REMOVAL OF TIN FROM SYNTHETIC WASTE WATER

A DISSERTATION

Submitted 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)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"REMOVAL OF TIN FROM SYNTHETIC WASTE WATER"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2006 to June 2007 under supervision of Dr. B. Prasad, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee.

The matter, embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: June 15-2007
Place: 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 and belief.

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ABSTRACT

Most heavy metals can affect microorganism at the concentrations which is normally found in the environment. However, toxicity of metal depends on the physiochemical characteristics of environment such as pH, temperature, pressure and ionic strength. Most studies on the toxic effects of tin have concentrated on organotin compounds. Toxicity studies of inorganic tin compounds are virtually noncoexistent, the earlier works have been proved that inorganic tin species would hydrolyze to form insoluble matter. However, recent works show that as little as 10 mg/l of tin as ($SnCl_2.5H_20$) significantly reduce microbial population. Exposure to inorganic tin occurs in the mining and smelting of tin are in the plating, alloys, toothpaste, ceramics and textile production. Acute gastrointestinal illness follows the intake of food containing high level of tin absorption from the guts less than five percent. Tin deposits in bones, liver, kidney and lymph nodes. Effects of tin on human beings are growth retardation, anemia, and change in enzyme activities. Absorption and excretion of copper, calcium, iron, and zinc leads to morphological change in liver and kidney. In order to recover valuable metal from printed circuit board and tin plating by solvent such as extraction, electrowinning, stripping, and precipitation method have been done at different cost.

The present work is adsorption of Tin(II) ion on granulated activated carbon from synthetic waste water. Proximate, ultimate analysis, particle size and thermo gravimetric analysis of GAC is carried out for detail characterization. Various batch parameters like *optimum pH, contact time, adsorbent dose, temperature etc. studied. The effective* pH found to be 4.0 and kinetic studies show that the adsorption equilibrium reached in 330 minutes. Optimum dose found to be 8 g/l of GAC in solution. Process of tin uptake followed pseudo-second order kinetics and equilibrium isotherm follows Langmuir and Redlich Peterson isotherms. Thermodynamic studies show that tin adsorption on GAC is endothermic in nature. Thermodynamic energy parameters such as ΔG^0, ΔH^0 and ΔS^0 for adsorption estimated based on equilibrium data.

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NAMENCLATURE

C_o	Initial concentration in solution (mg/l)
C_e	Concentration of adsorbate solution at equilibrium (mg/l)
K	Adsorption rate constant (min^{-1})
K_a	Rate constant, liquid/mg of adsorbate, (l/mg)
K_L	Longmuir isotherm constant, (l/mg)
K_T	Tempkin isotherm constant, (l/mg)
K_R	Redlich Peterson isotherm constant, (l/mg)
K_F	Freundlich isotherm constant $(\text{mg/l})^{-1/n}$
n	Freundlich isotherm constant
m	Adsorbent dose in solution (g/l)
q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg/g)
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)
q_m	Limiting adsorbing capacity, (mg/g)
R_L	Separation Factor
K_f	First order rate constant, (min^{-1})
Ks	Second order rate constant, (g /mgmin^{-1})
ΔG°	Gibbs free energy, (kJ/mol)
ΔH°	Enthalpy, (kJ/mol)
ΔS°	Entropy, (J K^{-1}/mol)

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

From antiquity tin was considered precious metal and known as early as 3500 B.C. Gold, silver and copper were metals preceding it. The copper–tin alloy bronze was invented about 2500 B.C. For a very long time tin was the only material for holding foods because it did not influenced the taste and flavor of meat and drinks, therefore tin was in great demand. In 1810 Nicholas Appert had the excellent idea of preserving foods by cooking and sealing them in tinned cans. Increasing tin concentration in human tissues of the inhabitant of *highly civilized countries are mirror images of the expanding consumption of canned food.* Today its is well known that canned foods contain more or less dissolved tin depending on the pH of the contents, storage temperature, and time and whether the food cans are coated or not. Accordingly, the biological effect of inorganic tin, tin compounds or tin complex in animals and humans is of great interest [Blunden and Wallace, 2003].

Many industries produce large quantities of waste streams containing low concentrations of tin along with other metal ions, for example, from processes such as (a) tin electroplating, (b) aluminium anodizing,(c) the manufacture of printed circuit boards. Where the stripping solutions used contain tin along with lead and copper and (d) metal-pickling processes that can lead to solutions containing, for example, tin with lead and indium. The recycling of metals from such solutions is attractive for environmental reasons and for the value of metals. Although most inorganic tin compounds are considered to present no health hazards or environmental problems, marked biocidal properties can be imparted by the formation of tin carbon bonds in triorganotin compounds.

There are many possible methods of tin recovery including ion exchange, solvent extraction and electrolysis. Very little work has been done on the electrolytic recovery of inorganic tin, from dilute solution, in the absence of other metal ions. Most of the work has concentrated on the recovery of tin as tin metal alloys from concentrated mixed metal solutions, for example, tin cadmium, tin antimony, tin bismuth, tin cobalt, tin nickel, tin lead, tin gold, tin silver, tin copper and tin zinc. The performance of an electrolytic cell is dependent on the concentration of metal ions in solution. In the case of dilute solutions, the formation of a diffusion layer near the cathode surface reduces the current efficiency and ultimately increases the cost of final disposal. All the methods of reducing the thickness of the diffusion layer involve agitation that is stirring, hydro cyclone-cell, turbulence promoters, rotating electrodes, 3-D electrodes, fluidized bed electrodes and fluidized bed of inert glass beads. Assessment of these methods in terms of capital cost, ease of operation and product quality indicate that a fluidized bed cell has the best performance. Developments in fluidized bed electrolysis with mesh electrodes and a fluidized bed of inert beads have demonstrated that this type of electro winning can result in efficient effluent purification, and has advantages, including (i) the metal can be extracted from dilute solutions, (ii) the metal is recovered in a directly reusable form, (iii) electrochemical separation of metals can be achieved, (iv) effluent disposal problems are reduced, (v) destruction of organic contaminants is possible [Kimbrough,1976].

1.2 HEAVY METALS

Heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include Tin(Sn), Mercury(Hg), Cadmium(Cd), Arsenic(As), Chromium(Cr), Thallium(Tl) and Lead (Pb).

Heavy metals are part of a large group of air pollutants called air toxics, which upon inhalation or ingestion can be responsible for a range of health effects like nausea, salivation, diarrhea, severe abdominal pain, renal degradation, constipation, anemia muscular cramps, vomiting, etc. Also, these heavy metals have been found to cause cancer, chronic disturbances including break down of the central nervous system and/or peripheral nervous system which may leads to death of human beings. The most important factor that distinguished metals pollutants from other pollutants is that they are not biodegradable pollutants once they have entered the environment.

1.3 SOURCES OF HEAVY METALS

Heavy metals find their way in the environment from a variety of sources-both from natural as well as industrial. But industrial discharges contribute more in the pollution. Large scale of industrial growth has caused 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 ground water level. This percolating water picks up a large number of heavy metals and reaches the aquifer system and hence degrades the ground water quality. The presence of the heavy metal in such cases have always been well defined by all the national and international pollution regulating agencies as given in the table 1.1 Heavy Metals are emitted out from various sources of industries the principal sources of contaminants of water quality are electroplating, mining, petroleum, chemical and petrochemical, steel, smelter plants, pulp and paper, textile, caustic, electroplating and agriculture industries.

Table 1.1: Heavy Metals Generated along with other Pollutants by Various Industries

Waste generators	**Waste types**
Paper industry	Dioxin, Furan, AOX, Chlorinated organics, dyes and pigments containing heavy metals, Corrosive liquids.
Refinery and Petrochemical Industry	Crude tank bottoms, process waste water containing hydro- carbons, sulphur compounds, chlorinated organics, coke containing chlorinated hydrocarbons, oil-containing sludge, oil containing acid, acid tar, sulphur containing residue, spent catalysts containing heavy metals, fluoride from Linear alkyl benzene plant, sludge from effluent treatment plant,
Leather products Industry	Waste toluene and benzene, Sludges containing sulphide and trivalent chromium, chromium (VI) bearing residue.

Metallurgical/Metal manufacturing and Electroplating	Acid, acid residue or acid mixture, alkali, alkali residue or alkali mixture, spent electrolytic solutions from copper, electro refining and electro winning operations, lead ashes, lead slags, lead containing filter material, cadmium or arsenic containing filter material, cupola oven dust, heavy metal containing oven debris arsenic chalk, seleniumor beryllium containing metal waste, metal hydroxide sludge containing chromium, cadmium, copper, zinc, nickel or silver, phosphating sludge, Halogen-free sludge from bath which used organic solvents, sludge from staining bath.
Fertilizer industry	Arsenic sludge, chromium sludge, heavy metals from spent catalyst, acid containing residues,
Pesticides industry	Chlorinated hydrocarbons, DDT, BHC, 2,4-D, malthion, palathion Pesticide *residues, off specification products,* Discarded *containers, synthetic liners,* sludge containing residues of paints and additives, sludge from wastewater treatment, hexa or hexa containing residue made with hexachlorocyclohexane or hexachlorobenzene.
Vehicle maintenance shops	Heavy metal paint wastes, Ignitable wastes, Used lead acid batteries, Spent solvents, oil water mixtures, oil containing sludge, oil emulsion, filters and filter material which have organic liquids on them. e.g. mineral oil, synthetic oil and organic chlorine compounds. Spent oil and other spent lubricating and system oil.
Electroplating Industries	Waste water may contain hazardous waste and heavy metals like Cd, Cr, Hg, Ni, Zn, Pb etc, voc and mist are goes to air
Dye and Paint industry	Process sludge, sludges from waste water treatment, Filtration residue, and heavy metals Containing Pb, Zn, Cu.
Textile industry	Sludge containing unreacted dyes, textile chemical residues, chlorinated

	organics
Printing industry	Printing ink residue, lacquer residue, liquid toner residue, etching fluid residue, dispersive oil residue, oxidizing agent residue, Heavy metal solutions, Waste inks, Spent solvents, Spent electroplating wastes
Cosmetics manufacturing	Heavy metal dusts, Ignitable wastes, Flammable solvents, Strong acids and bases
Chemical manufacturers	Strong acids and bases, Spent solvents, Reactive wastes, spent catalysts, refractory organics containing chlorinated compounds, phenol etc.

1.4 ELECTROPLATING WASTE

In comparison with other industries the electroplating industries generate little amount of such wastewater which are highly toxic in nature because of the presence of metals and acids along with dangerous chemicals. It is one of the largest users of many toxic chemicals in the world. Electroplating industry alone is the second largest end user of nickel and nickel compounds, the third largest end user of cadmium and cadmium compounds, and the user of a substantial amount of chromium and tin. The wastewater is thus very harmful to aquatic life, animals, human beings and environment and it gives rise to pollution of surface and ground water. Many industries like automotive, electronics, aerospace, hardware, jewelry, heavy equipment, appliances, tires and telecommunication, use metal electroplating in their manufacturing processes.

1.5 OBJECTIVE OF THE PRESENT STUDY

The objective of the present study is to investigate the removal of tin from synthetic waste water using granulated activated carbon as adsorbent. The whole study deals with various parameters dealing with adsorption and its kinetics. The experiments were carried out to study the following:

1. Characterization of granulated activated carbon, which includes particle size distribution, proximate and ultimate analyses and chemical analysis of ash.
2. Study the effect of adsorbent dose, initial tin concentration, contact time, pH and temperature on the removal of tin in a batch reactor.
3. Study the kinetics of tin adsorption using Lagergren, pseudo first and second order and Weber- Morris models.
4. Analysis of the equilibrium data of tin adsorbent into GAC using Freundlich, Langmuir, Redlich-Peterson, and Temkin isotherms and
5. Performing error analysis to find the best fit isotherm.

CHAPTER 2

LITRATURE REVIW

2.1 GENERAL

A compressive review is presented here on various reported out for the removal of various pollutant viz. heavy metals using adsorbent mainly by low cost adsorbent as well as high cost adsorbent like activated carbon and using of bagas fly ash and rice husk ash as adsorbent for removal of any substance .The literature review comprises following in the table 2.1.

Table2.1: Studies on removal of different pollutants from waste water using low cost adsorbent

S.No	Author	Adsorbent	Adsorbate	Operating condition	Conclusion
1.	Varshney et al. (2007)	Cation exchanger	$SnP0_4$ (IV)	Batch	1. Tin(IV) phosphate (SnP), a non-fibrous ion exchanger, for alkaline earths and heavy metal ions in different acidic media. 2. 200 mg of the exchanger in H ion form were added to a mixture containing 18mL of the acid solution and 2mL of the metal ion solution. 3.The content kept at 24 hr 4. distribution coefficients (K_d) of metal calculated by the formula: $K_d = \frac{I-F}{F}\frac{V}{M}(ml/g)$ 5. Fe(III), Co(II), Cu(II), Cd(II), Hg(II) and Pb(II) metal ions are totally adsorbed on the surface of SnP exchanger
2.	Fan and anderson (2005)	Mn oxide-coated granular activated carbon	Cu(II) and Cd(II)	Batch and column	1. Mn adsorb at 27 mg per g of GAC. 2. Removal capacity of Cu (II) 86.7 mg/g was three times more than Cd(II) 28.7mg/g. 3. pH used for metal removal 8, 6 ,5.8, 5. 4. Langmuir isotherms fitted
3.	Garcia et al. (2005)	Electrochemical	Sn and Pd	-	1.They used electrode of Ag/Agcl and voltage applied for both Sn and palladium 0.6 volt 2.Reactor used of pyrex glass of volume 250 cm^3 3. Mixture of both metal first deposited palladium metal on cathode 4. Recovery of tin (74%) and palladium (72%). 5. Process was operated on ambient temperature 6.Total recovery of tin is possible at current efficiency at 100%

4.	Gulnaziya et al. (2005)	Palm shell activated carbon	Pb	Batch	**1.** The adsorption experiments carried out at pH 3.0 and 5.0.and was maximum at pH 5 **2.** Addition of boric acid to the solution of lead improved total metal uptake especially at pH 5.0 **3.** Malonic acid presence resulted in the substantial decrease of metal uptake. **4.** The Langmuir isotherm used to estimate the maximal adsorption capacity of PSAC to remove lead ions.
5.	Karthikeyan et al. (2005)	Hevea Brasilinesis (Rubber wood) sawdust activated carbon	Cr(VI)	Batch	**1.** Cr(VI) removal is pH dependent and found to be maximum at pH 2.0 **2.** The Langmuir, Freundlich and Temkin isotherm used, Langmuir *isotherm shows better fit than* Freundlich and Temkin isotherm in the temperature range studied. **3.** Increases in adsorption capacity with increase in temperature indicate that the adsorption reaction is endothermic nature. **4.** Thermodynamic parameters like standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were evaluated. **5.** Pseudo first-order and pseudo second-order models analyzed the adsorbent, Pseudo second-order model was found to explain the kinetics of Cr(VI) adsorption most effectively. **6.** The activated carbon from rubber wood s proved to be a good adsorbing medium for Cr(V
6.	Kobya et al. (2005)	Activated carbon prepared from apricot stone	Ni(II), Co(II), Cd(II), Cu(II), Pb(II), Cr(III) and Cr(VI)	Batch	**1.** Adsorption capacities for the metal ions were obtained in the descending order of Cr(VI) > Cd(II) >Co(II) > Cr(III) > Ni(II) > Cu(II) > Pb(II). **2.** Cr (VI), the amount adsorbed decreased from 34.70 to 7.86 mg/g as the pH increased from 1 to 6.

