to the rise in levels of toxic metals and also organic matter in the environment. Interactions of heavy metals with humic substances typically control the fate and transport of metals through ground and surface water systems. Adsorption has been recognized as an effective technology for trace heavy metal removal and HA. Adsorption of HA causes change in the surface properties of adsorbent by increasing in the surface negative charges as well as pore blockage. Humic acid (HA) may improve metal adsorption by formation of metal–HA complexes on adsorbent surfaces. On the other hand, the HA can be present in a soluble form and form complexes with metals, which reduces metal adsorption onto the carbon. HA in aqueous solutions can change the metal adsorptive behaviour. The simultaneous adsorption of heavy metal and HA onto adsorbent is the best option.

Single and co-adsorption of cadmium and humic acid were carried out using Granular Activated Carbon (GAC), iron impregnated Granular Activated Carbon (Fe-GAC) and activated clay (A-Clay). Clay was activated by the acid treatment, while Fe-GAC was prepared by impregnation of Fe^{3+} onto the surface of GAC. Proximate analysis, chemical composition (EDS analysis), scanning electronic microscope (SEM) and surface area were carried out for detail characterization of adsorbents. Effect of parameters such as pH, adsorbent dosage (*m*), initial concentration of adsorbate (*Co*) and contact time (*t*) on adsorption of cadmium and humic acid were studied and optimum conditions were determined. Kinetic and isotherms studies were also carried out for single component. Co-adsorption of humic acid and cadmium were conducted and effect of pH, adsorbent dosage and contact time were found out. Effect of humic acid initial concentration on cadmium adsorption and also the effect of cadmium initial concentration on humic acid adsorption were determined.

GAC had the highest adsorption capacity in all the cases and the adsorption capacity of 3 adsorbents was in the order GAC > Fe-GAC >A-Clay i.e. in case in cadmium removal was 82.3%,78.4% and 74% for GAC, Fe-GAC and A-Clay respectively. It was found that the effective pH for cadmium and humic acid were 6 and

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Page No.

NOMENCLATURE

b	constant in Temkin equation
B_1	constant in Temkin equation
C_o	initial concentration of adsorbate (mg dm^{-3})
C_e	equilibrium concentration (mg dm^{-3})
K_{ad}	Equilibrium constant for adsorption (dm3 mg^{-1})
K_F	Freumdlich constant (dm^3 mg^{-1})
K_L	Langmuir constant (dm^3 mg−1)
K_R	Redlich–Peterson constant (dm^3 mg−1)
K_T	constant in Temkin equation (dm^3 mg^{-1})
m	adsorbent dose (g)
q	adsorptive uptake of Py (mg g^{-1})
q_e	adsorptive uptake of Py at equilibrium (mg g^{-1})
$q_{e,\,calc}$	calculated q_e (mg g^{-1})
$q_{e,\,exp}$	experimental q_e (mg g^{-1})
q_m	monolayer adsorptive uptake (mg g^{-1})
t	contact time (min)
T	temperature (K)

Chapter-I

INTRODUCTION

1.1 General

Water is one of nature's most important gifts to mankind. Although water covers more than 70% of the Earth, only 1% of the Earth's water is available as a source of drinking. Yet, our society continues to contaminate this precious resource. With the rapid increase in population and growth of industrialization in the country, quality of both surface and ground water is deteriorating day by day. Large volumes of poorly defined wastes, such as domestic sewage or pulp mill effluent etc, that are sometimes discharged directly or after treatment into rivers, lakes, and oceans. Anthropogenic sources supply specific organic compounds—agricultural chemicals, medicinal, heavy metals and products or by-products of industrial processes. The range of these is as broad as the range of organic chemistry itself. Many a times, the quality of such natural water sources become degraded and they are not fit for their usage, viz. drinking, irrigation, industrial processing, etc.

Besides the anthropogenic sources, there are natural inputs that contribute organic matter to water. Organic matters, which are result of both natural and anthropogenic activities, are consistent present in the water that requires removal, which is mixture of decomposition products of plants and animals. Organic matter in water plays important roles in controlling geochemical processes by acting as proton donors/acceptors and as pH buffers, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/precipitation reactions. Organic matter may also influence the availability of nutrients and serve as a carbon substrate for microbially mediated reactions. Numerous studies have recognized the importance of natural organic matter in the mobilization of hydrophobic organic species, metals (e.g. Pb, Cd, Cu, Zn, Hg, and Cr), and radionuclide (e.g. Pu, Am, U, and Co). The presence of NOM in the water is a major concern not only forms carcinogenic compounds such forms carcinogenic compounds such as trihalomethanes (THMs) during the chlorination of drinking water. Today, drinking water treatment at the point-of-use is no longer a luxury, it is a necessity!

1.1.1 Heavy Metals

In recent years, the presence of heavy metals in industrial wastewater and surface water has gained importance as they are dangerous and toxic. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are importance class of pollutants as they cannot be degraded or destroyed easily and they tend to bioaccumulate. Heavy metals may enter the human body through food, water, air, or absorption through the skin, are responsible for range oh health effects like nausea, vomiting, diarrhoea, renal damage, hypertension, proteinuria, kidney stone formation, testicular atrophy, skeletal deformation, cardiovascular diseases, hypertension etc (Kula et al., 2008). Also heavy metals are known as carcinogen and causes nervous breakdown and /or peripheral nervous system which lead to death of human beings.

Heavy metals find their way in the environment from a variety of sources both from nature as well as industries. But industrial discharges contribute more in the pollution. Large scale of industrial growth has cause serious concern regarding the susceptibility of ground water and stream water contamination due to heavy metals. A waste material near the factories, which is subjected to reaction with percolating, rain water and reaches the aquifer and hence degrades the ground water quality. Heavy metals are emitted out from various sources. The primary sources are electroplating, mining, Cd-Ni batteries, phosphate fertilizer, smelting, alloy manufacturing, petroleum, chemical and petro-chemical, pulp and paper, textile, caustic, steel, pesticides, leather, dye and paint etc.

Table 1.1 General standards for discharge of environmental pollutants:

Effluents (for industries operations or processes other than those industries specified in schedule of the environment protection Rules, 1989).

Sl. No	**Parameter**	**Inland surface water**	**Public sewers**	**Land for irrigation**	**Marine/coastal areas**
1.	Suspended solids mg/l, max.	100	600	200	(a) For process waste water. (b) For cooling water effluent 10% above total suspended matter of influent
2.	Particle size of suspended solids	Shall pass 850 micron IS sieve	-	-	(a) Floatable solids, solids max. 3mm (b) settlement solids, max 856 microns
3.	pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
4.	Temperature	Shall not exceed 5^0C above the receiving water			Shall not exceed 5^0C above the receiving water
5.	Oil and greases, mg/l max.	10	20	10	20
6.	Total residual chlorine, mg/l max	1.0	-	-	1.0
7.	Ammonical nitrogen (as N), mg/l, max.	50	50	-	50

(Continued..)

Sl. No	**Parameter**	**Inland surface water**	**Public sewers**	**Land for irrigation**	**Marine/coastal areas**
8.	Free ammonia (as NH_3), mg/l, max.	5.0	-	-	5.0
9.	Biochemical oxygen demand (3 days at 270C), mg/l, max.	30	350	100	100
10.	Chemical oxygen demand, mg/l, max.	250	-	-	250
11.	Arsenic (as As)	0.2	0.2	0.2	0.2
12.	Mercury (as Hg) mg/l, max.	0.01	0.01	-	0.01
13.	Lead (as Pb) mg/l, max.	0.1	1.0	-	2.0
14.	Cadmium (as Cd) mg/l, max	2.0	1.0	-	2.0
15.	Hexavalent chromium (as Cr^{+6}) mg/l, max.	0.1	2.0	-	1.0
16.	Total chromium (as Cr) mg/l, max	2.0	2.0	-	2.0
17.	Copper (as Cu) mg/l, max	3.0	3.0	-	3.0
18.	Zinc (as Zn) mg/l, max	5.0	15	-	15

(Continued..)

Sl. No	**Parameter**	**Inland surface water**	**Public sewers**	**Land for irrigation**	**Marine/coastal areas**
19.	Selenium (as Se)	0.05	0.05	-	0.05
20.	Nickel (as Ni) mg/l, max.	3.0	3.0	-	5.0
21.	Cynanide (as CN) mg/l, max	0.2	2.0	0.2	0.2
22.	Fluoride (as F) mg/l, max.	2.0	15	-	15
23.	Dissolved phosphates (as P), mg/l	5.0	-	-	-
24	Sulphide (as S) mg/l, max.	2.0	-	-	5.0
25.	Phenolic compounds (as C_6H_5OH) mg/l, max.	1.0	5.0	-	5.0
26.	Radioactive materials: (a) Alpha emitters microcurie mg/l, max. (b) Beta emitters micro curie mg/l	10^{-7} 10^{-6}	10^{-7} 10^{-6}	10^{-8} 10^{-7}	10^{-7} 10^{-6}
27.	Bio-assay test	90% suivial of fish after 96 hours in 100%	90% suivial of fish after 96 hours in 100%	90% suivial of fish after 96 hours	90% suivial of fish after 96 hours in 100% effluent

		effluent	effluent	in 100% effluent	
28.	Manganese	2 mg/l	2 mg/l	-	2 mg/l
29.	Iron (as Fe)	3 mg/l	3 mg/l	-	3mg/l
30.	Vanadium (as V)	0.2 mg/l	0.2 mg/l	-	0.2 mg/l
31.	Nitrate nitrogen	10 mg/l	-	-	20 mg/l

Source CPCB

Table 1.2 Maximum allowable limit of heavy metal discharge from industries according to CPCB

Sl. No	Parameter	Concentration not except, mg/l (expect for pH and temperature)
1.	pH	6.0 to 9.0
2.	Temperature	Shall not exceed 5 0 c above the ambient temperature of the receiving body
3.	Oil & Grease	10
4.	Suspended Solids	100
5.	Cyanides (as CN)	0.2
6.	Ammonical Nitrogen (as N)	50
7.	Total Residual Chlorine (as Cl_2)	1.0
8.	Cadmium (as Cd)	2.0
9.	Nickel (as Ni)	3.0
10.	Zinc (as Zn)	5
11.	Hexavalent Chromium (as Cr)	0.1
12.	Total Chromium (as Cr)	2.0
13.	Copper (as Cu)	3.0
14.	Lead (as Pb)	0.1
15.	Iron (as Fe)	3.0
16.	Total Metal	10

Source CPCB

1.2 Cadmium

Cadmium is a naturally occurring minor element, one of the metallic components in the earth's crust and oceans, and present everywhere in our environment. Cadmium (Cd) is a heavy metal which is not essential for growth of animals or plants. It is in the same subgroup of the Periodic Table (IIB) as zinc (Zn) and, like Zn, it occurs most frequently in aqueous systems as a divalent cation. Industrial applications for cadmium were developed in the late 19th and early 20th Century. Cadmium-sulfide based pigments were used as early as 1850 and appeared prominently in the paintings of Vincent Van Gogh in the late 1800s. Thomas A. Edison in the United States and Waldemar Junger in Sweden developed the first nickel-cadmium batteries early in the 20th Century. Cadmium levels in the environment vary widely. Since it can be transported continually between various matrices viz. air, water and soil. Cadmium can transform into number of salts such as cadmium oxide, cadmium chloride and cadmium sulphide. The mobility of these salts in the environment affects the ecosystem. Cadmium will invariably be present in our society, either in useful products or in controlled wastes. Today, its health effects are well understood and well regulated so that there is no need to restrict or ban cadmium products which, in any event, contribute so little to human cadmium exposure as to be virtually insignificant.

Chemical properties

Sl. No.	Properties	Cadmium
1.	Atomic Symbol	Cd
2.	Atomic Number	48
3.	Atomic Weight	112.40
4.	Density	8.64 g/cm^3
5.	Oxidation States	2
6.	Melting Point	321.07
7.	Boiling Point	767
8.	Electron Configuration	[Kr]5s^{2}4d^{10}

1.2.1 Application

Cadmium is intentionally added to six major classes of products where it imparts distinct performance advantages and is present as an impurity in five major classes of products where its presence is regarded as an environmental disadvantage but which generally does not affect the performance of the product. The fig () below shows applications of cadmium. The major intentional uses of cadmium are Ni-Cd batteries, cadmium pigments, cadmium stabilisers, cadmium coatings, cadmium alloys and cadmium electronic compounds such as cadmium telluride (CdTe).

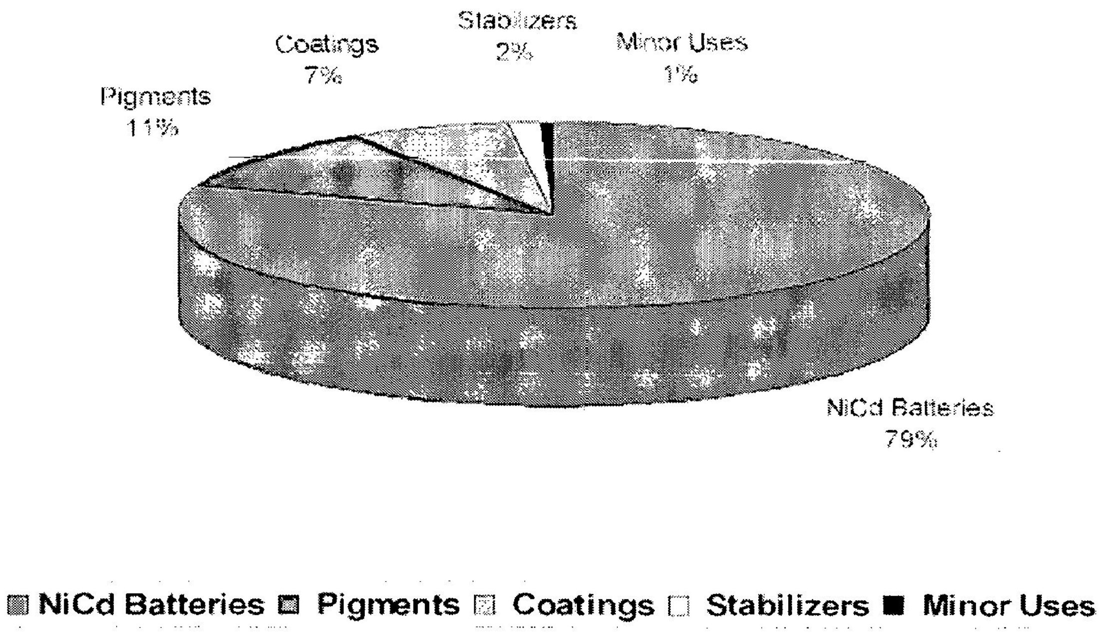


Fig 1.1 Applications of cadmium.

Ni-Cd Batteries - Cadmium hydroxide is utilised as one of the two principal electrode materials in Ni-Cd batteries which have extensive applications in the railroad and aircraft industry for starting and emergency power and in consumer applications such as cordless power tools, cellular telephones, camcorders, portable computers, portable household appliances and toys. Ni-Cd batteries are cost-effective well suited for high power applications, and have high cycle lives and excellent low temperature and high temperature performance relative to other battery chemistries (Morrow and Keating 1997).

Cadmium Pigments - Cadmium sulphide and cadmium sulphoselenide are utilised as bright yellow to deep red pigments in plastics, ceramics, glasses, enamels and artists colours. They are well known for their ability to withstand high temperature and high pressure without chalking or fading, and therefore are used in applications where high temperature or high pressure processing is required (Cook 1994).

Cadmium Stabilisers - Cadmium-bearing stabilisers retard the degradation processes in polyvinylchloride (PVC) which occur upon exposure to heat and ultraviolet light These stabilisers contain organic cadmium salts, usually carboxylates such as cadmium laurate or cadmium stearate, which are incorporated into PVC before processing and which arrest any degradation reactions during subsequent processing and ensure a long service life (Cadmium Association and Cadmium Council 1991).

Cadmium Coatings - Cadmium coatings are utilised on steel, aluminium, and certain other non-ferrous metal fasteners and moving parts to provide the best available combination of corrosion resistance, particularly in salt and alkali media, and lubricity or low coefficient of friction. They are also employed in many electrical or electronic applications where a good combination of corrosion resistance and low electrical resistivity are required. In addition, cadmium coatings exhibit excellent plating characteristics on a wide variety of substrates, have good galvanic comparability with aluminium, and are readily solderable (Morrow 1996).

Alloys and Minor Uses - Cadmium alloys include (a) alloys in which cadmium is present in small amounts to improve the physical, mechanical or electrochemical properties of copper, tin, lead or zinc-based alloys or (b) low melting point fusible alloys and high melting point joining alloys. Other minor uses of cadmium include cadmium telluride and cadmium sulphide in photovoltaic cells, and other semiconducting cadmium compounds in a variety of electronic applications (Cadmium Association and Cadmium Council 1991).

Industrial Occupation for Cadmium Exposures

- Alloys production
- Battery production

- Electroplating
- Enamelling
- Paint production and use
- Phosphorus production
- Pigment production and use
- Plastic production
- Plating
- Smelting and refining
- Solar cells production
- Soldering
- Stabilizer production
- Welding

1.2.2 Health Effects

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. Cadmium appears to be the largest single contributor to autoimmune thyroid disease

Cadmium, especially cadmium oxide is a 'probable carcinogen'. There is evidence of it causing prostate and kidney cancer in humans, it has been shown to cause lung and testicle cancer in animals. It is also a teratogen, and may cause reproductive damage. Inhalation of smoke from burning cadmium or from cadmium oxide is toxic to the respiratory system. It is unlikely that this sort of exposure would occur except in cases of unusual industrial accidents. Repeated low exposures can cause permanent kidney damage that may go unnoticed. Lung scarring can occur from a single high exposure or repeated low exposures. Long-term exposures can cause renal disfunction, anaemia, fatigue and loss of the sense of smell. High exposures can cause rapid lung damage, shortness of breath, chest pain, and a build up of fluid in the lungs. In severe cases death or permanent lung damage occurs. High exposure may also cause nausea, vomiting, cramps, and diarrhoea. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

1.2.3 Regulatory Environment Standards for Cadmium

Cadmium levels in the environment vary widely. Since it can be transported continually between various matrices viz. air, water and soil

Table 1.3 Maximum admissible concentration of Cadmium in drinking water

Country / Organization	**Max. admissible concentration/ Desirable limit/ Guideline**
IS: 10500 BIS (*Bureau of Indian Standards*)	0.01 mg/l
Australia	0.002mg/l
Japan, EQS (*Environmental Quality Standards*)	0.01 mg/l
EEC (*European Economic Community*)	0.005mg/l
German	0.005mg/l
USEPA (*United States Environment Protection Agency*)	0.005mg/l
WHO (*World Health Organization*)	0.003mg/l

Standards for Cadmium in Treated Leachate for disposal and MSW.

The Municipal Solid Waste (Management and Handling) Rules, 2000 of The Environment (Protection) Act, 1986 includes the standard for the compost derived from municipal solid wastes.

Table 1.4 Standards for Cadmium in Treated Leachate for disposal and MSW

Leachate	**Maximum discharge limit**
Disposal of treated leachate into:	
1. Inland surface waters	2.00 mg/l as Cd (max)
2. Public sewer	2.00 mg/l as Cd (max)
MSW Compost	5.00 mg/kg as Cd (dry Wt.)

Industry Specific Standards

The industries produce effluents of varied qualitative quantity and characteristics. In order to reduce the environmental pollution, industry specific standards have been notified by Government of India under schedule I of The Environment (Protection) Act, 1986.

Table 1.5 Waste water discharge standard for Cadmium concentration in different industry by CPCB

Industry	**Discharge standard**
Small scale industries (located in the Union Territories)	2.00
Dye and dye intermediate industries	2.00
Electroplating industries	2.00
Inorganic chemical industry (wastewater discharge)	0.02
Bullion refining	0.02
Treated effluent quality of CETP -Discharge into surface waters -Discharge into surface waters	 1.00 2.00

Table 1.6 Discharge (mg/l) Standards for Cadmium content in effluent in different water bodies :(Under Schedule II of the Environment (Protection) Act, 1986, general standards for discharge of effluent into different water bodies are notified.)

Water Sources	**Inland surface water**	**Public Sewer**	**Marine coastal areas**
Permissible limits	2.00 mg/l	1.00 mg/l	2.00 mg/l

1.3 Humic Acid

Organic matters, which are result of both natural and anthropogenic activities, are consistuent present in the water that requires removal. Humic substances (HS) are a general category of naturally occurring, biogenic, heterogeneous organic substances. Humic substances are the chemicals that are responsible for imparting the yellow to brown color found in most surface water sources and have extremely large molecular weights (in the range of 1000 to 1000,000). As a result of their large molecular weight, humic substances behave as colloids in solution which means they are sort of like transparent particles. They consist of several groups of substances that depending on their solubility can be grouped as follows: humin is the fraction of humic substances that is not soluble in water at any pH; humic acid (HA) is the fraction of humic substances that is not soluble in water under acidic conditions (below pH 2), but becomes soluble at greater pH; fulvic acid (FA) is the fraction of humic substances that is soluble under all pH conditions (Aiken et al., 1985). Humic acid is one of the major components of humic substances inturn organic matter in water. Humic substances as a group are found in the aqueous and terrestrial environments in a variety of forms and associations.

- Free HS consists of soluble or insoluble forms of the material itself.
- Complexed HS is chemically bound to metals, other inorganic species such as phosphate, or organic molecules. The complexed HS is either in solution or in particulate form.
- Surface-bonded HS is chemically bonded to other solids such as clay minerals or iron and aluminium oxides.

Humic acids are a complex mixture of partially "decomposed" and otherwise transformed organic materials. They occur in soil and sediment, peat, coal, lake water, sea water, plants and coral skeletons. Humic acid is one of the major components of humic substances. Humic acid is a condensed, refractive mixture of aromatic organic acids which has high molecular weight (typically 500-250,000 Daltons) and display both aliphatic and aromatic character. They are dark brown to black in colour. Humic acids are thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups.

1.3.1 Properties and Structure

Humic acid is a very complex organic material, the structure and reactions of which are not fully understood. Humic acid is a typical humic substance which has high molecular weight. Analysis of a wide variety of humic substances shows that it usually contains carbon, hydrogen, oxygen, and nitrogen within ranges (%) as follows:

Table 1.7 Elemental compositions of humic substances

Sl. No.	Elements	Composition
1.	C	45-60
2.	O	25-45
3.	H	4-7
4.	N	2-5
5.	Inorganic elements (ash)	0.5-5

Humic acid consist of nonuniform distribution of functional groups joined by a variety of aliphatic and aromatic units. The most important oxygen-containing functional groups along with typical ranges of content (mmol functional group per g of humic material) are carboxyl (2–6), phenolic-OH (1–4), alcoholic-OH (1–4), carbonyl, both ketones and quinones (2–6), and methoxyl (0.2–1). (Boily and Fein, 2000). The hypothetical structure for humic acid, shown in figure (), contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings (Stevenson, 1982)

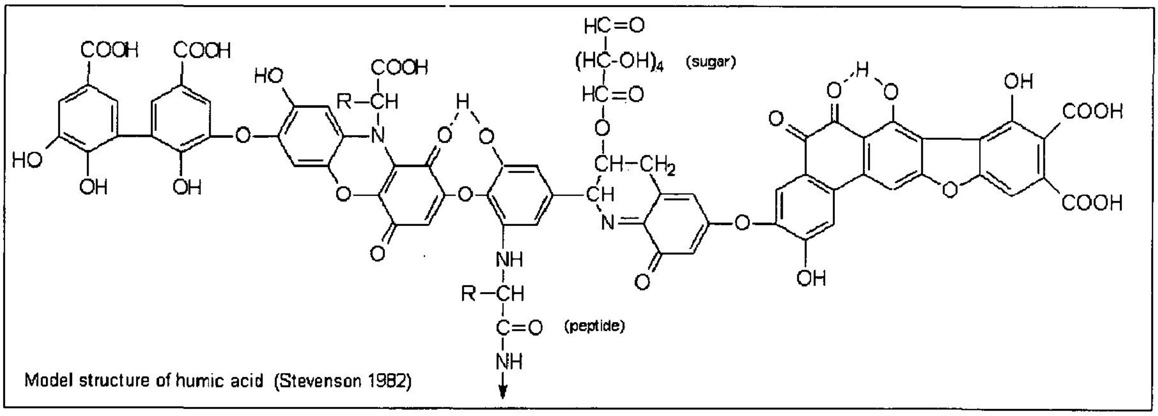


Fig. 1.2 Schematic of humic acid model structure (Stevenson, 1982)

Bio-Liquid Complex (Bio Ag Technologies International) derived from a type of leonardite (highly oxidized form of high organic matter) differs from their theoretical formula, because a part of its chemical structure has been oxidized. The oxidized sites give the entire molecule a negative charge enabling it to absorb micronutrients or react with metal ions (Fig.1.3)

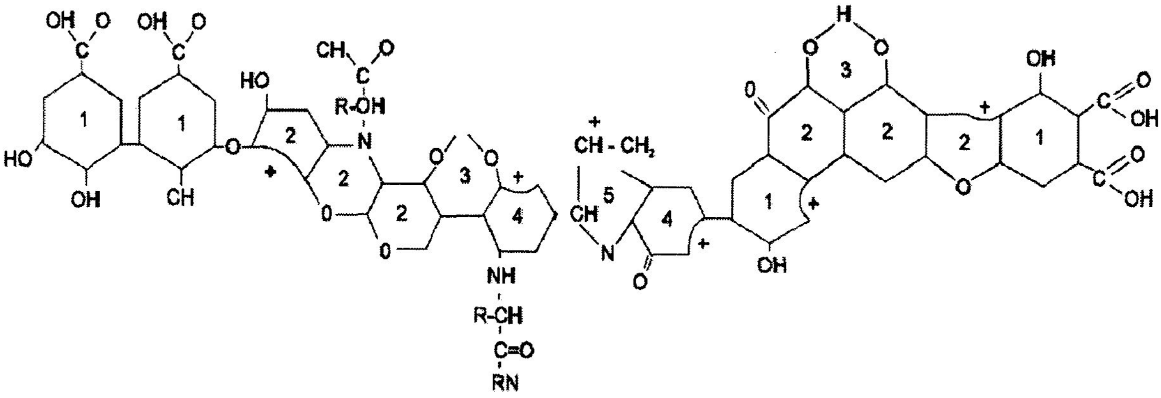


Fig. 1.3: Oxidized HA molecule (Bio Ag Technologies International)

The functional groups are the location of many of the important reactions with which HA is involved.

- It is these groups that, individually or together, enable specific reaction of humic substances with inorganic elements and with other organic molecules in soil–water systems.
- The functional groups are also major contributors to the ion exchange properties of soils and sediments. In addition to being present in the above groups, both oxygen and nitrogen appear as bridging units and in ring structures.

1.3.2 Humic Acid as a Complexing agent for Metal Ions

The complexation of metals by humic substances is of particular interest. Humic acid is a potent chelator as well. A chelator is a molecule that binds metals, including toxic heavy metals. The humic substances influence the biological and physico-chemical properties of toxic ions acting as an accumulation phase for heavy metals following the formation of metal–humate complex or chelates with different degrees of stability (Boily and Fein, 2000). Organic matter can have a dual role: it can reduce metal ion solubility through the binding of metal ions to solid organic sorbent or increase it through binding to dissolved organic matter. There are three possibilities of binding of humic acid with metal ions:

1. By chelation between carboxyl and phenolic hydroxyl groups.
2. By chelation between two carboxyl groups.
3. By complexation with carboxyl group.

The major binding sites in humic acids are usually attributed to the carboxylic and phenolic groups present, although other less abundant functional groups (e.g. N- and S-containing groups) may also be important for metal ion binding. The oxygen containing functional groups in HA represent about a quarter of the total molecular weight of HAs. The carboxyl (COOH) group increases in abundance with humidification, reacts readily with metals, and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO–) group. Wang et al. (1998) suggested that carboxylic groups dominate the uptake of metal cations by the dissolved organic matter fraction of wastewater and sludge, and demonstrated the important role of carboxylic groups in the uptake of metal ion. The phenolic hydroxyl (OH) group is more abundant in the early stages of decomposition, is derived from lignin in woody plants, reacts less with metals, and dissociates between pH 8 and 13.5 (Pillon et al., 1986). The carbonyl (C=O) group increases in abundance with humidification, is the main functional group and transforms into the COOH group under oxidizing conditions. (Andelkovic et al., 2006)

The infrared (IR) spectroscopic studies of metal–humic complexes suggested the participation of phenolic –OH and –COOH groups in binding of the metal ions followed –C=O and –NH– groups (Manunza et al., 1995). The reaction can be as follows:

$$\text{R–COOH} + \text{Me}^{+} \leftrightarrow \text{R–COOMe} + \text{H}^{+} \qquad (1)$$

$$\text{R–OH} + \text{Me}^{+} \leftrightarrow \text{R–OMe} + \text{H}^{+} \qquad (2)$$

Me^{+} is the metal ion. This reaction leads to the acidification of the sorption solution. The p*K* (dissociation constant) values of carboxylic groups are generally between 4 and 6. Thus, the increase of H^{+} concentration in the solution due to Eq. (1) decreases –COOH ionization and, consequently, the ion-exchange capacity. So, the pH of aqueous solution has to be higher than 4. (Evanko and Dzombak, 1999).

1.3.3 Environmental issues related to Humic Substance

Humic substances have many functions in the environment. In soils they participate in the formation of soil structure and thermal regime, but interacting with dissolved substances, they influence the accumulation and release processes of nutrients and trace elements. Humic substances much influence soil biota and especially microbial activity (Orlov et al., 2002). Humic substances can be considered as a matrix onto which environmental processes are imprinted, but on the other hand they can be considered as a reactive ingredient, actively participating in reactions and processes going on in the soil and aquatic environment. As far as the major reservoir of humic substances is soils, they are an important factor in various areas of agriculture, such as soil chemistry, fertility, plant physiology and others.

There is no doubt that HA has many beneficial effects humic substance has adverse effect on the aesthetic water quality as well as the biofouling of pipelines. Humic substances are the chemicals that are responsible for imparting the yellow to brown color found in most surface water sources. Humic substances present in the water are transformed into mutagenic organic chlorides such as trihalomethanes by chlorine treatment process for sterilization (Zhang and Minea, 2006).

Land disposal of municipal, leachate from municipal solid waste, industrial wastes and utilization of fertilizers and pesticides in agriculture all contribute to the rise in levels of toxic metals and also organic matter in the environment. Interactions of heavy metals with humic substances typically control the fate and transport of metals through ground and surface water systems. Adsorption has been recognized as an effective technology for trace heavy metal removal and HA. Adsorption of HA causes change in the surface properties of adsorbent by increasing in the surface negative charges as well as pore blockage. Humic acid (HA) may improve metal adsorption by formation of metal–HA complexes on adsorbent surfaces. On the other hand, the HA can be present in a soluble form and form complexes with metals, which reduces metal adsorption onto the carbon. HA in aqueous solutions can change the metal adsorptive behaviour. The simultaneous adsorption of heavy metal and HA onto adsorbent is the best option.

Activated carbon is usually used as adsorbent materials because of their extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. Furthermore, the presence of different surface functional groups on activated carbon, especially oxygen groups such as carboxylic, carbonylic, lactonic and phenolic [Bandosz et al. 1992] leads to the adsorption of ions of heavy metals (Al-Asheh et al., 2003; Naseem and Tahir, 2001). By the impregnation of Fe3+ onto the surface of untreated granular activated carbon (GAC) an amorphous layer of FeOOH is formed as per the following equation

$$Fe^{3+} + 3OH^{-} \rightarrow FeOOH + H_2O \qquad (1.1)$$

Formation of such layer of FeOOH increases the net positive charge (NPC) of the GAC-Fe and improves the adsorption capacity. The clay minerals in soils play the role of natural scavengers in removing and accumulating contaminants in water passing through the soil by ion exchange and adsorption. Clay minerals have great potential as inexpensive and efficient sorbents owing to their chemical and mechanical stability, high surface area and structural properties, high cation exchange capacity (CEC), tendency to hold water in the interlayer sites, and the presence of Brønsted and Lewis acidity. Treatment of clay minerals with concentrated inorganic acids usually at high temperature replaces exchangeable cations with H^+ ions with simultaneous partial elimination of Al and other cations from both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact. Hence acid activation increases the adsorbent capacity of clay.

1.4 Adsorption Fundamentals

1.4.1 General

Adsorption is a surface phenomenon. It is used as a separation process where a species present in a fluid phase is transferred to the solid phase and gets attached to the solid surface, if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid . In an adsorption process, molecules or atoms or ions in the fluid phase get concentrated or accumulated on the surface of a solid, where they bond with the solid surface or are held there by weak inter-molecular forces. The accumulated or concentrated species on the surface of solid is called the adsorbate, and the porous solid material is known as an adsorbent.

1.4.2 Adsorption Diffusion Study

In adsorption systems, the mass transfer of solute or adsorbate onto and within the adsorbent particle directly affects the adsorption rate. It is not only important to study the rate at which the solute is removed from aqueous solution in order to apply adsorption by solid particles to industrial uses but also it is necessary to identify the step that governs the overall removal rate in the adsorption process in order to interpret the experimental data. There are essentially four steps in the adsorption of a solute from the bulk liquid solution by an adsorbent.

1. Transport of solute from the bulk of the solution to the external film surrounding the adsorbent particle
2. Diffusion of the adsorbate from across the external liquid film to the external surface of the adsorbent particle.
3. Diffusion of the adsorbate from the pore mouth through the pores to the immediate vicinity of the internal adsorbent surface
4. Adsorption of the adsorbate onto the interior surface of the adsorbent.

All these processes play a role in the overall sorption of the solute from the bulk liquid solution to the internal surface of an adsorbent. In a rapidly stirred, well mixed batch adsorption, mass transport from the bulk solution to the external surface of the adsorbent is usually rapid. Therefore, the transport resistance of the adsorbate from the bulk of the solution to the exterior film surrounding the adsorbent may be small and can be neglected. In addition, the adsorption of adsorbate at surface sites (step 4) is usually very rapid, and thus offers negligible resistance in comparison to other steps, i.e. steps 2 and 3. Thus, these processes usually are not considered to be the rate-limiting steps in the sorption process.

Stages in adsorption process

Adsorption is thought to occur in three stages, as the adsorbate concentration increases.

Stage 1: First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it.

Stage 2: As the fluid concentration is further increased, second, third etc., layers form by physical adsorption; the number of layers which can form can limited by the size of the pores.

Stage 3: Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

1.4.3 Adsorption Kinetic Study

In order to investigate the adsorption processes, various kinetic models are used to describe the time-course of adsorption of a species onto an adsorbent. The kinetic models include pseudo-first-order, pseudo-second-order; rate expressions when the diffusional mass transfer resistances (external to solid, i.e. in the fluid phase, and internal-pore and surface diffusion) are considered to be negligible. The mass transfer based models include intra-particle diffusion model.

Pseudo-first order model

The rate of sorption to the surface should be proportional to a driving force times an area, and the pseudo first order equation is

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{1.2}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity in equilibrium (mg/g), k_f is the rate constant of pseudo-first order model (1/min), and t is the time (min). After definite integration by applying the initial conditions at t=0, q_t=0 and $t = t$, $q_t = q_t$, the equation becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \tag{1.3}$$

This equation is the so-called Lagergren equation (Lagergren, 1898). This equation is, however, valid only for the initial period of adsorption. A plot of $\log(q_e - q_t)$ versus t enables the determination of the kinetic constants.

Pseudo-Second Order

The pseudo-second-order model can be represented in the following form:

$$\frac{dq}{dt} = k_S(q_e - q_t)^2 \tag{1.4}$$

where k_S is the pseudo second order rate constant (g mg^{-1} min^{-1}), q_e the amount of solute ions adsorbed at equilibrium(mg g^{-1}) and q_t is the amount of solution ions adsorbed on the sorbent at any time, t (mg g^{-1}).

This equation can be integrated with $q_t = 0$ at $t = 0$, and $q_t = q_t$ at t=t, to give

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e} t \tag{1.5}$$

At $t \rightarrow 0$, $q_t \rightarrow 0$ and Eq. (2.3) gives the initial sorption rate,

$$\frac{dq}{dt}_{t \rightarrow 0} = h = k_S q_e^2 \tag{1.6}$$

where h, the initial sorption rate, has the units of mg g^{-1} min^{-1}.

The linearized plot of t/q_t versus t is the so-called ratio correlation. The q_e and the h along wit h the k_S can be determined experimentally from the slope and intercept of the plot of t/q_t versus t.

Intra-particle Diffusion Study

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with t-1/2, the Weber-Morris plot rather than with the contact time t.

$$q_t = k_{id} t^{0.5} + I \tag{1.7}$$

where, k_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and I (mg g^{-1}) is a constant that gives an idea about the thickness of the boundary layer, i.e., the larger the value of I, the greater is the boundary layer effect.

The slope of the Weber and Morris plots: q versus $t^{0.5}$, are defined as a rate parameter (k_{id}), characteristic of the rate of adsorption in the region where intra-particle diffusion is rate controlling. The higher the value of k_{id} the higher is the intraparticle diffusion rate.

1.4.4 Adsorption Isotherm

The successful representation of the dynamic adsorption of solute from a solution onto an adsorbent depends upon the equilibrium between the two phases. Adsorption equilibrium is established when the amount of adsorbate adsorbed on the solid surface of adsorbent is equal to the amount desorbed. At its equilibrium condition the amount of solute adsorbed on the solid adsorbent surface and the solution concentration remain constant. The relationship between the amount of adsorbate adsorbed and the adsorbate concentration remaining in solution is described by an isotherm. The adsorption isotherm can be depicted by plotting solid phase concentration against liquid phase concentration graphically. Equilibrium isotherms are measured to determine the capacity of the adsorbent for the adsorbate.

A variety of different isotherm equation have been proposed, some of which have a theoretical foundation and some being of a more empirical nature. Langmuir, Freundlich, Temkin, Brunauer-Emmet-Teller (BET), redlich-Peterson (P-R) etc. are commonly used adsorption isotherm models for describing the dynamic equilibrium. In practice, the two-parameter equations (Freundlich, Langmuir and Temkin) are more widely used than the three-parameter equations (Redlich-Peterson and Langmuir-Freundlich) due to the inconvenience of evaluating three isotherm parameters. However, a three parameter equation can often provide a better fit a the isotherm data than two-parameter one.

Langmuir isotherm:

Langmuir [1918] isotherm is derived with the basic assumption that the sorption takes place at specific homogeneous sites within the adsorbent.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (1.8)$$

where, K_L is a constant related to the free energy of adsorption ($K_L = e^{-\Delta G/RT}$) and is the reciprocal of the concentration at which the adsorbent is half-saturated. C_e is the equilibrium liquid phase concentration (mg dm^{-3}). It is a measure of the attraction forces between an adsorbate molecule and a solid adsorbent surface. q_m signifies the adsorption capacity (mg/g) corresponding to complete monolayer coverage. The assumptions of the Langmuir model are that the (1) surface is homogeneous, which means that the adsorption energy is constant over all surface adsorption sites (2) adsorbed atoms or molecules are adsorbed at definite sites, and (3) that each site can accommodate only one molecule or atom. A plot of either C_e/q_e versus C_e or the multiple regression fit of the equation with the experimental data enables the determination of the constants.

Freundlich isotherm

The Freundlich equation [Freundlich, 1906] is one of the earliest empirical equations used to describe equilibria data. This equation takes the following form:

$$q_e = K_F C_e^{1/n} \quad \text{or} \quad \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (1.9)$$

where, K_F is the Freundlich constant (l/mg), C_e is the equilibrium liquid phase concentration (mg dm^{-3}) and $1/n$ is the heterogeneity factor. The parameter n is usually greater than unity. These constants can be calculated from the plot of ln(C_e) versus ln(q_e). the Freundlich equation is most usefulfor dilute solutions over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on to activated carbon. A high K and high n value is an indication of high adsorption through out the concentration range. A low k and high n indicates a low adsorption through out the concentration range. A low n value indicates high adsorption at strong solute concentration.

Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into account the interactions between the adsorbing species and the adsorbent. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) that the adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy [Temkin and Pyzhev, 1940; Kim et al., 2004]. Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \qquad (1.10)$$

Eq. (3.4.9) can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad (1.11)$$

where, $B_T = \frac{RT}{b}$ and is related to the heat of adsorption. (1.12)

b and K_T is the equilibrium binding constant (dm^3 mol^{-1}) corresponding to the maximum binding energy. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_T and B_T.

1.4.5 Factors Controlling Adsorption

The amount of adsorbate adsorbed by an adsorbent from aqueous solution is depend upon a number of factors which are discussed below.

Nature of Adsorbent

The adsorption capacity of an adsorbent depends upon its physicochemical characteristics, specific surface area and its affinity for the adsorbate. Adsorption capacity is directly proportional to the exposed surface of the adsorbent. For the non-porous adsorbents, the adsorption capacity is inversely proportional to the particle diameter whereas for porous material it is practically independent of particle size. However, for porous substances particle size affects the rate of adsorption. For substances like GAC, the breaking of large particles to form smaller ones open up previously sealed channels making more surface accessible to the adsorbent.

Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC) [IUPAC, 1982], that is, micro-pores (diameter (d) < 20 Å), meso-pores (20 Å $< d < 500$ Å) and macro-pores ($d > 500$ Å). Micro-pores can be further divided into ultra-micropores ($d < 7$ Å) and super micro-pores (7 Å $< d < 20$ Å). For liquids, the adsorption of organic molecular would generally be facilitated by mesopores, which effect faster intra-particle migration of the adsorbate.

pH of Solution

Adsorption from solution is strongly influenced by "pH" of the solution. The adsorption of cations increases while that of the anions decreases with increase in pH. The solution pH affects the surface charge of the adsorbents and, therefore, the adsorption process through dissociation of functional groups, viz. surface oxygen complexes of acid character such as carboxyl and phenolic groups or of basic character such as pyrones or chromens, on the active sites of the adsorbent. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by pH of solution. Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. It is an evident observation that the surface adsorbs anions favourably at lower at pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of OH- ions.

Initial Concentration of Adsorbate

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of the adsorbate in the solution is very important. The amount adsorbed decreases with an increase in the adsorbate concentration as the resistance to the uptake of solute from the solution decreases with an increase in the solute concentration. Therefore, the rate of adsorption increases because of the increasing driving force

Contact time

The studies of the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption, most of the adsorbate species are absorbed species are adsorbed on the adsorbent surface with in short contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. Strong chemical binding of adsorbate requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of heavy metals is fast at the initial stages of the contact period, and there after it becomes slow near equilibrium.

Degree of agitation

Agitation in batch mode of operation is most important to ensure proper contact between the adsorbent and the solution. At lower agitation speed, the stationary fluid film around the particle is thicker and the process is mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film reduces and after a certain point the process becomes intra particle diffusion controlled. Whatever is the extent of agitation the solution inside the process remain unaffected and hence for intraparticle mass transfer controlled process agitation has no effect on the rate on the adsorption.