					3. As the pH increased from 1 to 6, the amount adsorbed increased from 3.08 to 33.57 mg/g for Cd(II), 7.74 to 30.07 mg/g for Co(II), 2.83 to 29.47 mg/g for Cr(III), 2.50 to 27.21 mg/g for Ni(II), 4.86 to 24.21 mg/g for Cu(II) and 6.69 to 22.85 mg/g for Pb(II), **4.**The pH experiments also showed maximum removal of 99.99% for Cr(VI) at pH 1, 99.86% for Pb(II) at pH 3, 99.67% for Cd(II) at pH 5, 99.11% for Co(II) at pH 6, 98.56% for Cr(III) at pH 4, 97.59% for Ni(II) at pH 4 and 96.24% for Cu(II) at pH 4, respectively.
7.	Mohanty et al. (2005)	Activated carbon developed fromTerminalia arjuna(agricultural waste) ,nuts activated with zinc chloride	Cr(VI)	Batch	**1.** The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. **2.** The maximum removal of chromium was obtained at pH 1.0 (about 99% for adsorbent dose of2 g/l and 10 mg/l initial concentration). **3.** The kinetic data best fitted to the Lagergren pseudo-first-order model. **4.** The cost of removal is expected to be quite low, as the adsorbent is cheap and easily available in large quantities
8.	Bazan (2004)	Electrochemical	Sn	-	**1.** The performance of a batch undivided electrochemical reactor with a rotating cylinder electrode of expanded metal sheets for the removal of tin from synthetic sulfate solution is studied. **2.** For a cathode potential of -0.65 V vs SCE at 500 rpm, the tin concentration decreased from 393 to 94 mg/l after 30 min of electrolysis with a specific energy consumption of 3.93 kWh/kg) and a normalized space velocity of 1.27/h. **3.** The results suggest that the applied potential must represent a compromise between the increase in

					space time yield or normalized space velocity and the increase in the specific energy consumption.
9.	Bishnoi et al.(2004)	Activated rice husk carbon and activated alumina	Cr(VI)	Batch	**1.** The smaller the particle size, greater is the adsorption capacity, as evident from 93.28% and 81.78% Cr(VI) removal with 0.3 and1.0 mm ARH, respectively **2**. The efficiency ARH was fairly high at pH 2whereas with AA it was at pH 4. 3. Adsorption increased with increasing dose and time at initial stages and then it became somewhat constant due to attainment of equilibrium. **4.** The adsorption pattern followed the Freundlich isotherm and the adsorption efficiency for different adsorbents was AA>ARH (0.3 mm) >ARH (1.0 mm).
10.	Kim (2004)	Granular activated carbon	Fe (III)	Batch	1.The absorbability of ferric ion increased with temperature and the estimated activation energy for adsorption substantiated the aspect of physisorption. **2.**Equilibrium adsorption observed to increase as the pH rise. **3.**The specific surface area of activated carbon was increased by swelling, resulting an increase in equilibrium adsorption. **4**.The activation energy for adsorption was approximately 2.23 kJ mol/l, which implied that Fe mainly physically adsorbed on activated carbon.
11.	Man-Seung et al. (2003)	Electro wining	Cu. Sn, Pb, Fe	Batch	1. Electrowinnig process was carried out in a 0.5-L vessel. **2.**The concentration of nitric acid in synthetic etching solution was 250 g/l(30-40 g/lCu,30-40 g/l Sn, 30-40 g/l Fe) 3. McCabe Thiele method was obtained for a feed solution the

					concentration of nitric acid in raffinate would be 13 g/l. **4.** Pure copper metal was obtained by electro winning from the etching solution after acid was removed by solvent extraction **5.**Tin ions were precipitated at 80 ^{0} c by adjusting the solution pH with $Pb(OH)_2$ **6.** By adding sodium pyrosulphide as reducing agent lead metal with purity of 99 % was obtained from the solution by concentration with iron powder
12.	Meena et al.(2003)	Carbon aerogel	Cd(II), Pb(II), Hg(II), Cu(II), Ni(II), Mn(II) and Zn(II)	Batch	**1.**The adsorption parameters determined using both Langmuir and Freundlich isotherm models. **2.**Thermodynamic constant (K_{ad}), standard free energy (ΔG_0), enthalpy (ΔH_0) and entropy (ΔS_0) calculated for predicting the nature of adsorption. **3.** The adsorption follows first order kinetics **4.** Agitation time was 48 hrs **5.** Pb(II) 93% removal at pH 7 and for Cd (II) 91.3% removal at pH 4.other metal at pH 6 **6.** Process was endothermic
13.	Adhoum and monser (2002)	Impregnated activated carbon	CN	Batch	**1.** The results indicate that carbon–Ag impregnation shown to have a cyanide removal capacity of nearly two times that of carbon–Ni impregnation and of four times that of plain activated carbon. **2.** The Langmuir and Freundlich isotherm models employed for experimental results obtained from the adsorption of Ag+ and Ni+ on plain activated carbon. **3.** The Langmuir adsorption isotherm of Ag+ and Ni+ on plain carbon gave a correlation coefficient higher than 0.99 and a percent deviation of 3.7 and 4.0%, respectively. **4.** The capacity of Ag-

					impregnating, Ni-impregnating and plain, carbon was 26.5, 15.4, and 7 mg/l carbon, respectively.
14.	Kadirvelu. et al.(2002)	Activated carbon from coconut coir pitch	Cd (II)	Batch	**1.** The Longmuir and freundlich isotherms used. **2.** Percent removal increase at pH (2-4) and temp.30 degree centi and remained constant at pH 10 **3.** Adsorption capacity was 93.4 mg/g Cd at pH=5.0 4. Agitation time was 2 hr
15.	Chaudhary et al. (2001)	Electrochemical	Sn	-	**1.**This work a 10 dm^3 capacity fluidized electrochemical cell used **2.**Two titanium mesh cathode and three iridium oxide –coated titanium mesh anode used **3.**Electrolyte solution were prepared from tin chloride crystal **4.** Tin metal ions was analysis by AAS **5.** The percentage removal of tin increase with increasing acid concentration from 0.2 to 0.4 mol dm^{-3} but further increase acid concentration from 0.4-0.48 moldm^{-3}. **6.** The higher the current density the greater the percentage removal of tin **7.**The greater electrode spacing increase the removal of tin and current efficiency
16.	Selvi and kadirvelu(2001)	Activated carbon from coconut saw dust saw mill	Cr(VI)	Batch	**1.** Maxi equilibrium attained at in 180 min **2.** Removal decrease 98.84% to 84.06% with concentration increase from 5 to 20 mg /l 3. Initial Cr concentration decreases the percent adsorption. 4. adsorption capacity is 3.46 mg /g at pH - 3.0 5.High adsorption occur at pH from3 to 5
17.	Jacome et al. (2000)	Activated carbon	Zn(II)	Batch	**1.**Removal of Zn is maximum at pH (3-7) and it is not adsorb below pH -2 and maximum at pH -7

					2. The Langmuir and freundlich isotherms used **3.** Temperature used 15, 25, 35 degree centigrade **4.** Type of activated carbon C, F-400, f-300 but C is better than other
18.	Tamas et al. (2000)	Electrochemical	Sn	Column	**1.**Tin dissolution rates in oxygenated NaOH solution are controlled by the oxygen transport to the reaction interface **2.**The efficiency of electrolytes in alkaline medium depends on the applied current density and temperature **3.** Cathodic extraction if tin could be stablised at current efficiency higher than 80% **4.**Leaching time was 6h in each case **5.** Tin sheet area was 3.8 cm^2 and r.p.m.- 352, temp-353K. **6.**Tin dissolved saw at different concent of NaOH(0.1-1.0 M)
19.	Aggarwal et al. (1999)	Activated carbon	Cr(III) and Cr(IV)	Batch	**1.** Modifying the activated carbon surfaces by oxidation with nitric acid, ammonium per Sulphate, hydrogen peroxide and oxygen gas at 3500C. **2.** The adsorption of Cr(III) ions increases on oxidation. On the other hand, the adsorption of Cr(VI) ions decreases on oxidation. The increase of Cr(III) and the decrease of Cr(VI) on oxidation have been attributed to the fact that the oxidation of the carbon surface enhances the amount of acidic carbon–oxygen surface groups .
20.	Ranganathan (1999)	Activated carbons prepared from Casurina equisetifolia leaves	Cr(VI)	Batch	**1.** Langmuir and Freundlich adsorption isotherms used, The sorption isotherms fit the Freundlich model accurately. **2.** Desorption studies show that 65±80% of adsorbed chromium could be desorbed by alkali followed by acid treatments.

					3. The waste leaves of C. equisetifolia can be used as a low-cost source material for the preparation of activated carbons and the carbons can be used for adsorption of chromium from aqueous solution. **4.** The optimum pH range for maximum Cr(VI) removal was 2.5±3.0
21.	Barakat (1998)	-	Sn ,Pb, Id	-	**1.** Tin recovered from the acidic solution as hydrated tin oxide by using NaOH at pH 2.0–2.8 **2.** Indium was recovered from the remaining solution by two different methods **3.** The recovery of these metals are found to be lead, tin ,indium 94.7, 99.5 and 99.7%,.respectivly **4.** The recovery processes are favored at a temperature of <45^{0}C for a maximum duration of 8 h and at a pH<2.4.
22.	Lamy-Pitara and benhima (1994)	Platinum metal	Sn(IV)	Batch	**1.**ThePt+Sn system was characterized by cyclic voltammeter and X-ray photoelectron spectroscopy (XPS) analysis. **2.** The ratio of the atomic fraction of tin to that of platinum is Sn/Pt = 2.4, which shows that the composition of the analysed surface volume is 29% platinum and 71% tin. **3.** Tin is still present at a depth of 200 A^0.at pt
23.	Rodes,et al. (1988)	Polyoreinted Gold electrode	Tin(II)	Column	1. This oxygenated tin species is more stable in the oxidized state when the pH increases. **2.** The quantity of adsorbed tin is increased up to 215uC/cm^2 (peaks A) at pH = 3,
24.	Apcioglu and huangt 1987)	Hydrous activated	Cu(II), Pb (II), Ni (II) and Zn	Batch	**1.** Pb(C104)$_2$, Cu(C104)$_2$, Zn(C104)$_2$ and Ni(C104)$_2$ used as solution

		carbon	(II)		**2**. The percent of heavy metal removal decreases with increasing surface loading. **3.** The percent Cu(II) removal is insensitive to surface loading at pH (2-3 or pH >7) **4.** In the cases of nickel(II) and zinc(II), the adsorption edge begins at higher pH values (at pH >4). As the temperature increases from 25 to 100°C, the amount of Cu(II) removed increases appreciably. **5**. The adsorption energy is ~4 kcal/mol per bonding
25.	Hbayg blankenship (1984)	Activated carbon	Hg(II)	Batch	**1.** Total Hg removal attained by all types of activated carbon especially at pH 4-5. **2.** The adsorption isotherm can be described by a Freundlich type of expression. **3.** The kinetics of reduction reaction is governed by intraparticle diffusion. **4.** The extent of adsorptive removal decreases with prolonged reaction time. time 1-2 hrs
26.	Jessen et al. (1979)	Octadecylsilyl	Organotin halides	Column	**1**. The column efficiency was strongly reduced, indicating irreversible reactions between the sample and adsorbent. **2.** The Cyanoalkyl silica (CN) column (column B) also gave strong adsorption of tin tetrachloride.

CHAPTER 3

ELECTROPLATING INDUSTRIES

3.1 GENERAL

There are large numbers of electroplating industries present worldwide on small scale; however, electroplating operation is also part of large number of heavy industries, manufacturing turbines, pumps, automotive parts, compressors and electronic parts. Large number of Industries like Jewelry shop, Steel plant, Automobile industries, Manufacturing industries needed Electroplating for their products for improving mechanical properties, physical properties, electrical properties; corrosive resistance; wear resistance; reflectivity and appearance; torque tolerance; solderability; tarnish resistance; chemical resistance; ability to bond to adhesives, organic coatings and rubber; and shape components etc, so the almost all products that are manufactured from or contain metal are subject to some type of finishing operation. The metal finishing industry uses a wide variety of processes and chemicals to clean, etc, and plate both metallic and non- metallic surfaces to enhance their appearance and surface properties In comparison with other industries, although, the electroplating industries generate little amount of wastewater, however, they are highly toxic in nature because of the presence of metal and acids along with the presence of highly dangerous cyanides. This wastewater is thus harmful to aquatic life in receiving bodies of water, give adverse effect on biological treatment processes and give rise to pollution of surface and ground water.

3.2 PRIMARY INDUSTRY CHEMICALS

3.2.1 Acids & Bases

Acids and bases are used in the metal plating industry in oxidizing, plating and stripping baths and in the waste treatment process. These materials are used to adjust the pH of a solution into operational limits or to provide oxidizing power to clean a surface. Acids used in the industry include: sulfuric, nitric, phosphoric, boric and hydrofluoric. The predominant base used is sodium hydroxide. A release of such acids and bases into the environment can be detrimental to living organisms. Their high corrosives make them extremely hazardous if inhaled, absorbed or ingested causing burns, and in severe cases death. Some acids such as nitric acids have chronic exposure risks and have been linked to anemia, leukopenia and esteoscherosis.