Temperature

Temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents.

1.5 Objective of the present study

The objectives of the present study are:

1. Characterization of Granular Activated Carbon (GAC), Iron impregnated Granular Activated Carbon (Fe-GAC) and Activated Clay (A-Clay), which includes proximate analysis, surface area, bulk density, SEM and FTIR etc.

2. Study the effect of pH, adsorbent dosage, initial concentration and contact time on the removal of humic acid and cadmium independently.

3. Study the effect of pH, adsorbent dosage, initial concentration of Humic acid and Cadmium and contact time on the removal of humic acid and cadmium by co-adsorption.

4. Study the kinetics for single and co-adsorption of humic acid and cadmium using Lagergran, pseudo second order and Weber Morris rate models.

5. Study of the isotherms used to find the adsorption capacity of the adsorbents.

Chapter –II

LITERATURE REVIEW

A comprehensive review is presented here on various studies, which have been reported out for the removal of heavy metal and humic acid by adsorption using various absorbents. The literature review comprises of the following:

2.1 TREATMENT METHODS OF CADMIUM

Several techniques have been used for the treatment of wastewater containing heavy metals. Techniques include physio-chemical processes, such as, adsorption, electro coagulation and biosorption etc.

2.1.1 Electrodialysis

Electrodialysis is an electrically driven membrane separation process that is capable of separating, concentrating, and purifying selected ions from aqueous solutions. The process is based on the property of ion exchange membranes to selectively reject anions or cations. Electrodialysis is a membrane separation technique where ionized species in solution are transported, through ion-exchange membranes, under the influence of an electric field. When a solution containing ionic species is introduced into the cell compartments, anions migrate toward the anode and cations migrate toward the cathode crossing anion-exchange and cation-exchange membranes. An alternate disposition of the membranes, separating the cell compartments, allows the ions that are able to cross the anion-exchange membrane to be stopped by the cation-exchange membrane and vice versa. With such technique it is possible to obtain a diluate and a concentrated solution containing ionic species (Marder et al., 2004).

2.1.2 Electro coagulation

The electrocoagulation technologies are essentially electrolytic processes that involve the destabilization of suspended, emulsified or dissolved pollutants in an aqueous medium, by the application of an electric current. In electrocoagulation (a process similar to chemical coagulation), there is a reduction of the net surface charge to a point where the colloidal particles can approach closely enough for Van der Waal's forces to hold them together and allow aggregation to take place. The surface charge reduction is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte having an opposite charge. This mechanism corresponds to the destabilization of colloidal particles. During electrocoagulation, the coagulant is generated in situ by electrolytic oxidation of an anode of appropriate material. Charged ionic species are removed from wastewater by allowing ions to react with oppositely charged ions, or with flocs of metallic hydroxides generated within the effluent (Escobar et al., 2006).

2.1.3 Ion exchange

Ion exchange has been in the use as treatment process for heavy metals fro decades. A typical heavy metal ion exchange system has a fixed bed resin with ability to exchange or remove cation or anion. Ion exchange resins are classified as cation exchangers, which has positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. In general, divalent and trivalent ions are easier to remove than monovalent ion using ion exchange (Wojtowicz and Stoklosa, 2002, Lin et al., 2008).

2.1.4 Biosorption

Biosorption is one of recent technique, used for removal of heavy metals from wastewater. Biosorption is the binding and concentration of heavy metals from aqueous solutions (even very dilute ones) by certain types of inactive, dead, microbial biomass. Research on biosorption is revealing that it is sometimes a complex phenomenon where the metallic species could be deposited in the solid biosorbent through different sorption processes of ion exchange, complexation, chelation, microprecipitation, etc. (Vilar et al., 2008,).

2.1.5 Adsorption

Adsorption is one among the most cost effective and simple technique. Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions.

Co-adsorption of heavy metals and humic acid on various absorbent has been studied widely since long time by several researchers see table 2.1.

Table 2.1 Studies on co-adsorption of heavy metals and humic acid using various adsorbents.

Sl. No	references	Adsorbent	Adsorbate	Inference
1.	Wang et al., (2008)	Fly ash	Humic acid and heavy metals (Cu^{2+}, $Pb^{2+)}$	1. Pb^{2+} and Cu^{2+} ions, and humic acid, exhibited adsorption capacity of 18, 7, and 36 mg/g, respectively. 2. For Pb–HA and Cu–HA systems, Pb^{2+} and Cu^{2+} adsorption was increased to 37 and 28 mg/g, respectively 3. In co-adsorption, heavy metals competed with adsorption of humic acid, resulting in decrease in the humic acid adsorption. 4. First and second order kinetics were used to describe adsorption. 5. Langmuir and Freundlich isotherms
2.	Wang et al., (2008)	Zeolite tuff	Humic acid and Cu^{2+}, Pb^{2+}	1. For single adsorption, the adsorption capacities of Cu^{2+}, Pb^{2+} and humic acid at 30 ◦C, pH 5 are 23, 68 and 78 mg/g, respectively. 2. In Pb^{2+}/humic-acid system, Pb^{2+} exhibited competitive adsorption with humic acid, resulting in reduced adsorption of both Pb2+ and humic acid. 3. In Cu^{2+}/humic-acid system, competitive adsorption and complexation between Cu^{2+} and humic acid influence the adsorption, resulting in decreased adsorption of humic acid but increased adsorption of Cu^{2+}. 3. The complexation structure of Pb–HA/zeolite and Cu–HA/zeolite in three-component system was proposed as S-Pb–HA and S-HA-Cu, respectively.

3.	Terdkiatburana et al., (2007)	Zeolite MCM-22 and Activated carbon	Humic acid and Cu^{2+}, Pb^{2+}	1. In single component system, the MCM-22 presents the adsorption capacities of Cu^{2+}, Pb^{2+}, and HA more than that of activated carbon. 2. Solution pH will significantly influence the adsorption, $Cu^{2+}$and Pb^{2+} adsorption will increase with increasing pH while HA shows a decreasing trend as pH is increase. 3. In binary-adsorbate system, on the MCM-22, Cu^{2+} and Pb^{2+}will present competitive adsorption with humic acid. 4. On the activated carbon, Pb^{2+} and HA also exhibit competitive adsorption, while Cu^{2+} and humic acid will have a complexation effect, resulting in an increase of Cu^{2+} adsorption on the activated.
4.	Long et al., (2007)	Crosslinked chitosan derivatives (carboxymethylchitosan)	Heavy metal ions (Cu^{2+},- Cd^{2+}) and humic acid	1. Crosslinked chitosan derivatives (carboxymethylchitosan) were prepared using the irradiation technique without any additives. 2. Cross-linked CM-chitosan was insoluble in both acidic and basic media, and showed relatively low-swelling properties. 3. Crosslinked chitosan derivatives possessed a porous morphological structure. 3. Adsorption of heavy metal ions (such as Cu^{2+}, Cd^{2+}) and humic acid onto crosslinked samples was found to be strongly pH-dependent. 4. Langmuir isotherm.
5.	Pehlivan and Arslan, (2006)	Lignite	Metal ions (Zn^{2+} and Cd^{2+})	1. Sorption depends strongly on pH, the origin of the young brown coal and on the nature of the metal ion. 2. Cd^{2+} was found to form the most stable HA complexes, followed by Zn.
6.	Yan and Bai, (2005)	Chitosan hydrogel beads	Lead and humic acid	1. Single species adsorption, sequential adsorption of one species after another and co-adsorption of both species were carried out. 2. Adsorption of either species mainly results from the complexation between adsorbate and functional groups at the surface of the hydrogel

				beads 3. Previously adsorbed species can either act as additional binding sites for, or occupy the same binding sites as the subsequent species to be adsorbed, resulting in enhanced or retarded adsorption of the subsequent species. 4. For co-adsorption, metal-organic interactions play a very important role in determining the extent of adsorption.
7.	Baker and Khalili, 2005	Humic acid	Zn^{2+} and Cd^{2+}	1. Investigation on the complexation of humic acid from Azraq Oasis with two heavy metal ions was done by using Schubert's ion-exchange equilibrium method. 2. The conditional stability constants (log βn) increased by increasing pH and temperatures for all metal–humate complexes. 3. The conditional stability constant log $\beta 1$ for Cd–humate is bigger than Zn–humate at all the desired temperatures and at pH 4 and 5. 4. The metal ion–humate complexation reaction overall was found to be endothermic. The values indicate spontaneous change (ΔG negative) with a large favourable entropy change (ΔS positive) at the two different pHs.
8.	Chen and Ju, (2004)	Activated Carbon	Copper ions and Humic acid (HA)	1. HA adsorption was highly dependent on solution pH. 2. At the HA concentration < critical concentration (CC), causes a decrease in copper adsorption and improves the adsorption at the HA concentration > CC 3. Presence of zinc and/or cobalt ions had less influence on the uptake of Cu. 4. HA causes slightly higher mass transfer resistance of copper ions in the adsorption 5. Intraparticle diffusion model is successfully used to describe the

				copper adsorption kinetics.
9.	Lai and Chen (2001)	Iron coated sand	Humic acid and metal ions ($Cu^{2+}$and Pb^{2+})	1. Batch and continuous mode of operation. 2. Maximum adsorption capacities for $Cu^{2+}$and Pb^{2+} were 0.259 mg/g and 1.211 mg/g 3. Presence of HA increased the adsorption of $Cu^{2+}$and Pb^{2+}. 4. Langmuir isotherm. 5. Desorption percentage of $Cu^{2+}$and Pb^{2+} were 98% and 58% respectively, while for HA it was 100%.
10.	Petrovic et al., (1999)	Sand, calcite and clay (kaolite)	Humic acid and metal ions (Pb^{2+}, Zn^{2+} and Cu^{2+})	1. Sorption of Pb^{2+}, Cu^{2+} and Zn^{2+} was favoured with increasing pH while HA sorption decreased with increasing in pH 2. Sorption of HA was higher on kaolin than on calcite or sand 3. Sorption of Cu^{2+} ions on all minerals studied rapidly increased as the concentration of dissolved HA increased 4. The amount of Pb^{2+} ions sorbed on sand slightly decreased as HA concentration increased, while on kaolin increased between 15 and 20%. 5. Sorption of Zn^{2+} ions onto all three minerals decreases as HA concentration was increased.
11.	Liu and Gonzalez, (1999)	Montmorillonite	Heavy metals (Pb^{2+}, Cd^{2+} and Cu^{2+}) and Humic acid	1. Humic acid adsorption was pH dependent. 2. In presence of bivalent metal, humic acid adsorption on montmorillonite increased slightly. 3. For preadsorption of HA, a slight increase in the amount of adsorption was observed for Cd and Cu when the adsorbed humic acid was increased. But no measurable change in the amount of adsorbed Pb on montmorillonite was observed 4. No difference between the preadsorption and coadsorption processes was observed for Pb and Cd. For Cu, there is a slightly higher amount of adsorption for the coadsorption process than the preadsorption process.

12.	Ferro-Garcia et al., (1998)	Activated carbon	Gallic acid (GA), Tannic acid (TA), and Humic acid (HA) and Cr^{3+}	1. Adsorption of GA is much higher than TA and HA, in the order HA < TA <<GA. 2. The adsorption of GA and TA was slightly higher out in the presence of Cr (III) than in the absence of the metal. 3. Adsorbent-adsorbate interactions for GA in the presence of Cr (III) were very strong. 4. At low acid concentration, a large decrease in the amount of Cr (III) adsorbed was observed. 5. Higher acid concentration, the amount of Cr adsorbed was enhanced, owing to the interactions of the cations Cr (III) with the negatively charged unbound functional groups of the adsorbed acids.
13.	Davis and Bhatnagar, (1995)	Hematite	Humic acid and cadmium	1. The modelling of Cd(II) adsorption onto hematite by the use of a non-electrostatic surface complexation model 2. Humic acid adsorption onto hematite decreases with increasing pH, exhibiting ligand exchange surface complexation characteristics. 3. The presence of humic acid increases Cd (II) uptake by hematite. 4. Cd (II) before HA > simultaneous adsorption ~ HA before Cd (II) general trend. 5. EDTA complexation significantly reduces the Cd (II) adsorption in the HA/hematite system.
14.	Xu et al., (1989)	Alumina	Humic acid and Cd (II)	1. Linear adsorption isotherms 2. The presences of fulvic acids would enhance the adsorption of cadmium at pH below PZC and reduce the adsorption above this pH.

Removal of Cadmium from wastewater using adsorption technique has been studied widely since last decades by several researches using various adsorbents see table 2.2.

Table 2.2 Studies on removal of cadmium using various adsorbents.

Sl. No.	References	Adsorbent	Adsorbate	Inference
1.	Argun and Dursun, (2008)	Pine tree Bark	Cd (II)	1. Modification of a bark with Fenton reagent enhanced its removal efficiency for heavy metal ions in comparison to raw bark. 2. The optimum Cd (II) removal by the FMB was obtained at pH 7. 3. The kinetics of sorption can be described by a model of pseudo-first-order. 4. The Langmuir and Freundlich isotherms were used to model isothermal sorption. 5. The adsorption capacity of the FMB adsorbent for Cd(II) equaled 30.2 mg g^{-1}. 6. The adsorption rate (k_1), the intraparticle mass transfer constant (k_d) and the external mass transfer constant (k_f) were 0.0027 min^{-1}, 1.57 mg g^{-1} $min^{-1/2}$, and 0.0061 cm s^{-1}, respectively.
2.	Kula et al., (2008)	Activated Carbon prepared from olive stone by $ZnCl_2$ activation.	Cd(II)	1. The equilibrium time, optimum pH, adsorbent dosage were found 60 min, pH > 6 and 1.0 g/50 ml respectively. 2. The kinetic data supported pseudo-second order model and intra-particle model but shows very poor fit for pseudo-first order model. 3. Langmuir and Freundlich isotherms were used. 4. The thermodynamic parameters, standard free energy (ΔG^0), standard enthalpy (ΔH^0), standard entropy (ΔS^0) of the adsorption process were calculated.

				5. Activated carbons produced with 20% $ZnCl_2$ solution was the best sample of the produced activated carbons from olive stone with the specific surface area of 790.25 $m^2 g^{-1}$. 6. Activated carbon from olive stone is an alternative low-cost adsorbent for removing Cd (II).
3.	Kadirvelu et al., (2008)	Carbon aerogel	Pb(II), Hg(II) and Cd(II)	1. Mono- and multi-component (binary and tertiary) systems with varying metal ion concentration (mg/l) were conducted to investigate the competitive adsorption characteristics. 2. Adsorption of the following metals in the order of Hg(II) > Pb(II) > Cd(II) in a single Systems. 3. Langmuir and Freundlich models are found to generally represent the experimental though but not consistently. 4. In the binary and tertiary systems, the sorption was suppressed by the presence of other metal ions in aqueous solution.
4.	Garg et al., (2008)	Sugarcane bagasse (SCB), Maize corncob (MCC) and Jatropha oil cake (JOC)	Cd (II)	1. Maximum metal removal was observed at pH 6.0 with a contact time of 60 min at stirring speed of 250 rpm with an adsorbent dose of 20 g/l. 2. The maximum adsorption of cadmium (II) metal ions was observed at pH 6 for all the adsorbents viz; 99.5%, 99% and 85% for JOC, MCC, and SCB, respectively, in the order JOC >MCC> SCB. 3. The applicability of Langmuir and Freundlich isotherm suggested the formation of monolayer of Cd (II) ions onto the outer surface of the adsorbent. 4. The intra-particle diffusion coefficient values obtained for Cd(II) sorption onto SCB, MCC and JOC confirm the feasibility and the spontaneous nature of the sorption process for Cd(II) ions.

5.	Al-Anber and Matouq (2008)	Olive cake	Cd(II)	1. The batch pH studies indicated that the optimum pH was 6 and the maximum cadmium removal at this pH was 66.6%. 2. The isotherm study indicates that the Langmuir and Freundlich models were adequately modelled our experimental data. 3. Increasing in temperature from 28 to 45 °C, the maximum adsorption capacity (*q*max) is decreased from 65.4 to 44.4 mg/g and Freundlich constant (K_f) decreased from 19.9 to 15.7. 4. The free energy change ($\Delta G°$) and the enthalpy change ($\Delta H°$) showed that the process was feasible and exothermic, respectively. 5. The kinetics study of sorption at pH 6 and temperature 28 ^{0}C indicates that the pseudo second-order model provides better correlation of the sorption data than the pseudo first-order model.
6.	Farinella et al, (2008)	Grape bagasse	Cd(II) and Pb (II)	1. The pH values found were 7 and 3 for Cd(II) and Pb(II), respectively 2. Adsorption capacity for metals were calculated from adsorption isotherms by applying the Langmuir model and found to be 0.774 and 0.428 mmol g−1 for Cd(II) and Pb(II), respectively. 3. The competition between metals for the same adsorption sites on grape bagasse was also evaluated, showing an increasing affinity for Pb(II) over Cd(II) when only these metals were present.
7.	Pehlivan et al., (2008)	Sugar Beet Pulp (SBP)	Cd(II) and Pb (II)	1. pH 5.3 and 5 were found optimum pH for Cd(II) and Pb (II), respectively. 2. Adsorption capacity for Cd (II) and Pb(II) were found to be 46.1 mg/g 43.5 mg/g respectively, 3. A dose of 8 g/ L was sufficient for the optimum removal of both the metal ions. 4. Freundlich isotherm. 5. SBP found to be promising substrate to entrap heavy metals in aqueous solutions

8.	Srivastava et al., (2007)	GAC	Cd(II), Zn (II) and Ni (II)	1. Maximum sorption of all the cations, viz. Cd(II), Ni(II) and Zn(II) was found to occur at pH0 6.0. 2. Optimum adsorbent dosage was found to be 20 g/dm3 for removal of Cd(II), Ni(II) and Zn(II) ions. 3. Optimum time was found to be 5 h. 4. The highest capacity for *C*0 = 500 mg/dm3 ,for Cd(II), Ni(II) and Zn(II) are found to be 11.0, 14.64 and 14.72 mg/g of ACC. 5. The sorption kinetics followed pseudo-second-order model
9	Gupta et al., (2003)	Bagasse fly ash	Cd(II) and Ni(II)	1. Maximum adsorption of cadmium and nickel occurred at a concentration of 14mg/l and 12mg/1. 2. Optimum pH value of 6.0 and 6.5for Cd (II) and Ni(II) respectively. 3. Dose of 10 g/l of adsorbent was found to be optimum. 4. Langmuir model better then the Freundlich model.
10.	Mathialagan and Viraraghavan (2002)	Perlite	Cd(II)	1. The batch pH studies indicated that the cadmium adsorption on perlite increased from 0 to 90%, when the pH was varied between 3 and 10. Beyond pH 9, cadmium removal was probably due to precipitation. The optimum pH was 6.0 and the maximum cadmium removal at this pH was 55%. 2. The kinetic studies at pH 6 indicated that equilibrium time for cadmium adsorption on perlite was 6 h. 3. The Ho et al.'s pseudo-second-order reaction rate model best described the kinetic data. 4. Isotherm analysis of the data showed that the adsorption pattern for cadmium on perlite followed the Freundlich isotherm. 5. The Thomas model was used to describe the column data and the adsorptive capacity of perlite for cadmium in column experiments using the Thomas model was 0.42 mg of Cd/g of perlite.

11.	Suraj et al., 1998	Kaolinites	Cd(II) and Cu(II)	1.Kaolinites was acid activated and thermal modified 2. Thermal modification alone deters the exchangeability of kaolinites_i.e., 3.08 mmol of Cd. and 3.06 mmol of Cu for TK and 3.15 mmol of Cd. and 16mmol of Cu. for MK. 4. Acid leaching improves the exchangeability of metal ions on to the clay lattice structure_i.e., 13.36mmol of Cd. and 18.80 mmol of Cu. for TK and 13.64mmol of Cd.and 18.09 mmol of Cu for MK.. 5. Cu and Cd shows higher uptake at 40^0C than those at 30^0C indicating its viability in pollution monitoring of warm industrial effluents.

Chapter – III

EXPERIMENTAL PROGRAMME

This chapter deals with the materials and methods of analysis, and the experimental procedures adopted to collect the experimental data.

3.1 Materials

3.1.1 Adsorbent

Adsorption of Cadmium and Humic acid were studied using three adsorbents, namely, Activated Clay (A-Clay), Iron impregnated Granular Activated Carbon (Fe-GAC) and the commercial grade Granular Activated Carbon (GAC). Clay was obtained from potters of Roorkee, Uttarkhand. Coconut-based GAC was purchased from ZeoTech Adsorbents Pvt. Ltd., New Delhi.

3.1.2 Adsorbate

All the chemicals used in the study were of analytical reagent (AR) grade. Cadmium was procured from, Rankem , Mumbai (India) and Humic acid, sodium salt was procured from Sigma Aldrich (Germany). The stock aqueous solutions of 1000 mg/l concentration has been prepared for each of the compound by taking respective amount of chemicals in distilled water (DW).

3.2 Preparation of Absorbent

3.2.1 Acid activation of Clay

Fifty grams of natural clay, with a particle size of 0.02–0.06 mm, were activated by refluxing with 250 ml of 1M H_2SO_4 at 80^0C in a round-bottom flask for 2 h. The slurry was air-cooled and filtered. The filter cake was repeatedly washed with distilled water until the filtrate was neutral. Finally, it was dried in an oven at 110^0C before use [Chang et al., 2004].

3.2.2 Preparation of Fe-GAC

Hundred grams of the granular activated carbon was treated with 240 ml of ferric chloride solution containing 2.5% Fe^{3+} (pH 6.8±0.2), the pH was raised to 12 by the addition of 1N NaOH solution. The high pH value for impregnation was considered for generation of maximum surface charges on the surface of GAC-Fe. The impregnation was carried out at 70^0C on a water bath till the complete evaporation of water was observed and then it was dried at 110^0C for 24 h. The dried material was washed with distilled water till the washing liquid became free from iron and then dried to constant weight (Mondal et al., 2008).

3.3 Adsorbent Characterization

The physico-chemical characteristics of the three adsorbents were determined by using standard procedure as described below.

3.3.1 Proximate Analysis

Proximate analyses of the adsorbents were carried out using the procedure given in IS 1350:1984. Sample was divided into two portions. The first portion of the sample was placed in a silica crucible and its moisture was determined. To determine the moisture content, sample was weighed and kept in oven at 105 ^{0}C, for 1 h. After 1 h the dry weight of sample was taken and % moisture was determined from the difference of initial weight and final weight (dry weight). After that, the sample was heated to 750 ^{0}C in a muffle furnace and maintained at this temperature for 2 h or more till a constant weight of the residue was obtained. The weight of the residue represented the ash content of the adsorbent. The second portion of the sample was placed in a crucible, covered with a lid and heated in the furnace at 600 ^{0}C for six minutes and thereafter at 950 ^{0}C in the furnace for another six minutes. Thereafter the crucible was kept in a dessicator for cooling and then the crucible was weighed. The volatile matter was found by subtracting the corresponding moisture determined previously

3.3.2 Density

Bulk densities of the adsorbents were determined by using MAC bulk density meter.

3.3.3 Scanning Electron Microscopic (SEM) Analysis

To understand the morphology of the adsorbents before and after the adsorption of adsorbate, the SEM micrographs were taken using LEO, Model 435 VP, UK. The particles were first gold coated using Sputter Coater, Edwards S150, to provide conductivity to the samples. The SEM micrographs were taken thereafter.

3.3.4 Surface area

Textural characteristics of adsorbents were determined by nitrogen adsorption at 77.15 K to determine the specific surface area and the pore diameter using an ASAP 2010 Micromeritics instrument and by Brunauer-Emmett-Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15 K).

3.3.5 Fourier Transform Infra Red (FTIR) Spectral Analysis

FTIR spectrometer (Thermo nicolet, Model Magna 760) was employed to determine the presence of functional groups in the adsorbents at room temperature. Pellet (pressed-disk) technique has been used for this purpose. The sample was mixed with KBr (IR spectroscopy, grade) thoroughly and pellet was made by using a special mold provided to make pellet under the pressure of 15 ton. The spectral range was from 4000 to 400 cm^{-1}.

3.4 Analytical methods

3.3.1 Analytical measurements for Humic Acid

The concentration of HA in the liquid sample was determined by a Perkin Elmer Lambda 35 double beam spectrophotometer. A standard solution of HA was taken and the absorbance was determine at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for HA was found to be 254nm. Calibration curve was plotted between the absorbance and the concentration of HA solution. The linearity of calibration curve (fig 3.1) from indicated the applicability of the Lambert-Beer's Law.

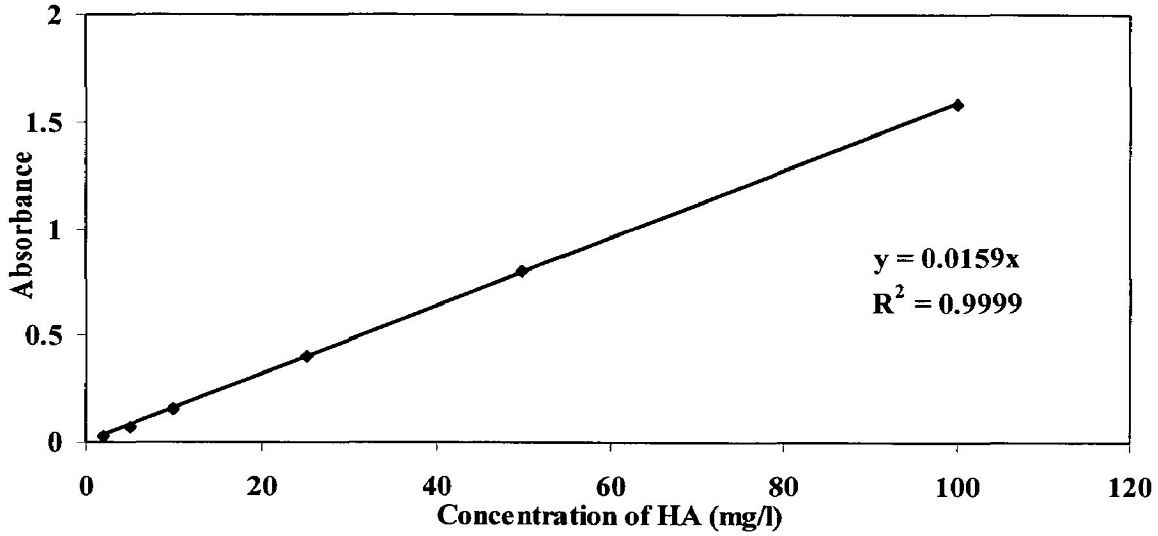


Fig 3.1 Calibration curve for Humic acid

3.3.2 Analytical measurements for Cadmium

Concentration of Cd was determined using Atomic Absorption spectroscopy (AAS) (GBC Avanta, Australia). The AAS used for Cd (II) concentration in the samples had the detection limit of 0.009 mg/l at the wavelength of 228.8 by using air–acetylene flame. Before the analysis, the sample was diluted to a metal ion concentration in the range of 0.2–1.8 mg/l with distilled water. Calibration curve was plotted between the absorbance and the concentration of Cd (II). The linearity of calibration curve (fig 3.2) from indicated the applicability of the Lambert-Beer's Law.

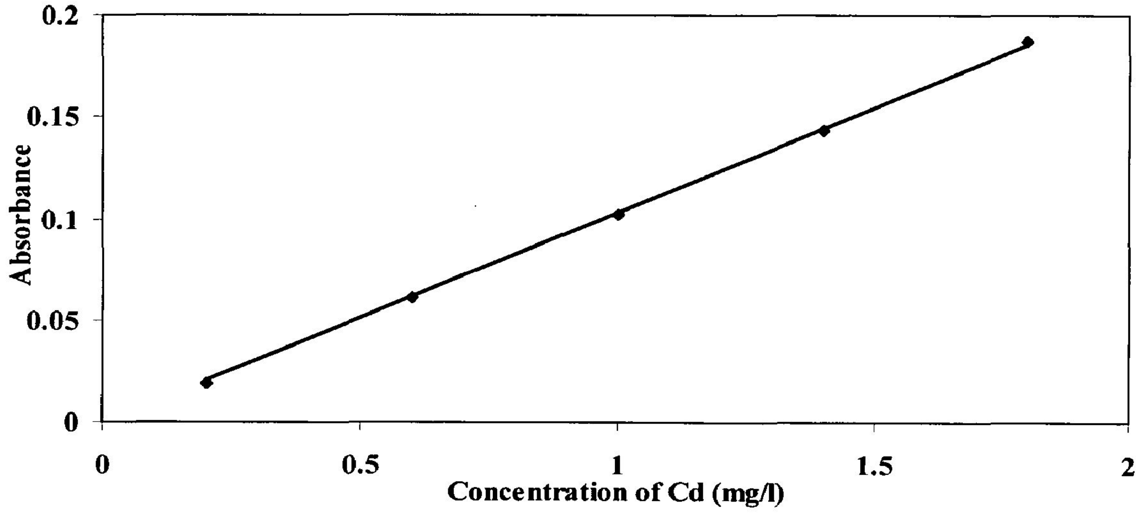


Fig 3.2 Calibration curve for Cadmium

3.5 Batch Experimental Programme

The batch adsorption studies were performed to study the effect of different parameter like initial pH, adsorbent dosage (*m*), initial adsorbate concentration (*Co*) and contact time (*t*) on adsorptive removal of HA and Cd (II). Batch experiments were conducted at 30±1 ^{0}C. For each experimental run, 50ml of the HA and Cd (II) of known concentration were taken in 100ml stoppered conical flask. The samples were agitated in a temperature controlled shaking water bath. Samples were withdrawn at appropriate time intervals. The filtrate solution was analyzed for remaining concentration of HA and Cd (II). The effect of pH was studied over a pH range of 2 to 8. For the optimum amount of adsorbent, 50 ml HA and Cd (II) solutions were contacted independently with different amounts of adsorbent till equilibrium was attained.

To study the adsorption kinetics, 50 ml of the aqueous solution containing known concentration of the adsorbate and known amount of absorbent was taken in a 100ml of conical flasks. The flasks were kept in a temperature-controlled shaker and the aqueous solution-adsorbent mixtures were stirred at 150 rpm. At the end of the predetermined time t, the flasks were withdrawn, their contents were filtered and the supernatant analyzed for the respective sorbate concentration. For adsorption isotherms, solutions of different concentration were agitated with known amount adsorbent till the equilibrium was achieved. Experiments were conducted out at the optimum pH by using a fixed amount of adsorbent with 50ml of the respective sorbate solutions having initial concentration in the range of 25-200 mg/l for Cd (II), 20-100mg/l for HA.

Similarly, for co-adsorption, effect of pH, contact time and adsorbent dosage were also studied in the same manner, by keeping concentration of HA and Cd(II) constant. For effect of initial concentration of HA, the Cd (II) concentration was kept constant while the HA concentration varied. Similarly for the effect of initial concentration of Cd (II), HA concentration was kept constant while the Cd (II) concentration varied.

The removals of metal ions from the solution and the metal uptake in the solid phase or surface loading, *q*e (mg/g), were calculated using the following relationships:

Percentage metal ions removal= $\frac{(C_0-C_e)}{C_e} * 100$ (3.1)

Amount of adsorbed metal ions per g of solid (qe) = $\frac{(C_0-C_e)V}{m}$ (3.2)

Where

C_0 is the initial metal ion concentration (mg/l),

Ce is the metal ion concentration (mg/l) at any time t,

V the volume of the solution (l)

m is the mass of the adsorbent (g).

Chapter –IV

RESULTS AND DISCUSSION

4.1 General

This chapter presents the results and discussion on the adsorption of humic acid and cadmium from aqueous solutions onto commercial grade granular activated carbon (GAC), iron impregnated granular activated carbon (Fe-GAC) and activated clay (A-Clay). This chapter has been divided into the following sections:

1. Characterization of adsorbents
2. Batch adsorption studies
3. Kinetic and isotherm studies

4.2 Characterization of Adsorbents

Proximate analysis was carried out for physico-chemical characteristics. The physico-chemical characteristics of GAC, Fe-GAC and A-Clay are given in the table 4.1. Proximate analysis showed that GAC and Fe-GAC has approximately same ash and fixed carbon percentage. Bulk density of A-clay was higher than both Fe-GAC and GAC. It can also be seen that bulk density of the GAC has increased drastically after iron impregnation.

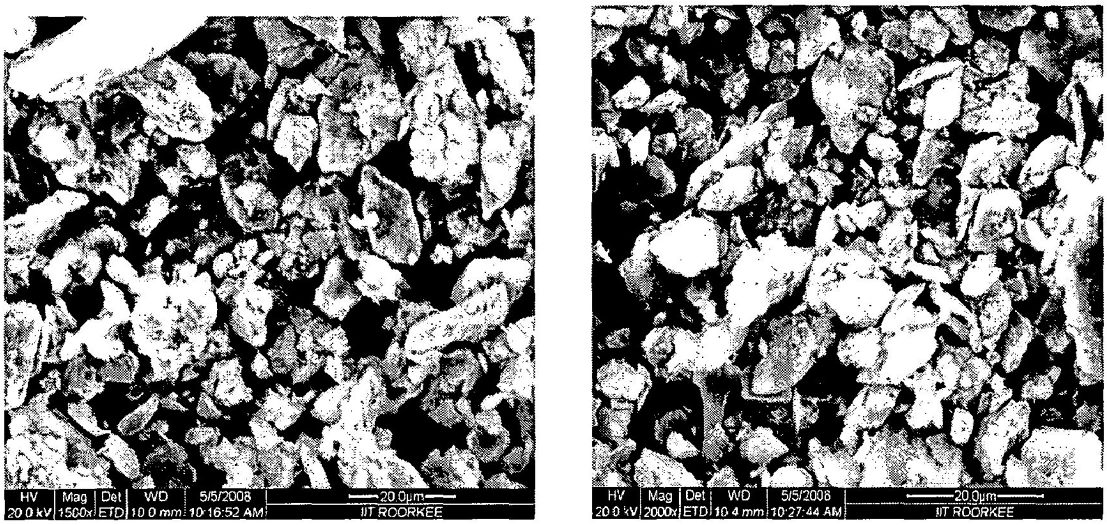
For structural and morphological characteristics, scanning electron microscope (SEM) analysis and Energy Dispersive Spectrum (EDS) were carried out. The SEMs of the blank GAC, Fe-GAC and A-Clay and HA, Cd (II) and HA-Cd loaded GAC, Fe-GAC and A-Clay are shown in Fig. 4.1 through 4.3. These figures revealed the surface texture and porosity of the blank and loaded adsorbents. Comparing the SEM of GAC and Fe-GAC blank (Fig. 4.2 and 4.3) it can be seen that an amorphous layer was formed on GAC due to the impregnation of Fe^{3+}. Due to this reason the specific surface area of GAC-Fe was less than GAC (Table 4.1).

The EDS X-ray detector measures the number of emitted X-rays versus their energy. The energy of the X-ray is characteristic of the element from which the X-ray was emitted. A spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume. Fig (4.4 - 4.9) shows the energy dispersive spectrum for the GAC, Fe-GAC and A-Clay before and after adsorption of Cd. Fig 4.10 shows the FTIR of GAC, Fe-GAC and A-Clay.Spectrum of GAC (fig 4.10) showed that there was only C to C stretching. In A-Clay spectra, (fig 4.10) there was O-H and N-H group stretching at 3433.46 cm^{-1}, 3622.87 cm^{-1} and 3698.44 cm^{-1}. There appeared to be a C=N group around the wavelength of 1630.88. Band at 796.94 cm^{-1} and 784.08 cm^{-1} is due to symmetric and asymmetric stretching of Fe-O stretching.

Fig 4.8 shows the FTIR of humic acid and humic acid-cadmium. FTIR provided the structural detail of HA and HA-Cd. For HA, a peak at 3400 cm^{-1} indicates hydrogen-bonded O-H stretching vibrations from phenolic and aliphatic OH groups. At 2920 cm^{-1} there was asymmetric stretching vibrations of aliphatic C-H bands in -CH3 and –CH2 units and Symmetric C–H stretch of aliphatic bonds in –CH3 and –CH2 units was appeared at 2851 cm^{-1}. A peak at 1550-1580 cm^{-1} may be due to C=C stretching in aromatic rings, asymmetric stretching stretching of –COO$^-$, hydrogen- bonded C=O, or C=C stretching alkenes conjugated with carbonyl groups or other double bonds. A peak at 1384 cm^{-1} may be due to O-H bending vibrations of alcohol. (Organic matter in water). For HA-Cd, there was a sharp peak at finger print region i.e. at 627.23 and 636.13 cm^{-1} due to symmetric and asymmetric stretching of Cd-O. There were sharp peaks at 1142.21 cm^{-1}, 1142.41 cm^{-1} and 1089.07 cm^{-1} due to formation of complex with Cd, which was not found in HA spectra. A peak at 1384.29 was due to N=O. There was a sharp peak at 1629.22 and broadening at 3467.36 cm^{-1} which indicated for Cd^{2+}.