3.2.2 Cyanide Compounds

Cyanide compounds are used in plating baths because they accommodate a wide range of electrical current, remove tarnish or other undesirable films from surfaces to be plated and cause an even metal deposit to form. Processes applying metal coatings of cadmium, iron, gold and zinc often use cyanide. Cyanide inhaled ingested or absorbed through the skin or mucous membranes are poisonous. Overexposure can interfere with the operation of the metabolic system and can cause death.

3.2.3 Metal Compounds

Metals are coated onto parts in metal plating shops to increase wear resistance, corrosion resistance or for enhanced appearance. Metals are supplied to plating baths either in their metallic form or combined with another compound. The industry's predominant metals are also it's most dangerous with regards to environmental and human health. These metals include:

Tin: Tin plating process is used extensively to protect both ferrous and non ferrous surface. Tin is useful metal for the food processing industry since it is non toxic ductile and corrosion resistant, the excellent of tin alloys a tin coated base metal sheet to be formed into a variety of sharp without damage to the surface tin layer. It provides protection for cooper, nickel and other non ferrous metal but not for steel. Tin is widely used in electronics industry because its ability to protect the base metal from oxidation. Thus preserving its solderability, in electronic application lead may be added to prevent the growth of metallic "whiskers" in compression stressed deposit which would otherwise cause electrical shorting.

Cadmium: Typically plated onto steel and iron parts to protect them from highly corrosive environments such as those found in the marine industry. Long term exposure to cadmium can result in emphysema, kidney disease, anemia, liver disorders, bone disease and possibly cancer.

Chromium: Provides excellent wear resistance and corrosion protection as well as a bright reflective surface. Certain forms of chromium are highly toxic due to strong oxidation characteristics and high membrane permeability. Long term exposures can result in ulcers and can contribute to various forms of cancer such as lung cancer.

Nickel: Coatings are used for decorative purposes or to improve corrosion resistance, wear resistance and magnetic characteristics. Nickel plating is a rapidly growing market that generates large amounts of hazardous waste. The electrolysis nickel baths have a short life after which they must be discarded generating hazardous waste. Nickel, if inhaled or ingested, can result in an increased risk of lung cancer.

3.2.4 Solvents

Solvents are used by the metal plating industry to clean parts. Traditional solvents are those such as trichloroethylene and trichloroethane that have the advantage of rapidly dissolving oils and greases on parts, and of rapidly evaporating thereby minimizing drying time. Exposure to either chemical in acute concentrations can be fatal. The electroplating process utilizes a wide variety of chemical, depending on the types of metal that are processed for electroplating and the types of metallic coatings that the facility applies to the processed substrates.

3.3 ENVIRONMENTAL PROBLEMS FROM ELECTROPLATING PROCESSES

Waste waters from electroplating operations are low in volume, contain relatively little organic matter but are highly toxic. Pollution effects of electroplating effluents can be broadly divided into four groups:

3.3.1 Toxicity to fish and other aquatic life: Toxicity of any one of the constituents present in the waste waters (acids, alkalis, cyanide and toxic metals) has been found to depend on the size, age and species of the fish or fish food. Toxicity depends also on other factors such as pH, temperature, hardness, alkalinity, oxygen content and other dissolved substances in the receiving water. Further, the type and quantity of biota in the water source, the degree and nature of other pollution sources, the extent of stratification, the amount of aeration and the presence of synergistic or antagonistic compounds in water has also to be taken into consideration.

3.3.2 Effects on sewers: Electroplating waste waters are highly corrosive due to the presence of acids. They attack metal and concrete structures, especially the concrete sewers, in which the waste waters are discharged. Further, the acids hydrolyze the soaps present in sewage, liberating fatty acids, which may form floating scum, because the floating objects to stick together and clog the sewers. Alkaline wastes are also corrosive but they are not as aggressive as acid wastes to most of the construction materials.

3.3.3 Effects on sewage treatment: Electroplating wastes have a deleterious effect on biological sewage treatment processes due to the presence of acids, alkalis and toxic metallic ions such as Cr(VI), Cu(II), Zn(II), etc. These compounds inhibit or kill the micro-organisms that take part in the purification of sewage. Although presence of small concentrations of the heavy metals in sewage may not affect its biological purification, most of these metals are precipitated during the process and get accumulated in sludge, rendering it unfit for use as manure.

3.3.4 Pollution of ground and surface waters: Discharge of untreated electroplating waste waters on land may pose a problem of ground-water contamination with toxic metals and may render it unfit for drinking purposes. The concentration of the toxic metals in surface water receiving the waste waters would be dependent solely on the dilution available in the surface water.

CHAPTER 4

TIN AND TIN COMPOUNDS

4.1 GENERAL

Tin is a chemical element in the periodic table that has the symbol Sn (Latin: *stannum*) and atomic number 50. This silvery, malleable poor metal that is not easily oxidized in air and resists corrosion is found in many alloys and is used to coat other metals to prevent corrosion. Tin is obtained chiefly from the mineral cassiterite, where it occurs as an oxide. It is the classic alloying metal to make bronze.

Tin is a soft, white, silvery metal that is insoluble in water. Tin metal is used to line cans for food, beverages and aerosols. Its is present in brass, bronze, pewter and some soldering materials.

Tin is a metal that combine with other chemical to form various compounds. When tin is combined with chlorine, sulfur or oxygen, its is called an inorganic tin compound. Inorganic tin compounds are found is small amounts in the earths crust. They are also present in tooth paste, perfumes, soap, coloring agents, food additives and dyes. There can be tin metal as well as inorganic and tin compounds in the air, water, and soil near places where they are naturally present in the rocks, mined, manufactured or used. In general, organic tin compound are from human -made sources and do not occur naturally in the environment. The time each tin compound stays in air water or soil differs from compound to compound [ATSDR, 2005].

4.2 OCCURRENCE

Tin is found in cassiterate from which the metal is obtained by reduction with coal in a reverberatory furnace. Most of the world supply comes from Malaysia, Bolivia, and Indonesia. The republics of Congo, Thailand and Nigeria. The united stats the main consumer, products almost none, although deposit have been found in Alaska and California. The type metal, fusible metal, bell metal, babbitt metal, white metal, pewter, bronze, phosper bronze, soft solder, and die casting alloy are some of the important alloy using tin. About 35 countries mine tin throughout the world. Nearly every continent has an important tin-mining country. Tin is produced by reducing the ore with coal in a reverberatory furnance. This metal is a relatively scarce element with abundance in the earth crust of about 2 ppm, compared with 94ppm for zinc, 63ppm for copper, and 12 ppm for lead. Most of the world's tin is produced from placer deposits; at least one half comes from Southeast Asia. Although small quantities of tin are recovered from complex sulphides such as stannite, cylindrite, franckeite, cafieldite, and teallite. Secondary, or scrap, tin is also an important source of the metal [ATSDR, 2005].

4.3 APPLICATIONS

Tin bonds readily to iron and has been used for coating lead or zinc and steel to prevent corrosion. Tin-plated steel containers are widely used for food preservation, and this forms a large part of the market for metallic tin. Speakers of British English call them "tins"; Americans call them "cans" or "tin cans". One thus-derived use of the slang term "tinnie" or "tinny" means "can of beer" The tin whistle is so called because it was first mass-produced in tin-plated steel.

OTHER USES:

1. Some important tin alloys are: bronze, bell metal, babbitt metal, die casting alloy, pewter, phosphor bronze, soft solder, and white metal.

2. The most important salt formed is stannous chloride, which has found use as a reducing agent and as a mordent in the calico printing process. Electrically conductive coatings are produced when tin salts are sprayed onto glass. These coatings have been used in panel lighting and in the production of frost-free windshields.

3. Most metal pipes in a pipe organ are made of varying amounts of a tin/lead alloy, with 50%/50% being the most common. The amount of tin in the pipe defines the pipe's tone, since tin is the most tonally resonant of all metals. When a tin/lead alloy cools, the lead cools slightly faster and makes a mottled or spotted effect. This metal alloy is referred to as spotted metal.

4. Window glass is most often made via floating molten glass on top of molten tin (creating floating glass) in order to make a flat surface (this is called the "Pilkington process").

5. Tin is also used in solders for joining pipes or electric circuits, in bearing alloys, in glass-making, and in a wide range of tin chemical applications. Although of higher melting point than a lead-tin alloy, the use of pure tin or tin alloyed with other metals in these applications is rapidly supplanting the use of the previously common lead–containing alloys in order to eliminate the problems of toxicity caused by lead.

6. Tin foil was once a common wrapping material for foods and drugs; replaced in the early 20th century by the use of aluminum foil, which is now commonly referred to as tin foil. Hence one use of the slang term "tinnie" or "tinny" for a small retail package of a drug such as cannabis or for a can of beer.

7. Tin becomes a super conductor below 276.72K. In fact, tin was one of the first superconductors to be studied; the Meissner effect, one of the characteristic features of superconductors, was first discovered in superconducting tin crystals. The niobium-tin compound Nb_3Sn is commercially used as wires for superconducting magnets due to the material's high critical temperature (18K) and critical magnetic field (25T). A superconducting magnet weighing only a couple of kilograms is capable of producing magnetic fields comparable to a conventional electromagnet weighing tons [ATSDR, 2005].

4.4 CHARACTERISTICS

Tin is a malleable, ductile, highly crystalline, silvery-white metal; when a bar of tin is bent, a strange crackling sound known as the “tin cry” can be heard due to the breaking of the crystals. This metal resists corrosion from distilled, sea and soft tap water, but can be attacked by strong acids, alkalis, and by acid salts. Tin acts as a catalyst when oxygen is in solution and helps accelerate chemical attack.

Tin forms the dioxide SnO_2 when it is heated in the presence of air. SnO_2, in turn, is feebly acidic and forms stannate (SnO_3^{-2}) salts with basic oxides. Tin can be highly polished and is used as a protective coat for other metals in order to prevent corrosion or other chemical action. This metal combines directly with chlorine and oxygen and displaces hydrogen from dilute acids. Tin is malleable at ordinary temperatures but is brittle when it is heated.

4.5 PHYSICAL PROPERTIES

Tin is a silvery-white malleable metal, somewhat ductile, and has a highly crystalline structure. The element has two allotropic forms: gray, or α-tin, with a cubic structure, which changes at 13.2°C into white, or β-tin, the ordinary form of the metal. White tin has a tetragonal structure. When tin is cooled below 13.2°C, it changes slowly from white to gray. This change is affected by impurities such as aluminum and zinc, and can be prevented by small additions of antimony or bismuth. The conversion was first noted as growths on organ pipes in European cathedrals, where it was thought to be the devils work. This conversion was also speculated to be caused by microorganisms and was called "tin plague" or "tin disease". The detailed physical properties of tin are given in table 4.1.

Table 4.1 Physical properties of tin

Name	Tin, Sn, 50
Chemical series	Poor metal
Group ,period, Block	14, 5, p
Standard atomic weight	118.710g/mole
Electron configuration	$4d^{10}\ 5s^2\ 5p^2$
Electron per cell	2, 8, 18, 18, 4
Phase	Solid
Density	(white) 7.265g/cm^{-3}
Liquid density at melting point	6.99 g/cm^{-3}
Melting point	505.08K (231.93°C, 449.47°F)
Boiling point	2875K

	(2602°C, 4716°F)
Heat of fusion	7.03 kJ·mol^{-1}
Heat of vaporization	296.1 kJ·mol^{-1}
Heat capacity	(25°C) white 27.112 j·mol^{-1}·K^{-1}
Crystal structure	Tetragonal

[Source: Encyclopedia of Tin]

4.6 PUBLIC HEALTH STATEMENT OF TIN AND TIN COMPOUNDS

Tin metal is release in electroplating industry. If you are exposed to tin and tin compound, many factors will determine whether you will be harmed. These factor include the dose (how much), the duration (how long), and how you come in contact with them. You must also consider any chemicals you are exposed to and your age sex, diet, family traits, lifestyle, and state of health.

4.6.1 Toxicology data of tin

It has been claimed that 1 to 2mg tin/kg diet is necessary for growth in rats. Tin has not been proven to be an essential trace element in man. On other hand for years the use of tin was considered to be nontoxic, as the in use as a theraptic drug demonstrated. A level of 250mg of inorganic tin/kg canned food is generally accepted a maximum tolerable level. The LD_{50} of $SnCl_2$ is given as 21 mg/kg body wt after in administration in mice and $SnCl_4$ as 41mg/kg body wt. experimental data in animals also indicates that toxic effect can be caused by ingestion of rather high dose of tin. Another problem is the simultaneous contaminated of canned food with lead dissolved from the tinned seams of cans [Schafer and Femfert, 1984].

A tolerable limit for tin concentration in canned food of 250ppm is generally accepted. However, biochemical effect attribute to tin have been observed even after administration of 1 and 3mgSn/kgbody wt. these doses reflect 10 and 30 ppm tin in the diet. The experiments of showed that hemoglobin concentration in the blood of rats decrease significantly feeding a diet containing 150 ppm in tin. The absorption of iron was diminished after simultaneous administration of 0.8 micromole Sn(II) and iron In however canned food usually plays a secondary role in daily nutrition. Fortunately, concentration of about 200 ppm tin as reported by Warburton et al. are not found in canned food, but values between 50 and 500 ppm are not unusual. If a large amount of canned food is eaten daily over along period, disturbance of gastric acid secretion and a reduction in iron absorption or metabolism cannot be excluded. The storage of food especially acid foods, in opened cans should be avoided as this practice increase the amount of tin in the food when it is consumed [Blunden and Wallace, 2003].

Table 4.2 Occupational exposure limits for tin and inorganic tin compounds in Air

Country	**mg/m^3**	**Comments**
Denmark	2	As Sn
Finland	2 5	As Sn As Sn, tin oxide fume
Germany	2	As Sn
Iceland	2	As Sn
Nether land	2 2	As Sn except as SnO_2,SnH_4 SnO_2
Norway	2	As Sn
Sweden	2	As Sn
United kingdom	2 4	As Sn except SnH_4 Short term
USA	2	As Sn metal, inorganic compounds except SnH_4
NIOSH	2 2	As Sn except oxide As SnO, SnO_2
OSAHA	2	As Sn except oxides

[Source: IPCS, 1980]

Table 4.3 Toxicity of inorganic tin compounds to aquatic species.

Organism	**Ion**	**Concentration mg/l**
Microorganism		
Bacterium(*pseudomonas fluorescenc)*	Sn^{4+}	245
Bacterium (*serratia sp.)*	Sn^{4+}	287
Marinebacterium(*Vibrio harveyi)*	Sn^{2+}	2.3
Cyanobacterium (*Anabaena flosaquae*	Sn^{2+}	>5
Grean alga (*Ankistrodesmus falcatus*	Sn^{2+}	12
Greenalga(*Scenedesmus quadricauda*	Sn^{2+}	>50
Diatom (*Skeletonemacostatum)*	Sn^{2+}	0.2
Diatom(*Thalassiosira guillardii)*	Sn^{2+}	0.2
Ciliate(*Tetrahymena pyriformis)*	Sn^{d}	132
Invertebrates		
Pulmonate snail (*Taphius glabratus*)	Sn^{2+}	10
Tubificid worm (*tubifex tubifex)*	Sn^{2+}	140
Amphipod(*Crangonyx pseudogracilis)*	Sn^{2+}	71.8
Waterflea (*Daphnia magna)*	Sn^{2+}	27
Midge(*Chironomus plumosus)*	Sn^{2+}	8.3
Fish--- Goldfish(*carassius)*	Sn^{2+}	2.1
Carp (*Cyprinus carpio)*	Sn^{2+}	295
Largemouthbass(*Micropterus salmoides)*	Sn^{2+}	1.9

[Source: IPCS, 1980]

Table 4.4 Tin Exposure limit in air.

Metal	OSHA(PEL)	ACIGH(TLV)	NIOH(REL)
Sn	2mg/m^3(TWA)	2mg/m^3(TWA)	2mg/m^3(TWA)

[Source: Health Council of Netherland, 2005]

ACIGH: American conference of governmental industrial hygienist

OSHA: US occupational safety and health administration

NIOH: National institute of occupational safety and health

PEL: Permissible exposure limit

TWA: Time weighted average

TLV: Threshold limit value

REL: Recommended exposure limit

Table 4.5 Tin levels in food

Food item	Concentration mg/kg
Mineral waters	<0.003
Nonalcoholic beverages	0.04
Fish and crustacean	<0.003
Breads	<0.003
Pasta	<0.003
Meats	<0.003
Cooked pork meat	<0.003
Milk	<0.003
Dairy product	<0.003
Sugar	<0.003
Chocolate	<0.003
Oil	<0.003

[Source: EPA NPL HAZ, 2004]

Table 4.6 Tin levels in fruits

Food item	Concentration mg/kg
Preserved food in unlacquered food	
Tomatoes	84
Mushroom	34
Pineapples	82
Fruit cocktails	97
Grape fruits	128
Preserved food in lacquered	
Tomatoes	6.0
Mushroom	6.9
Apricot	5.8
Strawberry	0.6
Papaya	2.9
Meat	4.5
Fish	0.7
Salad	0.02
Apples	0.04
Orange	0.07

[Source: EPA NPL HAZ, 2004]

Table 4.7 Emission limit value for discharge to water of organotin coating

Constitute group and parameter	Limit value
pH	6-9
BOD	25
Toxic unit(mg/l)	10
Organotin(ng/l)	200
Copper(mg/l)	0.5
Mineral oil(mg/l)	20
metals	As per licence present in metal

[Source: EPA NPL HAZ, 2004]

4.6.2 Tin compound in environment

Tin may release in dusts from wind storms, roads and farming activities, Gases dusts and fumes containing tin may be released from smelting and refining process, burning of waste and burning of fossil fuels [coal and oil]. Particle in the air containing tin may transport by wind or washed of the air by rain or snow. Tin binds to soils and to sediments in water and generally regarded as being relatively imbibe in the environment. Tin cannot be destroyed from particles in environment. It can be change its form or become attached or separated from particle in soil, sediments and water. Organic tin compound stick to soil, sediment and particle in water. Organic tin compounds can be degraded into inorganic tin compound. In water tin compound are mostly attached particle in water. Organic tin compounds may also settle out of the water into sediments and remain unchanged for years. Organic tin compounds may be up taken into the tissues of animals that live in water containing these compounds [ATSDR, 2005].

Air: The vapour pressure of elemental tin is negligible and the high boiling points of elemental tin and many inorganic tin compounds indicate that they are non-volatile under environmental conditions. However, the wind may carry airborne particles for long distances before deposition, depending on the type of emitting source, physical form and properties (e.g. size, density), physical or chemical changes that may occur during transport, adsorption processes, and meteorological conditions. Tin is detected in air infrequently and at low concentrations, except in the vicinity of industrial sources. Air concentrations of tin in US cities from several studies were as high as 0.8 μg/m3. Average concentrations are generally below 0.1 μg/m3, with higher concentrations near some industrial facilities [IPCS, 1980].

Water: Tin occurs in trace amounts in natural waters. Inorganic tin concentrations of up to 0.003 μg/litre were reported for rainwater in the USA during 1981. Industrial pollution was found to increase inorganic tin levels in the river estuary to up to 0.7 μg/litre [ATSDR, 2005]. In the environment, Tin compounds are generally only sparingly soluble in water and are likely to partition to soils and sediments. In water, inorganic tin may exist as either divalent (Sn^{2+}) or tetravalent (Sn4+) cations under environmental conditions. Cations such as Sn^{2+} and Sn^{4}+ will generally be adsorbed by soils to some extent, which reduces their mobility. Tin(II) dominates in reduced (oxygen-poor) water and will readily precipitate as tin(II) sulfide or as tin(II) hydroxide in alkaline water. Tin(IV) readily hydrolyses and can precipitate as tin(IV) hydroxide. The solubility product of tin(IV) hydroxide has been measured at approximately 10–56 g/litre at 25°C [IPCS, 1980].

Soils and sediments: From the information available, it appears likely that inorganic tin will partition to soils and sediments and will not volatilize from water. Transfer coefficients for tin in a soil–plant system were reported to be 0.01–0.1. Mean total tin concentrations in Antarctic sediment were 2.1 and 5.1 mg/kg dry weight for the <2 mm and <63μm fractions, respectively. Inorganic tin was detected in 100 of 235 sediment samples collected from Canadian waterways. Concentrations ranged up to 8 mg/kg dry weight in coastal areas and up to 15.5 mg/kg in rivers and lakes. Sediment concentrations of inorganic tin in Toronto Harbour, Canada, during 1983 were found to be highest (up to 13.8 mg/kg) near areas of tributyltin contamination [ATSDR, 2005].

Food: In most unprocessed foods, inorganic (and total) tin levels are generally less than 1 mg/kg. Higher concentrations can arise as tin(II) in canned foods due to dissolution of the tin coating or tin plate. Tin levels are usually below 25 mg/kg in lacquered food cans, but may exceed 100 mg/kg in unlacquered cans. Tin concentrations in canned foods increase with storage time and temperature. Once opened, the tin content in foods stored in metal cans increases more quickly over time, since tin can rapidly dissolve in the presence of oxygen. Acidic foods are more aggressive to the tin coating in metal cans, and canned acidic foods have higher tin contents. Oxidizing agents (nitrates, iron salts, copper salts, and sulfur) accelerate detinning, whereas tin salts, sugars, and gelatins reduce the dissolution rate. Tin concentrations of vegetables, fruits and fruit juices, nuts, dairy products, meat, fish, poultry, eggs, beverages, and other foods not packaged in metal cans are generally below 2 mg/kg. Tin concentrations in pastas and breads have been reported to range from <0.003 to 0.03 mg/kg. Mean tin concentrations ranging from <1 to 1000 mg/kg have been found in foods packaged in unlacquered or partially lacquered cans, whereas the average tin concentration in foods in lacquered cans has been reported to be up to 6.9 mg/kg [ATSDR, 2005].

4.6.3 Exposed of tin and tin compounds

Tin is presents in the air, water soil and landfills and normal part of many plants animals that live on land and in water. Tin is also presents in the tissues of your body. There is no evidence that tin is an essential elements for humans. It will be founds in small amounts in foods. Tin concentration of vegetable, fruits and juices, nuts dairy products, meat fish poultry. Eggs beverage and other food not packaged in metal cans are generally less than 2 part per million. Tin concentration in pastas and breads has been reported to range from lass than 0.003 ppm. You can be exposed to tin when you eat food or drink juice or other liquid from tin- lined cans. Canned food from lacquered tin -lined cans contains less than 25 ppm of tin since the lacquer prevents the food from reacting with the tin. food from unlacquered tin-lined contains up to 100 ppm of tin since the reaction of the food with the can causes some of the tin to dissolve in the contents of the can. Tin concentration in food also increases if food is stored in opened cans stannous fluoride, a tin containing compound is added to toothpaste.

You can also be exposed to higher–than normal levels of tin you in a factory that makes or uses tin, because tin compound have many uses. You can be exposed by breathing in tin dusts or fumes or getting tin compounds or your skin. Tin compound can also be spilled accidentally. If you live near a hazardous waste site, you could by breathing dusts touching materials or drinking water contaminated with tin [ATSDR, 2005].

4.6.4 Tin compounds enter and leave human body

Tin compounds can enter your body from nearby hazardous waste sites by expose to contaminated air, water and soil. When you eat tin in your food, very little leaves the gastrointestinal tract and gets into your blood stream. Most tin travels through the intestines and leaves your body in the faces. Some leaves your body in the urine. If you breathe air containing tin dust or fumes, some of the tin could be trapped in your lungs, but this does not affect your breathing if it is a small amount. If you swallow some metallic tin particle, they will leave your body in the faces. Very little tin can enter the body through unbroken skin. Your body can rid itself of most inorganic tin in weeks, but some can stay in your body from 2-3 months. In organic tin compound leave your body very quickly, most are gone within a day. Very small amounts of tin stay some tissues of your body, like the bones, for longer periods of time [ATSDR, 2005].

4.6.5 Effect on health of tin and tin compounds

Because inorganic tin compound usually enter leave your body rapidly after breathe or eat them, they do not usually causes harmful effect. However, humans who swallowed large amounts of tin inorganic tin in research studies suffered stomachs, anemia, and liver and kidney problems [ATSDR, 2005]. Studies with inorganic tin in animals have shown effect to those observed in humans. There is no evidence that inorganic tin compound affect reproductive functions produce birth defects or cause genetic change. Inorganic tin compound are not known to cause cancer. Inhalation, oral or dermal exposure to some organ tin compound has been shown to cause harmful effect in humans. But the main effect will depends on the particular organ tin compound. There have been reports of skin and eye irritation, respiratory irritation, gastrointestinal effect. And neurologist problems in humans exposed for short periods of time to high amounts of certain organotin compound. Some neurologist problems have persisted for years after the poisoning occurred. Lethal cases have been reported following ingestion of very high amounts. Studies in animals have shown that certain organotin mainly affect the immune system, but a different type primarily affects the nervous system. Yet there are some organotin that exhibits very low toxicity. Exposure of pregnant rat and mice to some organotin compound has reduced fertility and stillbirth, but scientists still are not sure whether this occurs only with doses that also are toxic to the mother. Some animal studies also suggested that reproductive organs of males may be affected. There are no studies of cancer in humans exposed to organotin compounds. Studies of few organotin in animals suggest that some organotin compound can produce cancer. EPA has determined that one specific organotin, tributyltinoxide, is not classified as to human carcinogenicity; that is its is not known whether or not it cause humans cancer.

Acute effects are:

Eye and skin irritations. Headaches, Stomachaches, Sickness and dizziness, Severe sweating, Breathlessness, Urination problems,

Long-term effects are:

Depressions, Liver damage, malfunctioning of immune systems, Chromosomal damage, Shortage of red blood cells, Brain damage (causing anger, sleeping disorders, forgetfulness and headaches)[Health Council of Netherland,2005]

4.6.6 Effect on children of tin and tin compounds

Children can be exposed to tin compounds in some manner as adults through the diet or by contact with contaminated soil at near hazardous waste sites where these compounds are found. Some children eat significant amounts of dirt, which may lead to increased exposure if the soil is contaminated. Tin addition children can be exposed if mainly members work with tin compounds and bring residues in their clothing or tools. There are no studies on health effect exposed to tin compounds. However its is reasonable to assume that children would exhibits the type of health effect observed in exposed adults. We do not know whether children are some susceptible to the effect of exposed to tin and tin compound or of inorganic tin animals. Studies in animals have shown that organotin compounds can cross the placenta and reach the fetus. Exposure of rodents to some organotin during pregnancy has produced birth defect in the new born animals. The results of several studies suggest that may occur only at high exposure levels that cause maternal toxicity, but further research is needed to clarify this issue. One study found that rats whose mothers exposed tributyltin during pregnancy showed altered performance in some neurologist tests conducted when they young adults. Another study, also with tributyltin, found that exposure during gestation, lactation, and post lactation affected some development landmarks in female rats. There are no reports of tin or tin compounds in human breast milk, and there is no direct evidence in animals of transfer of these compounds to the young nursing [ASDR, 2005].

CHAPTER 5

ADSORPTION FANDAMENTAL

5.1 GENERAL

Adsorption (also known as adsorptive separation) can be simply defined as the concentration of solute, which may be molecule in gas stream or a dissolved or suspended substance in a liquid stream, on the surface of a solid. The major application had been in the separation of solute from liquid streams and removal of impurities from gas streams. In an adsorption process, molecule or atoms or ions in a gas or liquid diffuse to the surface of a solid, where they bond the solid surface or are held there by weak intermolecular forces. The adsorbed solute is called the adsorbate, and the solid material is the adsorbent.

During adsorption, the solid adsorbent becomes saturated or nearly saturated with the adsorbate. To recover the adsorbate and allow the adsorbent to be reused it's regenerated by desorbing the adsorbed substance (i.e.adsorbates). When a feed streams containing a contaminated component is passed through a solid adsorbent, the contaminated component is retained in the adsorbent. Now, if a second liquid feed (known as the adsorbent) containing a different component that also has an affinity for adsorbing to the solid adsorbent, there will be competition between the contaminated and this component for limited number of adsorption site available. This result in the removal or desorption of the contaminated component from the solid.