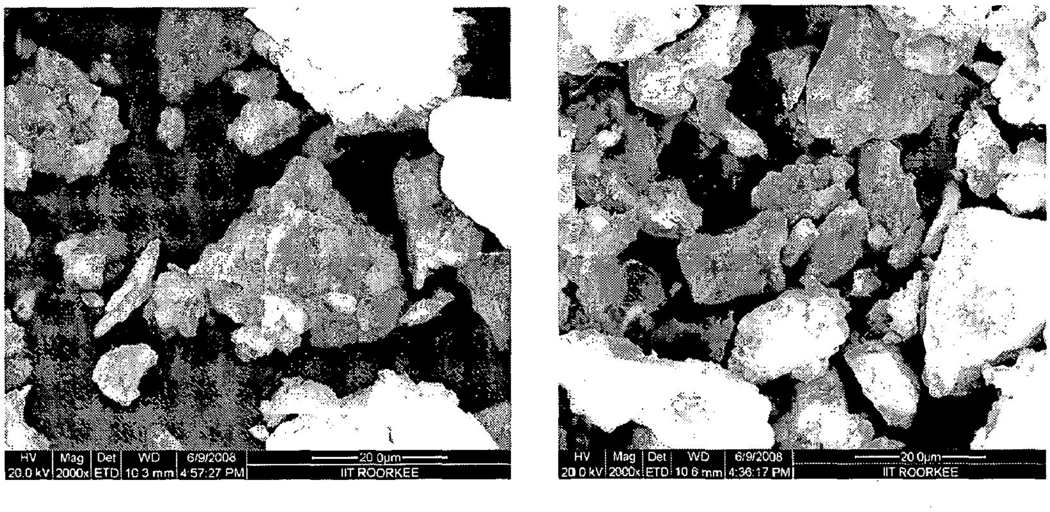
Table 4.1: Physico-chemical characteristics of adsorbents

Characteristics	**GAC**	**Fe-GAC**	**A-Clay**
Proximate analysis			
Moisture (%)	4.41	3.79	4.158
Volatile matter (%)	3.32	3.9	-
Ash (%)	50.4	51.9	-
Fixed Carbon (%)	41.91	40.37	-
Bulk density (kg/m^3)	599.32	850.2	1131.8
Chemical composition **EDS analysis**			
C	75.18	9.19	12.95
O	9.88	37.27	44.23
Si	10.0	16	30.37
Al	2.83	6.33	7.83
Fe	1.11	22.68	2.66
Ca	-	3.04	-
Mg	-	4.5	-
Surface area (BET) m^2/g	358.3	348	90.3
Monolayer Volume cm^3/g	82.308	79.948	20.735



A-Clay – Blank

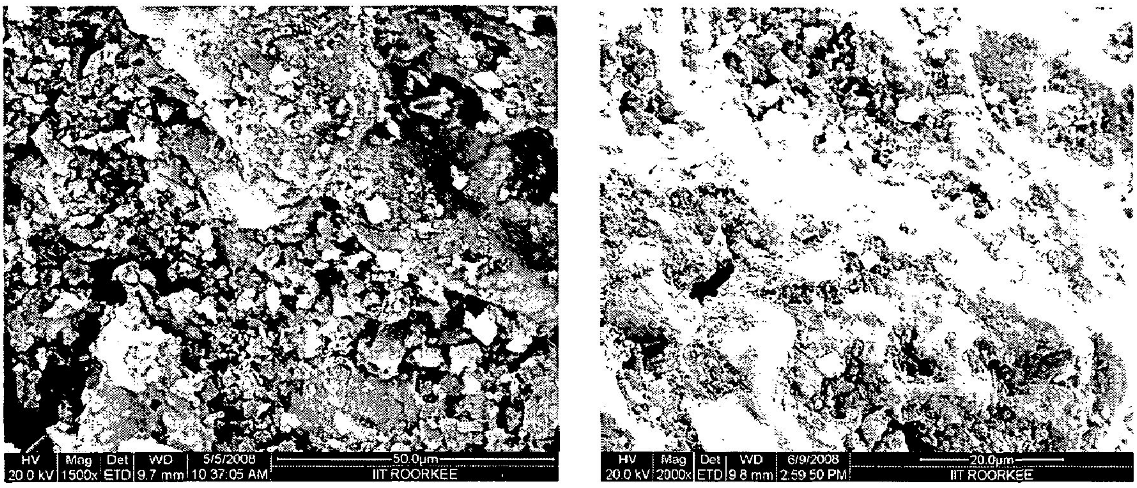
A-Clay -- Cd



A-Clay -- Cd-HA

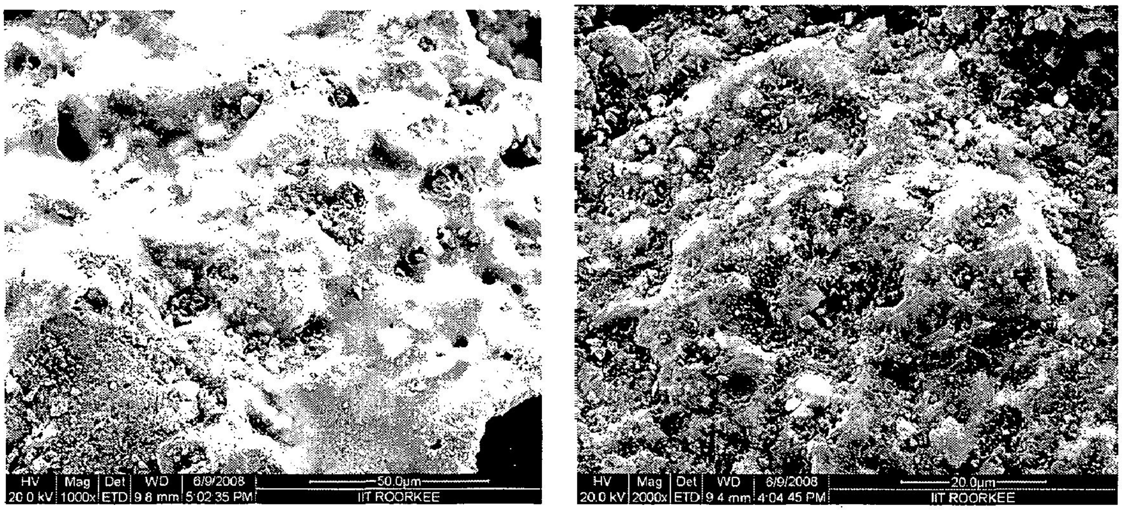
A-Clay -- HA

Fig 4.1 SEM of blank and loaded A-Clay with HA and Cd



GAC -- blank

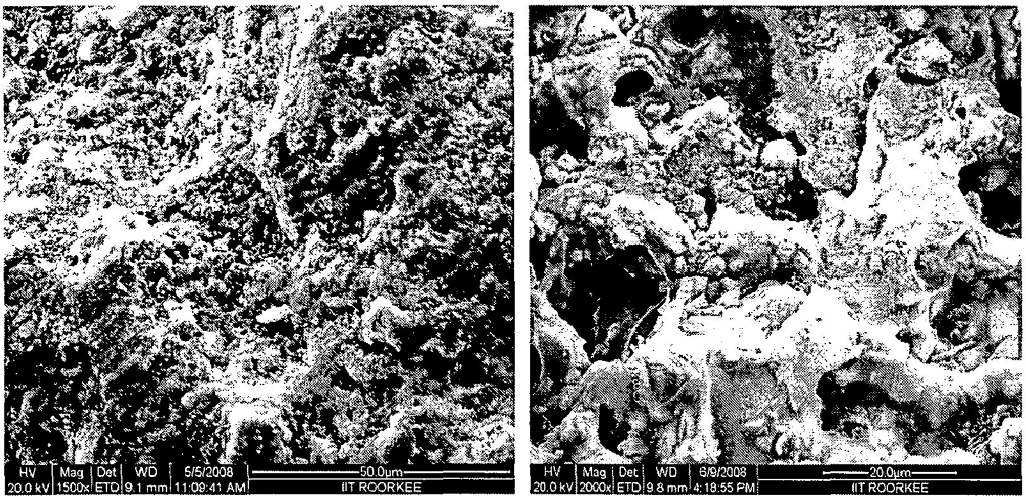
GAC -- Cd



GAC -- HA-Cd

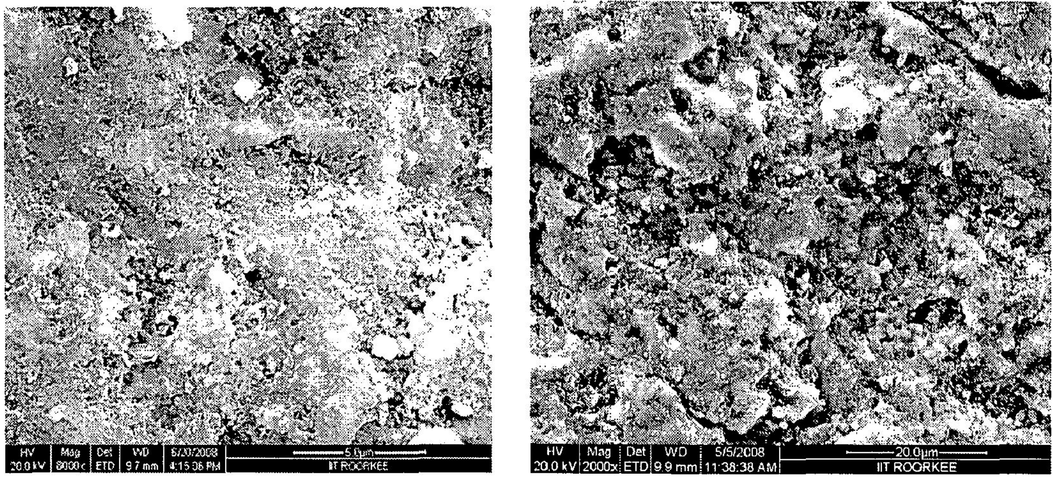
GAC -- HA

Fig 4.2 SEM of blank and loaded GAC with HA and Cd



Fe-GAC – Blank

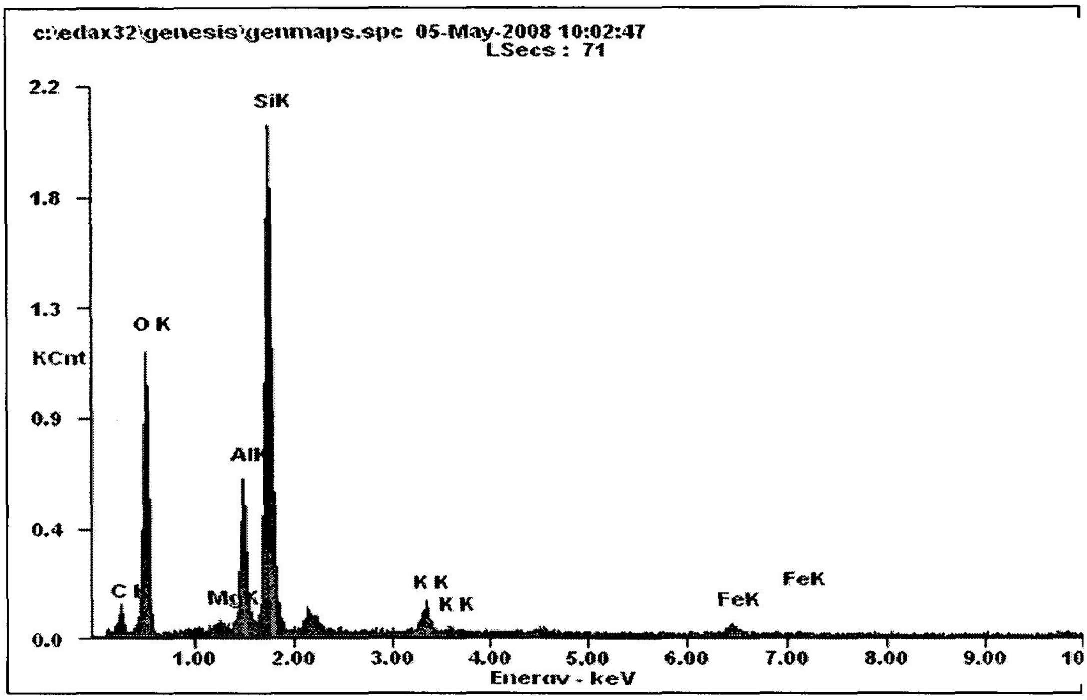
Fe-GAC – HA



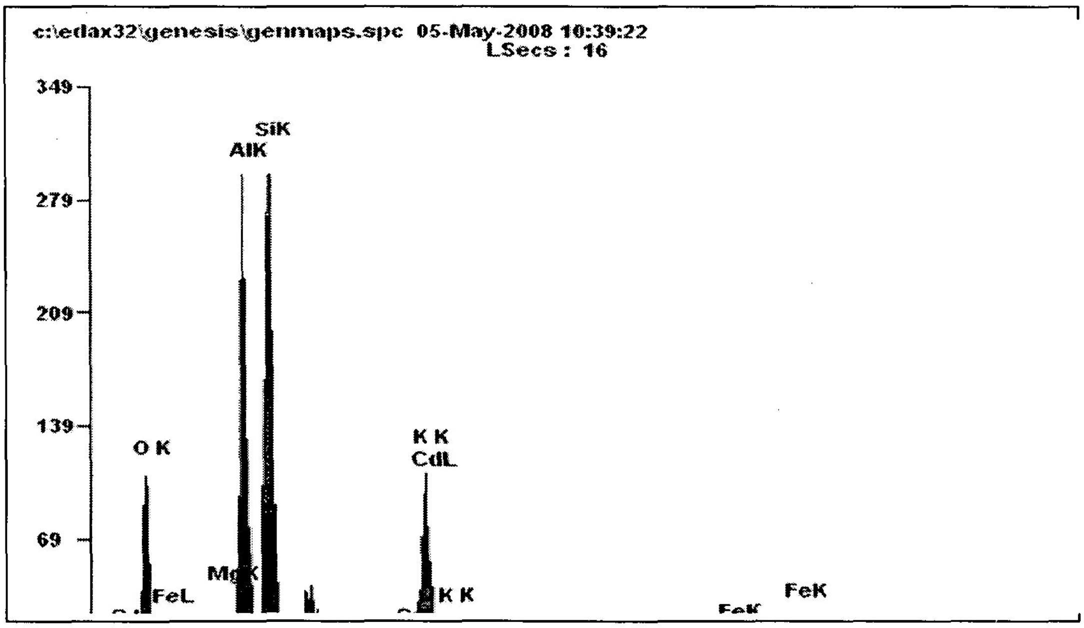
Fe-GAC – HA- Cd

Fe-GAC–Cd

Fig4.3 SEM of blank and loaded Fe-GAC with HA and Cd

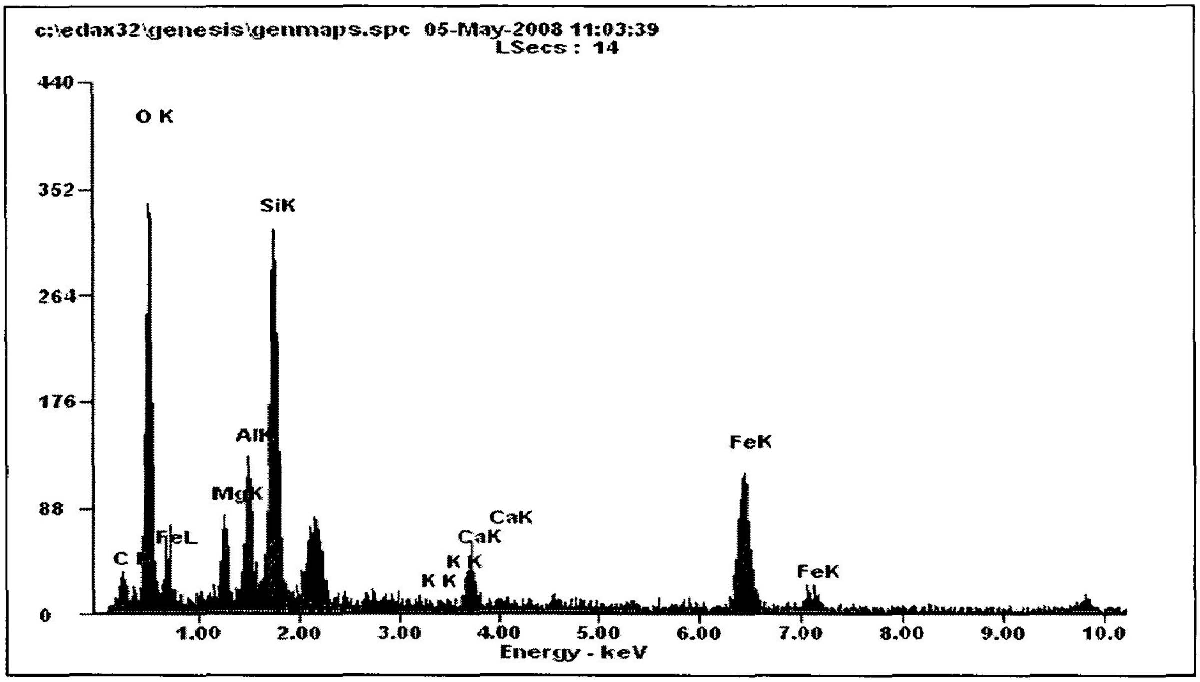


A-Clay Blank

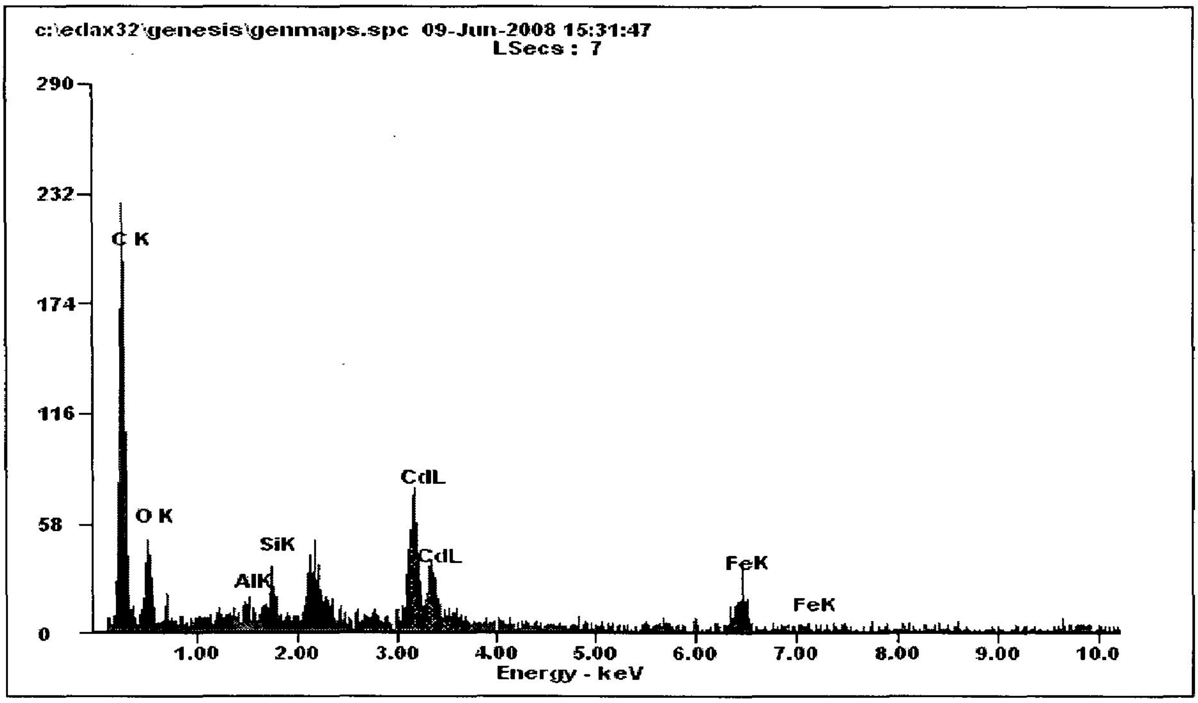


A-Clay - Cd

Fig 4.4 EDS blank and loaded A-Clay with Cd

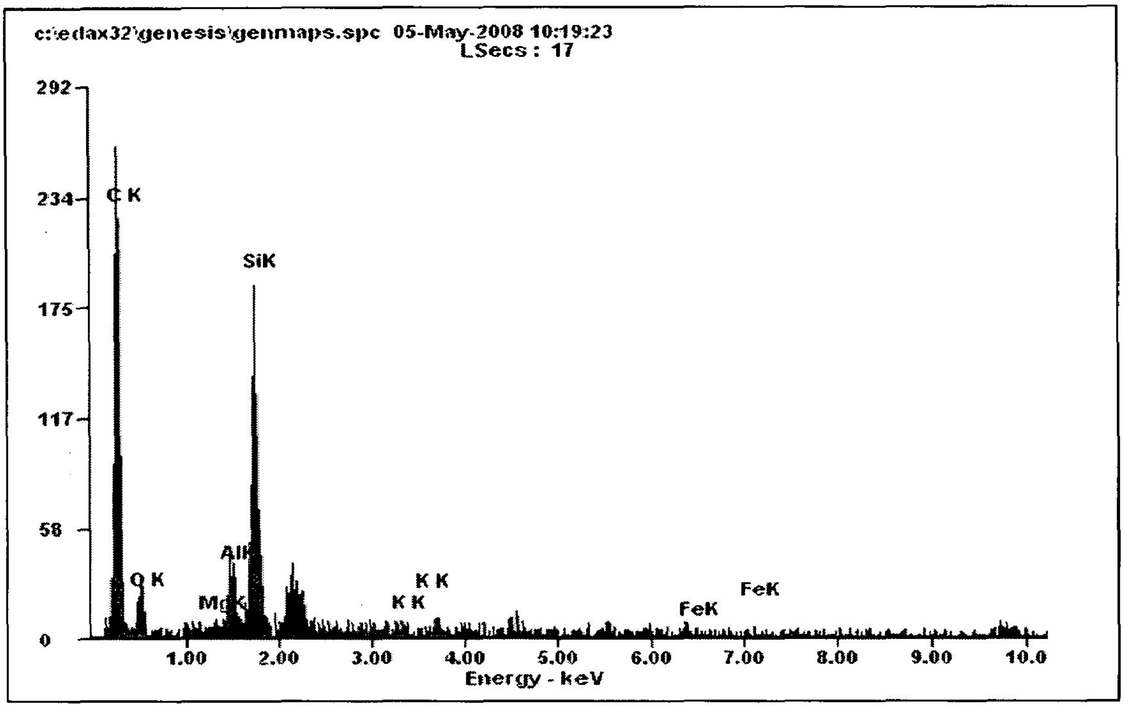


Fe-GAC Blank

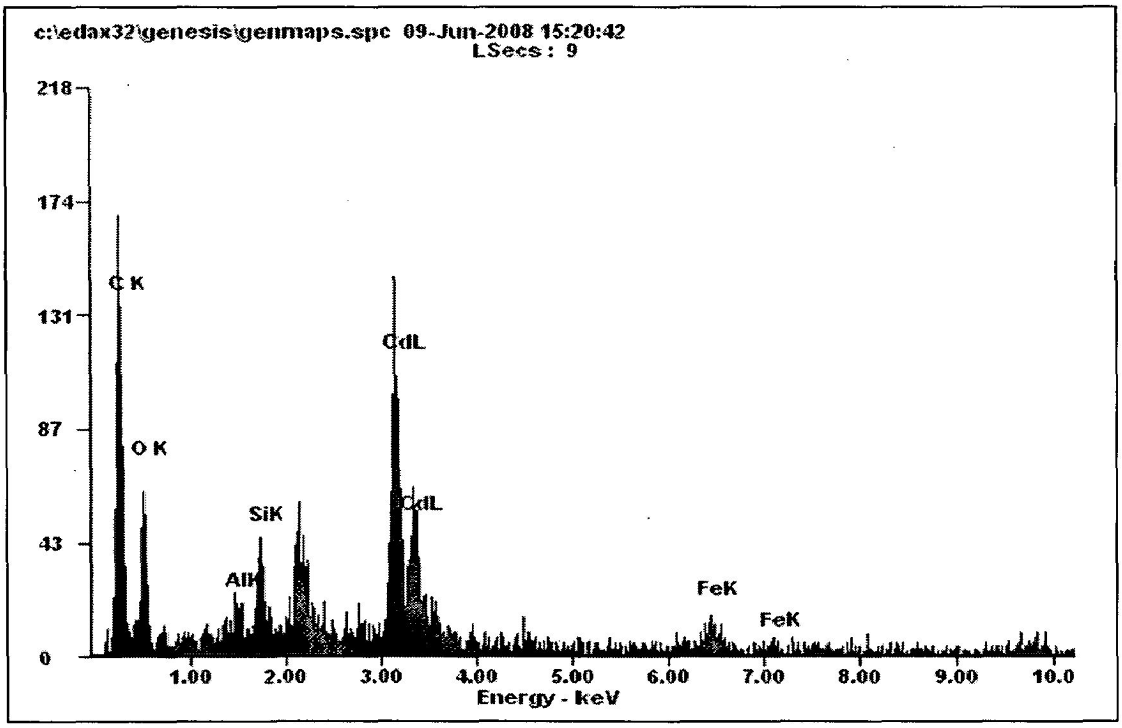


Fe-GAC -Cd

Fig 4.5 EDS blank and loaded Fe-GAC with Cd

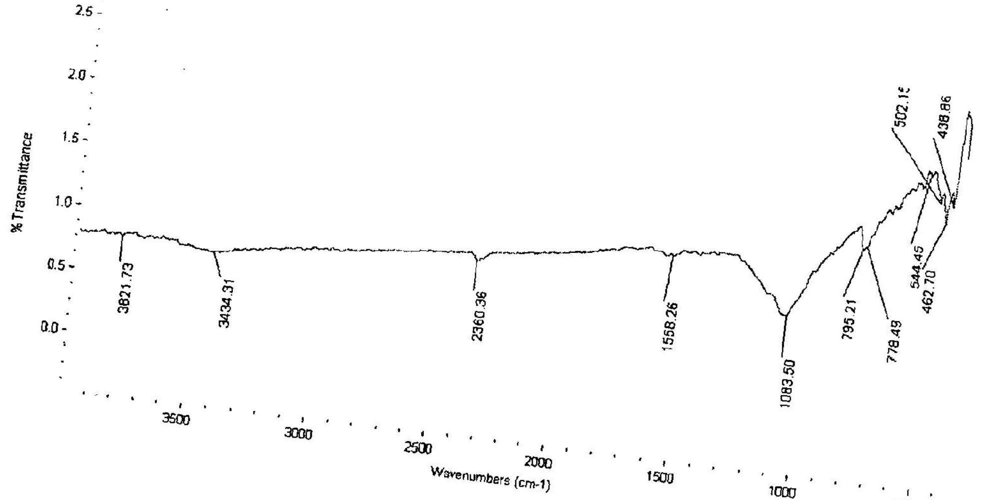


GAC Blank

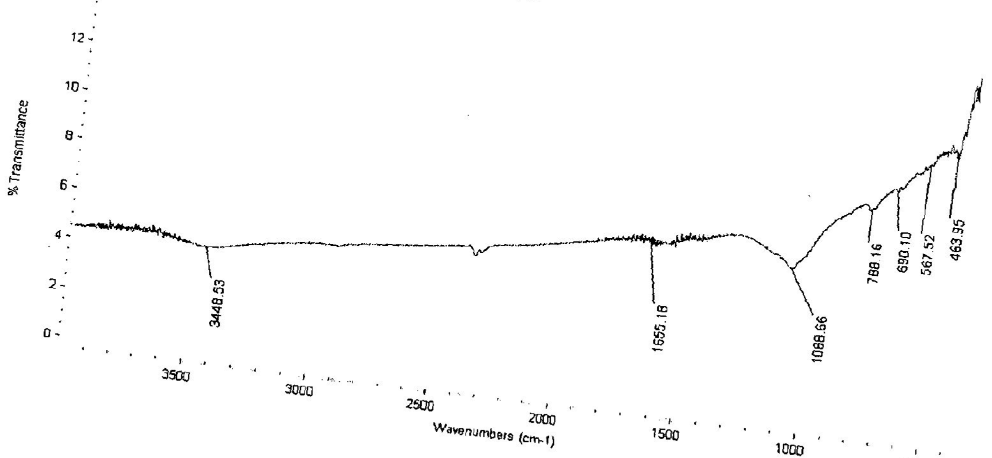


GAC -Cd

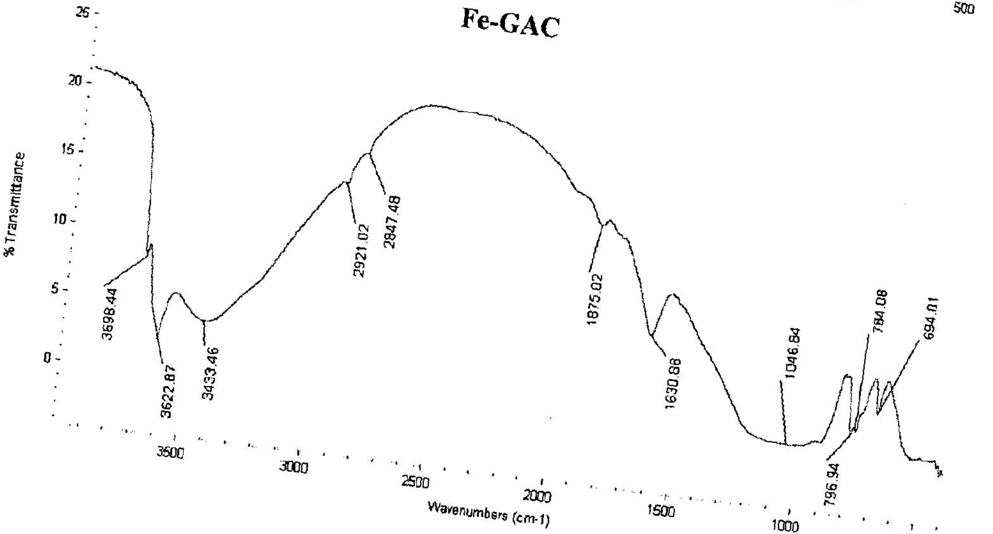
Fig 4.6 EDS OF blank and loaded GAC with Cd



GAC

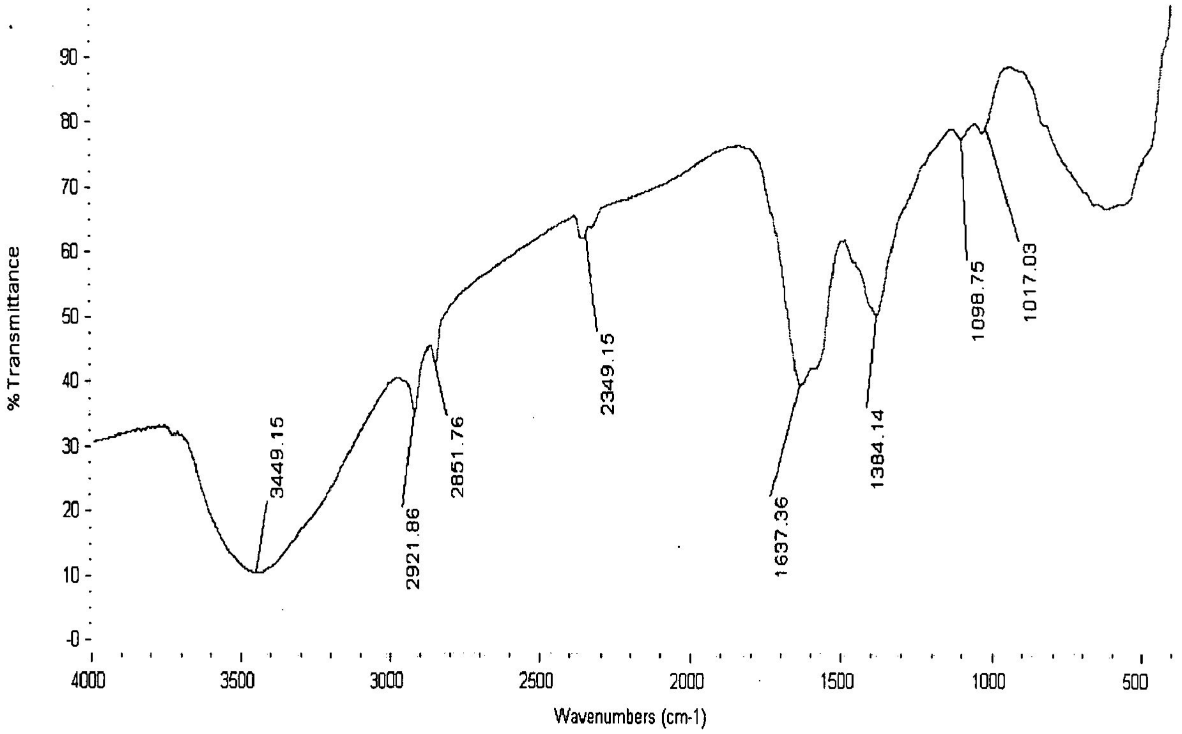


Fe-GAC

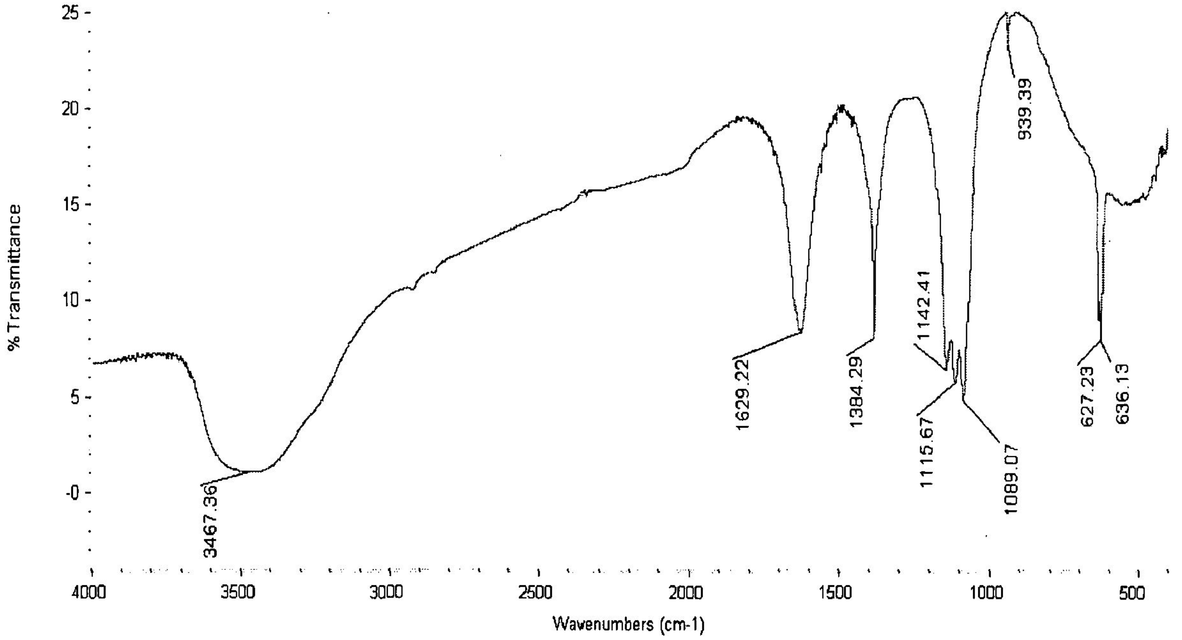


A-Clay

Fig 4.7 FITR spectra of GAC, Fe-GAC and A-Clay



Humic acid



Humic acid-Cadmium

Fig 4.8 FTIR spectra of Humic acid and Humic acid-Cadmium

4.3 Batch Adsorption Studies

In order to study the effect of different parameters the batch operations were found most suitable. Batch adsorption experiments were carried out in 100 ml stoppered conical flask for removal of Cd(II), HA and Cd-HA from the solution of known concentrations. Effect of various parameters viz. adsorbent dose (m), initial pH (pH_0), contact time (t) and initial concentration (C_0) on the adsorption of HA and Cd(II) onto GAC, Fe-GAC and A-Clay adsorbents have been discussed in this section.

4.3.1 Effect of pH:

The pH is one of the key parameters in the adsorption process. The pH has significant effect on adsorption, as it affects the surface charge of adsorbent and also chemical speciation of the adsorbate. Effect of pH on the adsorption of Cd (II) is shown in the fig 4.9. Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_{2(S)}$ are the forms of cadmium, present in deionised water [Garg et al., 2008]. Adsorption of Cd (II) increased with increase in the pH of the solution. The removal efficiencies increased sharply from pH 2 to pH 6 and thereafter remained constant. The % removals at pH 2 were 30.4%, 24.3% and 15.2% whereas it was 84%, 78.7% and 75% at pH 6 for GAC, Fe-GAC and A-Clay respectively. Based on the results, all the experiments were conducted at pH 6. There was no significant change in rate of adsorption due to precipitation of Cd ions at higher pH (Gaballah and Kilbertus, 1998, Al-Anber et al., 2008). At low pH, the H^+ ions compete with cadmium ions on the active sites, as a result removal was very low. As the pH increases, the H^+ ion concentration decreases and hence the positively charged Cd ions are adsorbed at negatively charged sites on adsorbent (Gupta et al., 2006, Al-Anber et al., 2008). Reed and Matsumoto showed the Cd (II) ion predominates at pH below 7 and it begins to precipitate out as $Cd(OH)_2$ at pH values just above 9. At pH 8, the species distribution is approximately 90% Cd(II) and 10% $Cd(OH)^+$.

Effect of pH on the adsorption of HA is shown in the fig 4.10. Humic acid contains both hydrophobic and hydrophilic moieties as well as many chemical functions of carboxylic, phenolic, carbonyl, and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules (Davies and Ghabbour, 1998).

The existence of carboxylic and phenolic groups predominantly in humic acid results in carrying negative charges in the aqueous solution. As shown in fig. 4.10, the capacity for HA adsorption was found to increase in general with decreasing pH. At low pH, the HA exist as partly or fully undissociated/protonated forms while adsorbents present positive charge, which favours the HA adsorption due to the electrostatic abstraction. The surface of adsorbents becomes negatively charged as the pH increased. Thus, HA adsorption was less. It was observed from the fig 4.12 that between pH 2 and 5 there was no significant change in the removal. As the pH increased there was drastic decrease in the removal from 68%, 63% and 60% at pH 5 to 30%, 29% and 24.6% at 8 for GAC, Fe-GAC and A-Clay respectively. Based on this result pH 5 was chosen as the optimum pH.

Figs 4.11 and 4.12 show the effect of pH on co-adsorption of HA-Cd on GAC, Fe-GAC and A-Clay. It was be seen that even in the co-adsorption system the adsorption capacity for Cd(II) increased with increase in the pH. Similarly HA also showed the same trend as in single adsorption. It was found at pH 5, the capacity for HA adsorption starts to decrease drastically while for Cd(II) adsorption capacity was almost constant. So pH 5 was the considered to be optimum pH for co-adsorption.

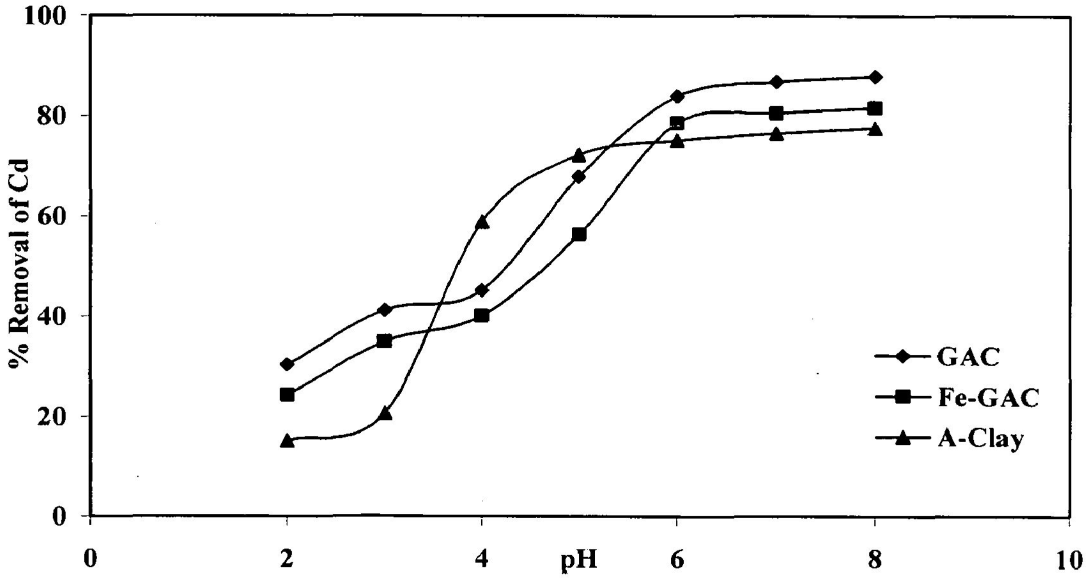


Fig 4.9 Effect of pH on removal of Cadmium using GAC, Fe-GAC and A-Clay

(Co= 50mg/l, Adsorbent dosage=5g/l, T=300 K)

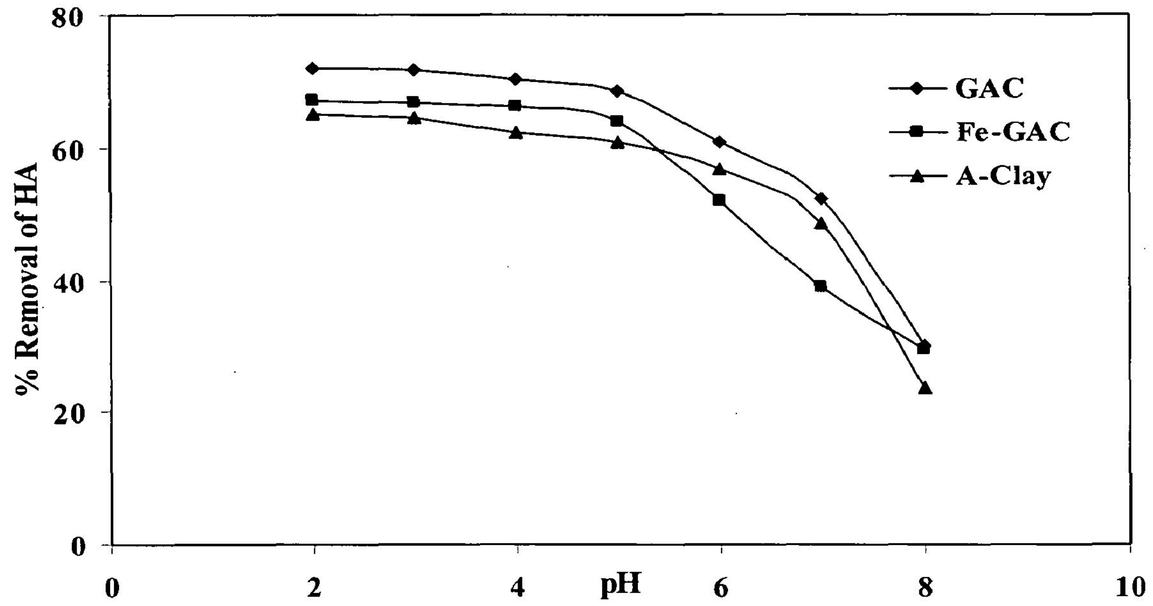


Fig 4.10 Effect of pH on removal of humic acid using GAC, Fe-GAC and A-Clay (Co= 50mg/l, Adsorbent dosage=5g/l, T=303 K)

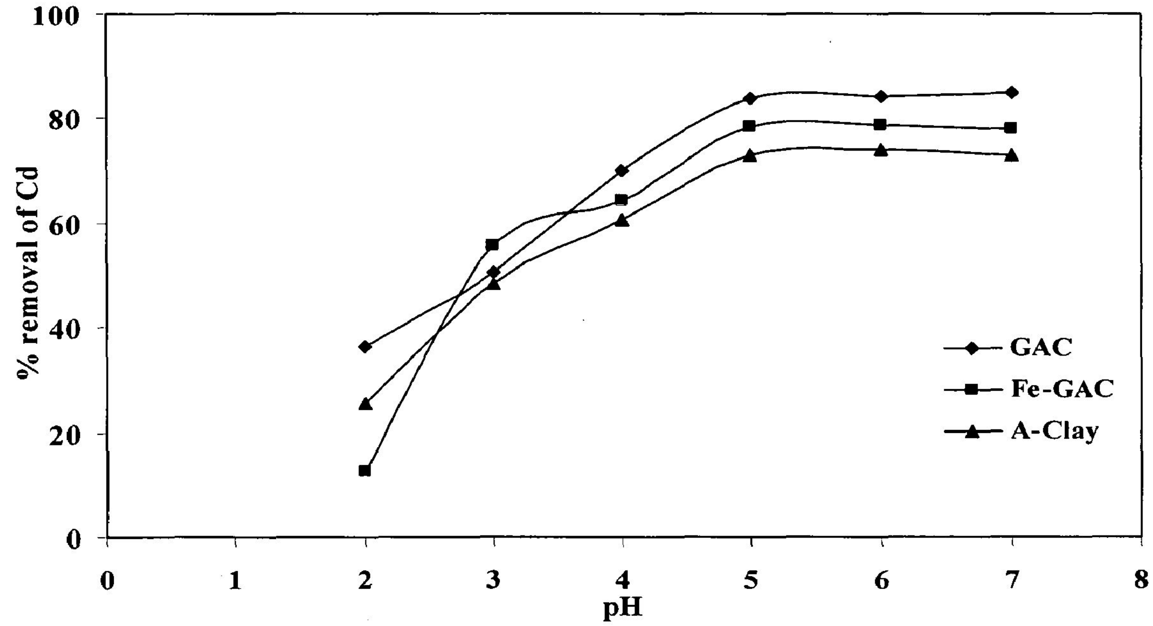


Fig 4.11 Effect of pH on removal of Cadmium in coadsorption (HA-Cd) using GAC, Fe-GAC and A-Clay (Co= 50mg/l of HA &Cd, Adsorbent dosage=10g/l, T=303 K)

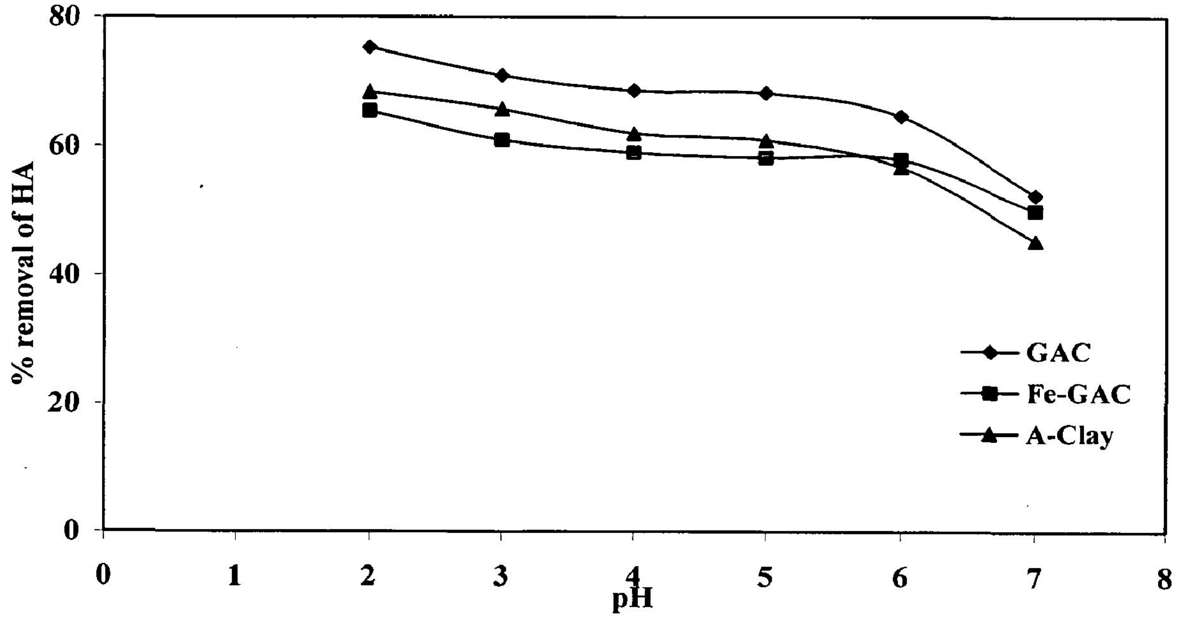


Fig 4.12 Effect of pH on removal of humic acid in coadsorption (HA-Cd) using GAC, Fe-GAC and A-Clay (Co= 50mg/l of HA &Cd, Adsorbent dosage=10g/l, T=303)

4.3.2 Effect of Adsorbent Dosage (m)

The effect of adsorbent dosage (m) on removal of HA (Co=50mg/l), Cd(II) (Co=100mg/l) and HA-Cd (Co=50mg/l both HA and Cd(II)) by GAC, Fe-GAC and A-Clay have been shown in Figs. 4.13 – 4.16. From the figures, it was generally found that the removal for a fixed concentration increased with an increase in amount of adsorbent but the capacity of the adsorbent for the sorption of adsorbate, i.e. the amount of adsorbate sorbed per unit weight of adsorbent decreased with an increase in adsorbent dose. The removal percent increased with increase in adsorbent dose due to increase in the total available surface area of the adsorbent particle.