5.2 PHYSICAL ADSORPTION VS CHEMISORPTION

Adsorption process can be classified as either physical adsorption (Vander Walls adsorption or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and adsorbent. In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved in chemisorption, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals, which are bound separately.

Physical adsorption from a gas occurs when the inter-molecular attractive between molecules of the solid adsorbent and the gas are greater than between molecule of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat, similar in magnitude to the heat of condensation. Physical adsorption occurs quickly and may be monomolecular (unimolecular) layer or monolayer or two, three or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multilayer and ten, if the pores are close to the size of the molecule, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a pores adsorbent can be more related to the pore volume than to the surface area.

In contrast, chemisorption is molonolayer, involves the formation of chemical bonds between the adsorbate and adsorbent, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place at temperature greater than 200^0C, and may be slow and irreversible.

Most commercial adsorbents rely on adsorption: while catalyses rely on physical adsorption: A comparison between physical adsorption and chemical adsorption is given in table 5.1

5.3 ADSORBENTS

Major type of adsorbents in use is; activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents. Most adsorbents are manufactured (such as activated carbons), but a few, such as some zeolites, occur naturally. Each material has its own characteristic such as porosity, pore structure and nature of its adsorbing surface. Pore sizes in adsorbents may be distributed throughout the solid. Pore size are classified generally into 3 ranges: macrospores have "diameters" in excess of 50 nm, mesopores (also know as transitional pores) have "diameters" in the range 2-50nm, and microspores have "diameters" which are smaller than 2-nm.
The application of some commercial Adsorbents given in table 5.2

Table 5.1: Physical adsorption vs Chemisorption

S.No	**Physical adsorption**	***Chemical adsorption***
1.	Vander Walls adsorption	Activated adsorption
2.	The individuality of the adsorbate and the adsorbent are preserved	There is transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals , which are bound separately
3.	Heat of adsorption = 5kcal/mole	Heat of adsorption=20-100 kcal/mole
4.	Adsorption only at temperature less than the boiling point of the adsorbate.	Adsorption takes only at temperature greater than 200 degree centigrade and may be slow and irreversible
5.	Mono and multilayer adsorption	Almost monolayer adsorption
6.	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is slow i.e. only active surface sites are important
7.	Extent of adsorption depends upon the properties of adsorbent	Extent of adsorption depends upon both adsorbate and adsorbent
8.	Rate of adsorption control by resistance mass transfer.	Rate of adsorption depends upon both adsorbate and adsorbent
9.	No activated energy involved in the adsorption process	Activation energy may be involved

Table 5.2 Commercial adsorbents their properties, method of production and application.

Adsorbent	**Properties & method of preparation**	**Applications**
Silica gel	Hard, very granular, very porous product made from gel precipapted by acid treatment of sodium silicate solution	.Drying of gases ,refrigeration, organic solvents, transformer oils, desiccants in packing and double glazing dew point control of natural gas
Activated alumina	Hard, hydrated aluminum hydroxide which is activated by heating to drive moisture.	.Drying of gases ,organic solvents, transformer oils removal of HCL

		from hydrogen removal of fluorides in alkaline process
Carbons	Activated carbon is the residue obtained from various carbonaceous materials like coal, nutshells. wood, paper mill sludge, petroleum based and activation	.Nitrogen from air .Hydrogen from syngas .Ethane from methane and hydrogen Vinyl chloride monomer(VCM) from air .Removal of odours from gases .Removal of solvents vapors .Removal of SOX and NOX .Removal of helium .Clean up of nuclear off gases .Water purification
Polymeric &resin	These are hydrophobic adsorbents which are obtained from pyrolysis and activation of polymeric compounds.	.Water purification .Recovery and purification of steroids, amino acids .Separation of fatty acid from water and toluene .Separation of aromatics from aliphatic .Recovery of proteins and enzymes .Removal of colours from syrups .Removal of organics from hydrogen peroxide
Fuller earth	These are natural clays. The clay is heated and dried during which it developed a porous structure.	.Treatment of edible oils .Removal of organic pigments .Refining of mineral oils .Removal of polychlorinated biphenyls (PCB)
Zeolites	Its is unique mineral with a cage –like skeletal	.Oxygen from air

	structure that allow it to trip, hold and exchange materials from its internal structure. It is an insoluble and chemically stable aluminum silicate mineral that was formed from glass components of volcanic ash *millions of years ago.*	.Drying of gases .Removing water from azeotrops .Sweetening sour gases and liquids .Purification of hydrogen *separation of ammonia* .Recovery of carbon and argon .Removal of acetylene, propane and butane from air .Separation of xylene and ethyle benzene .Separation of normal from branched paraffins .Separation of olefins and aro atics from paraffins .Drying of refrigerants and organic liquids .Pollution control, including removal of Hg, NOX and SOX

Table 5.3 Typical non conventional adsorbents and their applications

Coal ash fly ash	Heavy metal organic compounds, COD of waste water, phosphate, colour from paper mill effluents dyes ammonia from fertilizer units, phenolic compounds.
Bagasse fly ash	Sugar and distillery effluents, chlorinated phenols, 2-4-D pulp and paper mill effluents, heavy metals
Peat	Heavy metals, cyanides phosphate ,oil in water, 2-4-d.detergents septic tank waste metal finishing waste ,colour and dyes,
Lignite	Ammonia dyes

Activated carbon from lignin sludge bark, rice husk	Color heavy metal dyes, distillery waste
Coconut husk, peanut skin.bagasse pith, rice husk etc.	Heavy metals, dyes
Hardwood, softwood, saw dust bark	Heavy metal, dyes, COD lead battery effluent
Water rubber	Heavy metals
Hematite, slag	Heavy metals
Tannery hair	Heavy metals, TOC, soluble organic dyes, virus
China clay, Wollastonite	Heavy metal dyes oxalic acid fluoride
Soil, sand	Colour heavy metal, dyes

[Sources: www. Separationprocess.com]

5.4 INTRAPARTICLE DIFFUSION PROCESS

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites with the particles. This can be bracken conceptually into a series of consecutive steps.

1. Diffusion of adsorbate across a stationary solvent film surrounding each adsorbent
2. Diffusion through the macro pore
3. Diffusion through micro pore
4. Adsorption at an appropriate site

It is assumed that the fourth step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So it can be assumed that the main resistance to the adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the limited step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system process the term "intrapaticle transport" which comprises of surface diffusions and molecular diffusion. Several researchers have shown that surface diffusion is the dominants mechanism and is the rate–determining step. A functional relationship common to most of the treatment of intraparticle transport is that the uptake varies almost proportionality with square root of time.

5.5 STAGES IN ADSORPTION PROCESS

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

Stage I- First a single layer of molecule build up over the surface of soil. 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 II- As the fluid concentration is further increase. Second, third etc. layer form by physical adsorption. The numbers of layer which can form are limited by size of the pores.

Stage III- Finally, for adsorption from the gas phase , capillary condensation may be occur in which capillaries filled with condensed adsorbate, when its partial pressures reaches critical value relative to size of the pore.

5.6 ADSORPTION ISOTHERMS

When a solution is contacted with a solid adsorbent, molecule of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amount of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium data at a given temperature are represented by adsorption isotherms ranging from the design of heterogeneous chemical reactor to purification of compounds by adsorption

A variety of different isotherms equation have been proposed, some of which have a theoretical foundation and some being of amore empirical nature. Many of this equation are valid over small relative ranges but do not fit experimental data when tested over the full range of relative pressures. Langmuir, Freundlich, Brunauer-Emmet-Teller (BET), Redlich–Peterson(R-P) atc. Are most commonly used adsorption isotherms models for describing the dynamic equilibrium. The isotherms equations used for the study described follows:

5.6.1 Langmuir Isotherm

This isotherm described adsorbate-adsorbent system in which the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached. The isotherms were formulated on the basis of a dynamic equilibrium between the adsorbed phases and gaseous or vapour phase. The implicit assumptions are:

1. No lateral interaction between adsorbed molecules, thus the heat of adsorption is constant and independent of coverage.
2. Each adsorbate molecule occupies only one site.
3. The adsorbed molecule remained at the site of adsorption until its is desorbed the adsorption is localized.

If θ is the fraction of adsorbent surface covered by adsorbate, then $(1-\theta)$ is the fraction of surface remaining uncovered and therefore available as adsorption sites. The rate of adsorption is proportional to $(1-\theta)$ while the rate desorption is proportional to. At equilibrium, those two rates are equal. Thus

$$k_a p\,(1-\theta) = k_d\,\theta$$

$$\theta = \frac{q}{q_e} = \frac{k_a p}{k_d + k_a p} = \frac{KP}{1+KP} \qquad \text{where } K = \frac{k_a}{k_d}$$

Where θ = the fraction of adsorbent surface covered by adsorbate

p = partial pressure of gas

q = mass of solute adsorbed/ mass of adsorbent

q_e = maximum loading correspond to complete of coverage of the surface by solutes

k_a = rate of constant for adsorption.

k_d = rate constant for desorption.

Alternative form of solute in solution, mass/volume.

$$\theta = \frac{q}{q_e} = \frac{KC}{1+KC} \tag{5.1}$$

Langmuir isotherm can be rearranged to the following linear forms.

$$\frac{C_e}{q_e} = \frac{1}{K_A q_m} + \frac{C_e}{q_m} \tag{5.2}$$

or

$$\frac{1}{q_e} = \left(\frac{1}{K_A q_m}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{q_m}\right) \tag{5.3}$$

5.6.2 The Freundlich Isotherm

The heat of adsorption in many instances decrease in magnitude with increasing extent of adsorption. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill monolayer ($\theta=1$). The equation that describes such isotherm is the freundlich isotherm, given as

$$q = K_F p^{1/n} \qquad \text{where } n>1 \qquad (5.4)$$

Empirical constant `n` is a measure of the measure the adsorption intensity.

K_F is a temperature-dependent constant, adsorption coefficient, is a measure of adsorption capacity or fundamental effectiveness of the adsorption. Its is a directly related to the standard free energy change.

Alternative form of the freundlich isotherm equation is

$$q = K_F C^{1/n} \qquad (5.5)$$

or

$$\log q = \log K_F + \frac{1}{n}\log C \qquad \text{where } n>1 \qquad (5.6)$$

A high K_F and `n` value is an indication of high adsorption throught the concentration range. A low K_F and high `n` indicates a low adsorption throught the studies concentration range. A low `n` value indicates high adsorption at strong solute concentration

The freundlich equation is the most useful for dilute solution over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on the activated carbon.

5.6.3 Redlich-Peterson isotherm

It combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R–P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation. It can be described as follow

$$q_e = \frac{K_R C_e}{1 + a_R C^{\beta}} \tag{5.7}$$

Where K_R is R-P isotherm constant (l/g), a_R is R-P isotherm constant (l/mg) and β is the exponent which lies between 1and 0 where β =1

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{5.8}$$

It becomes a langmuir equation. Where $\beta = 0$

$$q_e = \frac{K_R C_e}{1 + a_R} \tag{5.9}$$

i.e. the Henry's equation

Eq. (5.8) can be converted to linear taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1 \right) = \ln a_R + \beta \ln C_e \tag{5.10}$$

Plotting the left-hand side of equation (5.10) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure was adopted to solve equation (5.10) by maximizing the correlation coefficient between the theoretical data for qe predicted from equation (5.10) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with any suitable computer programme.

5.6.4 The BET Isotherm

This model is an extension of Langmuir monolayer approach for apparent multilayer adsorption, following assumptions is made.

1. Adsorbed surface is composed of uniform energies of adsorption and the energies of located sites don't interfere with neighboring sites.

2. Adsorbed molecules don't migrate on the surface of adsorbent.

3. The first monolayer is held by the energy of adsorption and the subsequent layers are adsorbed due to condensation energy of adsorbate.

4. A layer need not be complete before the next layer starts forming.

In its most useful form, the BET equation is written as:

$$\frac{p}{q(p_s - p)} = \frac{1}{q_m K_B} + \frac{(K_B - 1)p}{q_e K_B p_s} \tag{5.11}$$

Where p_s = saturated vapour pressure

K_B = constant related to energy of adsorption

For small values of p/p_s, the BET equation reduces to the langmuir equation. For the adsorption from a liquid solution, the BET equation is

$$\frac{C}{Q(C_s - C)} = \frac{1}{Q_m k_B} + \frac{(K_B - 1)C}{Q_e K_B C_s}$$

or

$$Q = \frac{Q_e K_B C}{(C_s - C)[1 + (K_B - 1)\frac{C}{C_s}]}$$

Where C_s= concentration of solute at saturation of all layers

5.7 FACTOR CONTROLLING ADSORPTION

The amount of adsorbate adsorbed by an adsorbent from adsorbate solution is influenced by a number of factors as discussed below:

(I) **Nature of adsorbent:** Both the physical state and nature of adsorption is important. Adsorbents differ in their specific surface area and affinity for adsorbate. Adsorption capacity is directly proportional to exposed surface. For the non porous adsorbents. The adsorption capacity is inversely proportional to the particle size. Many solids are used as adsorbents to remove the impurities from fluids. Commercial adsorbents generally have large surface area per unit mass. Most of the surface area is provided by a network of small pores inside the particle. Common industrial adsorbents for fluids include activated carbon, silica gel; activated alumina molecular sieves etc. Adsorption capacity is directly proportional to the exposed surface. For the non-porous adsorbents, the adsorption capacity is directly proportional to the particle size diameter where for porous materials it is practically independent of particle size.

(II) **pH of solution**: adsorption from solution is strongly by pH the solution. The adsorption of cations increases while that of the anions decreases with increase in pH. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and there for the adsorption of others ions are affected by pH of solution. Change in pH affect the adsorptive process through dissociation of functional group on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. The surface charge as well as the degree of ionization is affected by the pH of solution since the hydrogen and hydroxyl ions adsorbed readily on the adsorbent surface, the adsorption of others molecule and ions is affected by pH. It is common observation that a surface adsorbs anions favorably at low and cations in high range.

(III) **Contact time:** The studies on the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. The uptake of adsorbate is fast in the initial stage of contact and becomes slow near equilibrium. However, strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of adsorbate species is fast at the stages of the contact period, and thereafter, it becomes slower near the equilibrium.

(IV) **Initial Concentration:** A given mass of adsorbent can adsorb only a fixed amount of adsorbate, so the initial concentration of adsorbate solution is very important. The amount adsorbed decrease with increasing of adsorbate concentration as the resistance to the uptake of solute from solution of adsorbate decrease with increasing solute concentration. The rate of adsorption is increased because of the increasing driving force.

(V) **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 case decrease with increasing temperature of the system. Some of the adsorption studies show increased adsorption 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.

(VI) **Degree of agitation:** Agitation in batch adsorption is important to ensure proper contact between the adsorbent and the solution at lower agitation speeds, the stationary fluid film around the particle is thicker and the process is external mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film is reduced and after a certain point the process becomes intraparticle diffusion controlled. Whatever is the extent of agitation, the solution inside the pores remains unaffected and hence, for intraparticle mass transfer controlled process agitation has no effect on the rate of adsorption.

CHAPTER 6

EXPERIMENTAL PROGRAMME

6.1 GENERAL

Batch studies have been carried out for the removal of Tin(II) from synthetic wastewater using granulated activated carbon (GAC) as an adsorbent. GAC was obtained from the industry. The characterization of GAC by SEM (Scanning Electron Microscope), TGA(Thermal Degradation Studies) and XRD (X-Ray Diffraction Analysis) analysis and proximate and ultimate analysis of GAC.

6.2 CHARACTERIZATION OF ADSORBENT

The physico-chemical characteristic of the GAC was determined using standard Procedures as discussed below:

6.2.1 Proximate Analysis

Proximate analysis of the GAC was carried out using the procedure as per IS 1350:1984.

6.2.2 Bulk Density

The Bulk density of GAC was determined using MAC bulk density meter.

6.2.3 X-Ray Diffraction Analysis

X-Ray diffraction analysis of GAC was carried out by using Phillips (Holland) Diffraction unit (Model PW1140/90).

6.2.4 Scanning Electron Microscope (SEM)

SEM analysis of GAC was carried out by using LEO 435 VP Scanning electron microscope.

6.2.5 Ultimate or CHN Analysis

The ultimate analysis was performed on finely ground and oven-dried GAC to determine the weight fractions of carbon, hydrogen and nitrogen. The weight fractions of carbon, hydrogen and nitrogen analysis were determined by using Perkin Elmer CHN elemental analyzer.

6.2.6 Thermal Degradation Studies

The thermal degradation of (pyrolysis) of the GAC was studied using the thermo gravimetric and differential analysis techniques. The thermal decomposition of GAC was carried out non-isothermally in a Pyris diamond TG/TGA of Perkin Elmer Instruments. The samples were prepared carefully to obtain homogenous material properties. The degradation runs were taken at heating rate of 20^{0C}min^{-1} under an inert atmosphere (flowing nitrogen) for pyrolysis. The tests were conducted from the ambient temperature to 1000^{0} C. Flowing rate in both cases was kept constant at 200 ml/min. The thermo gravimetric (TG), differential thermo gravimetric (DTG) and differential thermal analysis (DTA) curves obtained in each case were analyzed to understand the behaviour of thermal degradation.

6.3 ADSORBATE

Synthetic wastewater solutions of Sn(II) of desired concentrations (500mg/l) were prepared by dissolving accurately weighed quantity of $SnCl_2$ (AR grade) in distilled water.

6.3.1 Analysis of Metals by Atomic Absorption Spectrometer (AAS)

The atomic absorption spectrometer is used to determine the concentration of element presents in a sample. The technique makes of the fact that natural or ground state atom of elements can absorb electromagnetic radiation over a series of very narrow sharply defined wave length. The sample in solution is aspirated as a fine mist into a flame where it is converted to atomic vapor. Most of the atom remains in the ground state and there for capable of absorbing radiation of a suitable wavelength. This discrete radiation is usually supplied by a hallow cathode lamp. Which is sharp line source consisting of a cathode containing elements to be determined along with the tungsten anode. The line characteristics of the elements are emitted by the hallow cathode lamp and passes through the flame where they may be absorbed by the atomic vapor. Since generally only the test element can absorb this radiation. The method becomes very specific in addition to being sensitive. The application area of the spectrometer can very. It is frequently used for elements analysis in metal alloy and medicine etc.

6.3.2 Analytical Measurements

Concentration of Sn (II) is determined by Atomic Adsorption Spectroscopy, GBC Avanta instrument. Standard solutions of Sn (II) were taken and their absorbance was determined by AAS at different concentrations. The linearity of calibration curves indicates applicability of the Lambert-Beer's Law.

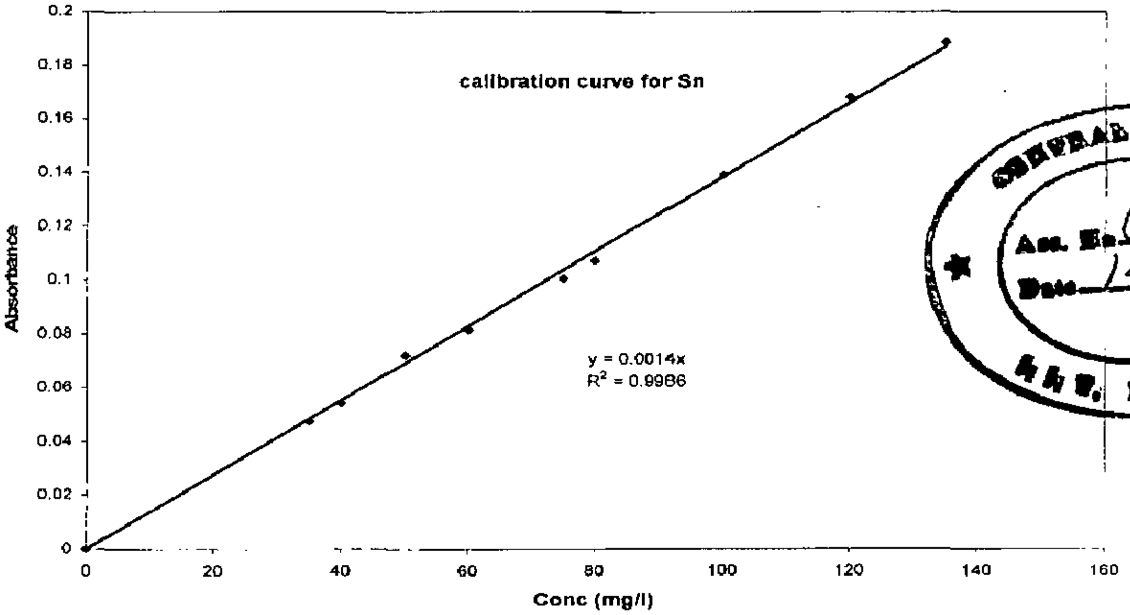

Fig 6.1 Calibration curve of Tin

6.4 EXPERIMENTAL PROGRAMME

The experimental programme was conducted by Batch adsorption studies

6.4.1 Batch Adsorption Experiments

In order to study the effect of different parameters like adsorbent dose, initial concentration, pH, contact time, temperature effect etc. batch experiments were conducted.

For each experimental run, 500mg/l of synthetic wastewater of known metal concentration was taken with known amount of GAC(8g/l) in a 50 ml stoppered conical flask. These samples were agitated in a temperature controlled shaking water bath. The temperature was maintained at 303.15K. Samples were withdrawn at appropriate time intervals. The filtrate solution was analyzed for remaining metal concentration by AAS.

For adsorption isotherms, metal solutions of known concentration were agitated with different known amount of GAC till equilibrium was achieved. For optimum amount of adsorbent per unit mass adsorbate Sn(II) in 500 ml synthetic wastewater were agitated separately with different GAC doses till equilibrium was attained. To see the effect of temperature for the adsorption of metal from solution by GAC, experiments were also conducted at 288.15 K, 303.15 K, 318.15, and 333.15K.

CHAPTER 7

RESULT AND DISCUSSION

7.1 GENERAL

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

- Characterization of Granulated Activated Carbon
- Adsorption of Tin from synthetic tin waste water by Granulated Activated Carbon
- Batch adsorption studies.

7.2 CHARACTERIZATION OF GRANULATED ACTIVATED CARBON

Particle size analysis, proximate analysis and ultimate analysis were carried out for physico-chemical characteristics. Thermo gravimetric analysis was also done nitrogen atmospheres to see the effect of temperature on the GAC stability. Morphological characteristics are given through scanning electron microscope (SEM) analysis.

Ultimate analysis (Table 7.1) showed that the GAC has very high Carbon content. It has low amount of ash content as also shown by the proximate analysis (Table7.2). The physico-chemical characteristics of the adsorbents are given in Table (7.3). GAC has higher bulk density. GAC also has a high surface area of 864.67 m^2/g which comprises mainly of pore surface area, with average pore diameter of 25.42A^0 (Table 7.3). Particle size is important in systems having external mass transfer resistance. The aqueous solution-adsorbents mixture was agitated at the maximum rpm, and the external mass transfer resistance is assumed to be absent.

Adsorption of tin is basically governed by intra-particle surface diffusion, where pore size distribution and surface area are important. Average particle size of GAC is 3-5mm. For structural and morphological characteristics, scanning electron microscope (SEM) analysis and X-ray diffraction were carried out. Scanning electron microscopic photograph (Fig 7.1-7.2) of GAC reveals their surface texture and porosity. This photomicrograph shows the size and the number of pores in GAC. The d-spacing values (Fig.7.3 and Table 7.4) provided by the X-ray spectrum of GAC reflected the presence of $Fe_2(SO_4)9H_20$, $Pb_5Cl(ASO_3)$ and major peak indicates the Presence of silica in form tridynite and alpha cristobalite compounds. Diffraction peaks corresponding to crystalline carbon were observed in GAC. Amorphous form of silica was identified in GAC.

Thermal stability of GAC is directly dependent on the decomposition temperature of its various oxides and functional groups. The surface groups present on carbons and those formed as a result of interaction with oxidizing gases or solutions are generally quite stable even under vacuum at temperatures below 150°C, irrespective of the temperature at which they were formed.

The thermo-gravimetric analysis curves of GAC under inert (nitrogen) atmosphere are shown in Fig.7.4-7.5. At unloaded sample it tell us that at temp increasing from 25^0C to 99^0C weight loss occur 2.79%, 99^0C to 200^0C wt. loss 2.90%, 200^0C to 500^0C wt. loss 1.22%, 500^0C to 700^0C wt. loss 0.88%, 700^0C to 1013^0C wt. loss 2.79%. At loaded sample temp increasing from 24^{0C} to 100^0C wt. loss occur 2.22%, 151^0C to 400^0C wt. loss 1.35%, 500^0C to 700^0C wt. loss 1.91% and 799 ^{0}C to 934^0C wt. loss 1.16% to distinct zones can be investigated from room temperature to 1000^0C in GAC.

Thermal degradation characteristics of GAC in flowing nitrogen atmosphere shows removal of moisture and light volatiles of about 7.7 % up to temperature of 1000°C. It can be inferred that the GAC is highly stable.

Table 7.1 Ultimate analysis of GAC

S.No	Element	Value
1.	C (%)	79.52
2.	H (%)	0.271
3.	O (%)	20.139
4.	S (%)	0.070

Table 7.2 Proximate analysis of GAC

Characteristics	GAC
Moisture (%)	7.23
Volatile Matter (%)	5.20
Ash (%)	9.28
Fixed carbon (%)	78.29

Table7.3 Physico-chemical characteristics of GAC

Characteristics	**GAC**
Surface area(m^2/g)	864.67
Pore Volume(cm^3/g)	0.51
Pore diameter(A^o)	25.42
Bulk density (kg/m^3)	720.52

Table 7.4 XRD analysis of GAC

S.N0	**2θ**	**d**
1.	6.200	14.24403
2.	8.6500	10.21431
3.	26.807	3.32302
4.	32.249	2.77364
5.	44.809	2.02101
6.	55.470	1.65521
7.	61.911	1.49756
8.	70.668	1.33191
9.	87.018	1.11886
10.	98.497	1.01683

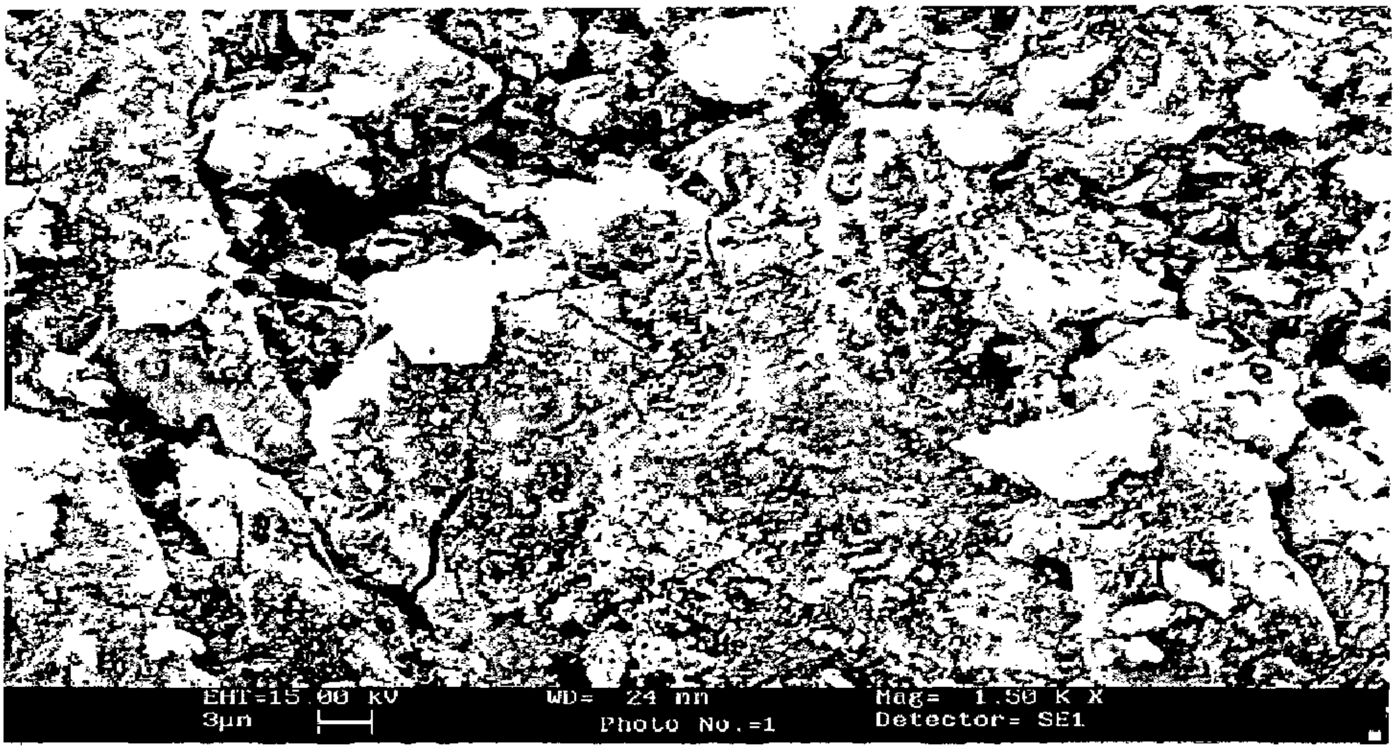

Fig.7.1 Scanning electron micrograph of GAC (unloaded of Tin)