From fig 4.13, it was observed that Cd(II) removal increased significantly with increase in m upto 10 g/l for Fe-GAC and A-Clay, while for GAC upto m=5g/l Beyond m =10 g/l , the removal remained almost unaffected by the adsorbent dosage. At m < 10g/l, the adsorbent surface becomes saturated with Cd. For m > 10 g/l the Cd(II) removal became very low. Thus m = 10 g/l is chosen as the optimum dose for the removal of Cd(II). For HA, it was observed from fig 4.14, that there was a drastic increase in the removal upto m=5g/l, i.e from 18.5%, 14.5 and 23.1% at m=1g/l to

68%, 63% and 58% at *m*=5g/l for GAC, Fe-GAC and A-Clay respectively. For *m*>5g/l the removal was almost constant. Hence the optimum dose was 5g/l for HA. Fig 4.15 and 4.16 shows the effect adsorbent dosage on co-adsorption. In co-adsorption HA-Cd, Cd(II) removal gradually increased as *m* increased, while for HA the increase was sudden upto *m*=5g/l for GAC and A-Clay than Fe-GAC. The optimum adsorbent dosage was found to be 10g/l for co-adsorption.

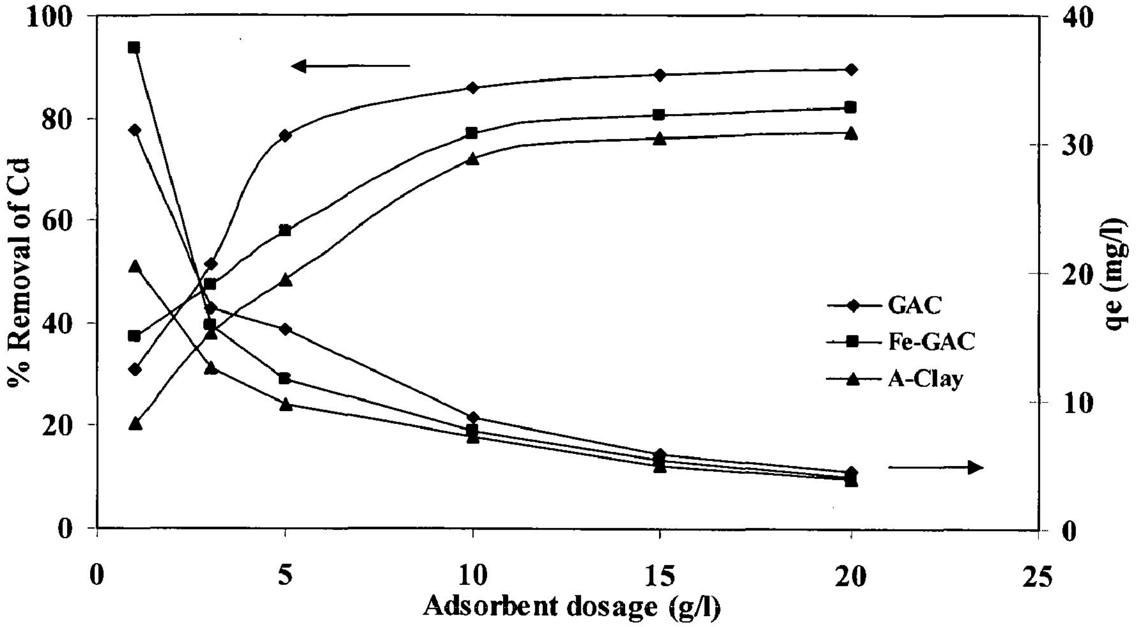


Fig 4.13 Effect of adsorbent dosage on removal of Cadmium using GAC, Fe-GAC and A-Clay (Co= 100mg/l, pH=6, T= 300K)

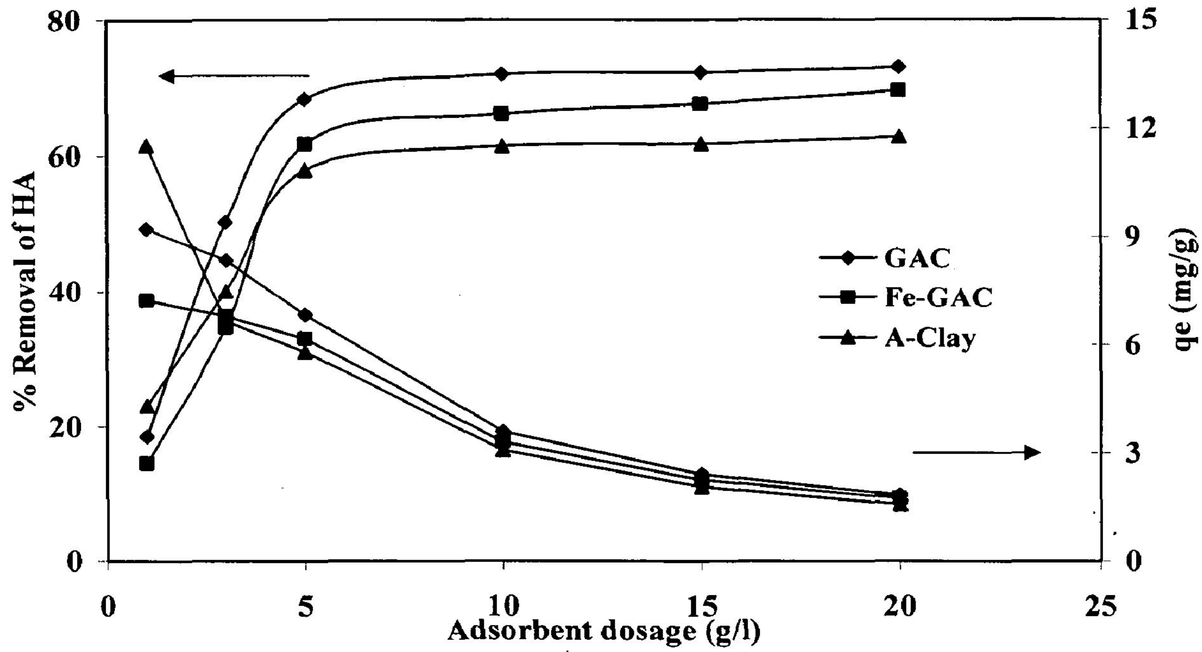


Fig 4.14 Effect of adsorbent dosage on removal of humic acid using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T= 300K)

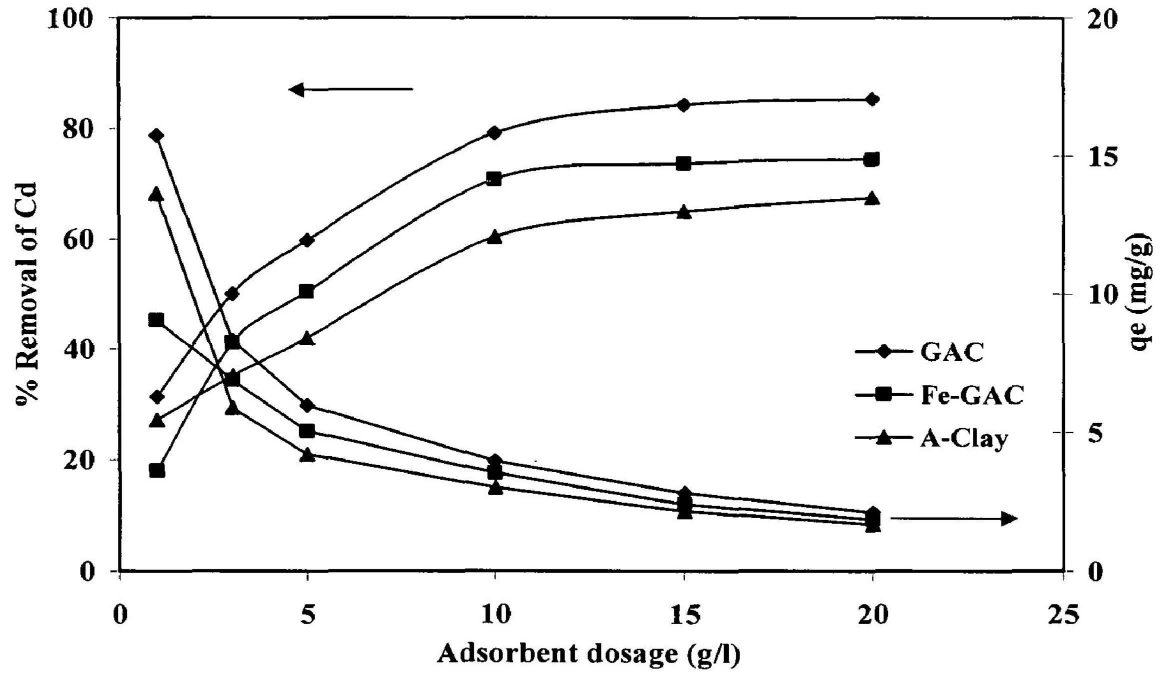


Fig 4.15 Effect of adsorbent dosage on removal of Cadmium in Co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T= 300K

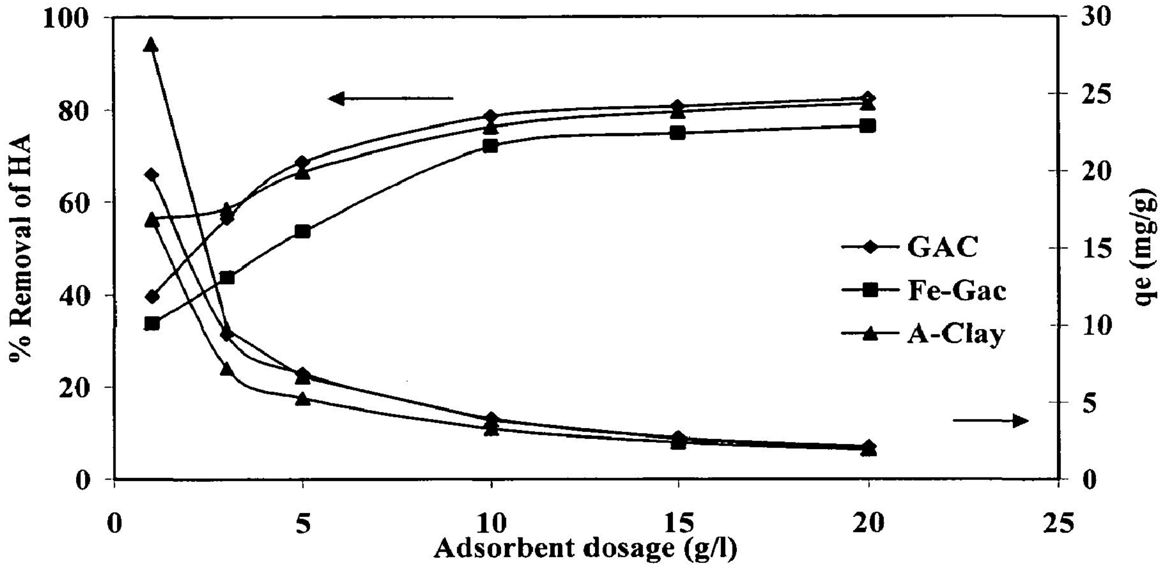


Fig 4.16 Effect of adsorbent dosage on removal of Humic acid in Co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T= 300K)

4.3.3 Effect of Initial Concentration (C_0)

The effect of C_0 on the adsorption of HA, Cd (II) and HA-Cd is shown in Figs. 4.17 - 4.26. For single adsorption, the removal of HA and Cd (II) decreased with an increase in C_0, although the total amount of adsorbate adsorbed per unit mass of adsorbent, i.e. q_e increased with increase in C_0. The increase in adsorption uptake with an increase in C_0 is attributed to an increase in the driving force for adsorption and a decrease in resistance to the uptake of adsorbate by the adsorbents from the solution.

From the fig 4.17 and 4.18, it was found that the adsorption capacity q_e increased rapidly from 2.5mg/g, 2.45mg/g and 2.4mg/g at Co=25mg/l to 9.65mg/g, 8.55mg/g and 7.45mg/g at Co=125 mg/l for GAC, Fe-GAC and A-Clay, respectively. Later increase in *Co* had no significant change in q_e. As the q_e increased the removal percent decreased. It was also observed that all the three adsorbents followed the same trend but only the efficiency differed in the order GAC>Fe-GAC>A-Clay. Fig 4.19 and 4.20 shows the effect of initial concentration of HA. Similarly the q_e started to increase significantly in the initial concentration and later was almost constant.

Co-adsorption of heavy metal ion and HA adsorption was different from that in single-component adsorption. The adsorption of Cd (II) was reduced in the presence of HA while adsorption of HA significantly increased in presence of metal ion. Fig (4.21-4.22) shows the effect of Cd(II) initial concentration on humic acid adsorption. As per Wang et al., (2008) during the co-adsorption process, competitive adsorption of humic acid and heavy metal ions will occur on surface hydroxyl sites. In the presence of humic acid, complexation of metal ions with humic acid can occur via the functional groups, carboxylic and phenol, which are not binding to the solid surface:

$\text{HA–COOH} + \text{Me}^{2+} \rightarrow \text{HA–COOMe} + \text{H}^{+}$

$\text{HA–OH} + \text{Me}^{2+} \rightarrow \text{HA–OPb} + \text{H}^{+}$

There are two possible structures for the adsorption of metal and organic complex compounds on mineral surfaces. One is the S–Me–HA and the other is the S–HA–Me, where S represents the adsorption site on the solid surface and Me is the metal ion Many researchers have suggested S–Me–HA is the suitable model (Liu and Gonzalez, 1999, Katsumata et al., 2008). It can be seen from the fig (4.23 - 4.24) that HA adsorption increased as concentration of Cd (II) increased. Single component adsorption of HA, the removal was around 72%, 66% and 61%, while in presence of Cd(II) removal increases to around 80%, 75% and 76% for GAC, Fe-GAC and A-Clay respectively. The effect of initial concentration of HA on Cd (II) adsorption has been shown in the fig (4.23 - 4.24). It can be seen that initially the removal of Cd(II) increased slightly, as the concentration of HA increases the removal of Cd (II) decreases from 82%, 77.4% and 68.8% to 66.6%, 50.8% and 57% for GAC , Fe-GAC and A-Clay respectively.

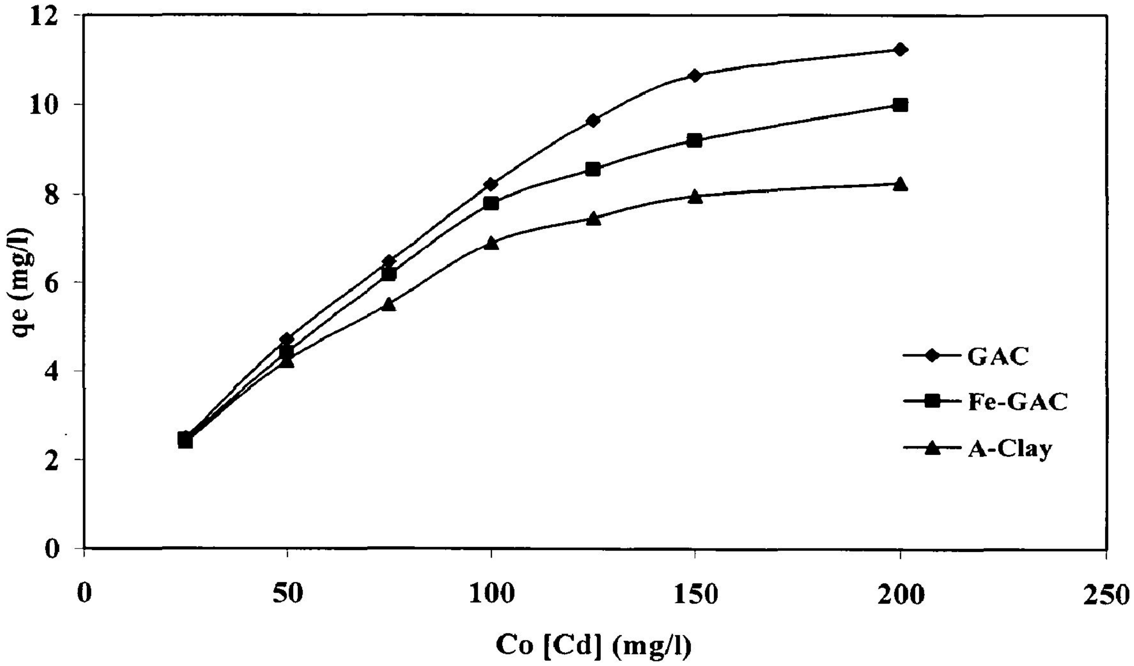


Fig 4.17 Effect of initial concentration of Cadmium on its removal using GAC, Fe-GAC and A-Clay (pH=6, Adsorbent dosage=10g/l, T=300 K)

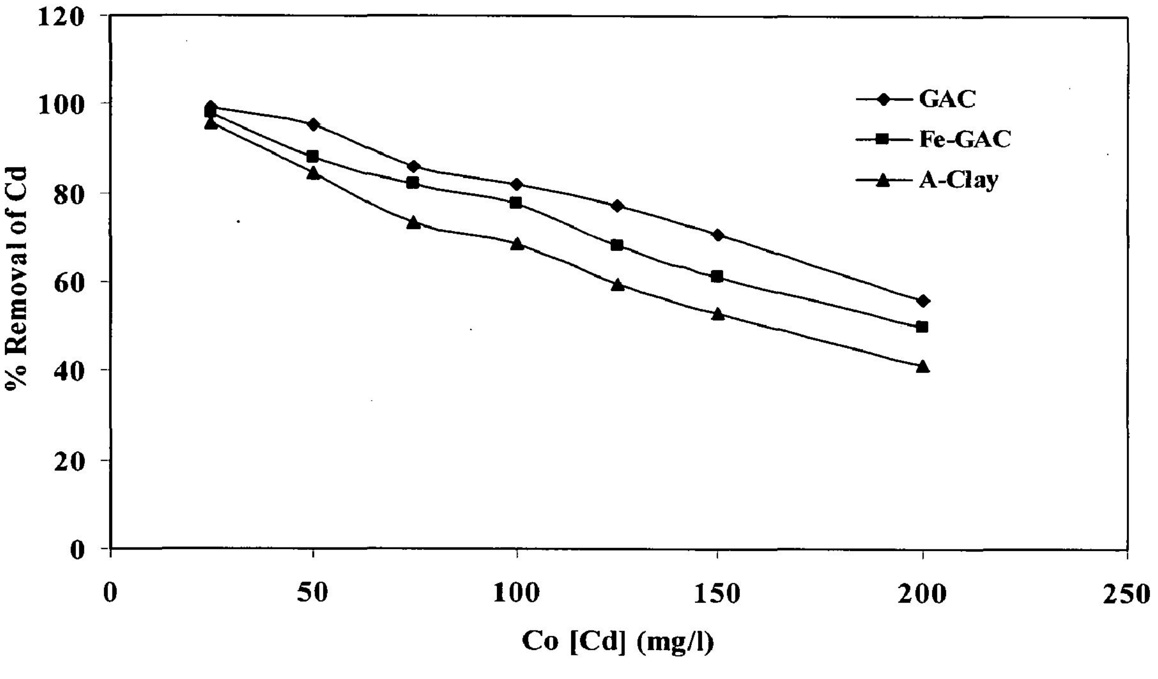


Fig 4.18 Effect of initial concentration on removal of Cadmium using GAC, Fe-GAC and A-Clay (pH=6, Adsorbent dosage=10g/l, T=300 K)

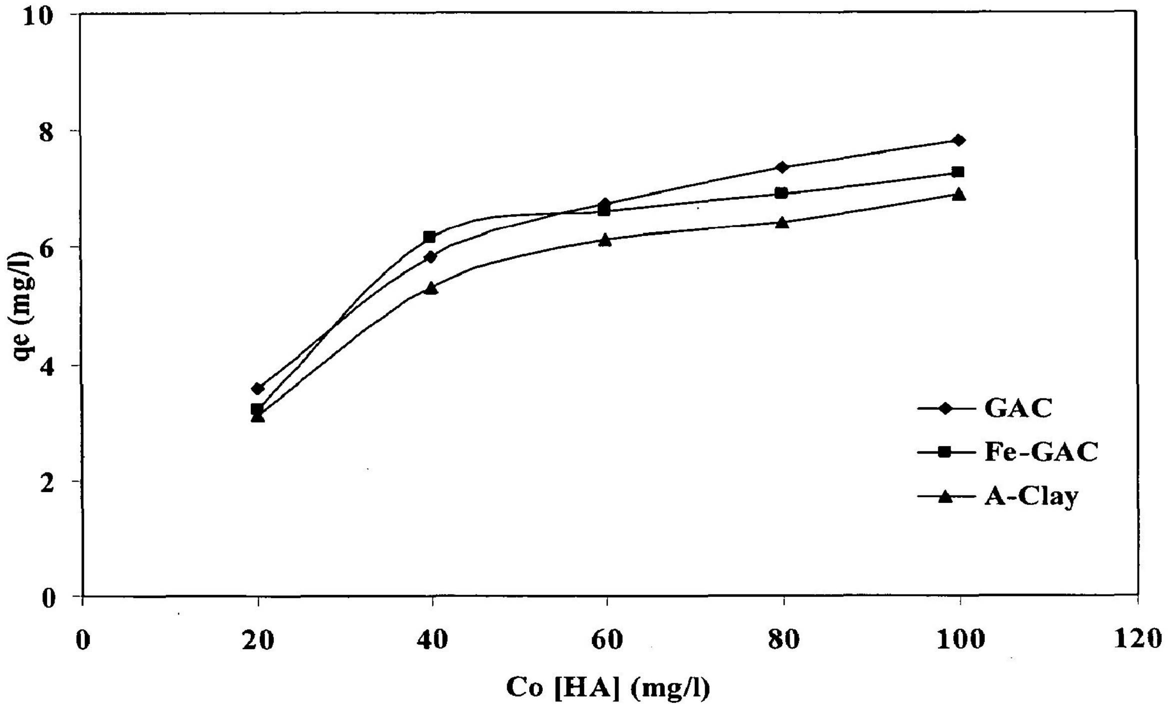


Fig 4.19 Effect of initial concentration on removal of Humic acid using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 5g/l, T=300 K)

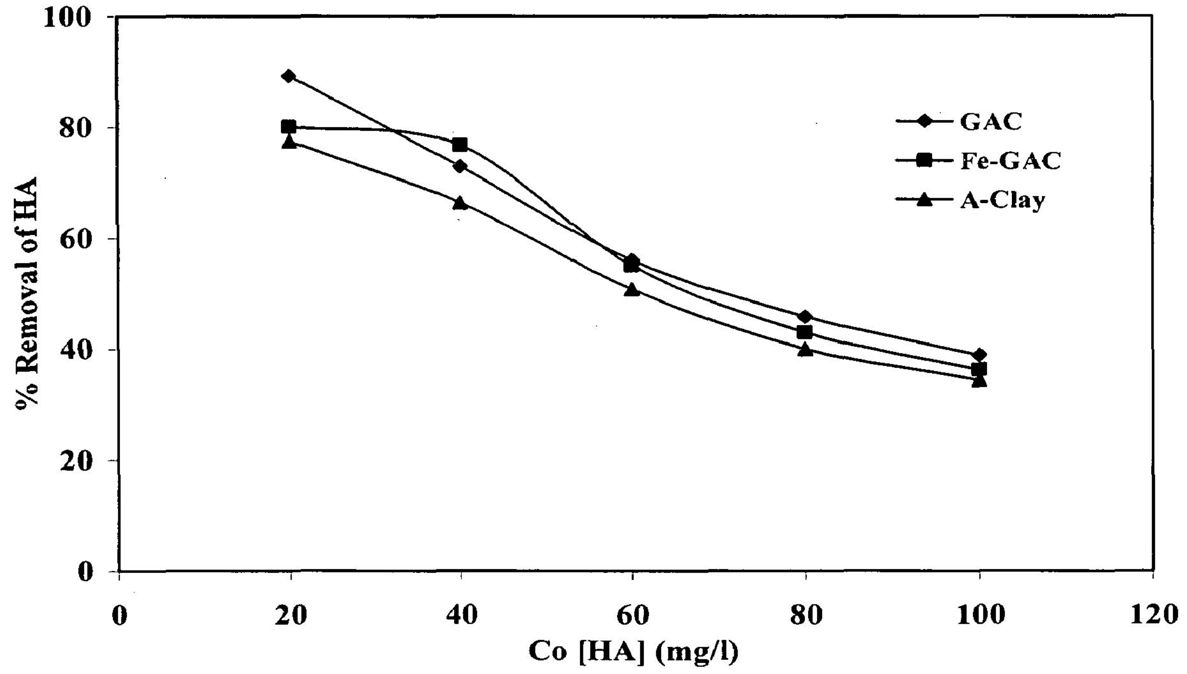


Fig 4.20 Effect of initial concentration on removal of Humic acid using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 5g/l, T=300K)

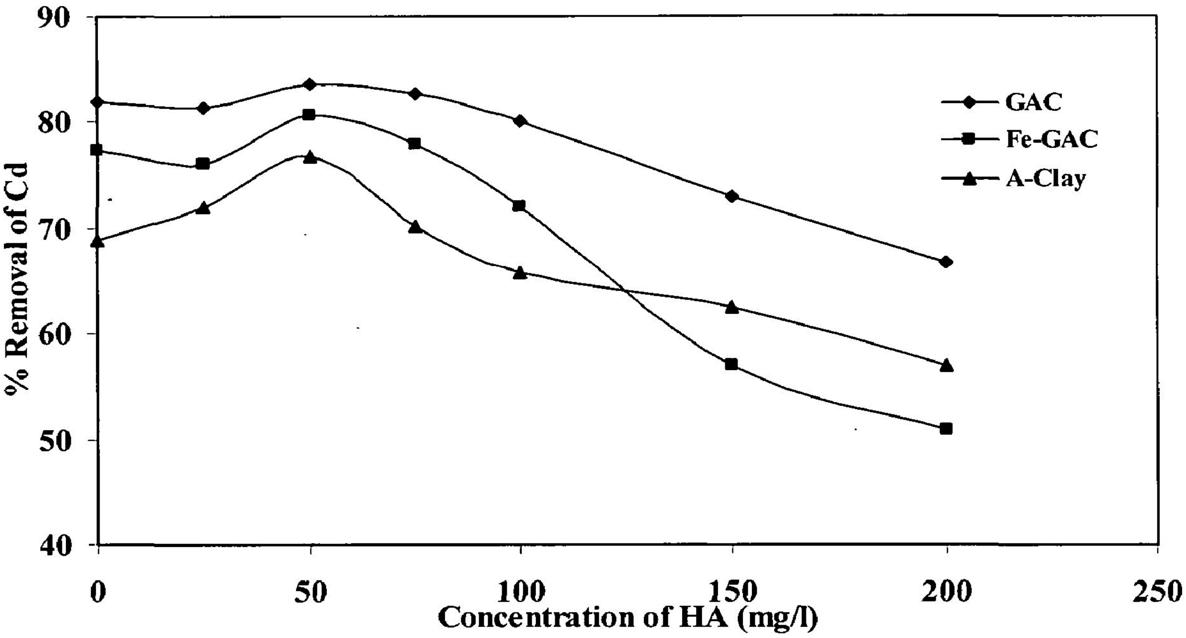


Fig 4.23 Effect of initial concentration of HA on removal of Cd in Co-adsorption using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, Co=50mg/l [Cd], T=300 K)

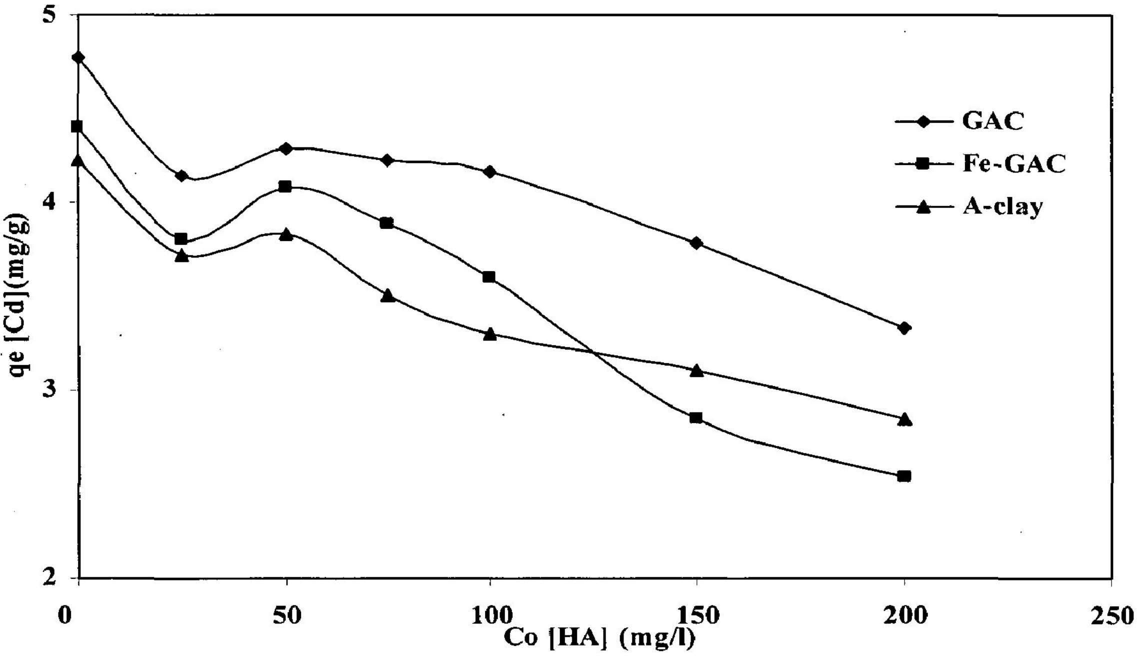


Fig 4.24 Effect of initial concentration of HA on removal of Cd in Co-adsorption using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, Co=50mg/l [Cd], T=300 K)

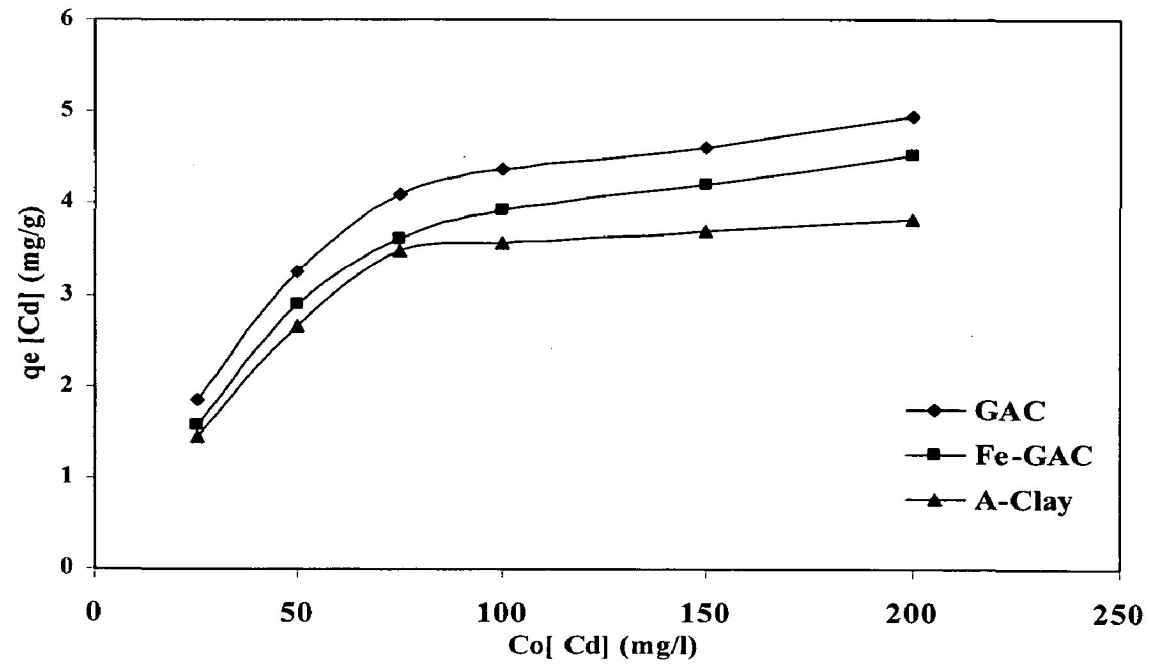


Fig 4.25 Effect of initial concentration of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [HA] = 50mg/l, pH=5, T=303 K, m=10g/l)

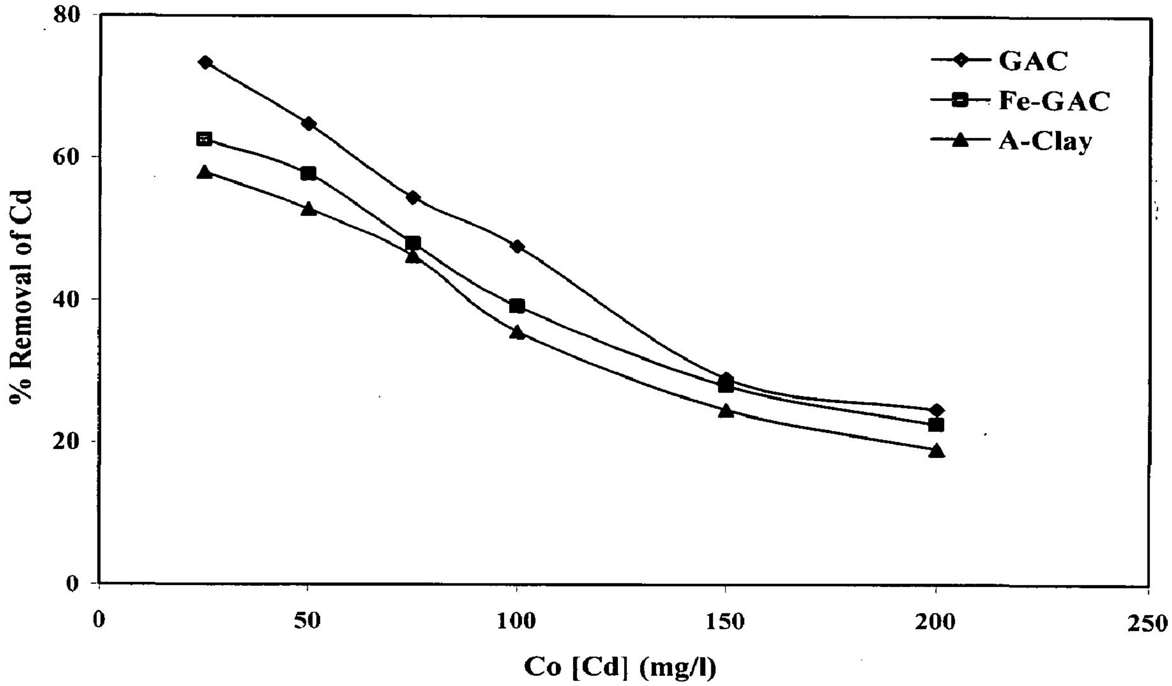


Fig 4.26 Effect of initial concentration of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [HA] = 50mg/l, pH=5, T=303 K, m=10g/l)

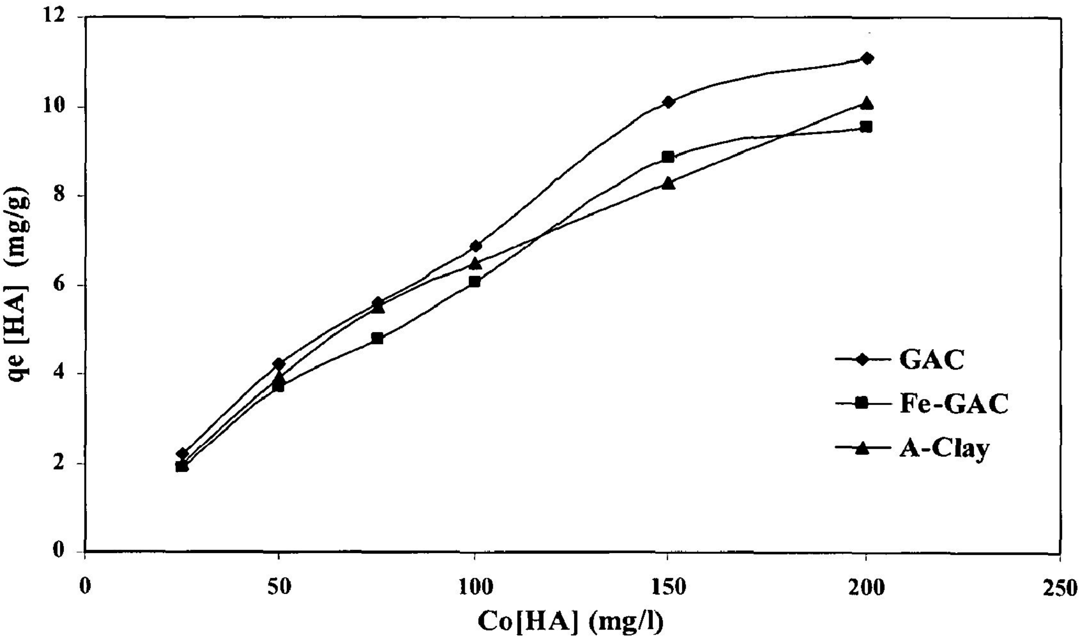


Fig 4.27 Effect of initial concentration of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [Cd] = 50mg/l, pH=5, T=303 K, m=10g/l)

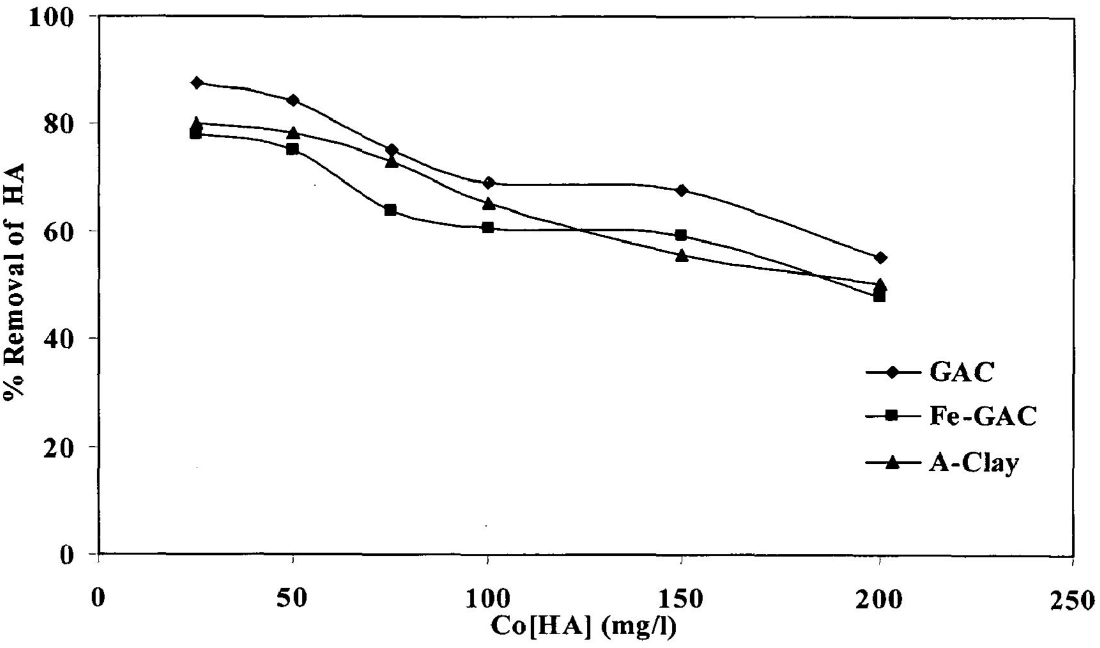


Fig 4 .28 Effect of initial concentration of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [Cd] = 50mg/l, pH=5, T=303 K, m=10g/l).

4.3.4 Effect of Contact Time

The contact time, *t* between adsorbate and adsorbents is an important factor in the adsorption process. A rapid uptake of the adsorbate and the establishment of equilibrium in a short period signifies the efficacy of the adsorbent for its use in the wastewater treatment. Fig 4.29-4.30 shows the effect of contact time for removal of HA by GAC, Fe-GAC and A-Clay. From the Fig 4.29- 4.30 it can be observed that initially the removal was rapid around 60% for first 60 mins and thereafter, the adsorption rate decreased gradually, finally reached to around 68%. It was found that the removal was constant after 3h for HA. Hence 3h was optimum contact time. For Cd(II), fig 4.31 - 4.32 shows the effect of contact time. Even Cd (II) also followed the same trend as HA but the optimum time was 5h. Fig 4.33-4.34 shows the effect of contact time for co-adsorption of HA-Cd. Similarly in co-adsorption optimum time was 3 h.