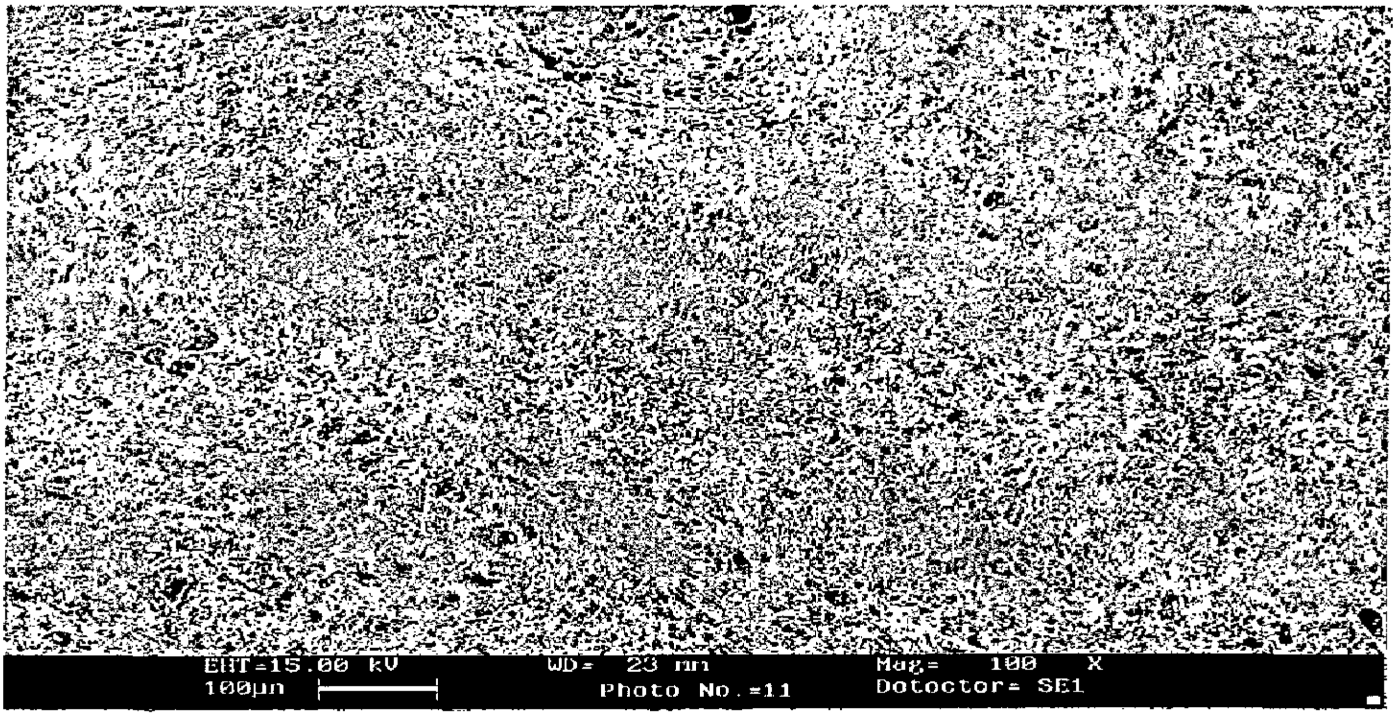

Fig.7.2 Scanning electron micrograph of GAC (loaded of Tin)

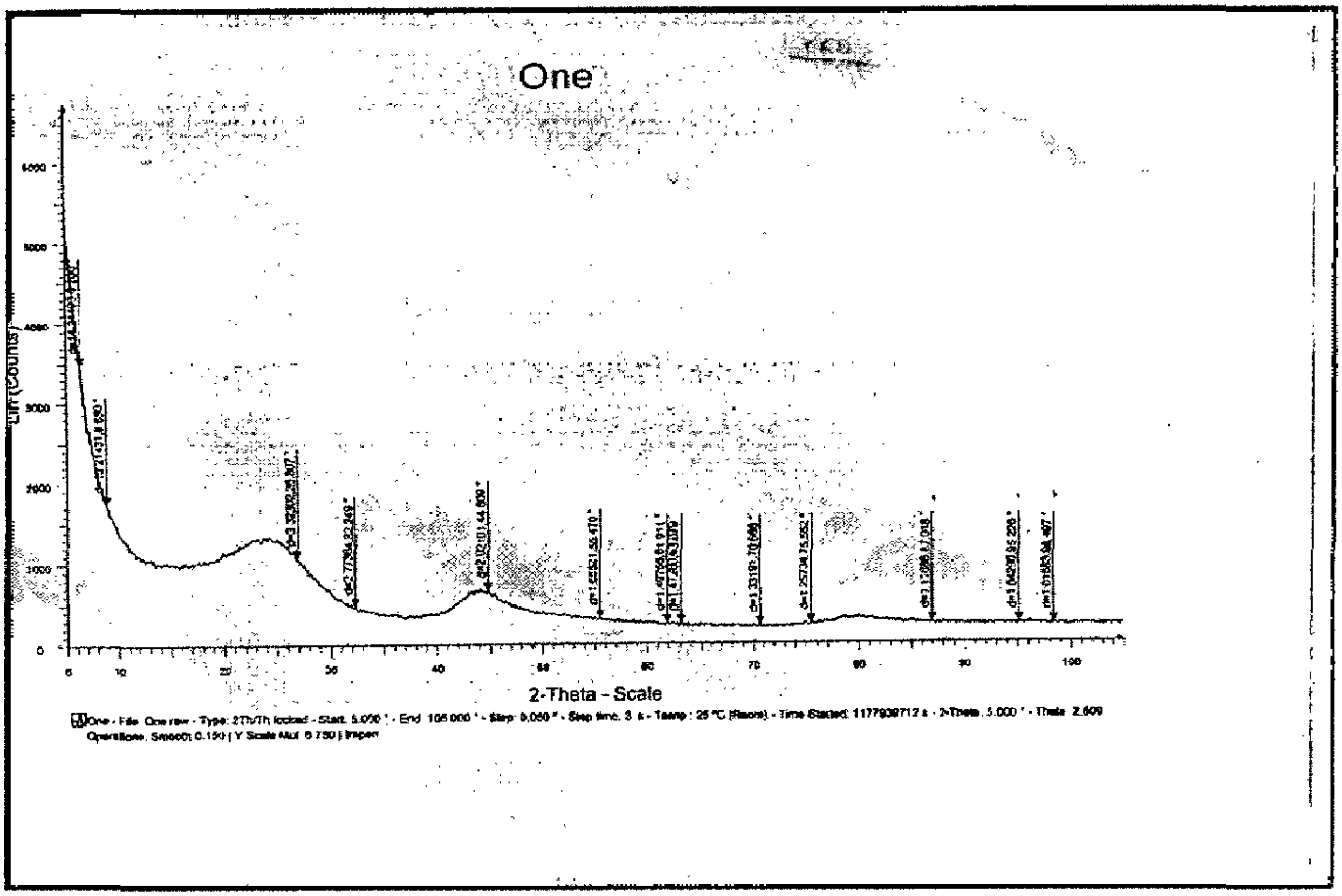

Fig. 7.3 X-Ray diffraction analysis of GAC

Institute Instrumentation Centre, IITR, Roorkee.

Sample Name: 1
Data Name: Shiv-1
Measurement Date: 4/19/2007
Sample Weight: 8.769 mg
Reference Weight: 10 mg
Reference Name: Alumina Powder

Temperature Program:

Cel	Cel	Cel/min	min	s
24	070	100	0	0.5

Instrument: Perkin Elmer (Pyris Diamond)
Operator: A.K.Saini
Pan: Alumina
Atmosphare: Nitrogen (200 ml/min)

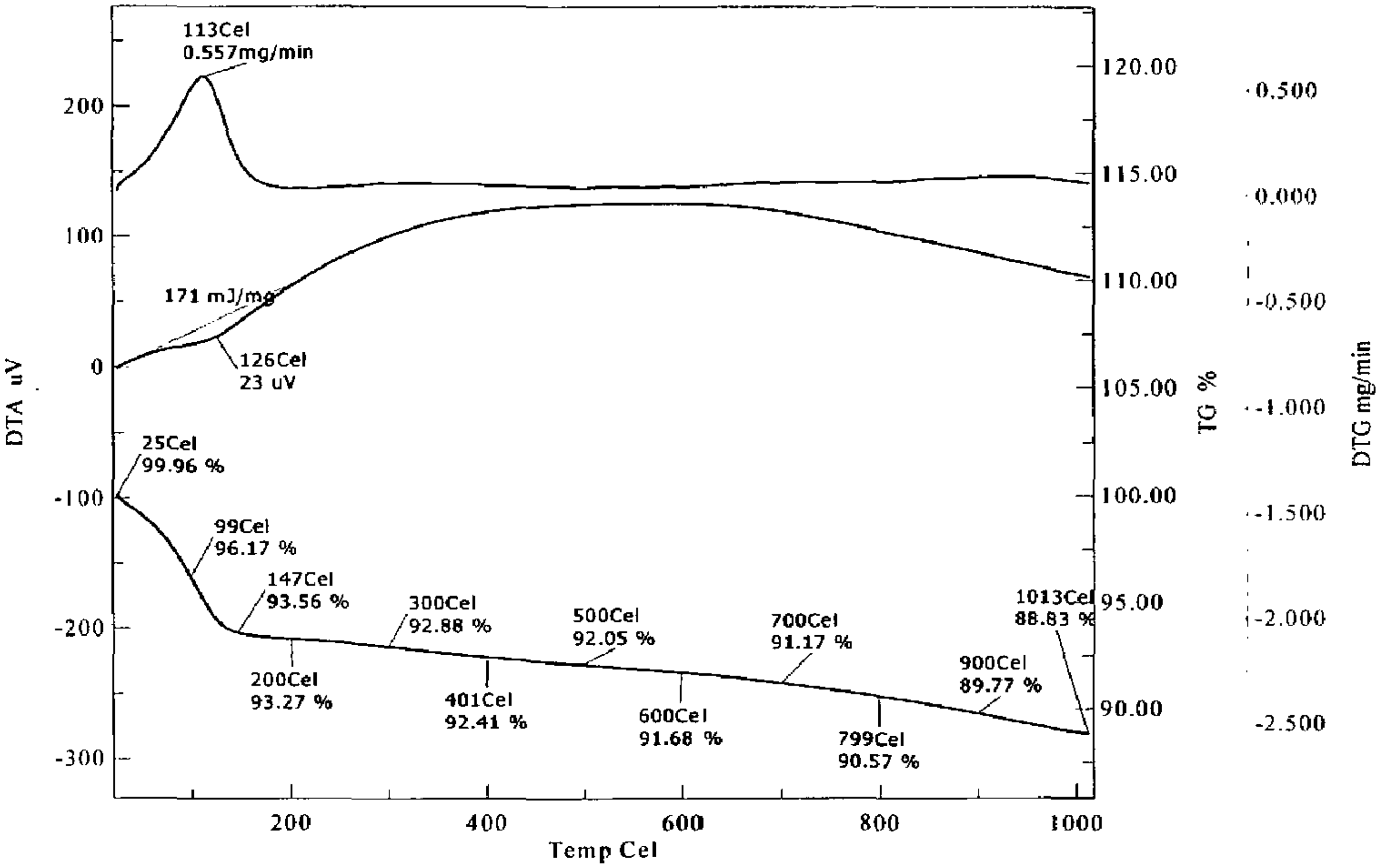

Fig.7.4 Thermal degradation plot for GAC flowing in nitrogen (unloaded of Tin)

Institute Instrumentation Centre, IITR, Roorkee.