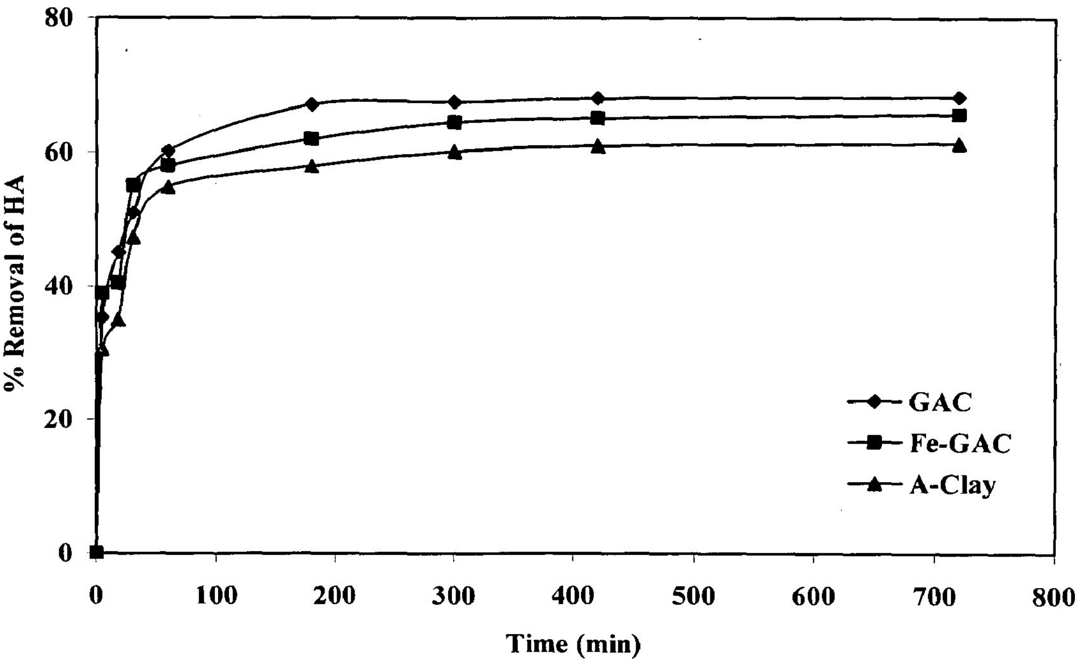


Fig 4.29 Effect of contact time on removal of Humic acid using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 5g/l, T=300 K, Co=50mg/l)

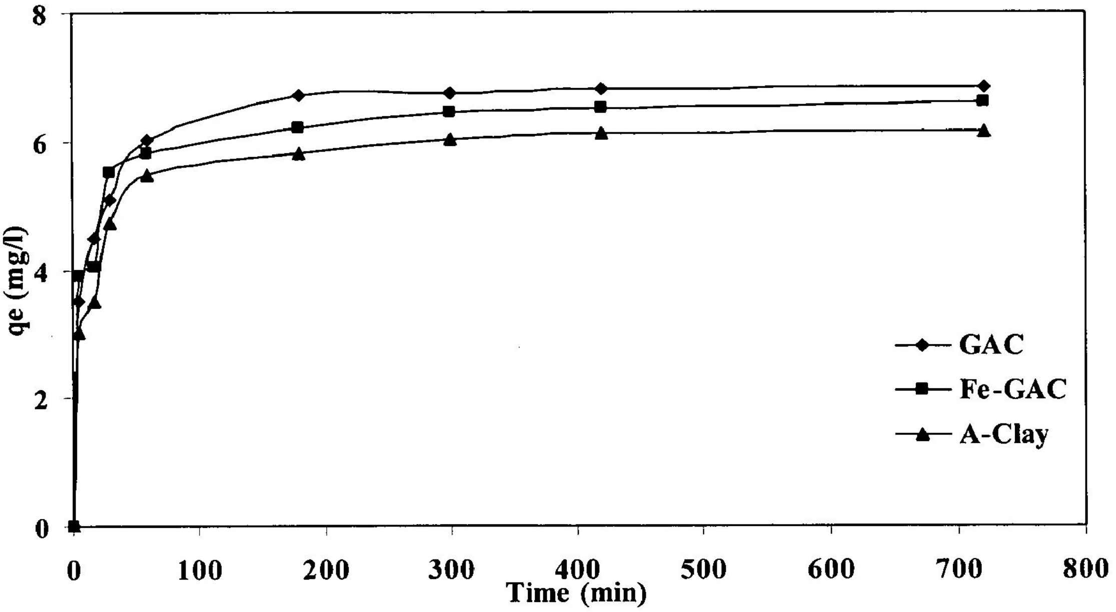


Fig 4.30 Effect of contact time on removal of Humic acid using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 5g/l, T=300 K, Co=50mg/l)

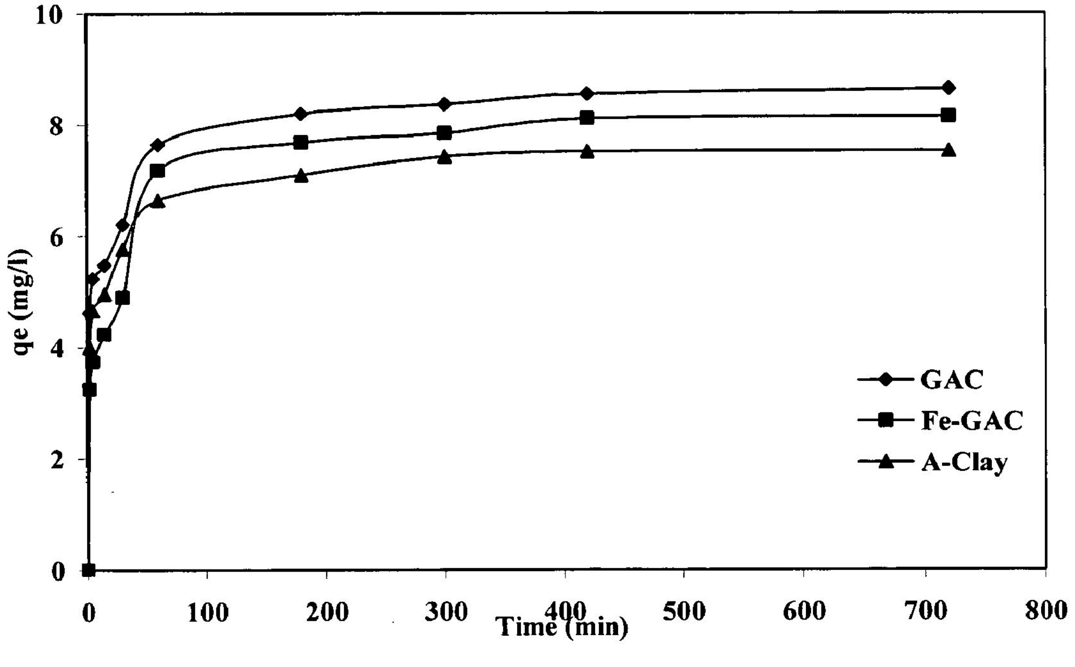


Fig 4.31 Effect of contact time on removal of Cadmium using GAC, Fe-GAC and A-Clay (pH=6, Adsorbent dosage= 10g/l, T=300 K, Co=100mg/l)

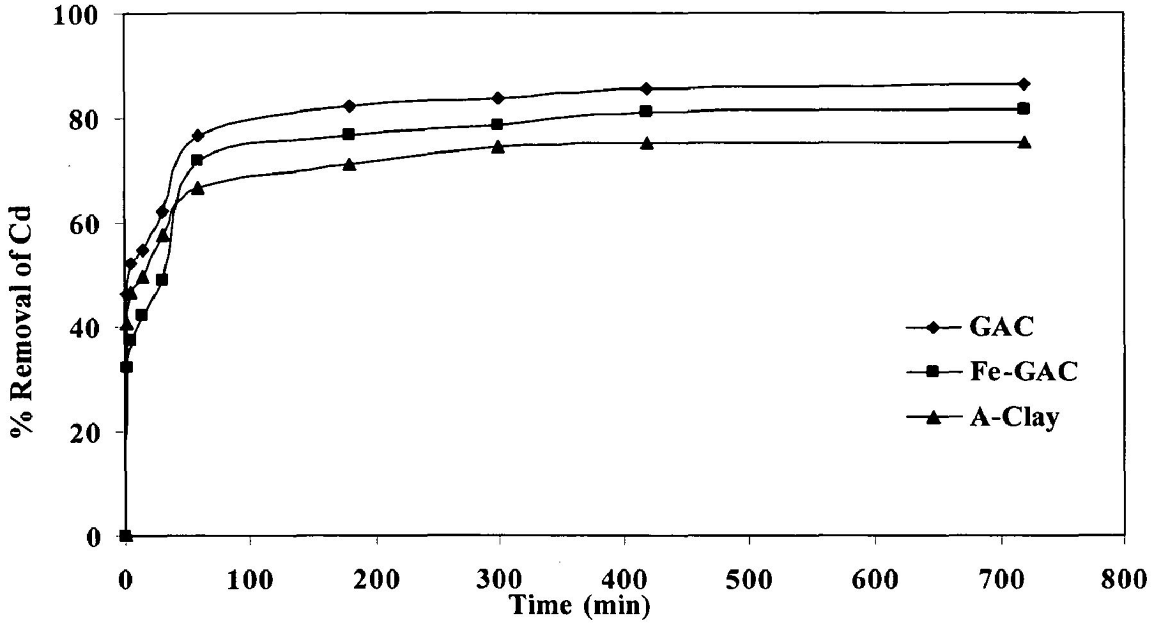


Fig 4.32 Effect of contact time on removal of Cadmium using GAC, Fe-GAC and A-Clay (pH=6, Adsorbent dosage= 10g/l, T=300 K, Co=100mg/l)

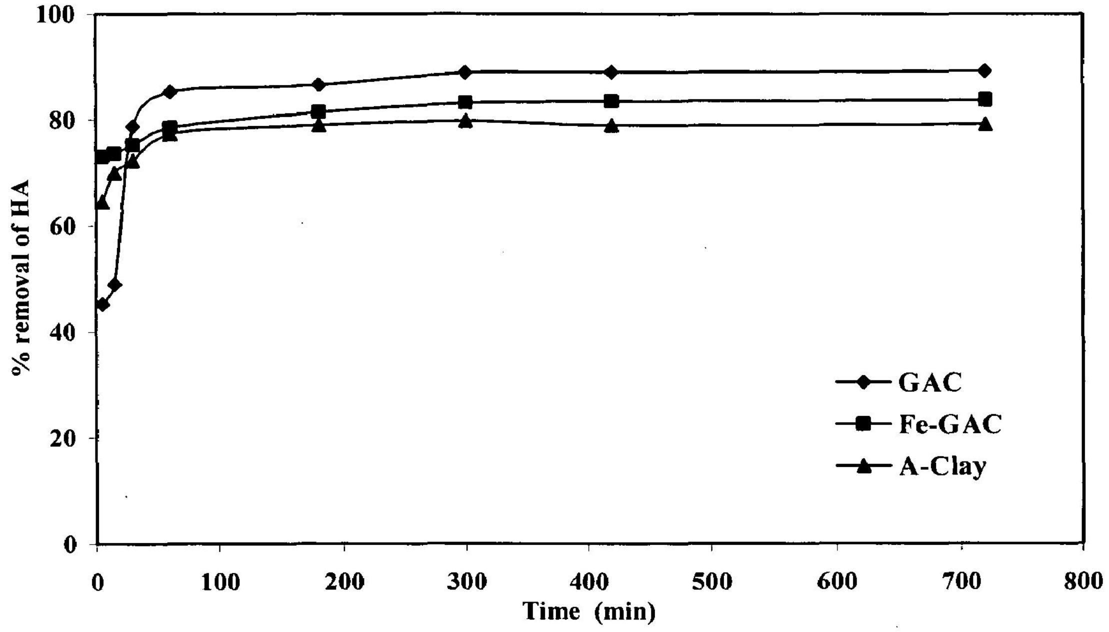


Fig 4.33 Effect of contact time on removal of HA in Co-Adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, T=300 K, Co=50mg/l for HA and Cd)

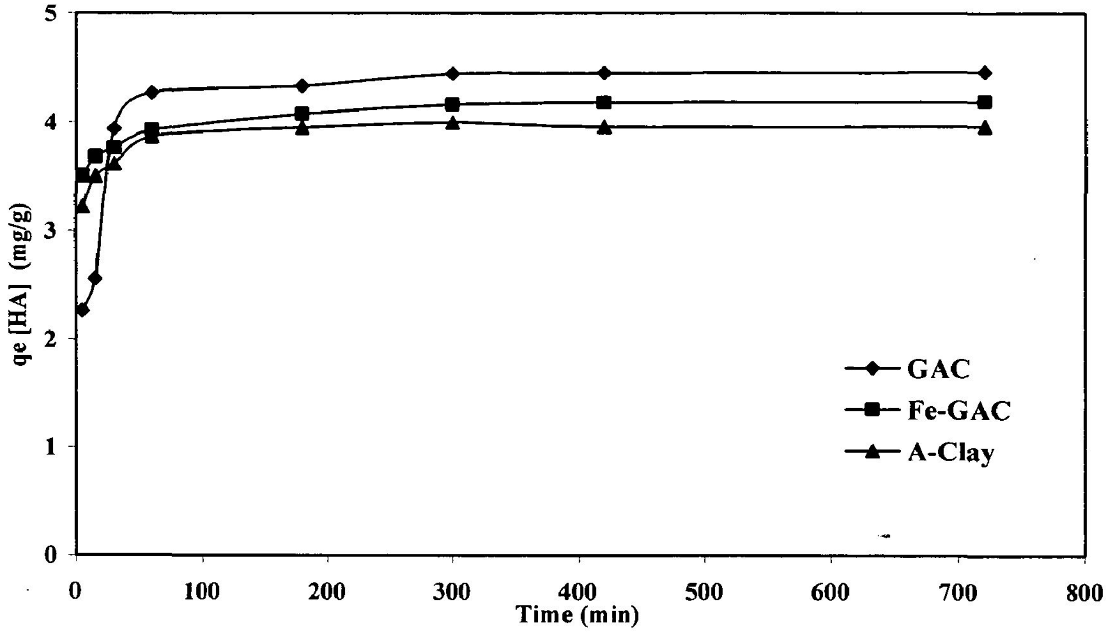


Fig 4.34 Effect of contact time on removal of HA in Co-Adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, T=300 K, Co=50mg/l for HA and Cd)

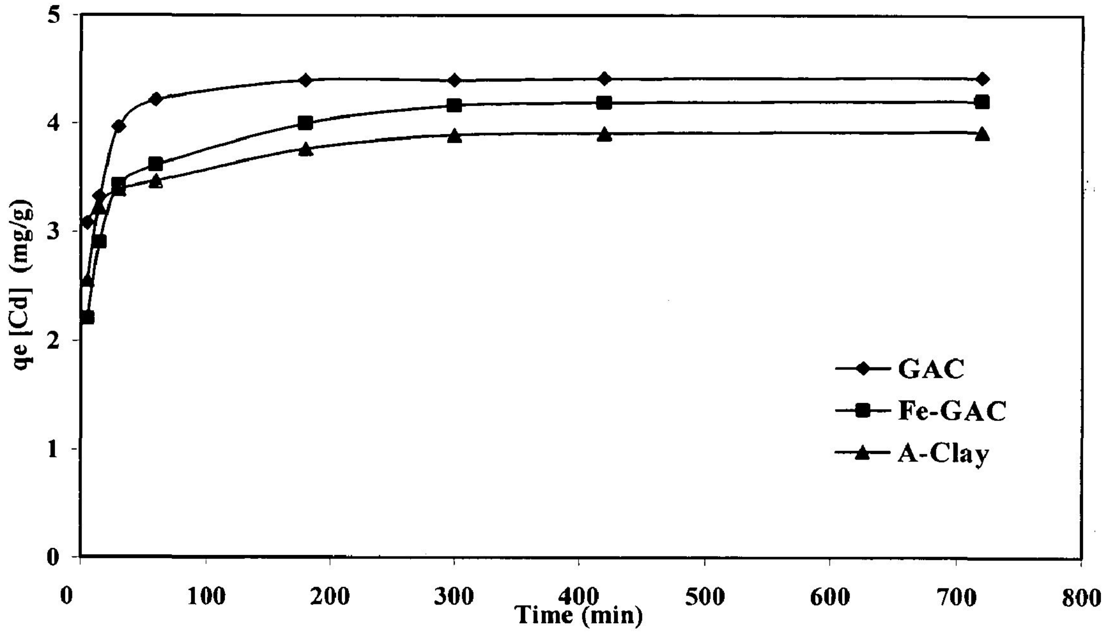


Fig 4.35 Effect of contact time on removal of Cd in Co-Adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, T=300 K, Co=50mg/l for HA and Cd)

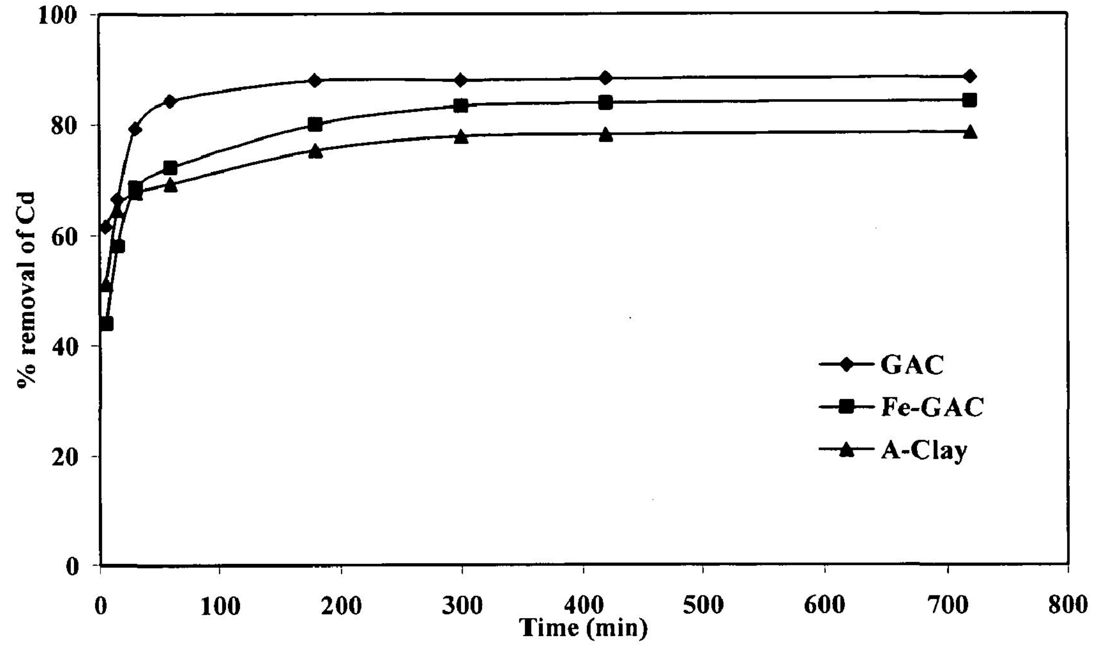


Fig 4.36 Effect of contact time on removal of Cd in Co-Adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (pH=5, Adsorbent dosage= 10g/l, T=300 K, Co=50mg/l for HA and **Cd)**

4.4 Adsorption Kinetic Study

There are various models available to explain the kinetics of the adsorption. In order to investigate the adsorption processes of Cd(II) on GAC, Fe-GAC and A-Clay, three kinetic models viz. pseudo-first-order model, pseudo-order-model and intra-particle diffusion model are used.

4.4.1 Pseudo-first order model

The pseudo first order equation is

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \qquad (4.1)$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity in equilibrium (mg/g), k_f is the rate constant of pseudo-first order model (1/min), and t is the time (min). After definite integration by applying the initial conditions at t=0, q_t=0 and $t = t$, $q_t = q_t$, the equation becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \tag{4.2}$$

The values of the pseudo-first-order adsorption rate constant (k_f) (Tables 4.2 - 4.5) are determined from Eq. (4.2) by plotting $\log(q_e - q_t)$ against t for HA, Cd (II) and HA-Cd onto GAC, Fe-GAC and A-Clay. Figs (4.37-4.39, 4.46 -4.48, 4.55-4.57, 4.64-4.66) show the plot of $\log(q_e - q_t)$ against t for adsorption HA, Cd (II) and HA-Cd onto GAC, Fe-GAC and A-Clay.

4.4.2 Pseudo-Second Order

The pseudo-second-order model can be represented in the following form:

$$\frac{dq}{dt} = k_S(q_e - q_t)^2 \tag{4.3}$$

where k_S is the pseudo second order rate constant (g mg^{-1} min^{-1}), q_e the amount of solute ions adsorbed at equilibrium(mg g^{-1}) and q_t is the amount of solution ions adsorbed on the sorbent at any time, t (mg g^{-1}).

This equation can be integrated with $q_t = 0$ at $t = 0$, and $q_t = q_t$ at t=t, to give

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e}t \tag{4.4}$$

The initial sorption rate h (mg/g min),

$$h = k_S q_e^2 \tag{4.5}$$

The initial sorption rate (h), the equilibrium adsorption capacity q_e, and the pseudo second order constant k_S can be determined experimentally from the slope and intercept of the plot of t/q_t versus t. Figs (4.40-4.42, 4.49-4.51, 4.58-4.60, and 4.67-4.69) show plot of t/q_t versus t for adsorption HA, Cd (II) and HA-Cd onto GAC, Fe-GAC and A-Clay. Tables (4.2-4.5) show the value of second order rate constants. The qe,exp and the qe,cal values for the pseudo-first-order model and pseudo-second-order models are being shown in Tables 4.2-4.5. The qe,exp and the qe,cal values from the pseudo-second-order kinetic model were very close to each other. Also, the calculated correlation coefficients were equal to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetic model. Therefore, the sorption can be approximated more appropriately by pseudo-second-order kinetic model than the other kinetic models for the adsorption of, HA, Cd(II) and HA-Cd onto GAC, Fe-GAC and A-Clay.

4.4.3 Intra-particle Diffusion Study

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with t-1/2, the Weber-Morris plot rather than with the contact time t.

$$q_t = k_{id} t^{0.5} + I \tag{4.6}$$

where, k_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and I (mg g^{-1}) is a constant that gives an idea about the thickness of the boundary layer, i.e., the larger the value of I, the greater is the boundary layer effect.

The slope of the Weber and Morris plots: q versus $t^{0.5}$, are defined as a rate parameter (k_{id}), characteristic of the rate of adsorption in the region where intra-particle diffusion is rate controlling. The higher the value of k_{id} the higher is the intraparticle diffusion rate. If a Weber and Morris plot satisfies the linear relationship with the experimental data, then the sorption is found to be controlled by intra-particle diffusion only. Figs (4.43-4.45, 4.52-4.54, 4.61-4.63, 4.70-4.72) represents the plot of q versus $t^{0.5}$ for adsorption HA, Cd (II) and HA-Cd onto GAC, Fe-GAC and A-Clay. The deviation of straight lines from the origin figs (4.43-4.45, 4.52-4.54, 4.61-4.63, 4.70-4.72) may be due to difference in the rate of mass transfer in the initial and final stages of adsorption. Further such deviation of straight line from the origin indicates the pore diffusion is not the sole-rate-controlling step (Srivastavaet al., 2006).

From figs (4.43-4.45, 4.52-4.54, 4.61-4.63, 4.70-4.72), it can be seen that there are two separate regions the initial bulk diffusion and linear portion to intra particle diffusion. The values of $k_{id,1}$ and $k_{id,2}$ are listed in the table (4.2-4.5). Again it may be the both film and pore diffusion is involved in this process.

4.5 Adsorption Equilibrium Study

To optimize the design of an adsorption system for the adsorption system for the adsorption of adsorbate, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been to describe the equilibrium have been used to describe the equilibrium characteristics of adsorption.

4.5.1 Langmuir and Freundlich isotherm

Linearized form of Freundlich and Langmuir isotherm equation are given as

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \text{(Linear form)} \qquad (4.7)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad \text{(Linear form)} \qquad (4.8)$$

Figs (4.76 and 4.79) shows the Freundlich isotherm plots (lnq_e versus lnC_e) for adsorption of HA and Cd(II) onto different adsorbents. A plot of C_e/q_e versus C_e in figs (4.75-4.78) shows the Langmuir isotherm. Freundlich and Langmuir isotherm parameter along with linear and non linear correlation co-efficient for HA and Cd are given in table (4.6-4.7). Langmuir isotherm represented a better fit of the experimental data than that of Freundlich isotherm. This suggested that adsorption of HA and Cd (II) by GAC, Fe-GAC and A-Clay was apparently with monolayer coverage of adsorbed molecules. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, which describes the type of patter and is defined as $R_L = 1/(1+K_L Co)$ indicates the nature of adsorption as if

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The value of R_L was found to be less 1. Hence, adsorption using GAC, Fe-GAC and A-Clay for HA and Cd(II) was favorable.

4.5.2 Temkin isotherm

Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad (4.9)$$

Eq. (3.4.9) can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad (4.10)$$

where, $B_T = \frac{RT}{b}$

b and K_T is the equilibrium binding constant corresponding to the maximum binding energy. Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. A plot of q_e versus $\ln C_e$ shown in the figs (4.77 and 4.80) enables the determination of the isotherm constants K_T and B_T. Temkin isotherm parameters are being listed in the tables 4.6-4.7.

Table 4.2 Kinetic parameter for the removal of cadmium by GAC, Fe-GAC and A-Clay (pH=6, T=300 K, Co=100 mg/l, m=10 g/l)

<table>
<tr><th colspan="6">Pseudo- first order</th></tr>
<tr><td>Adsorbent</td><td>$q_{e,exp}$ (mg/l)</td><td>$q_{e,cal}$ (mg/l)</td><td>k_f</td><td>R_1^2 (linear)</td><td>R_1^2 (non linear)</td></tr>
<tr><td>GAC</td><td>8.36</td><td>3.36</td><td>0.017</td><td>0.9594</td><td>0.9869</td></tr>
<tr><td>Fe-GAC</td><td>7.84</td><td>4.23</td><td>0.019</td><td>0.9329</td><td>0.9722</td></tr>
<tr><td>A-Clay</td><td>7.43</td><td>2.718</td><td>0.0126</td><td>0.9101</td><td>0.9948</td></tr>
<tr><th colspan="6">Pseudo-second order</th></tr>
<tr><td>Adsorbent</td><td>$q_{e,cal}$ (mg/l)</td><td>h (mg/g min^{-1})</td><td>k_s</td><td>R_1^2 (linear)</td><td>R_1^2 (non linear)</td></tr>
<tr><td>GAC</td><td>8.503</td><td>1.395</td><td>0.019</td><td>0.9992</td><td>0.9994</td></tr>
<tr><td>Fe-GAC</td><td>8.08</td><td>0.8292</td><td>0.012</td><td>0.9977</td><td>0.9978</td></tr>
<tr><td>A-Clay</td><td>7.501</td><td>1.241</td><td>0.022</td><td>0.9991</td><td>0.9997</td></tr>
<tr><th colspan="6">Intra-particle diffusion</th></tr>
<tr><td>Adsorbent</td><td>k_{id} (mg/g min$^{-1/2}$)</td><td>I_1 (mg/g)</td><td>R_1^2 (linear)</td><td colspan="2">R_1^2 (non linear)</td></tr>
<tr><td>GAC</td><td>0.4465</td><td>3.9853</td><td>0.9598</td><td colspan="2">0.9815</td></tr>
<tr><td>Fe-GAC</td><td>0.5843</td><td>2.2357</td><td>0.9365</td><td colspan="2">0.9875</td></tr>
<tr><td>A-Clay</td><td>0.3995</td><td>3.5504</td><td>0.981</td><td colspan="2">0.981</td></tr>
<tr><td>Adsorbent</td><td>k_{id} (mg/g min$^{-1/2}$)</td><td>I_2 (mg/g)</td><td>R_2^2 (linear)</td><td colspan="2">R_2^2 (non linear)</td></tr>
<tr><td>GAC</td><td>0.0758</td><td>7.0977</td><td>0.9601</td><td colspan="2">0.9999</td></tr>
</table>

Fe-GAC	0.0703	6.6646	0.9669	0.9999
A-Clay	0.0813	6.0169	0.9971	0.9999

Table 4.3 Kinetic parameter for the removal of Humic acid by GAC, Fe-GAC and A-Clay (pH=5, T=300 K, Co=50 mg/l, m=5 g/l)

Pseudo- first order					
Adsorbent	$q_{e,exp}$ (mg/l)	$q_{e,cal}$ (mg/l)	k_f	R_l^2 (linear)	R_l^2 (non linear)
GAC	6.71	3.672	0.0278	0.9998	0.9998
Fe-GAC	6.2	2.877	0.0345	0.8806	0.8917
A-Clay	5.8	3.84	0.041	0.976	0.9808
Pseudo-second order					
Adsorbent	$q_{e,cal}$ (mg/l)	h (mg/g min^{-1})	k_s	R_l^2 (linear)	R_l^2 (non linear)
GAC	7.01	0.79	0.01609	0.9988	0.9994
Fe-GAC	6.4	1.0305	0.0251	0.9985	0.9980
A-Clay	6.07	0.725	0.0196	0.9981	0.9981
Intra-particle diffusion					
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_1 (mg/g)	R_1^2 (linear)	R_1^2 (non linear)	
GAC	0.4681	2.6373	0.989	0.9964	
Fe-GAC	0.3898	2.9238	0.8691	0.873	
A-Clay	0.4433	1.9252	0.9669	0.9672	
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_2 (mg/g)	R_2^2 (linear)	R_2^2 (non linear)	
GAC	0.0564	5.0773	1	1	
Fe-GAC	0.0765	5.2536	1	1	
A-Clay	0.1217	5.0429	1	1	

Table 4.4 Kinetic parameter for removal of Cadmium in Co-adsorption by GAC, Fe-GAC and A-Clay (pH=5, T=300 K, Co=50 mg/l, m=10 g/l)

Pseudo- first order					
Adsorbent	$q_{e,exp}$ (mg/l)	$q_{e,cal}$ (mg/l)	k_f	R_1^2 (linear)	R_1^2 (non linear)
GAC	4.4	1.637	0.0378	0.9732	0.9798
Fe-GAC	4	1.713	0.027	0.9035	0.9986
A-Clay	3.77	0.965	0.022	0.7588	0.7588
Pseudo-second order					
Adsorbent	$q_{e,cal}$ (mg/l)	h (mg/g min^{-1})	k_s	R_1^2 (linear)	R_1^2 (non linear)
GAC	4.49	0.058	1.17	0.9998	0.9999
Fe-GAC	4.11	0.04	0.676	0.9996	0.9999
A-Clay	3.83	0.071	1.047	0.9995	1
Intra-particle diffusion					
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_1 (mg/g)	R_1^2 (linear)	R_1^2 (non linear)	
GAC	0.15454	2.4132	0.7618	0.9318	
Fe-GAC	0.2561	1.7987	0.8993	0.9983	
A-Clay	0.2198	2.584	0.9427	0.9796	
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_2 (mg/g)	R_2^2 (linear)	R_2^2 (non linear)	
GAC	0.0529	3.0602	1	1	
Fe-GAC	0.0679	3.0891	1	1	
A-Clay	0.0326	3.9623	1	1	

Table 4.5 Kinetic parameter for removal of Humic acid in Co-adsorption by GAC, Fe-GAC and A-Clay (pH=5, T=300 K, Co=50 mg/l, m=10 g/l)

Pseudo- first order					
Adsorbent	$q_{e, exp}$ (mg/l)	$q_{e, cal}$ (mg/l)	k_f	R_1^2 (linear)	R_1^2 (non linear)
GAC	4.4	3.82	0.0755	0.9881	0.9838
Fe-GAC	4	1.744	0.0324	0.9885	0.9899
A-Clay	3.945	1.1269	0.3915	0.9819	0.9895
Pseudo-second order					
Adsorbent	$q_{e, cal}$ (mg/l)	h (mg/g min^{-1})	k_s	R_1^2 (linear)	R_1^2 (non linear)
GAC	4.46	0.037	0.7386	0.9979	0.9985
Fe-GAC	4.1	0.124	2.10	0.9999	1
A-Clay	3.987	0.123	1.95	0.9999	0.9999
Intra-particle diffusion					
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_1 (mg/g)	R_1^2 (linear)	R_1^2 (non linear)	
GAC	0.4014	1.3077	0.8973	0.9077	
Fe-GAC	0.0735	3.3596	0.9789	0.9889	
A-Clay	0.1118	3.0111	0.978	0.9867	
Adsorbent	k_{id} (mg/g min$^{-1/2}$)	I_2 (mg/g)	R_2^2 (linear)	R_2^2 (non linear)	
GAC	0.0071	4.2054	1	1	
Fe-GAC	0.0265	3.7151	1	1	
A-Clay	0.0141	3.7557	1	1	

Table 4.6 Isotherms parameters for removal of Cadmium by GAC, Fe-GAC and A-Clay (pH=6, T=300 K, Co=100mg/l adsorbent dosage=10 g/l)

Freundlich constants

Adsorbent	K_F ((mg/g)(mg/l)$^{-1/n}$)	$1/n$	R_l^2 (linear)	R_l^2 (non linear)
GAC	3.807	0.2593	0.9888	0.9891
Fe-GAC	2.935	0.2805	0.9828	0.983
A-Clay	1.115	0.274	0.9842	0.9885

Langmuir constants

Adsorbent	K_L (l/g)	q_m (mg/g)	R_L	R_l^2 (linear)	R_2^2 (non linear)
GAC	0.1998	11.75	0.0477	0.9921	0.9957
Fe-GAC	0.1399	10.51	0.0667	0.9937	0.9967
A-Clay	0.1319	8.718	0.0704	0.9955	0.9964

Temkin isotherm

Adsorbent	K_T (1/mg)	B_l	R_l^2 (linear)	R_2^2 (non linear)
GAC	15.746	1.5134	0.9435	0.9786
Fe-GAC	6.557	1.5016	0.949	0.9797
A-Clay	4.76	1.5134	0.9686	0.9784

Table 4.7 Isotherms parameters for removal of Humic acid by by GAC, Fe-GAC and A-Clay (pH=5, T=300 K, Co=100 mg/l adsorbent dosage=5 g/l).

Freundlich constants

Adsorbent	K_F ((mg/g)(mg/l)$^{-1/n}$)	$1/n$	R_1^2 (linear)	R_1^2 (non linear)
GAC	3.013	0.2328	0.977	0.9977
Fe-GAC	2.702	0.2556	0.763	0.936
A-Clay	2.204	0.2858	0.9203	0.9908

Langmuir constants

Adsorbent	K_L (l/g)	q_m (mg/g)	R_L	R_1^2 (linear)	R_2^2 (non linear)
GAC	0.2396	8.1767	0.077	0.9972	0.9999
Fe-GAC	0.2367	7.668	0.087	0.9973	0.9973
A-Clay	0.1604	7.44	0.11	0.9982	0.9988

Temkin isotherm

Adsorbent	K_T (l/mg)	B_l	R_1^2 (linear)	R_2^2 (non linear)
GAC	5.602	1.2542	0.9963	0.9963
Fe-GAC	5.64	1.2775	0.8175	0.9428
A-Clay	2.67	1.3589	0.9618	0.9921

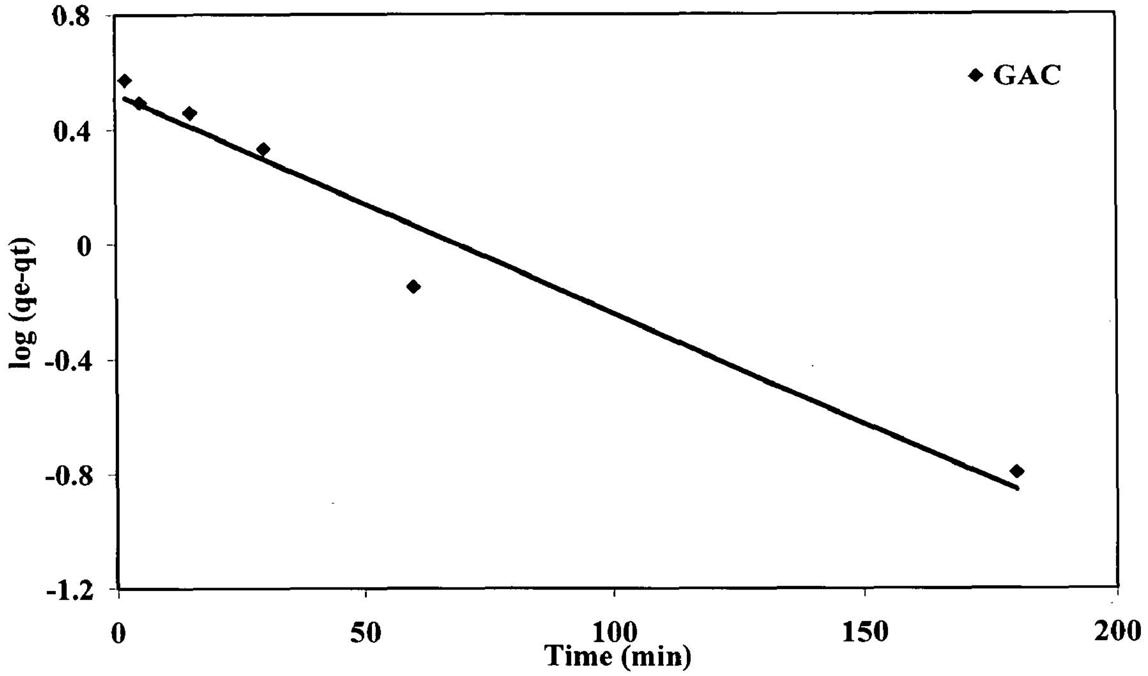


Fig 4.37 Lagergren plot for removal of Cadmium for GAC,
(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

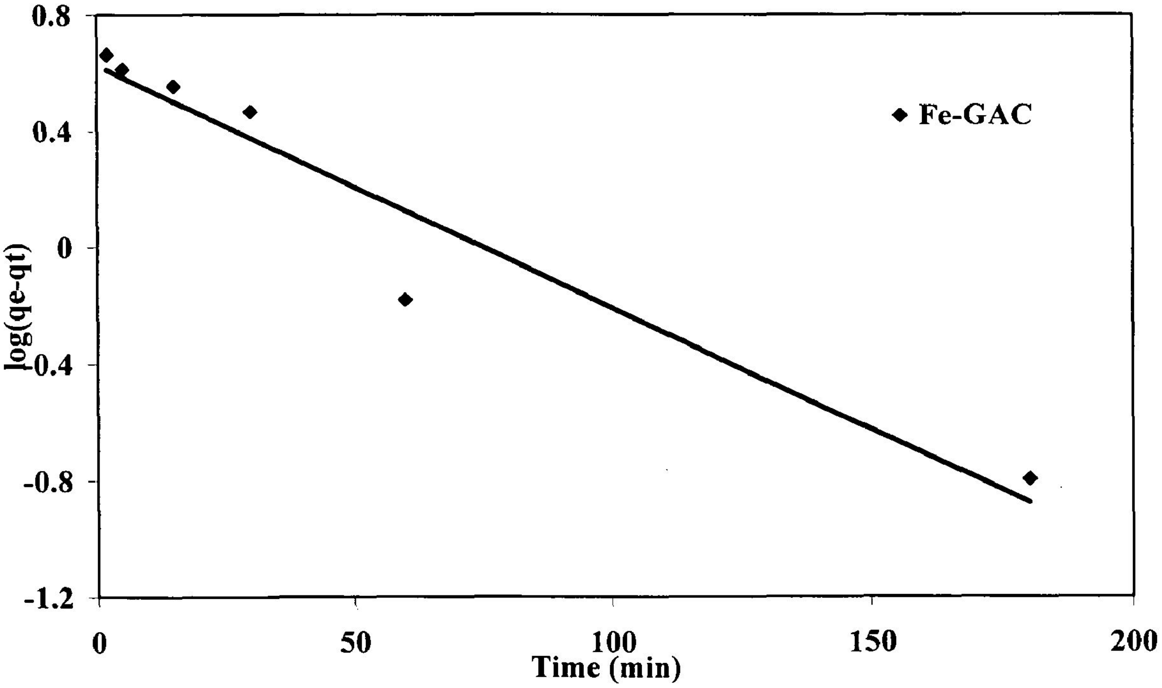


Fig 4.38 Lagergren plot for removal of Cadmium for Fe-GAC (Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

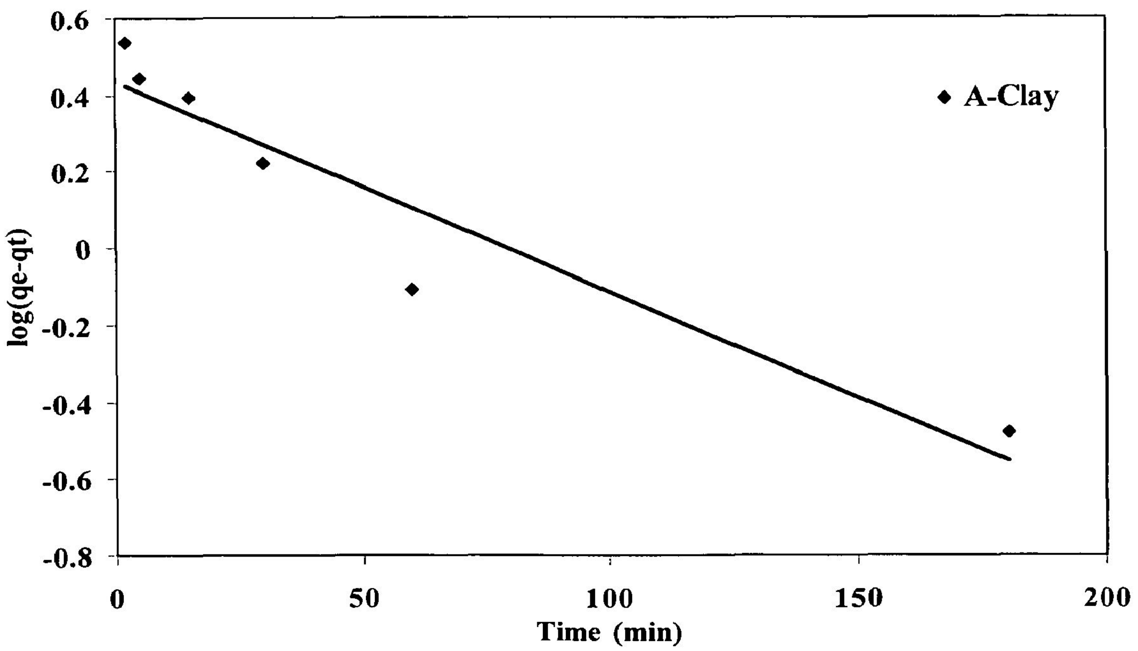


Fig 4.39 Lagergren plot for removal of Cadmium A-Clay (Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

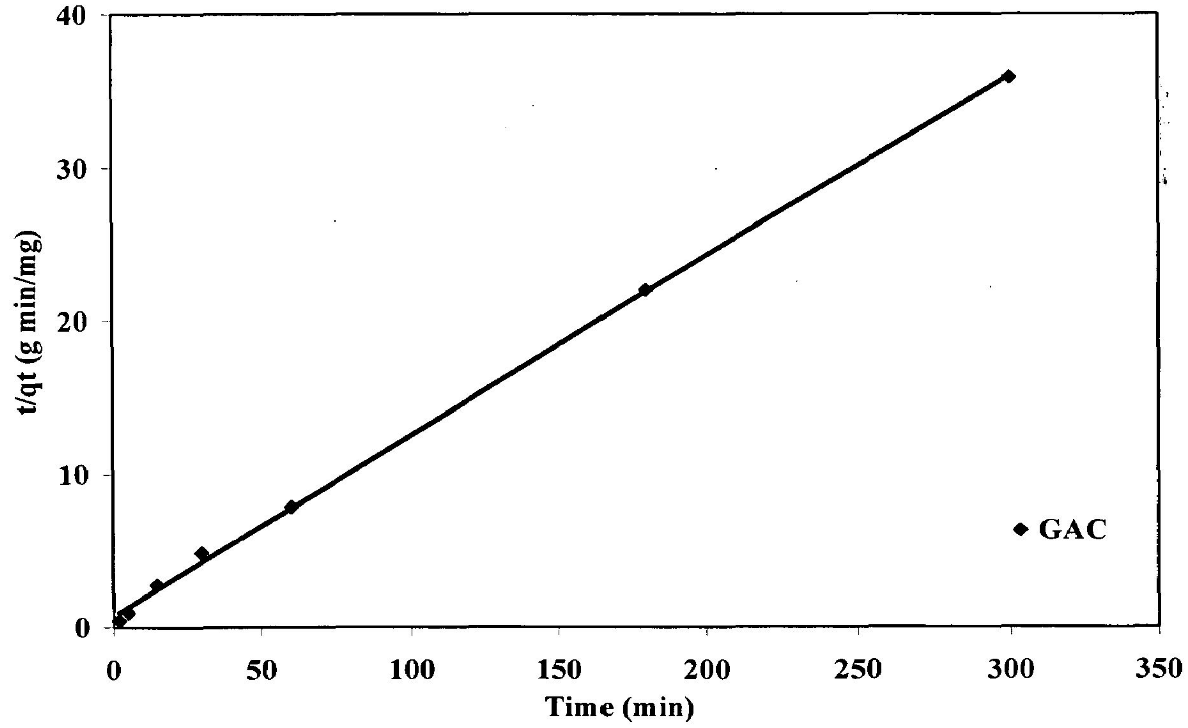


Fig 4.40 Pseudo second order kinetics for removal of Cadmium for GAC

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

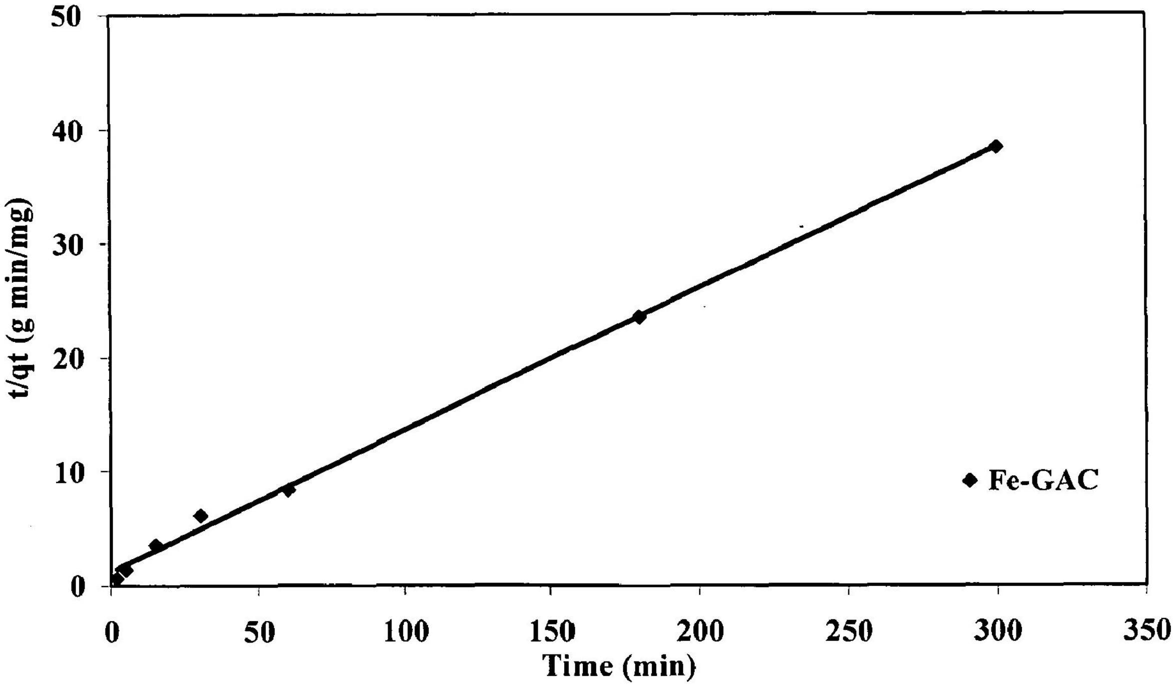


Fig 4.41 Pseudo second order kinetics for removal of Cadmium for Fe-GAC

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

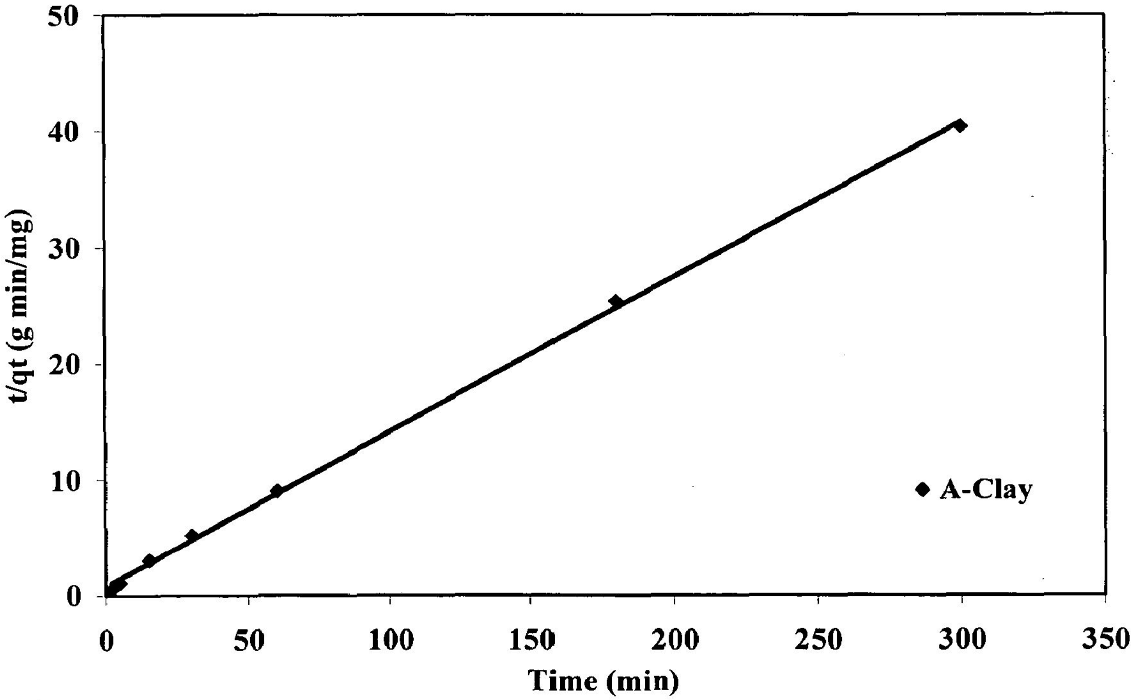


Fig 4.42 Pseudo second order kinetics for removal of Cadmium for A-Clay

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

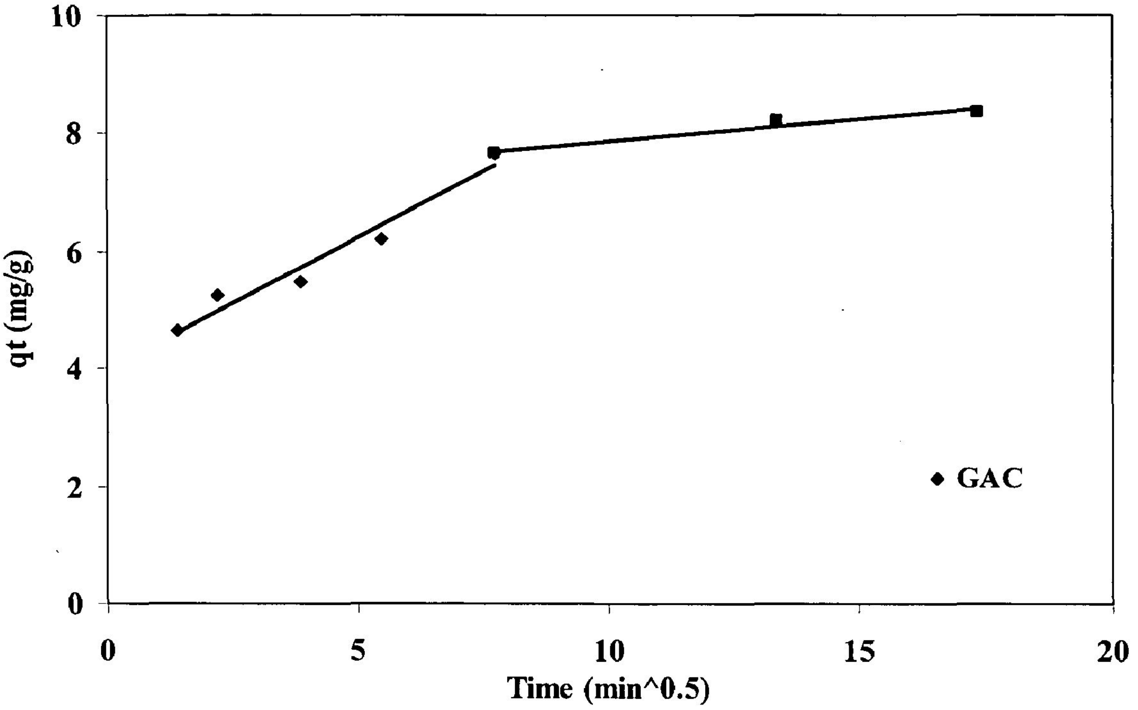


Fig 4.43 Weber Morris plot for removal of Cadmium for GAC

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

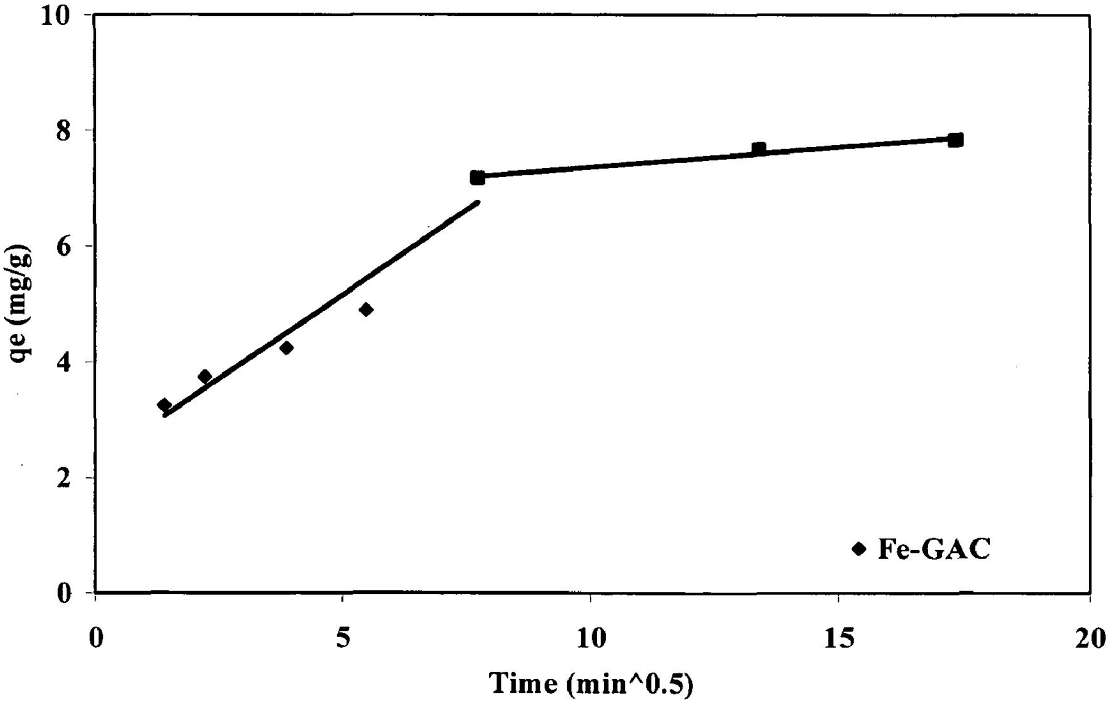


Fig 4.44 Weber Morris plot for removal of Cadmium for Fe-GAC

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

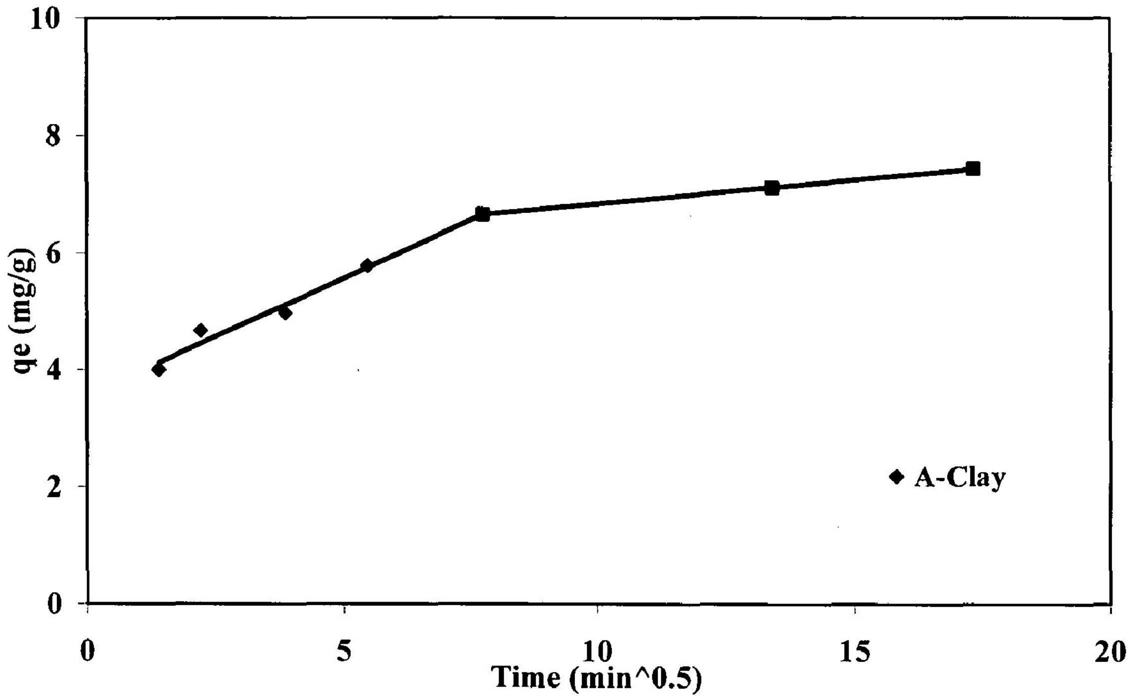


Fig 4.45 Weber Morris plot for removal of Cadmium for Fe-GAC

(Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

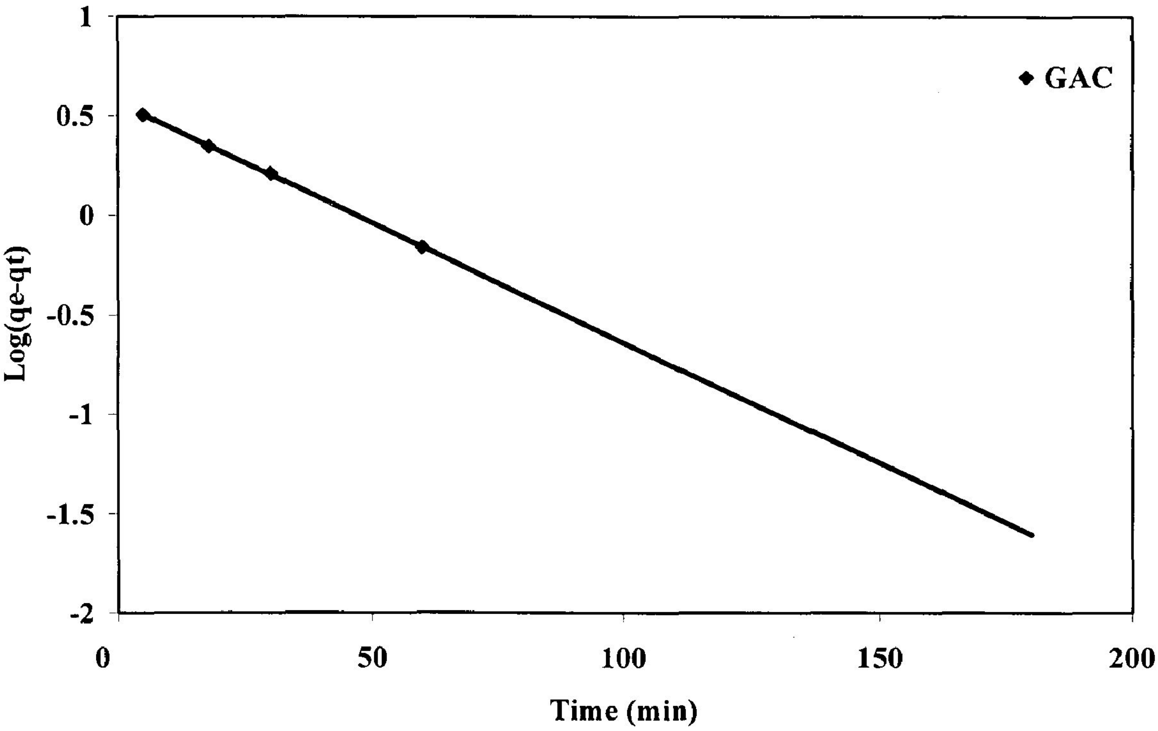


Fig 4.46 Lagergren plot for removal of Humic acid for GAC,

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

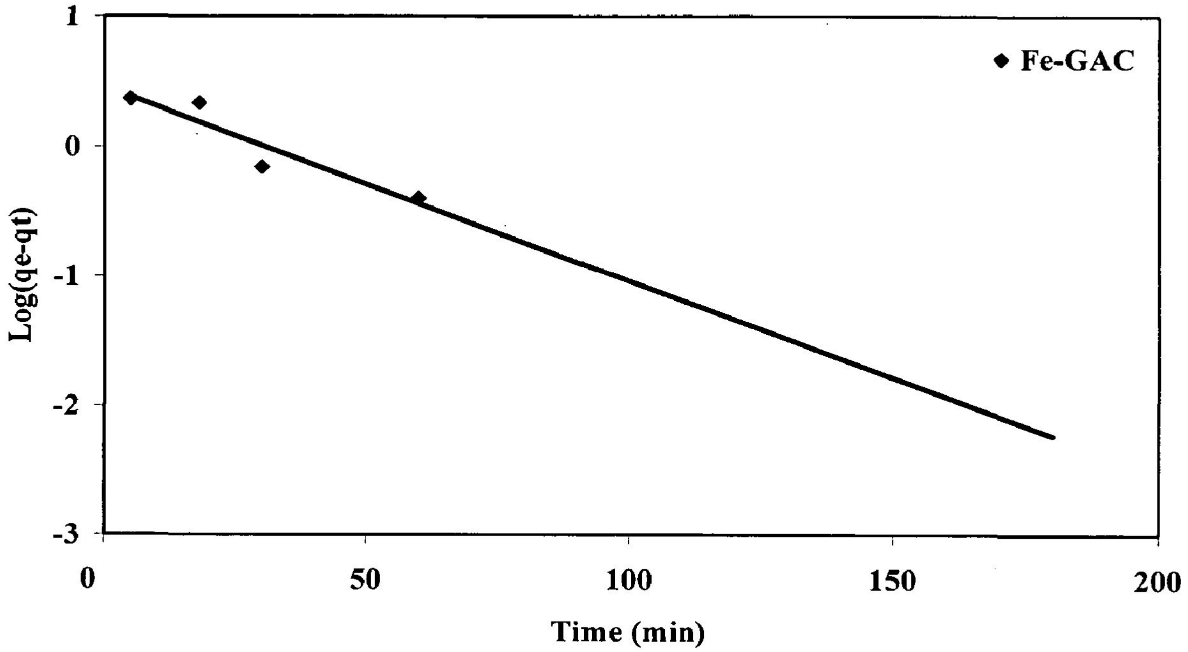


Fig 4.47 Lagergren plot for removal of Humic acid for Fe-GAC,
(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

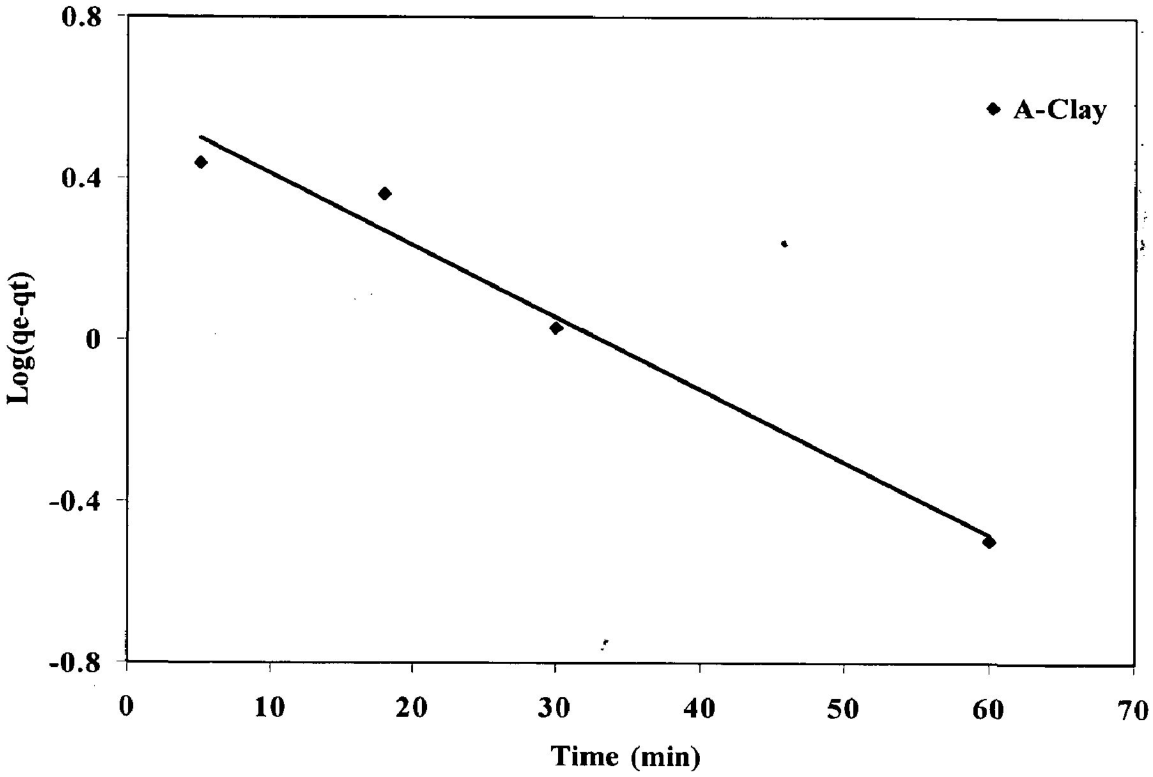


Fig 4.48 Lagergren plot for removal of Humic acid for A-Clay,
(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

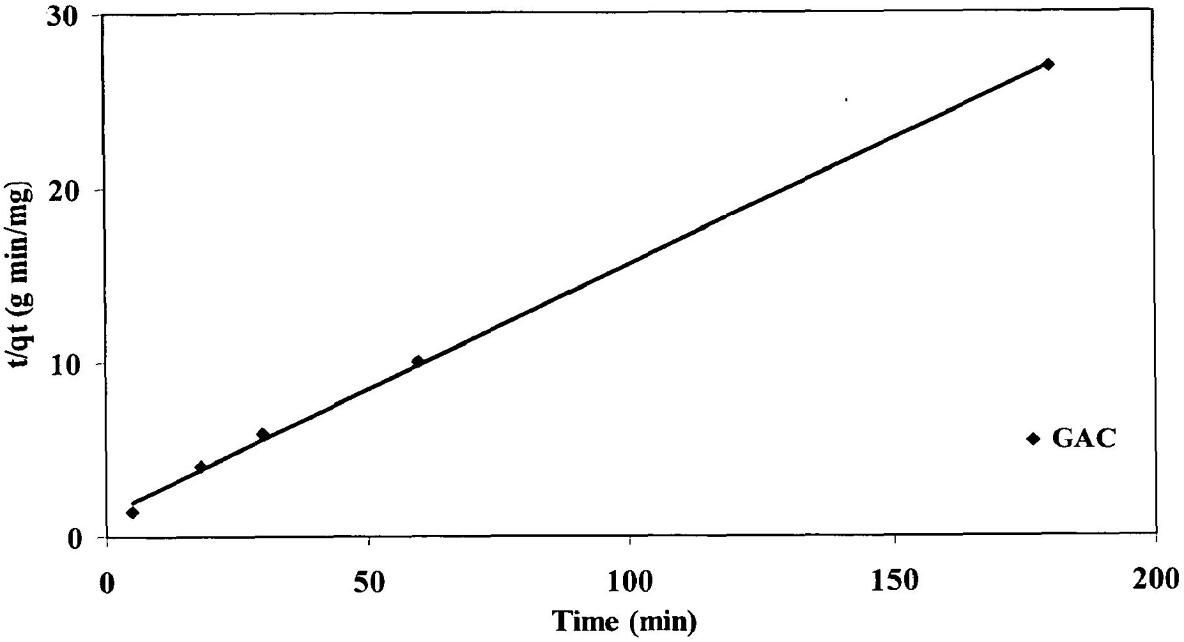


Fig 4.49 Pseudo second order kinetics for removal of Humic acid for GAC

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

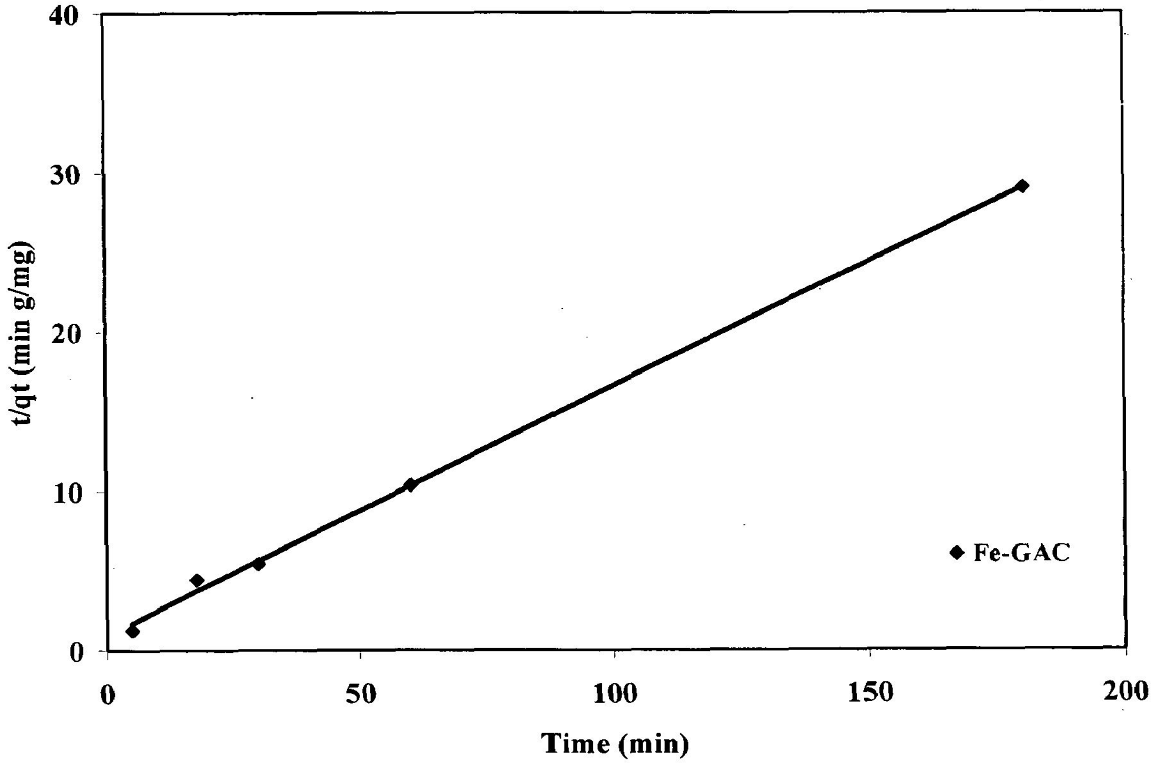


Fig 4.50 Pseudo second order kinetics for removal of Humic acid for Fe-GAC

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

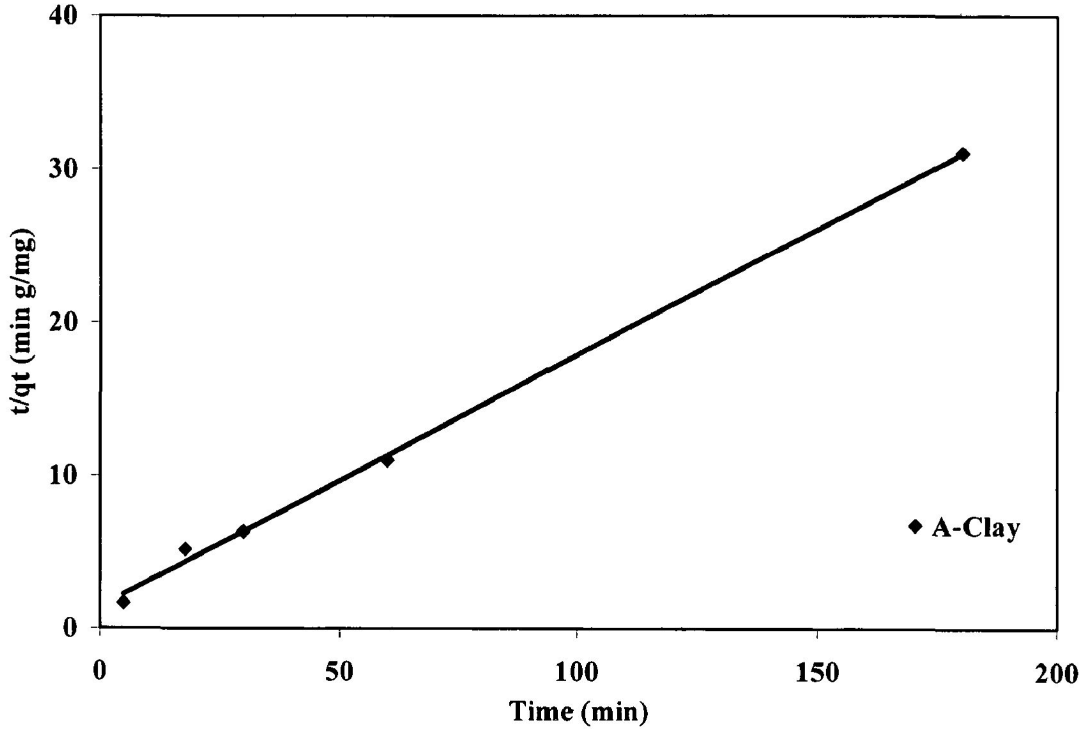


Fig 4.51 Pseudo second order kinetics for removal of Humic acid for A-Clay

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

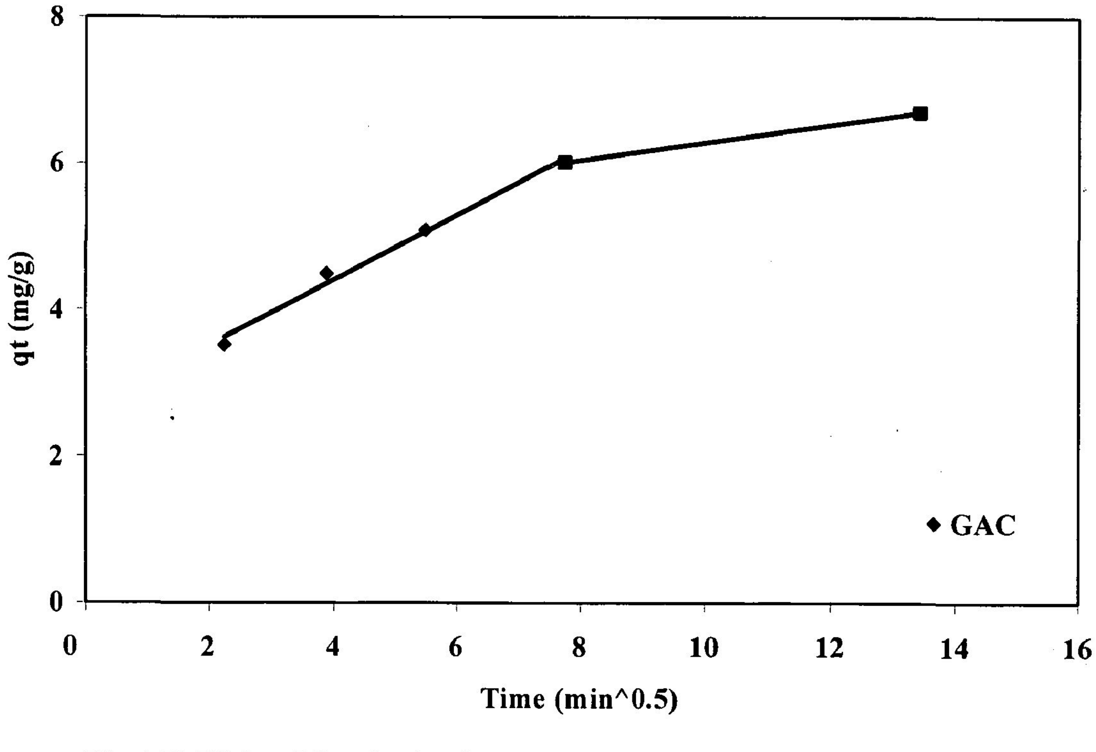


Fig 4.52 Weber Morris plot for removal of Humic acid for GAC,

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

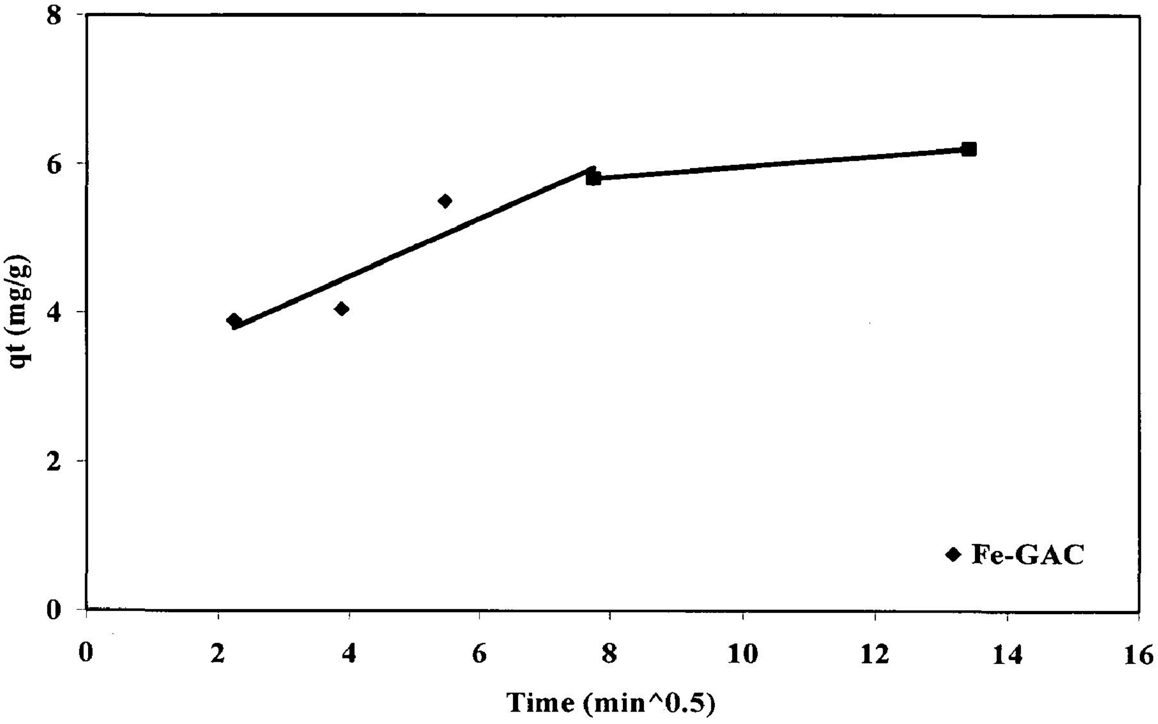


Fig 4.53 Weber Morris plot for removal of Humic acid for Fe-GAC,

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

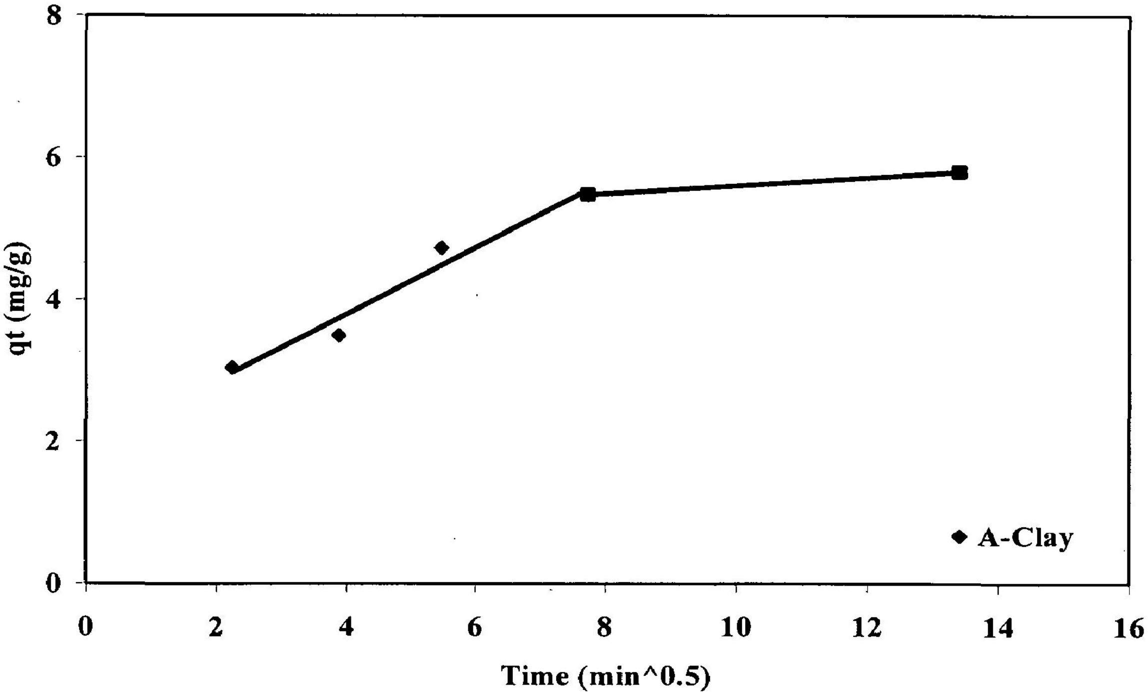


Fig 4.54 Weber Morris plot for removal of Humic acid for A-Clay,

(Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

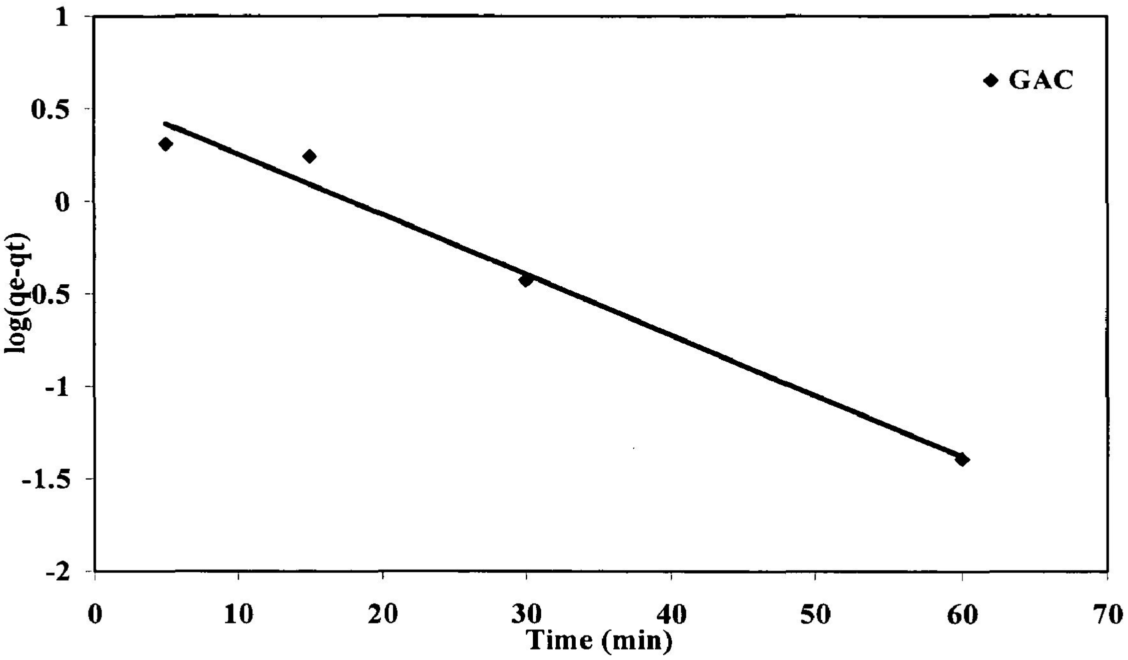


Fig 4.55 Lagergren plot for removal of Cadmium in co-adsorption for GAC
(Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K).

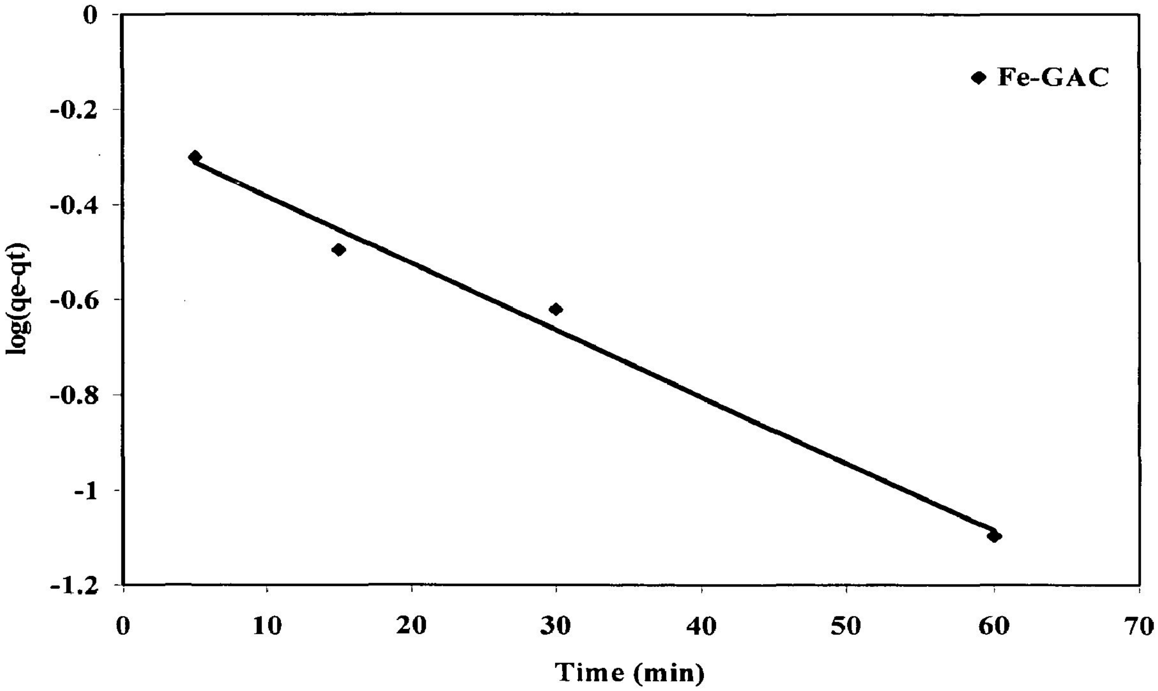


Fig 4.56 Lagergren plot for removal of Cadmium in co-adsorption Fe-GAC
(Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

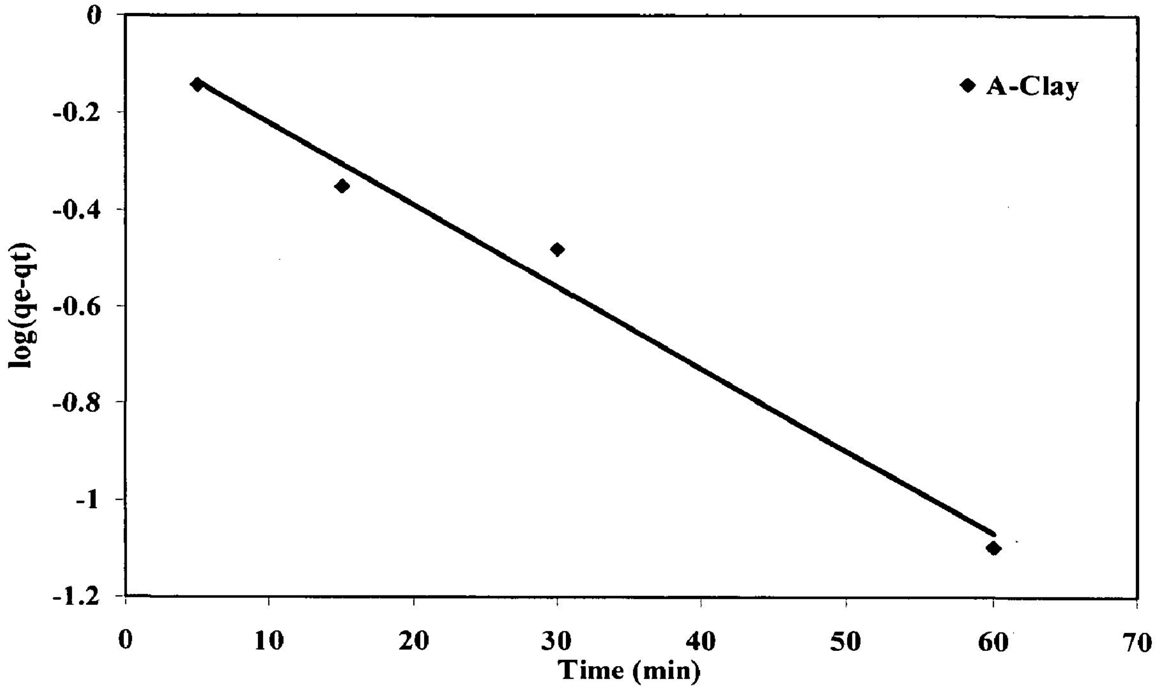


Fig 4.57 Lagergren plot for removal of Cadmium in co-adsorption A-Clay
(Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

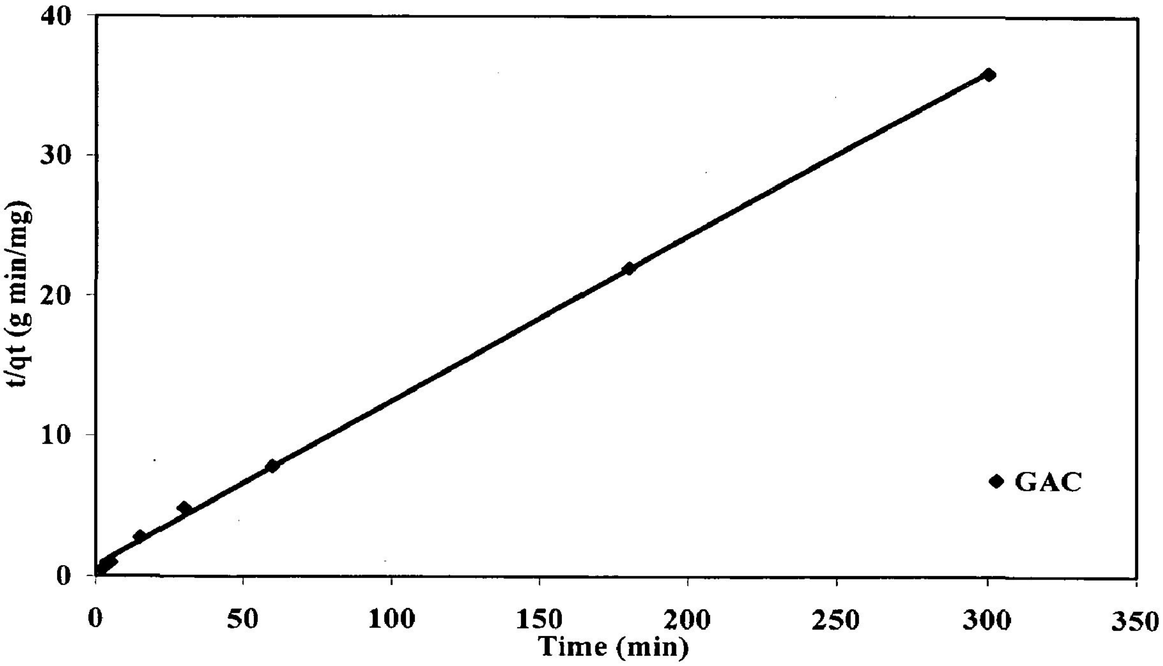


Fig 4.58 Pseudo second order kinetics plot for removal of Cadmium in co-adsorption for GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

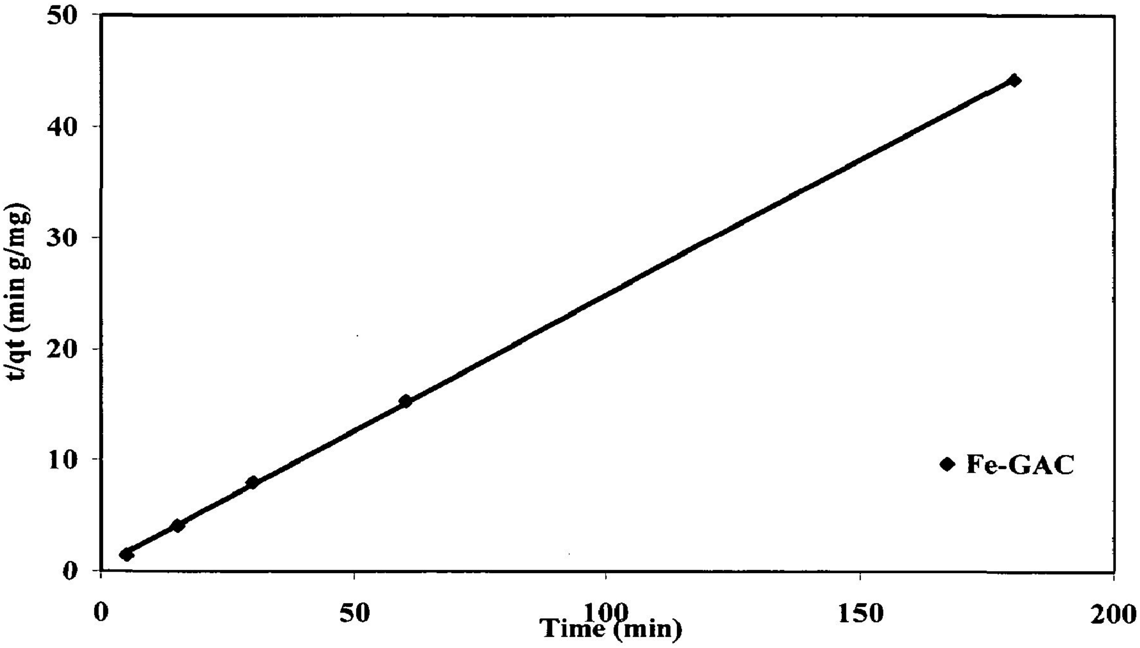


Fig 4.59 Pseudo second order kinetics plot for removal of Cadmium in co-adsorption for Fe- GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

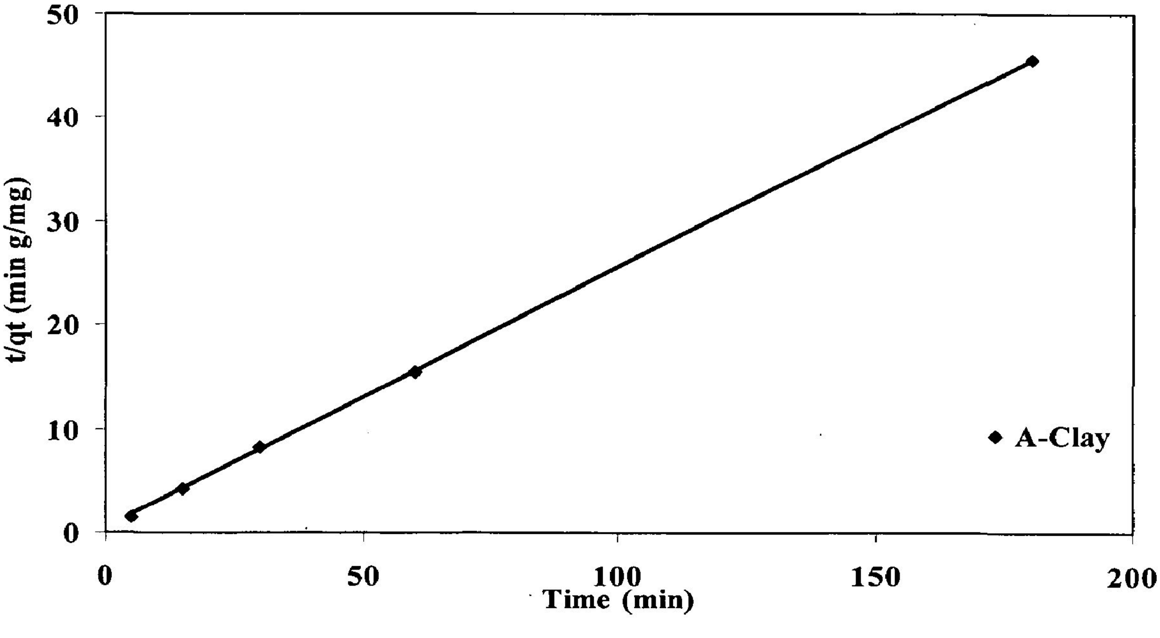


Fig 4.60 Pseudo second order kinetics plot for removal of Cadmium in co-adsorption for A-Clay (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

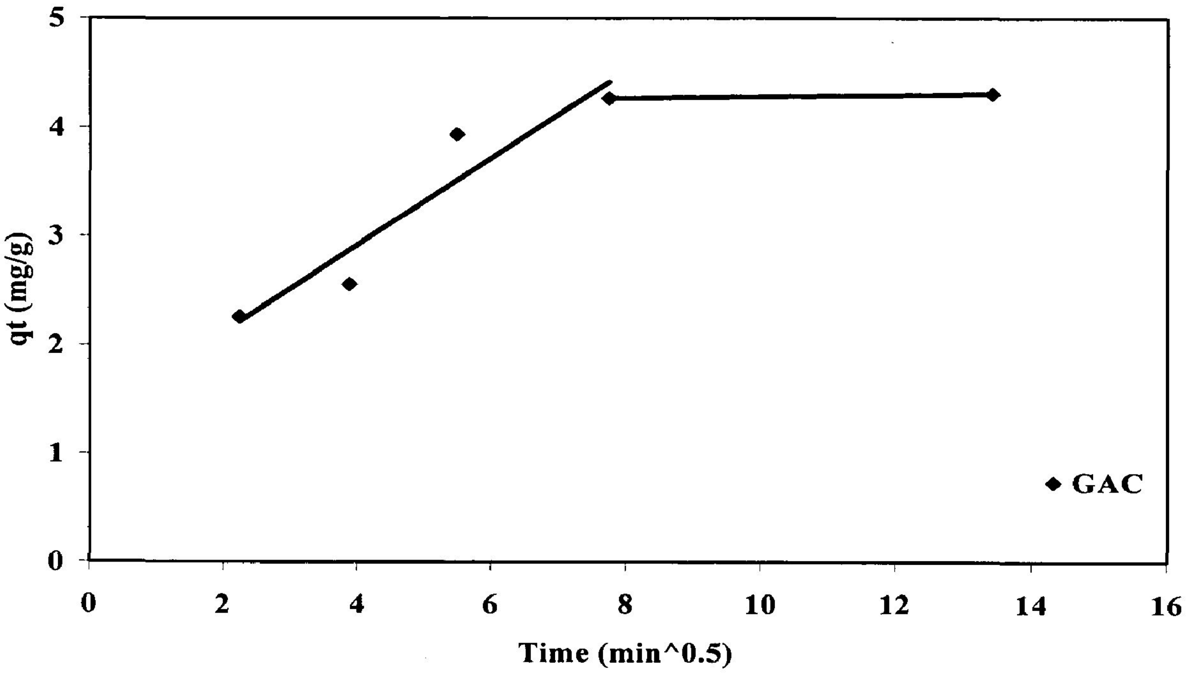


Fig 4.61 Weber Morris kinetics plot for removal of Cadmium in co-adsorption for GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K

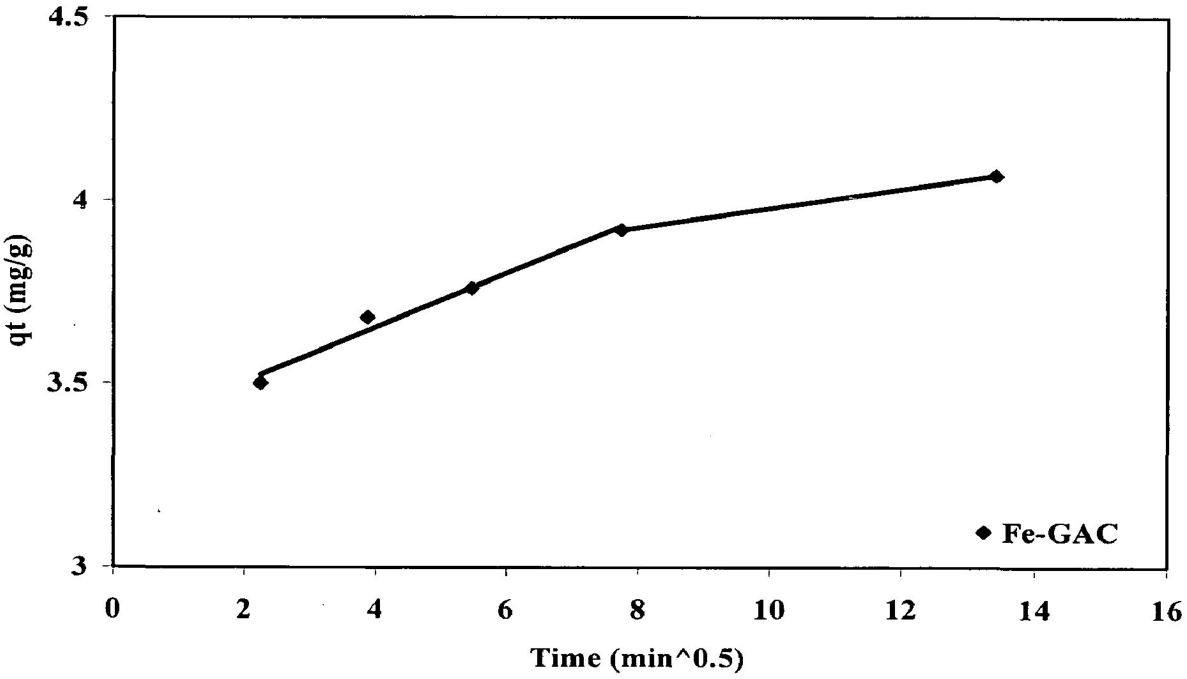


Fig 4.62 Weber Morris kinetics plot for removal of Cadmium in co-adsorption for Fe-GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K

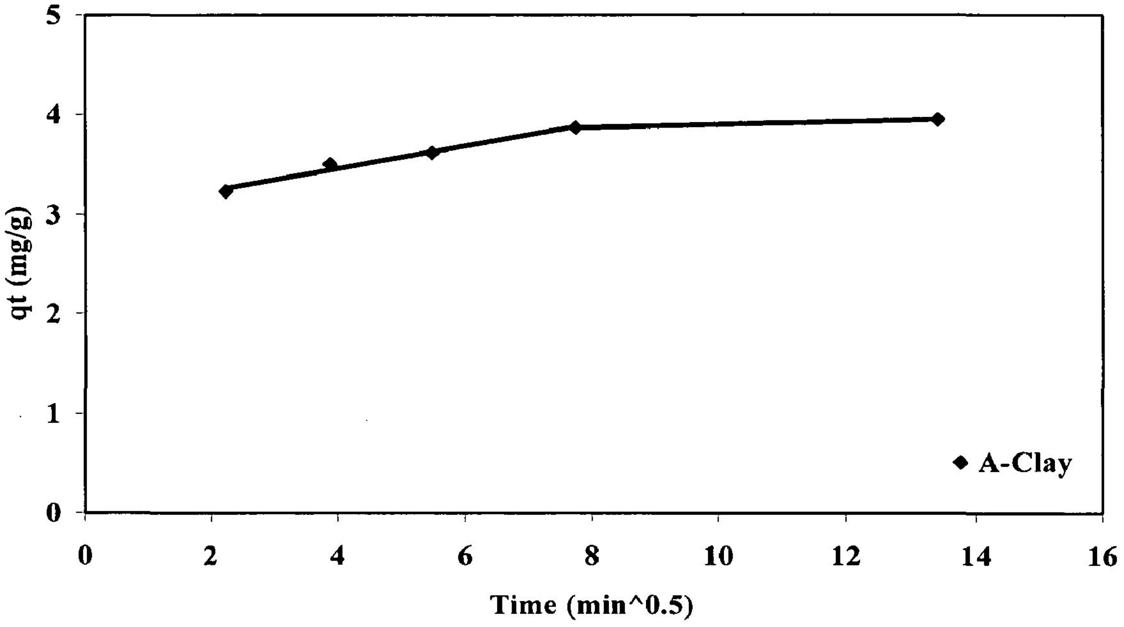


Fig 4.63 Weber Morris kinetics plot for removal of Cadmium in co-adsorption for A-Clay (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

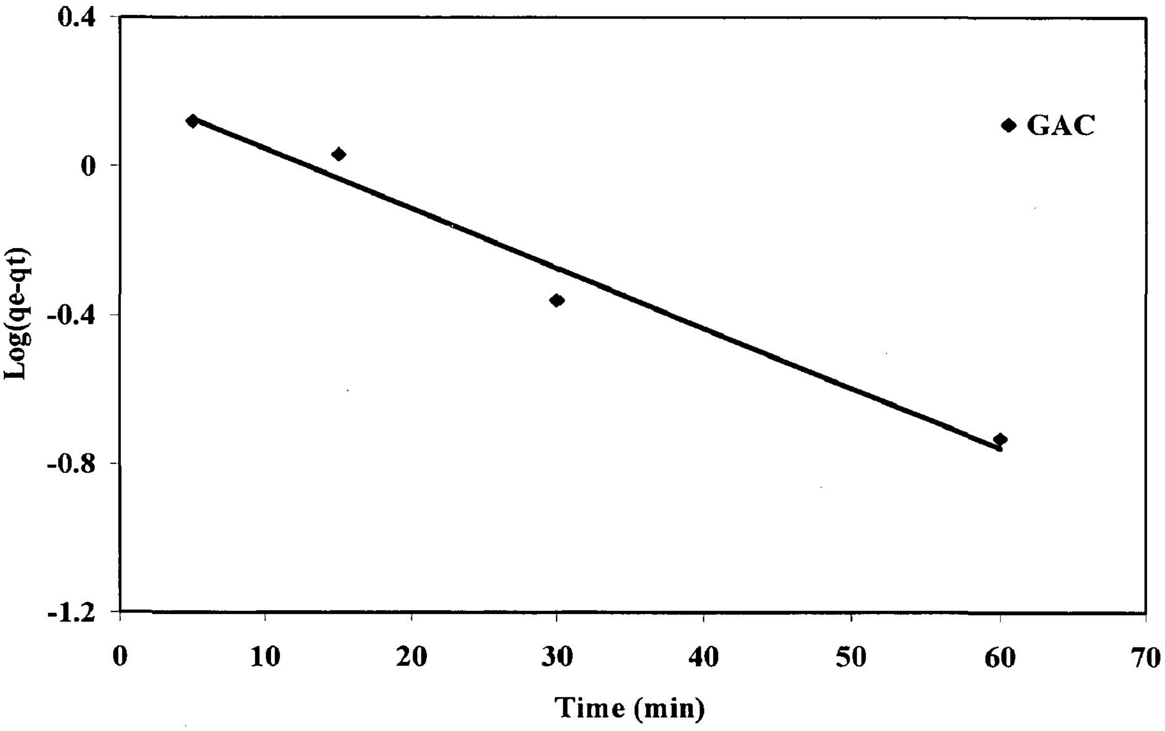


Fig 4.64 Lagergren plot for removal of Humic acid in co-adsorption GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

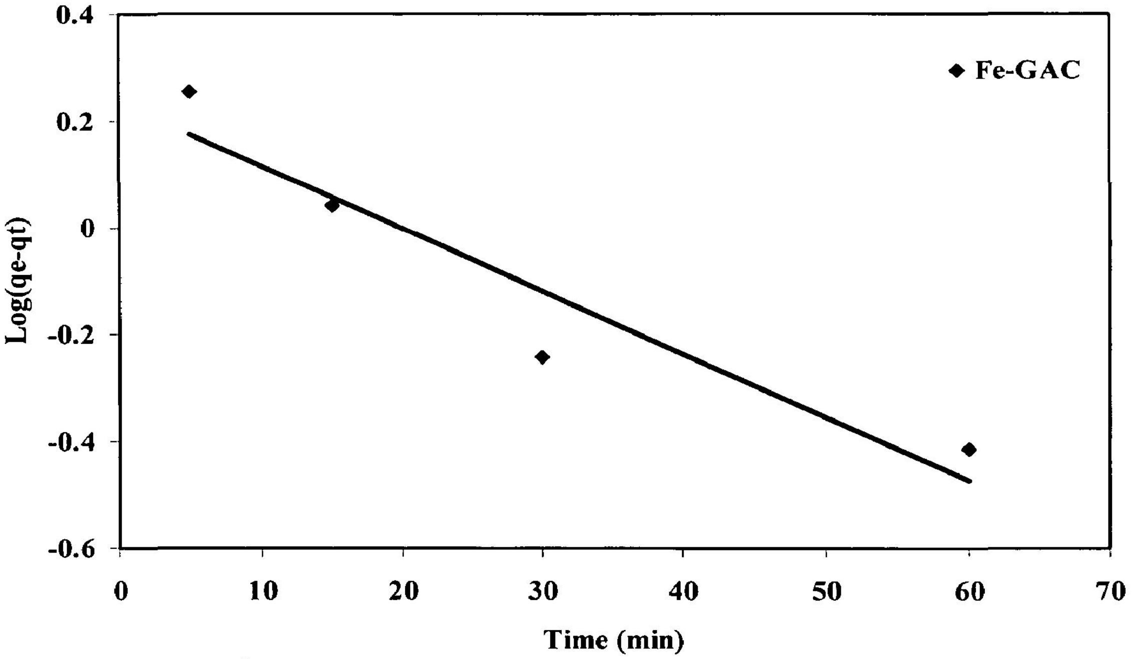


Fig 4.65 Lagergren plot for removal of Humic acid in co-adsorption Fe-GAC
(Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

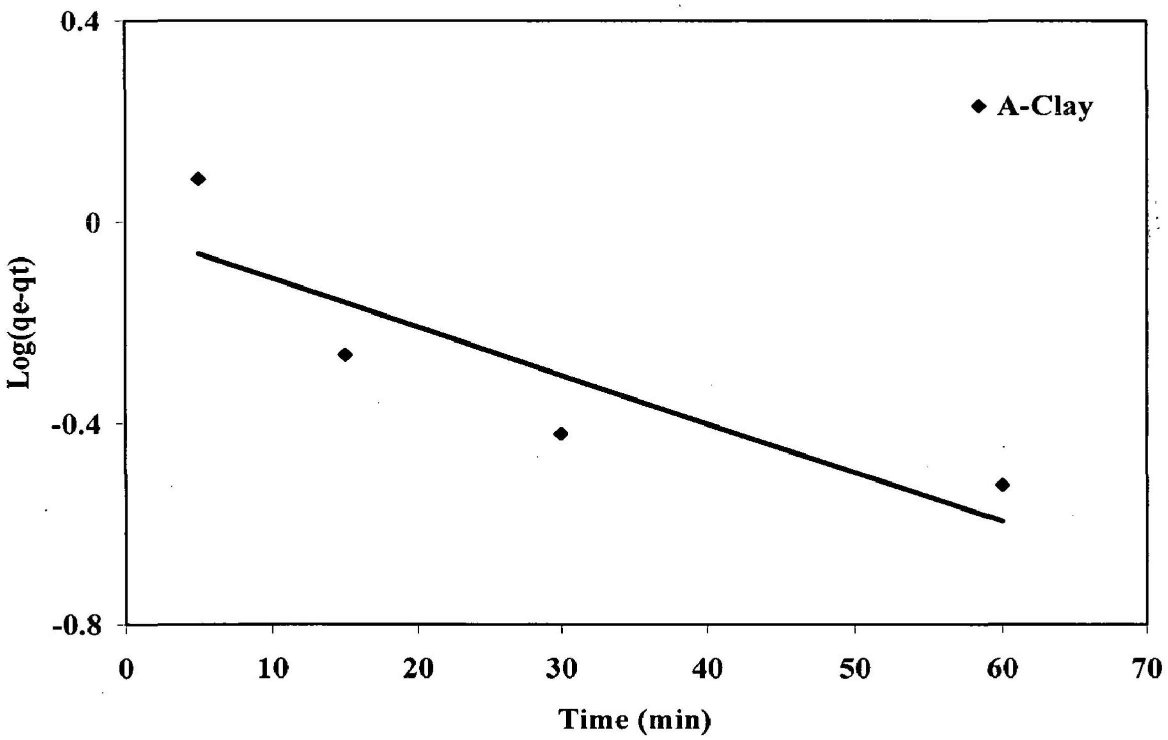


Fig 4.66 Lagergren plot for removal of Humic acid in co-adsorption A-Clay
(Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

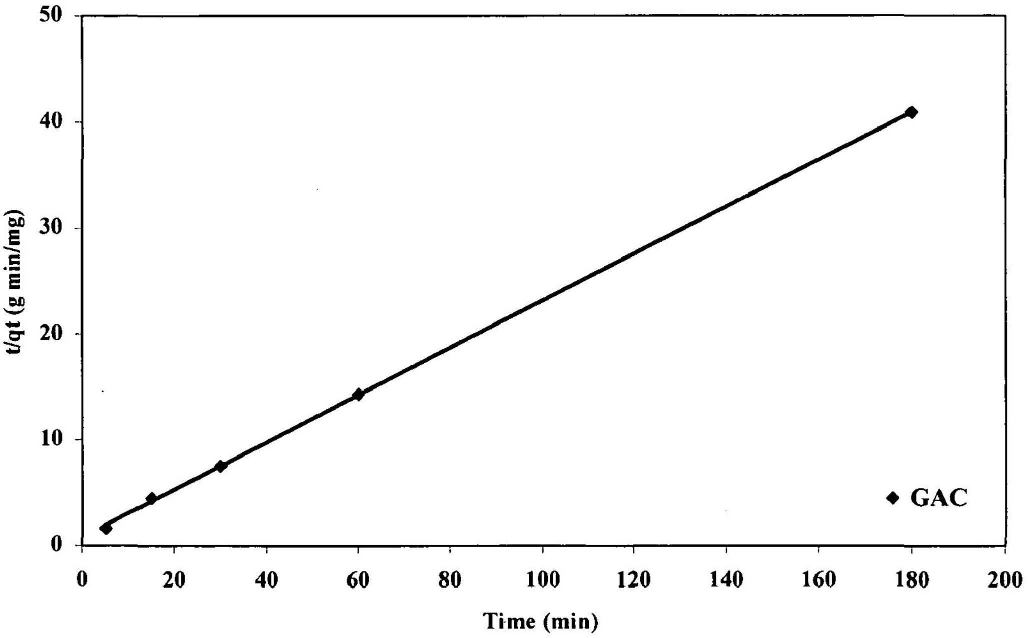


Fig 4.67 Pseudo second order kinetics plot for removal of Humic acid in co-adsorption for GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

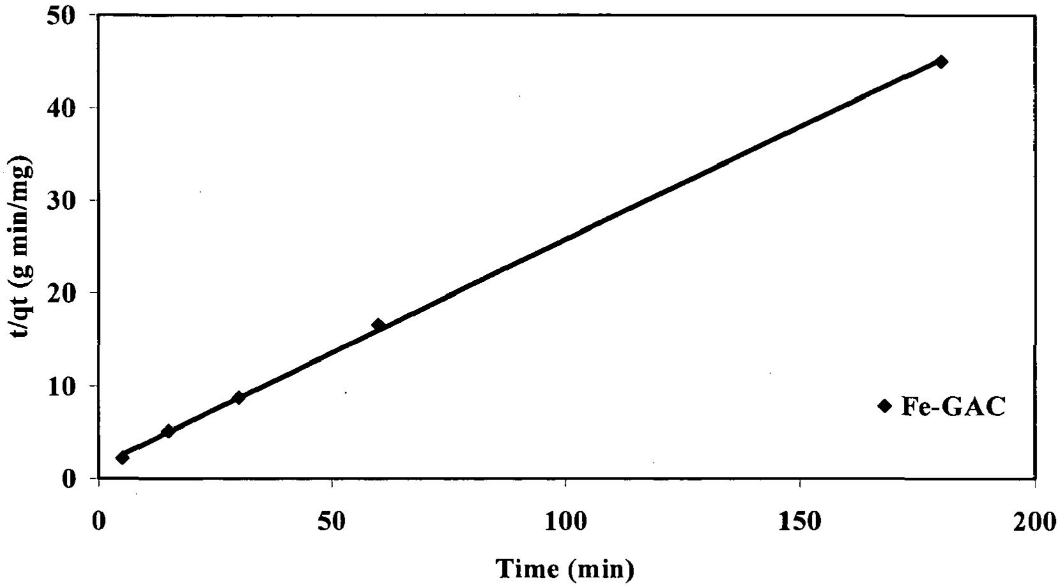


Fig 4.68 Pseudo second order kinetics plot for removal of Humic acid in co-adsorption for Fe-GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

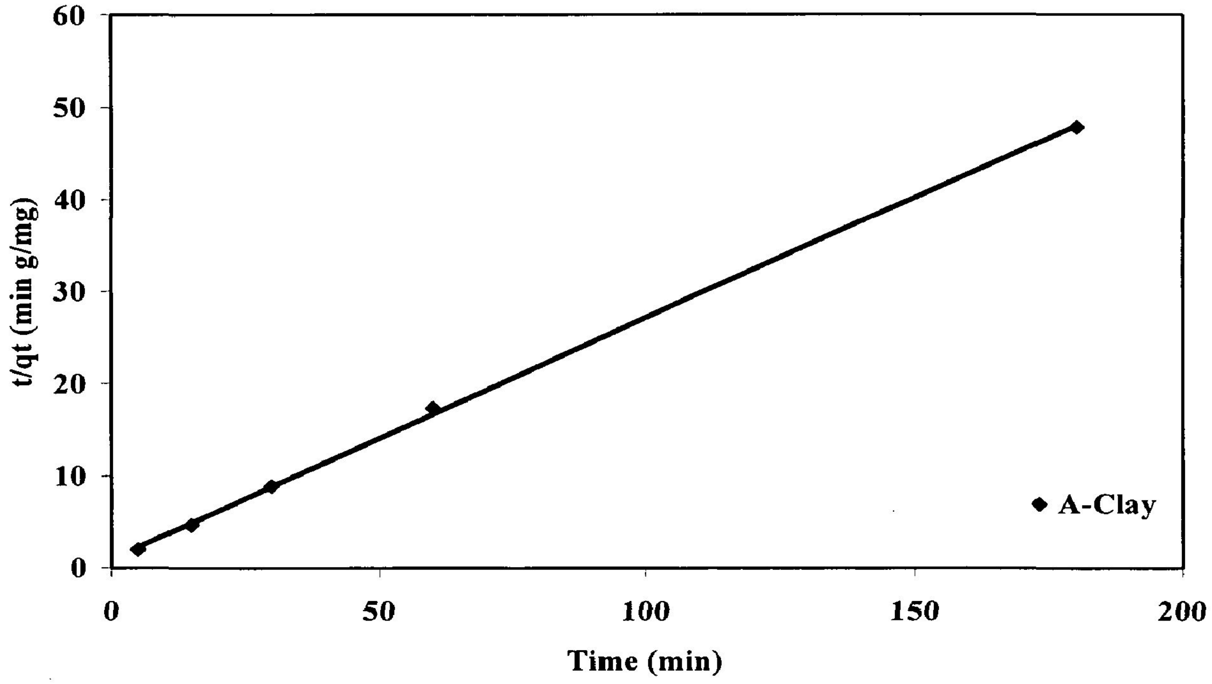


Fig 4.69 Pseudo second order kinetics plot for removal of Humic acid in co-adsorption for A-Clay (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

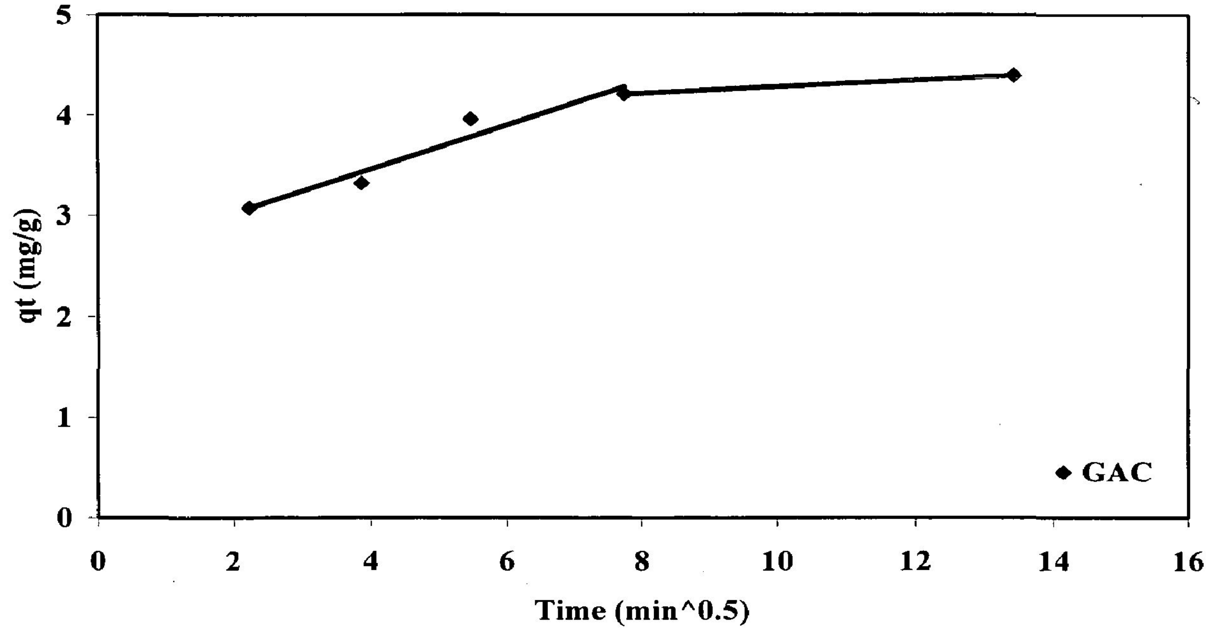


Fig 4.70 Weber Morris kinetics plot for removal of Humic acid in co-adsorption for GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

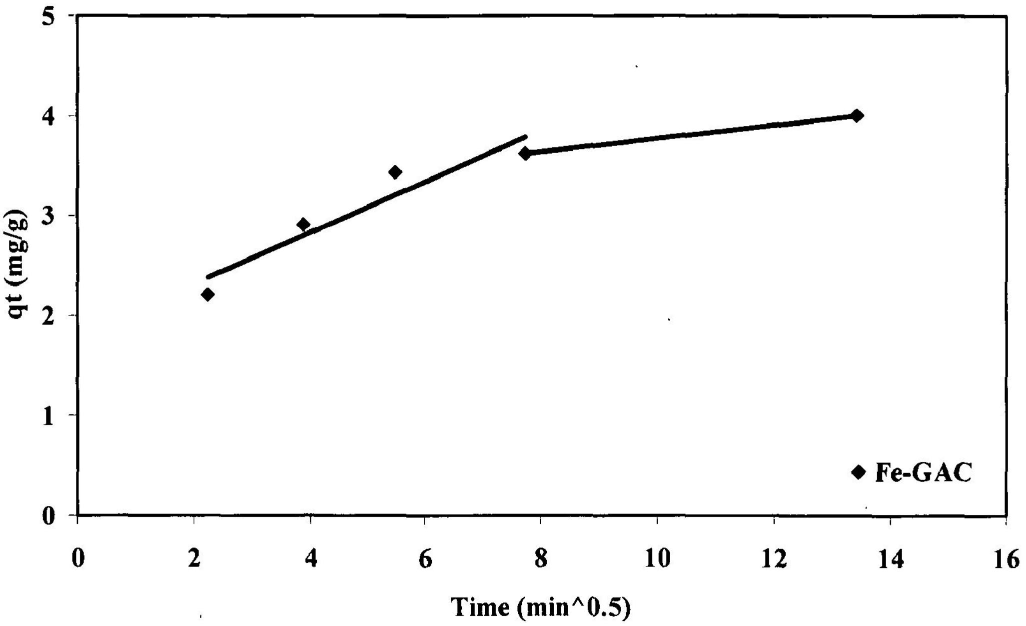


Fig 4.71 Weber Morris kinetics plot for removal of Humic acid in co-adsorption for Fe-GAC (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

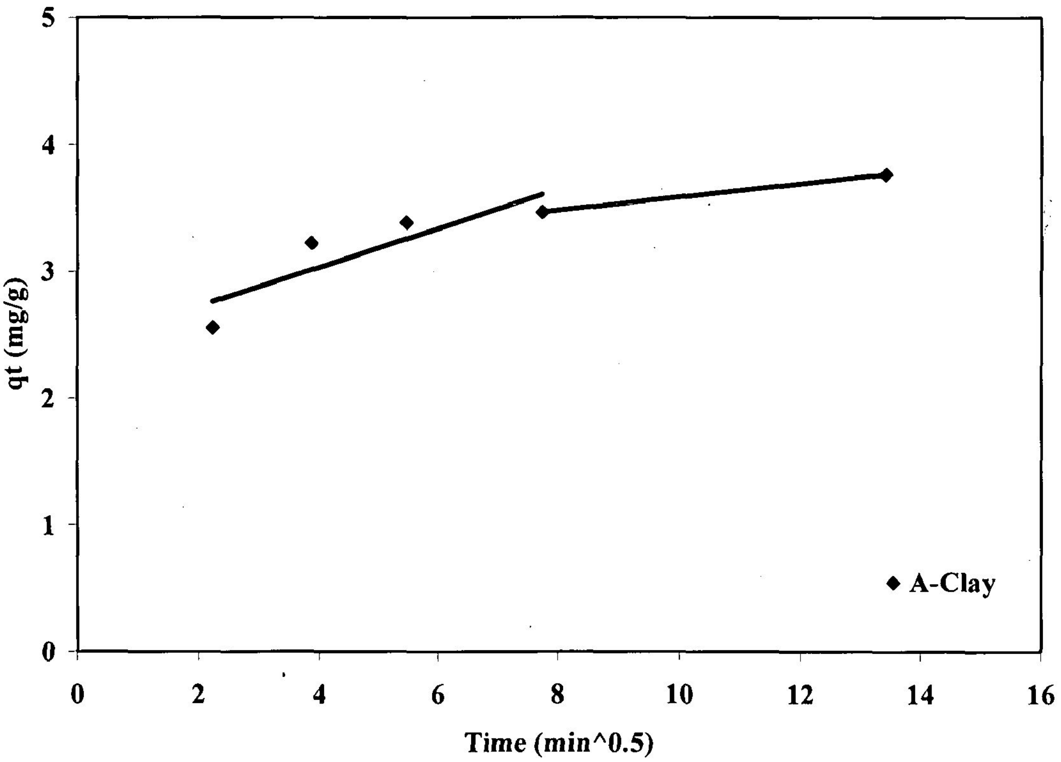


Fig 4.72 Weber Morris kinetics plot for removal of Humic acid in co-adsorption for A-Clay (Co=50mg/l for HA and Cd, adsorbent dosage = 10g/l, pH=5, T=303K)

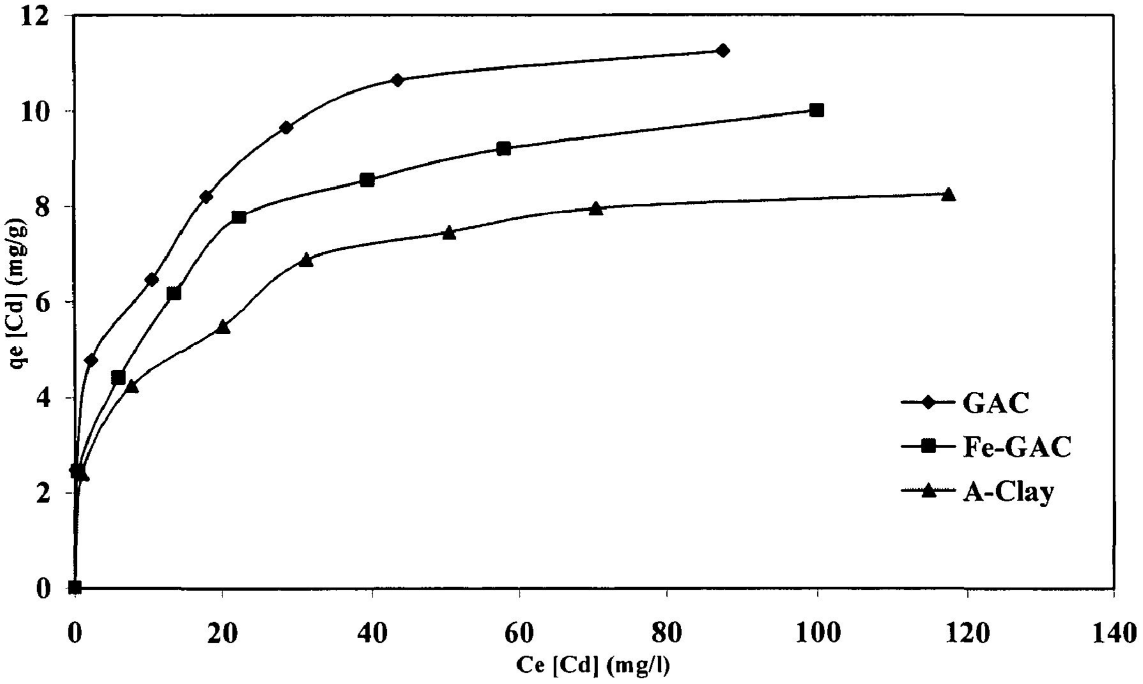


Fig 4.73 Equilibrium adsorption isotherms for cadmium removal using GAC, Fe-GAC and A-Clay (t=5h, pH=6, adsorbent dosage= 10g/l)

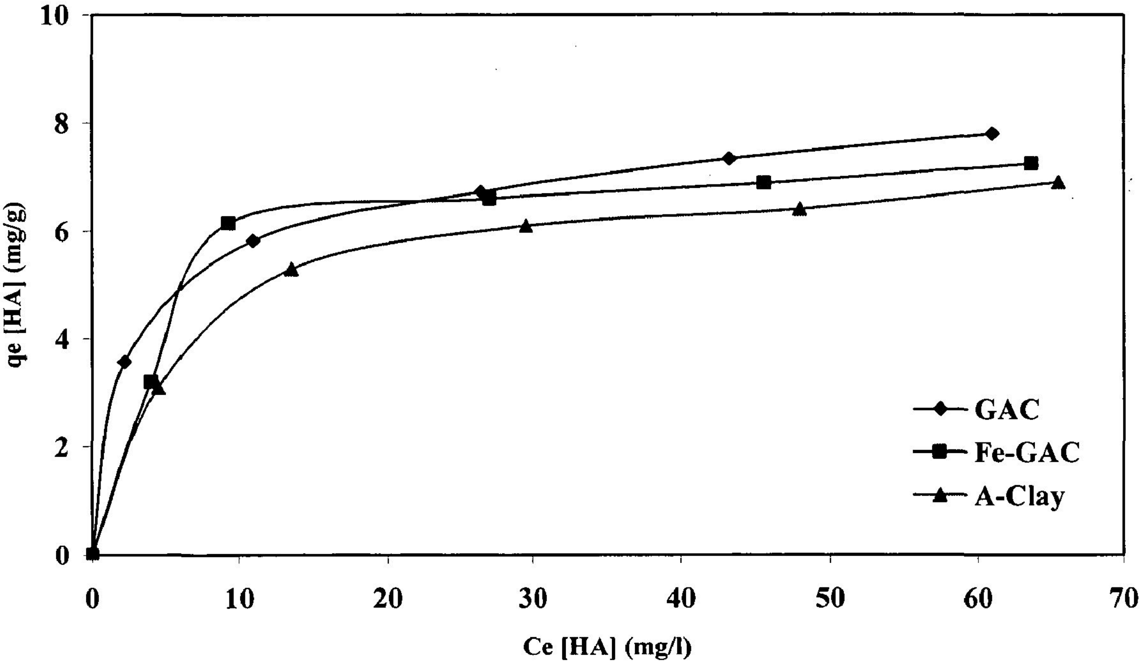


Fig 4.74 Equilibrium adsorption isotherms for humic acid removal using GAC, Fe-GAC and A-Clay (t=5h, pH=5, adsorbent dosage= 5g/l)

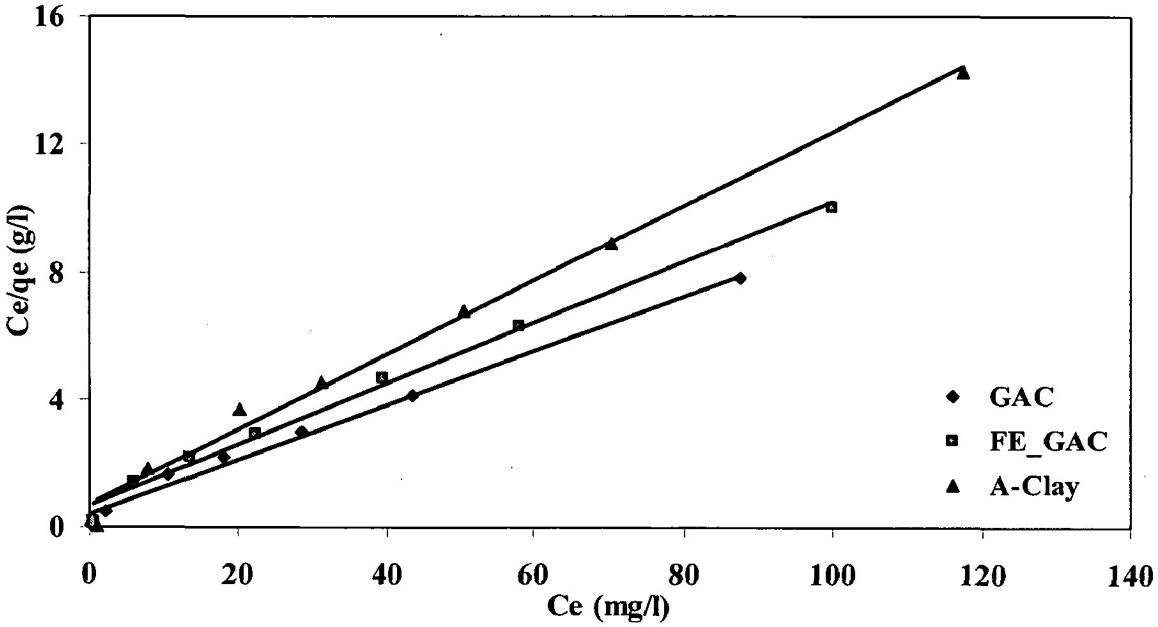


Fig 4.75 Langmuir Isotherms for removal of Cadmium for GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

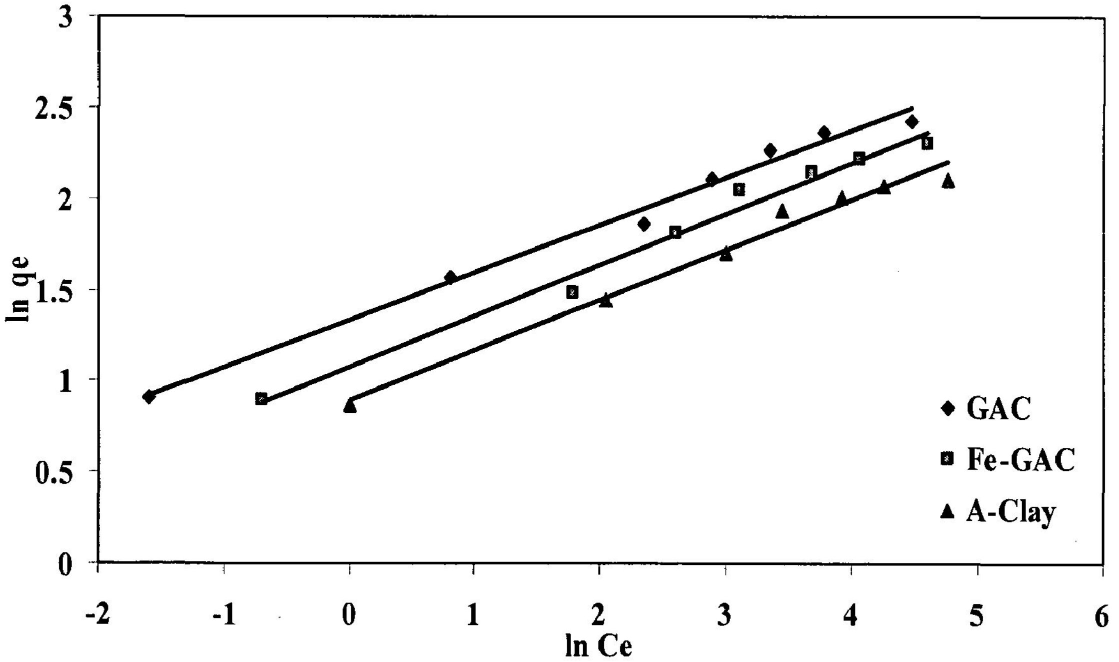


Fig 4.76 Freundlich Isotherms for removal of Cadmium using GAC, Fe-GAC and A-Clay. (Adsorbent dosage = 10g/l, pH=6, T=303K)

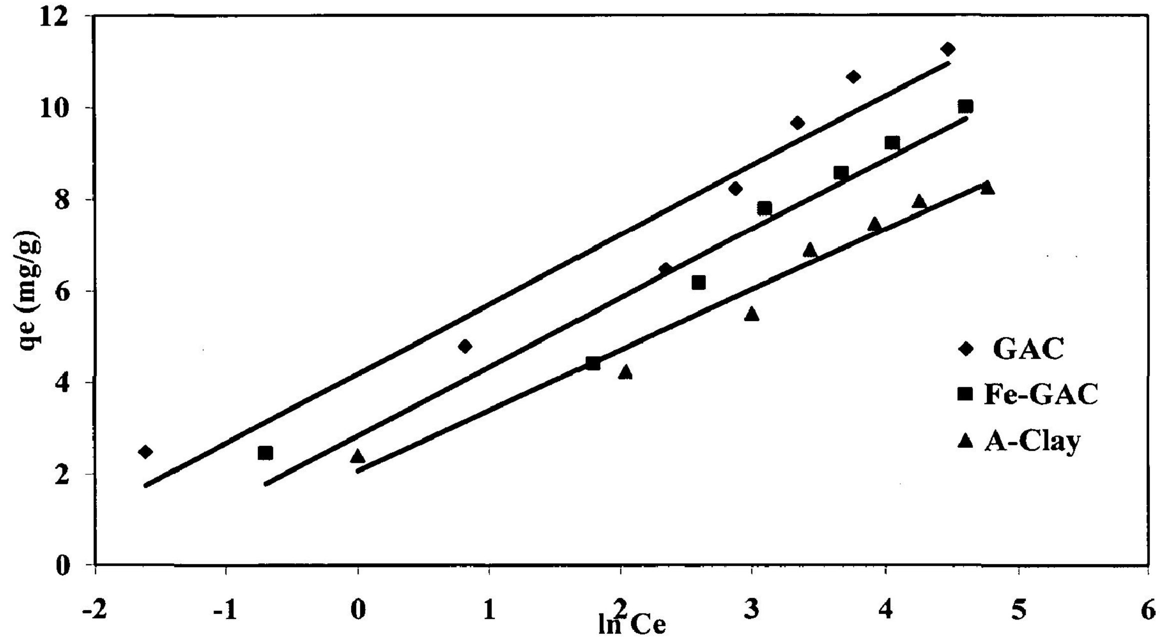


Fig 4.77 Temkin Isotherms for removal of Cadmium using GAC, Fe-GAC and A-clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

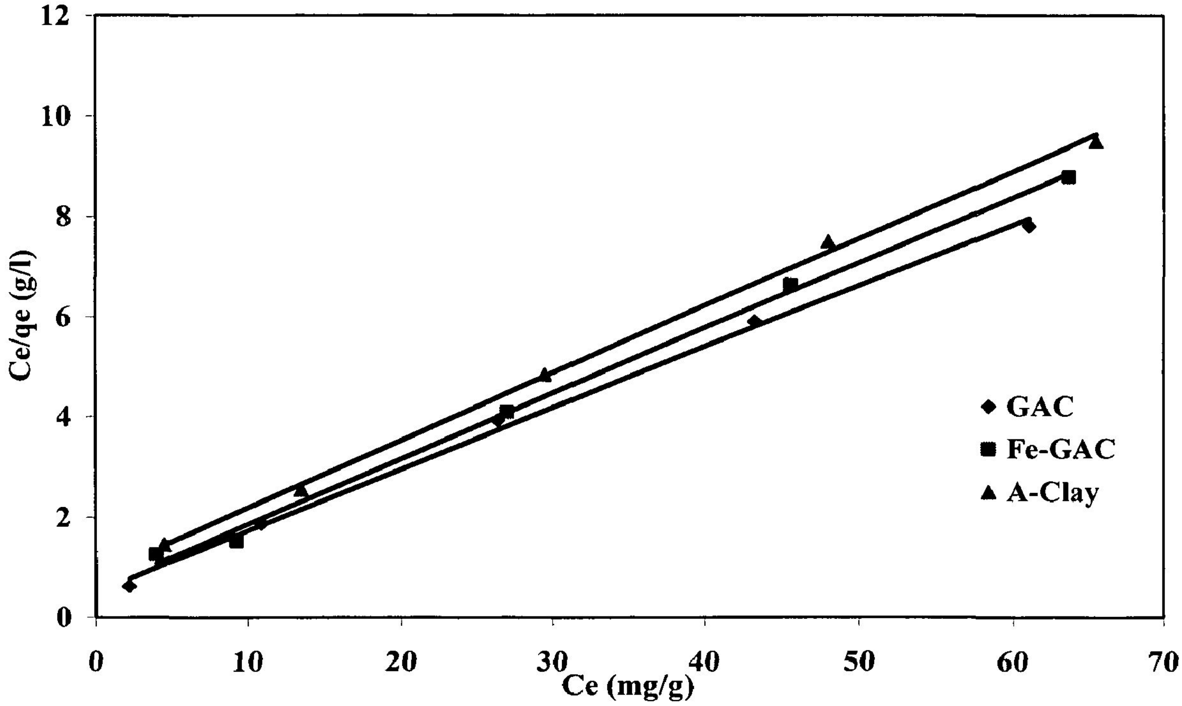


Fig 4.78 Langmuir Isotherms for removal of Humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5g/l, pH=5, T=303K)

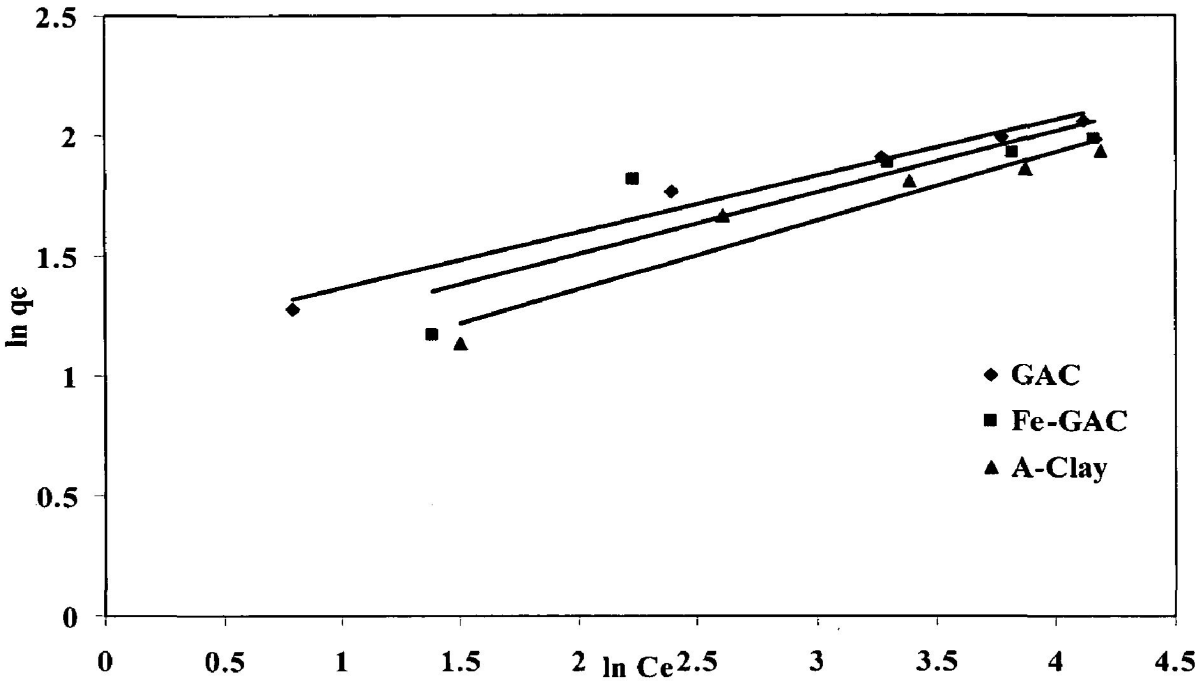


Fig 4.79 Freundlich Isotherms for removal of Humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

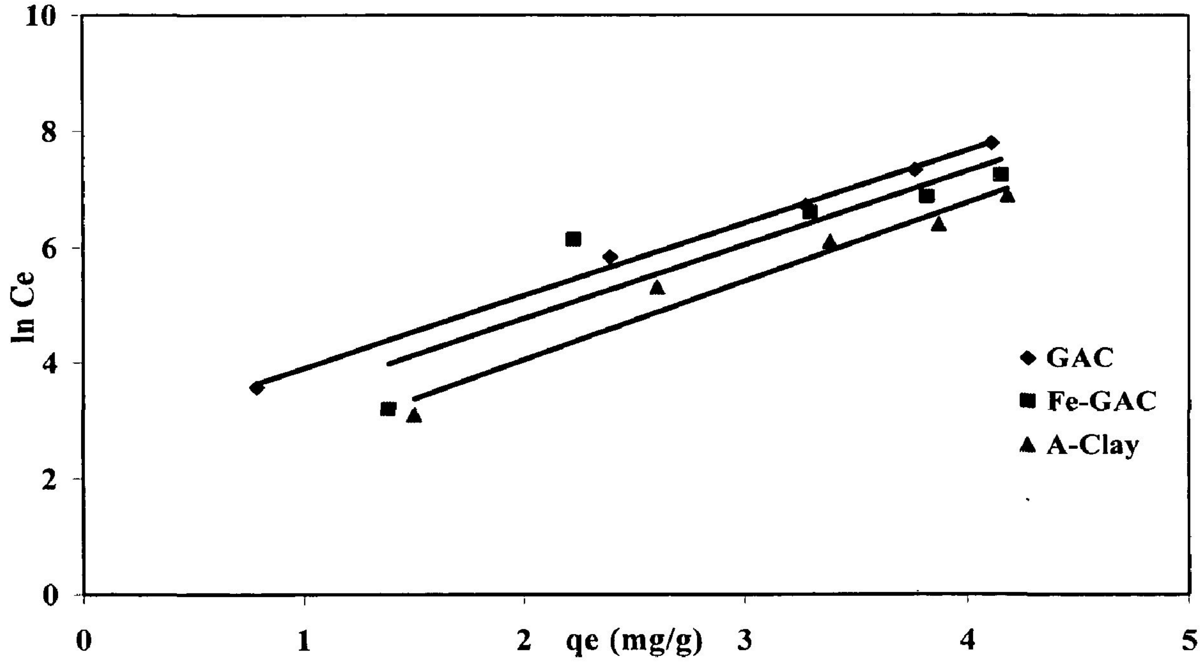


Fig 4.80 Temkin Isotherms for removal of Humic acid for Fe-GAC
(Adsorbent dosage = 5g/l, pH=5, T=303K)

Chapter – V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the present study, the following conclusions can be drawn:

1. The density of A-Clay and Fe-GAC were 1131.8 kg/m^3 and 850.2 kg/m^3, while GAC was 599.32 kg/m^3.
2. The BET surface area of GAC and Fe-GAC were 358m^2/g and 348m^2/g respectively whereas for A-Clay it was 90m^2/g.
3. An amorphous layer was formed on GAC due to the impregnation of Fe^{3+} as evident from SEM.
4. The optimum pH was found to be 5 and 6 for HA and Cd(II) single component adsorption by GAC, Fe-GAC and A-Clay. While for co-adsorption of HA-Cd the optimum pH was 5.
5. The optimum adsorbent dosage for HA and Cd(II) independent removal was found to be 10g/l and 5g/l respectively. For co-adsorption of HA and Cd optimum adsorbent dosage was found to be 10g/l.
6. Co-adsorption of Cd (II) and HA was different from that of independent adsorption.
7. Adsorption capacity of humic acid at optimum conditions was 68%, 65% and 61% and increased to 89%, 83% and 79% for GAC, Fe-GAC and A-Clay respectively in presence of cadmium and was found that humic acid showed better adsorption in presence of cadmium.
8. Cadmium removal was 82.3%, 78.4% and 74% for GAC, Fe-GAC and A-Clay respectively and found that GAC had greater efficiency than the other two adsorbent i.e. Fe-GAC and A-Clay. All the three adsorbents followed the same trend of adsorption as a function of different parameters and the efficiency was in the order GAC>Fe-GAC>A-Clay.

9. The sorption kinetics could be represented by the pseudo-second-order kinetic model.
10. Weber–Morris plot revealed that the intraparticle transport (pore diffusion) was the rate controlling step.
11. Equilibrium data was very well described by the Langmuir isotherm

5.2 Recommendations:

1. Mutli component isotherm such as non-modified Langmuir, modified Langmuir, extended Langmuir, extended Freundlich and Sheindorf–Rebuhn–Sheintuch (SRS) studies should be carried out for this system.
2. Thermodynamic studies for both single and co-adsorption should be carried out.
3. Detailed characterization of adsorbents such as chemical analysis, pore size, pore volume distribution should be carried out.
4. Batch study parameters can be scaled up for the continuous process.

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APPENDIX-A

Table A-1 Calibration curve for Cadmium

Sl. No.	Concentration	Absorbance
1.	0.2	0.019
2.	0.6	0.061
3.	1	0.1021
4.	1.4	0.1433
5.	1.8	0.1872

Table A-2 Calibration curve for Humic acid

Sl. No.	Concentration	Absorbance
1.	2	0.0226
2.	5	0.0703
3.	10	0.1542
4.	25	0.4026
5.	50	0.8002
6.	100	1.5863

Table A-3 Effect of pH on removal of Cadmium using GAC, Fe-GAC and A-Clay (Co= 50mg/l, Adsorbent dosage=5g/l, T=303 K)

Sl. No.	pH	% Removal of Cadmium		
		GAC	Fe-GAC	A-Clay
1.	2	30.4	24.3	15.2
2.	3	41.1	34.88	20.5
3.	4	45.1	40	58.9
4.	5	68	56.4	72.3
5.	6	84	78.7	75.2
6.	7	86.9	80.7	76.7
7.	8	88	81.8	77.7

Table A-4 Effect of pH on removal of humic acid using GAC, Fe-GAC and A-Clay (Co= 50mg/l, Adsorbent dosage=5g/l, T=303 K)

Sl. No	pH	% Removal of Humic acid		
		GAC	Fe-GAC	A-Clay
1.	2	72	67.2	65.2
2.	3	71.6	66.9	64.4
3.	4	70.3	66.1	62.3
4.	5	68.6	63.8	60.8
5.	6	60.8	51.8	56.8
6.	7	52.2	38.7	48.6
7.	8	29.9	29.2	23.6

Table A-5 Effect of pH on removal of humic acid in co-adsorption using GAC, Fe-GAC and A-Clay (Co= 50mg/l, Adsorbent dosage=10g/l, T=303 K)

Sl. No	pH	% Removal of Humic acid		
		GAC	Fe-GAC	A-Clay
1.	2	75.3	65.4	68.4
2.	3	70.9	60.9	65.7
3.	4	68.6	58.9	61.9
4.	5	68.2	58.2	60.9
5.	6	64.6	57.9	56.7
6.	7	52.4	50	45.3

Table A-6 Effect of pH on removal of cadmium in co-adsorption using GAC, Fe-GAC and A-Clay (Co= 50mg/l , Adsorbent dosage=10g/l, T=303 K)

Sl. No	pH	% Removal of cadmium		
		GAC	Fe-GAC	A-Clay
1.	2	36.36	12.5	25.6
2.	3	50.5	55.6	48.5
3.	4	70.1	64.4	60.5
4.	5	83.6	78.5	72.9
5.	6	84	78.8	74
6.	7	84.7	78	72.9

Table A-7 Effect of adsorbent dosage on removal of Cadmium using GAC, Fe-GAC and A-Clay (Co= 100mg/l, pH=6, T=303 K)

Sl No.	Adsorbent dosage (g/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	1	31.1	31.1	37.4	37.4	20.5	20.5
2.	3	17.2	51.65	15.8	47.4	12.6	37.9
3.	5	15.48	76.6	11.58	57.9	9.68	48.4
4.	10	8.59	85.9	7.68	76.8	7.2	72
5.	15	5.89	88.4	5.37	80.5	5	76
6.	20	4.48	89.7	4.1	82.1	3.86	77.2

Table A- 8 Effect of adsorbent dosage on removal of humic acid using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T=303 K)

Sl No.	Adsorbent dosage (g/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	1	9.25	18.5	7.25	14.5	11.55	23.1
2.	3	8.36	50.2	6.8	34.6	6.66	40
3.	5	6.84	68.4	6.32	63.2	5.8	58
4.	10	3.6	72	3.305	66.1	3.07	61.4
5.	15	2.41	72.3	2.25	67.6	2.06	61.8
6.	20	1.825	73	1.74	69.6	1.57	62.8

Table A-9 Effect of adsorbent dosage on removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T=303 K)

Sl No.	Adsorbent dosage (g/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	1	15.75	31.5	9.05	18.1	13.65	27.3
2.	3	8.33	50	6.87	41.2	5.88	35.2
3.	5	5.97	59.7	5.04	50.4	4.21	42.1
4.	10	3.955	79.1	3.535	70.7	3.015	60.3
5.	15	2.81	84.3	2.4	73.6	2.16	64.9
6.	20	2.1	85.3	1.86	74.4	1.685	67.4

Table A-10 Effect of adsorbent dosage on removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T=303 K)

Sl No.	Adsorbent dosage (g/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	1	19.8	39.6	16.85	33.7	28.25	56.5
2.	3	9.41	56.5	7.2	43.7	9.76	58.6
3.	5	6.86	68.6	5.26	53.5	6.66	66.6
4.	10	3.93	78.5	3.26	72	3.81	76.2
5.	15	2.68	80.6	2.4	74.8	2.6	79.4
6.	20	2.1	82.2	1.91	76.2	2.02	81.1

Table A- 11 Effect of initial concentration of Cadmium using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10 g/l, T=303 K, pH= 6)

Sl No.	Initial conc. (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	25	2.48	99.2	2.45	98	2.4	96
2.	50	4.775	95.5	4.4	88	4.23	84.6
3.	75	6.45	86	6.15	82	5.49	73.2
4.	100	8.21	82.1	7.77	77.7	6.88	68.8
5.	125	9.65	77.2	8.55	68.4	7.45	59.6
6.	150	10.65	71	9.2	61.3	7.95	53
7.	200	11.25	56.25	10	50	8.25	41.25

Table A-12 Effect of initial concentration of humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5 g/l, T=303 K, pH= 5)

Sl No.	Initial conc. (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	20	3.57	89.3	3.2	80.1	3.1	77.5
2.	40	5.83	72.9	6.14	76.7	5.3	66.3
3.	60	6.72	56	6.6	55	6.1	50.8
4.	80	7.34	45.8	6.88	43	6.4	40
5.	100	7.8	39	7.25	36.3	6.9	34.5

Table A-13 Effect of Cadmium initial concentration on removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [HA] = 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Initial conc. [Cd] (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	0	3.6	72	3.305	66.1	3.07	61.4
2.	25	4.024	80.48	3.75	75	3.82971	76.5942
3.	50	4.04	80.8	3.836957	76.73913	3.905797	78.11594
4.	75	4.043	80.86	4.014493	80.28986	3.914	78.28
5.	100	4.043478	80.86957	4.025362	80.50725	3.924	78.48
6.	150	4.0993	81.986	4.112319	82.24638	3.941	78.82
7.	200	4.1035	82.07	4.15942	83.18841	4.059	81

Table A-14 Effect of Humic acid initial concentration on removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [Cd] = 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Initial conc. [HA] (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	0	4.77	82	4.4	77.4	4.23	68.8
2.	25	4.14	81.3	3.8	76	3.72	71.9
3.	50	4.29	83.6	4.08	80.7	3.84	76.8
4.	75	4.23	82.6	3.89	77.8	3.51	70.2
5.	100	4.17	80	3.6	72	3.3	65.8
6.	150	3.78	72.9	2.85	57	3.1	62.4
7.	200	3.33	66.6	2.54	50.8	2.85	57

Table A-15 Effect of initial concentration of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [HA] = 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Initial conc. [Cd] (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	25	1.835	73.4	1.565	62.6	1.45	58
2.	50	3.24	64.8	2.89	57.8	2.645	52.9
3.	75	4.0875	54.5	3.6	48	3.4725	46.3
4.	100	4.36	47.6	3.92	39.2	3.56	35.6
5.	150	4.6	29.04	4.2	28	3.69	24.6
6.	200	4.94	24.7	4.52	22.6	3.82	19.1

Table A- 16 Effect of initial concentration of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co [Cd] = 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Initial conc. [HA] (mg/l)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	25	2.19	87.6	1.9	78.1	2	80.2
2.	50	4.228	84.56	3.7	75.3	3.9	78.2
3.	75	5.6	75.1	4.77	63.7	5.5	72.9
4.	100	6.9	69.3	6.08	60.8	6.5	65.4
5.	150	10.1	67.9	8.85	59.06	8.3	55.7
6.	200	11.1	55.4	9.56	47.8	10.1	50.5

Table A-17 Effect of contact time on removal of Cadmium using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10 g/l, T=303 K, pH= 6, Co=100mg/l)

Sl No.	Time (min)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	2	4.62	46.2	3.24	32.4	4	40.8
2.	5	5.24	52.4	3.74	37.4	4.66	46.6
3.	15	5.48	54.8	4.24	42.4	4.96	49.6
4.	30	6.2	62.2	4.9	48.8	5.77	57.7
5.	60	7.65	76.5	7.18	71.8	6.65	66.5
6.	180	8.2	82.3	7.68	76.8	7.1	71
7.	300	8.36	83.6	7.84	78.4	7.43	74.3
8.	420	8.55	85.5	8.11	81.1	7.51	75.1
9.	720	8.64	86.4	8.14	81.4	7.52	75.2

Table A- 18 Effect of contact time on removal of humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5 g/l, T=303 K, pH= 5, Co=50mg/l)

Sl No.	Time (min)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	5	3.52	35.2	3.89	38.9	3.04	30.4
2.	15	4.5	45	4.04	40.4	3.5	35
3.	30	5.09	50.9	5.5	55	4.73	47.3
4.	60	6.02	60.2	5.8	58	5.48	54.8
5.	180	6.71	67.1	6.2	62	5.8	58
6.	300	6.75	67.5	6.45	64.5	6.02	60.2
7.	420	6.8	68	6.51	65.1	6.1	61
8.	720	6.83	68.3	6.58	65.8	6.14	61.4

Table A-19 Effect of contact time on removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Time (min)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	5	3.08	61.6	2.2	44	2.555	51.1
2.	15	3.325	66.5	2.9	58	3.225	64.5
3.	30	3.965	79.3	3.43	68.6	3.39	67.8
4.	60	4.215	84.3	3.615	72.3	3.47	69.4
5.	180	4.4	88	4	80	3.77	75.4
6.	300	4.4	88	4.165	83.3	3.895	77.9
7.	420	4.415	88.3	4.195	83.9	3.91	78.2
8.	720	4.425	88.5	4.21	84.2	3.93	78.6

Table A-20 Effect of contact time on removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co= 50mg/l, pH=5, T=303 K, m=10g/l)

Sl No.	Time (min)	GAC		Fe-GAC		A-Clay	
		qe (mg/g)	% Removal	qe (mg/g)	% Removal	qe (mg/g)	% Removal
1.	5	2.26	45.18	3.5	73	3.225	64.5
2.	15	2.55	49	3.68	73.6	3.5	70
3.	30	3.9	78.72	3.76	75.22	3.615	72.3
4.	60	4.26	85.27	3.92	78.5	3.865	77.3
5.	180	4.32	86.55	4.07	81.4	3.945	78.9
6.	300	4.44	88.8	4.155	83.1	3.99	79.8
7.	420	4.45	89	4.175	83.5	3.95	79
8.	720	4.46	89.2	4.185	83.7	3.96	79.2

Table A-21 Lagergren plot for removal of Cadmium using GAC, Fe-GAC and A-Clay (Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

Sl. No	Time (min)	Log(qe-qt) GAC	Log(qe-qt) Fe-GAC	Log(qe-qt) A-Clay
1.	2	0.572872	0.662758	0.535294
2.	5	0.494155	0.612784	0.44248
3.	15	0.459392	0.556303	0.392697
4.	30	0.334454	0.468347	0.220108
5.	60	-0.14874	-0.18046	-0.10791
6.	180	-0.79588	-0.79588	-0.48149
7.	300	-	-	-

Table A-22 Pseudo second order kinetics for removal of Cadmium using GAC, Fe-GAC and A-Clay (Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

Sl. No	**Time (min)**	**t/qt**	**t/qt**	**t/qt**
		GAC	**Fe-GAC**	**A-Clay**
1.	2	0.4329	0.617284	0.5
2.	5	0.954198	1.336898	1.072961
3.	15	2.737226	3.537736	3.024194
4.	30	4.83871	6.122449	5.199307
5.	60	7.843137	8.356546	9.022556
6.	180	21.95122	23.4375	25.35211
7.	300	35.88517	38.26531	40.37685

Table A- 23 Weber Morris plot for removal of Cadmium using GAC, Fe-GAC and A-Clay (Co=100mg/l, adsorbent dosage = 10g/l, pH=6, T=303K)

Sl. No	**Time (min)**	**Time $^{0.5}$ (min) $^{0.5}$**	**qt**	**qt**	**Qt**
			GAC	**Fe-GAC**	**A-Clay**
1.	2	1.414214	4.62	3.24	4
2.	5	2.236068	5.24	3.74	4.66
3.	15	3.872983	5.48	4.24	4.96
4.	30	5.477226	6.2	4.9	5.77
5.	60	7.745967	7.65	7.18	6.65
6.	180	13.41641	8.2	7.68	7.1
7.	300	17.32051	8.36	7.84	7.43

Table A-24 Lagergren plot for removal of Humic acid using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	Log(qe-qt)	Log(qe-qt)	Log(qe-qt)
		GAC	Fe-GAC	A-Clay
1.	5	0.503791	0.363612	0.440909
2.	18	0.344392	0.334454	0.361728
3.	30	0.209515	-0.1549	0.029384
4.	60	-0.16115	-0.39794	-0.49485
5.	180	-	-	-

Table A-25 Pseudo second order kinetics for removal of Humic acid using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	t/qt	t/qt	t/qt
		GAC	Fe-GAC	A-Clay
1.	5	1.420455	1.285347	1.644737
2.	18	4	4.455446	5.142857
3.	30	5.89391	5.454545	6.342495
4.	60	9.966777	10.34483	10.94891
5.	180	26.82563	29.03226	31.03448

Table A-26 Weber Morris plot for removal of Humic acid using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	Time $^{0.5}$ (min) $^{0.5}$	qt	qt	Qt
			GAC	Fe-GAC	A-Clay
1.	5	2.236068	3.52	3.89	3.04
2.	15	3.872983	4.5	4.04	3.5
3.	30	5.477226	5.09	5.5	4.73
4.	60	7.745967	6.02	5.8	5.48
5.	180	13.41641	6.71	6.2	5.8
6.	300	17.32051	6.75	6.45	6.02

Table A-27 Lagergren plot for removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 10g/l, pH=5, T=303K)

Sl. No	Time (min)	Log(qe-qt)	Log(qe-qt)	Log(qe-qt)
		GAC	Fe-GAC	A-Clay
1.	5	0.311754	-0.30103	-0.14267
2.	18	0.243038	-0.49485	-0.35164
3.	30	-0.4318	-0.61979	-0.48149
4.	60	-1.39794	-1.09691	-1.09691
5.	180	-	-	-

Table A- 28 Pseudo second order kinetics for removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	t/qt	t/qt	t/qt
		GAC	Fe-GAC	A-Clay
1.	5	2.222222	1.428571	1.550388
2.	18	5.882353	4.076087	4.285714
3.	30	7.633588	7.978723	8.298755
4.	60	14.08451	15.30612	15.52393
5.	180	41.86047	44.22604	45.62738

Table A- 29 Weber Morris plot for removal of Humic acid in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	Time $^{0.5}$ (min) $^{0.5}$	qt	qt	Qt
			GAC	Fe-GAC	A-Clay
1.	5	2.236068	2.25	3.5	3.225
2.	15	3.872983	2.55	3.68	3.5
3.	30	5.477226	3.93	3.76	3.615
4.	60	7.745967	4.26	3.92	3.865
5.	180	13.41641	4.3	4.07	3.945

Table A-30 Lagergren plot for removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 10g/l, pH=5, T=303K)

Sl. No	Time (min)	Log(qe-qt)	Log(qe-qt)	Log(qe-qt)
		GAC	Fe-GAC	A-Clay
1.	5	0.120574	0.255273	0.084576
2.	18	0.031408	0.041393	-0.2636
3.	30	-0.36151	-0.24413	-0.42022
4.	60	-0.73283	-0.41454	-0.52288
5.	180	-	-	-

Table A-31 Pseudo second order kinetics for removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	t/qt	t/qt	t/qt
		GAC	Fe-GAC	A-Clay
1.	5	1.623377	2.272727	1.956947
2.	18	4.511278	5.172414	4.651163
3.	30	7.566204	8.746356	8.849558
4.	60	14.23488	16.59751	17.29107
5.	180	40.90909	45	47.74536

Table A- 32 Weber Morris plot for removal of Cadmium in co-adsorption [HA-Cd] using GAC, Fe-GAC and A-Clay (Co=50mg/l, adsorbent dosage = 5g/l, pH=5, T=303K)

Sl. No	Time (min)	Time $^{0.5}$ (min) $^{0.5}$	qt	qt	Qt
			GAC	Fe-GAC	A-Clay
1.	5	2.236068	3.08	2.2	2.555
2.	15	3.872983	3.325	2.9	3.225
3.	30	5.477226	3.965	3.43	3.39
4.	60	7.745967	4.215	3.615	3.47
5.	180	13.41641	4.4	4	3.77

Table A-33 Langmuir Isotherms for removal of Cadmium using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	Ce/q_e (g/l)	Ce (mg/l)	Ce/q_e (g/l)	Ce (mg/l)	Ce/q_e (g/l)	Ce (mg/l)
1.	0.080645	0.2	0.204082	0.5	0	1
2.	0.471204	2.25	1.363636	6	1.820331	7.7
3.	1.627907	10.5	2.195122	13.5	3.661202	20.1
4.	2.180268	17.9	2.870013	22.3	4.534884	31.2
5.	2.953368	28.5	4.619883	39.5	6.778523	50.5
6.	4.084507	43.5	6.304348	58	8.867925	70.5
7.	7.777778	87.5	10	100	14.24242	117.5

Table A-34 Freundlich Isotherms for removal of Cadmium using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	ln q_e	ln Ce	ln q_e	ln Ce	ln q_e	ln Ce
1.	0.9082	-1.6094	0.896	-0.693	0.875495	0
2.	1.5633	0.8109	1.481	1.7917	1.442245	2.041432
3.	1.864	2.3513	1.816	2.6026	1.70298	3.001031
4.	2.105	2.885	2.05	3.1045	1.928677	3.440775
5.	2.2669	3.35	2.145	3.676	2.008274	3.92238
6.	2.3656	3.772	2.219	4.06	2.073234	4.256054
7.	2.42	4.472	2.3035	4.605	2.110277	4.766933

Table A- 35 Temkin Isotherms for removal of Cadmium using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 10g/l, pH=6, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	q_e (mg/g)	ln Ce	q_e	ln Ce	q_e	ln Ce
1.	0.9082	2.48	2.45	-0.693	2.4	0
2.	1.5633	4.775	4.4	1.7917	4.23	2.041432
3.	1.864	6.45	6.15	2.6026	5.49	3.001031
4.	2.105	8.21	7.77	3.1045	6.88	3.440775
5.	2.2669	9.65	8.55	3.676	7.45	3.92238
6.	2.3656	10.65	9.2	4.06	7.95	4.256054
7.	2.42	11.25	10	4.605	8.25	4.766933

Table A- 36 Langmuir Isotherms for removal of Humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5 g/l, pH=6, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	Ce/q_e (g/l)	Ce (mg/l)	Ce/q_e (g/l)	Ce (mg/l)	Ce/q_e (g/l)	Ce (mg/l)
1.	0.616246	2.2	1.25	4	1.451613	4.5
2.	1.86964	10.9	1.514658	9.3	2.54717	13.5
3.	3.928571	26.4	4.090909	27	4.836066	29.5
4.	5.899183	43.3	6.627907	45.6	7.5	48
5.	7.820513	61	8.786207	63.7	9.492754	65.5

Table A-37 Freundlich Isotherms for removal of Humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5g/l, pH=5, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	ln q_e	**ln Ce**	**ln q_e**	**ln Ce**	**ln q_e**	**ln Ce**
1.	1.272698	0.788539	1.163271	1.386438	1.131519	1.504233
2.	1.7632	2.38901	1.815013	2.230246	1.66788	2.60296
3.	1.905286	3.273703	1.887265	3.296179	1.808476	3.384741
4.	1.993546	3.768543	1.928819	3.820304	1.85649	3.871602
5.	2.054337	4.1113	1.981207	4.154615	1.931722	4.182484

Table A-38 Temkin Isotherms for removal of Humic acid using GAC, Fe-GAC and A-Clay (Adsorbent dosage = 5g/l, pH=6, T=303K)

Sl No.	GAC		Fe-GAC		A-Clay	
	q_e (mg/g)	**ln Ce**	**q_e (mg/g)**	**ln Ce**	**q_e (mg/g)**	**ln Ce**
1.	3.57	0.788539	3.2	1.386438	3.1	1.504233
2.	5.83	2.38901	6.14	2.230246	5.3	2.60296
3.	6.72	3.273703	6.6	3.296179	6.1	3.384741
4.	7.34	3.768543	6.88	3.820304	6.4	3.871602
5.	7.8	4.1113	7.25	4.154615	6.9	4.182484