Sample Name: 2
Data Name: Shiv-2
Measurement Date: 4/25/2007
Sample Weight: 11.18 mg
Reference Weight: 10 mg
Reference Name: Alumina Powder

Temperature Program:

Cel	Cel	Cel/min	min
23	1000	100	0

Instrument: Perkin Elmer (Pyris Diamond)
Operator: A.K.Saini
Pan: Alumina
Atmosphare: Nitrogen (200 ml/min)

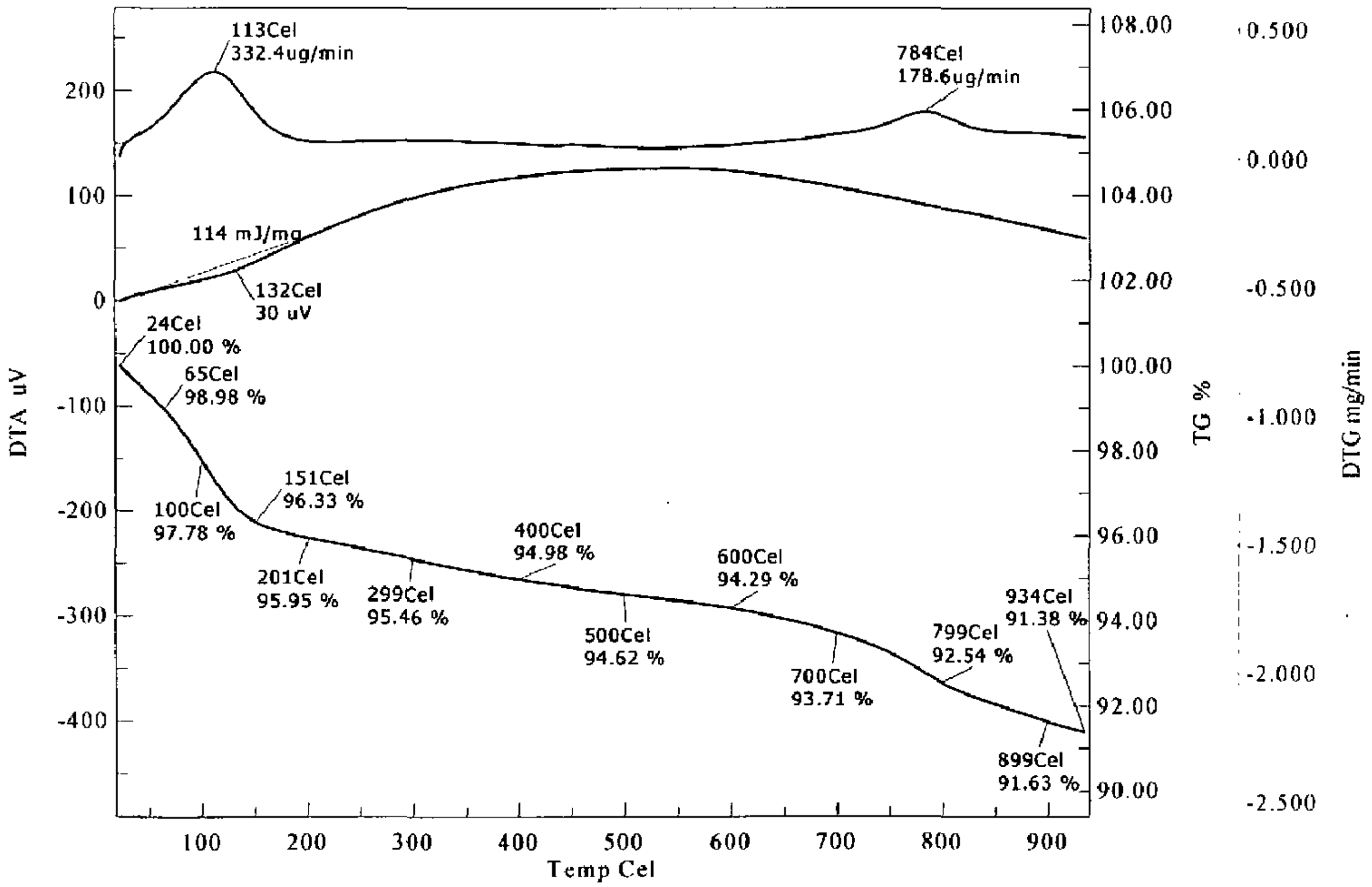

Fig.7.5 Thermal degradation plot for GAC flowing in nitrogen (loaded of Tin)

7.3 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 50 ml stoppered conical flask for removal of heavy metals from synthetic solutions of individual metal ions solutions of known concentrations. The effect of solution pH (2.0–14.0), contact time (0–330 min), *initial metal concentration (500–2000 mg/l), GAC dose (8 g/l) and temperature (288.15 K - 333.15 K)* were studied. The solutions were filtered and the remaining concentrations of metal ions after adsorption were determined by atomic absorption spectrometer.

7.3.1 Effect of adsorbent dose

Effect of GAC dose for the removal of Sn(II) from 500mg/l metal solutions each at temperature of 303.15 K for contact time of 5.30 h shown in Fig. 7.6. It is seen that percent adsorption increased with increase in GAC dose from 0.05 to 0.4g per 50 ml solution. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites.

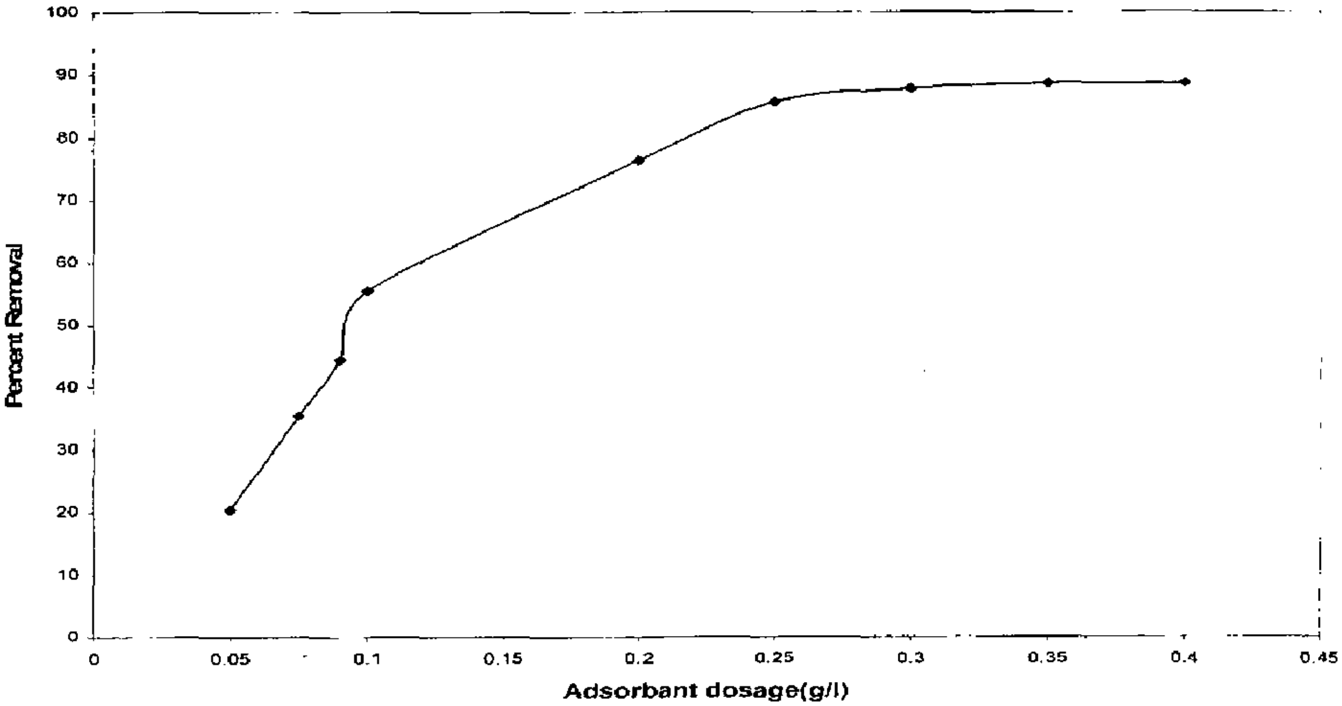

Fig.7.6 Effect of adsorbents dosage on the adsorption of Sn(II) By GAC (pH=4,T=303K, t=330 min Co=500mg/l)

7.3.2 Effect of pH

The effect of pH on the degree of metal removal for Sn(II) ions was investigated; the results are shown in Fig.7.7. In these experiments, the GAC loading was 0.4 g in 50 ml of solution containing 8g/l each of Sn(II) at 303.15 K. The contact time was 5.30 h to attain in equilibrium, as discussed earlier. The removal of tin by adsorption on GAC was found maximum at pH 4.0 and it decrease sharply when the pH was increased from 4.0 pH.

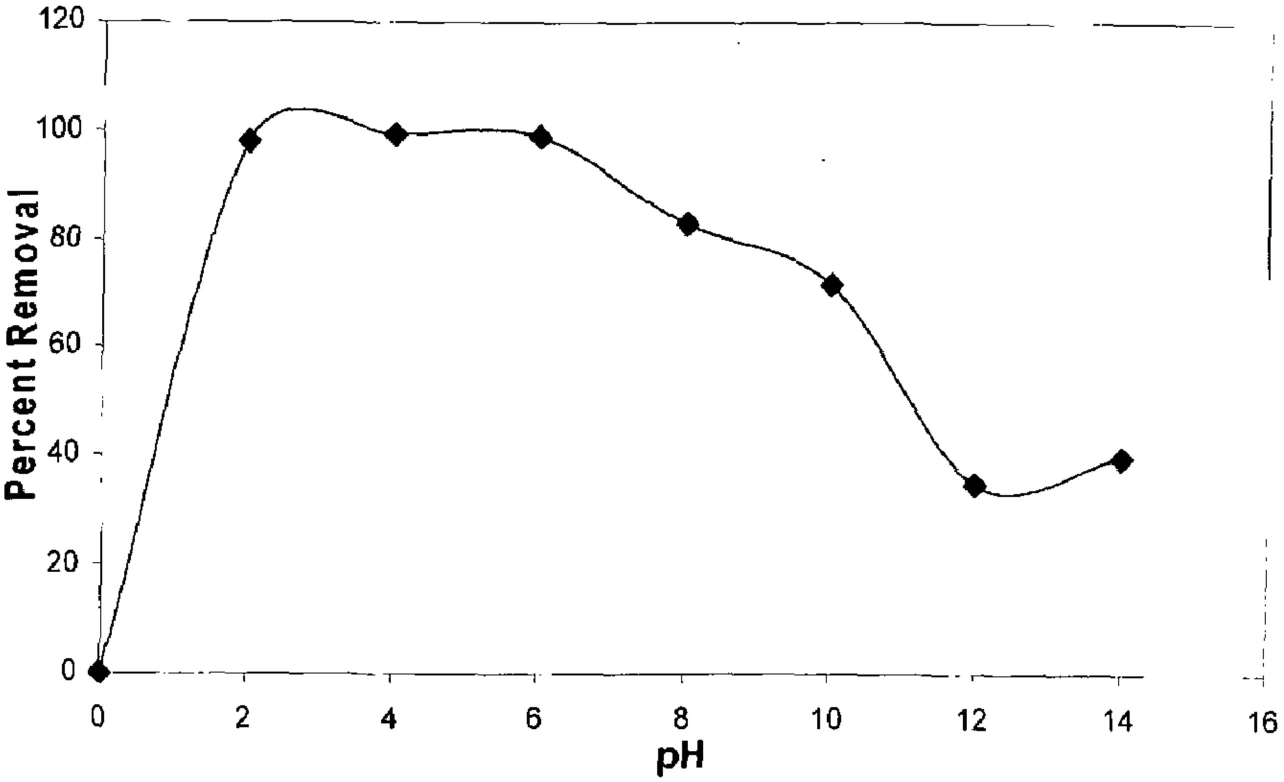

Fig.7.7 Effect of pH on the adsorption of Sn(II) BY GAC (T=303K,T=330min,Co=500mg/l, m=8g/l)

7.3.3 Effect of contact time

Contact time between the metal and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of metal and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for it use in waste water treatment.

Fig.7.8 shows the percentage removal of Sn(II) by GAC for 0.4g/50 ml. Sn(II) solutions of 500 mg/l initial concentrations at different contact times. The contact time curves show that initially the removal is very rapid in first 75 min, then the adsorption rate gradually decreases and the removal reaches equilibrium in around 330 min. It is also seen that the time required to attain equilibrium is dependent on the initial concentration of tin for the same concentration, the percent removal of tin increases with increases with increase in contact time till equilibrium attained in 330 min. The curves are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of metal on the surface of GAC.

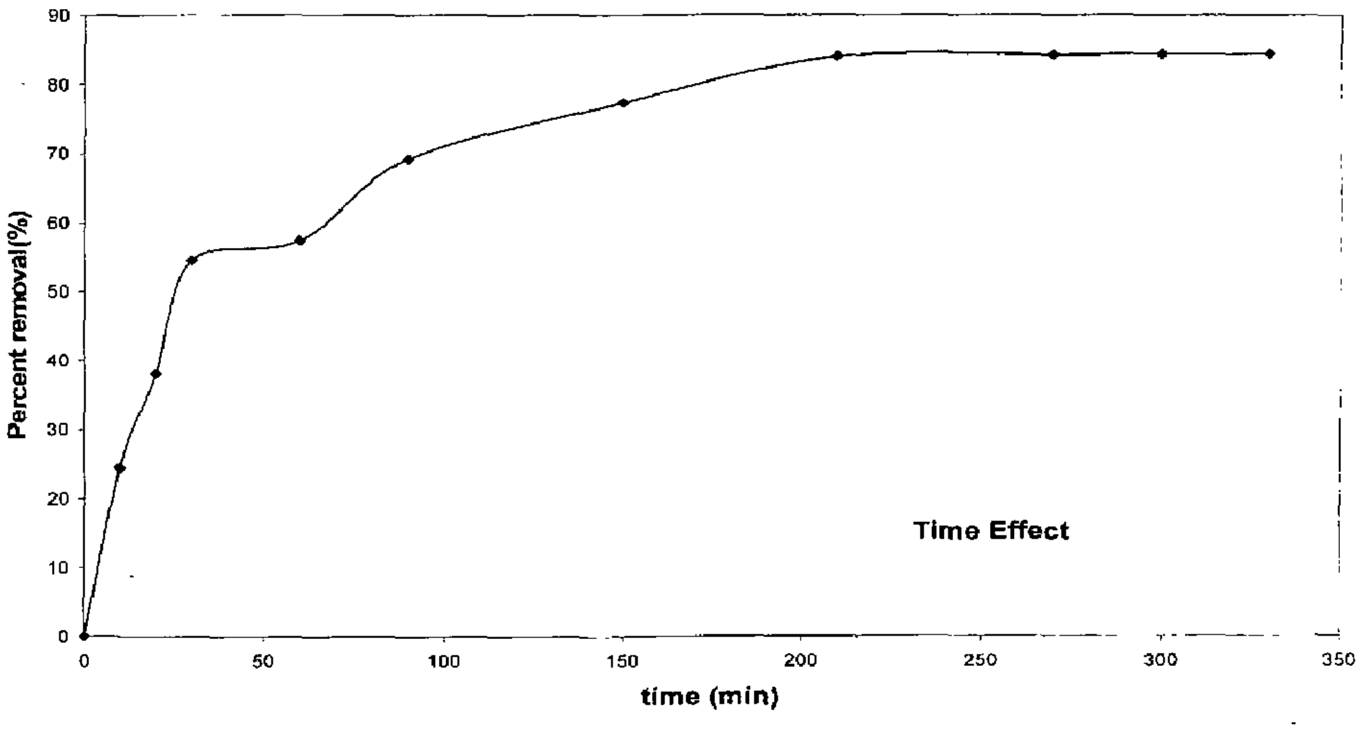

Fig.7.8 Effect of contact time on adsorption of Sn(II) by GAC (pH=4,T=303K Co= 500mg/l, m=8g/l)

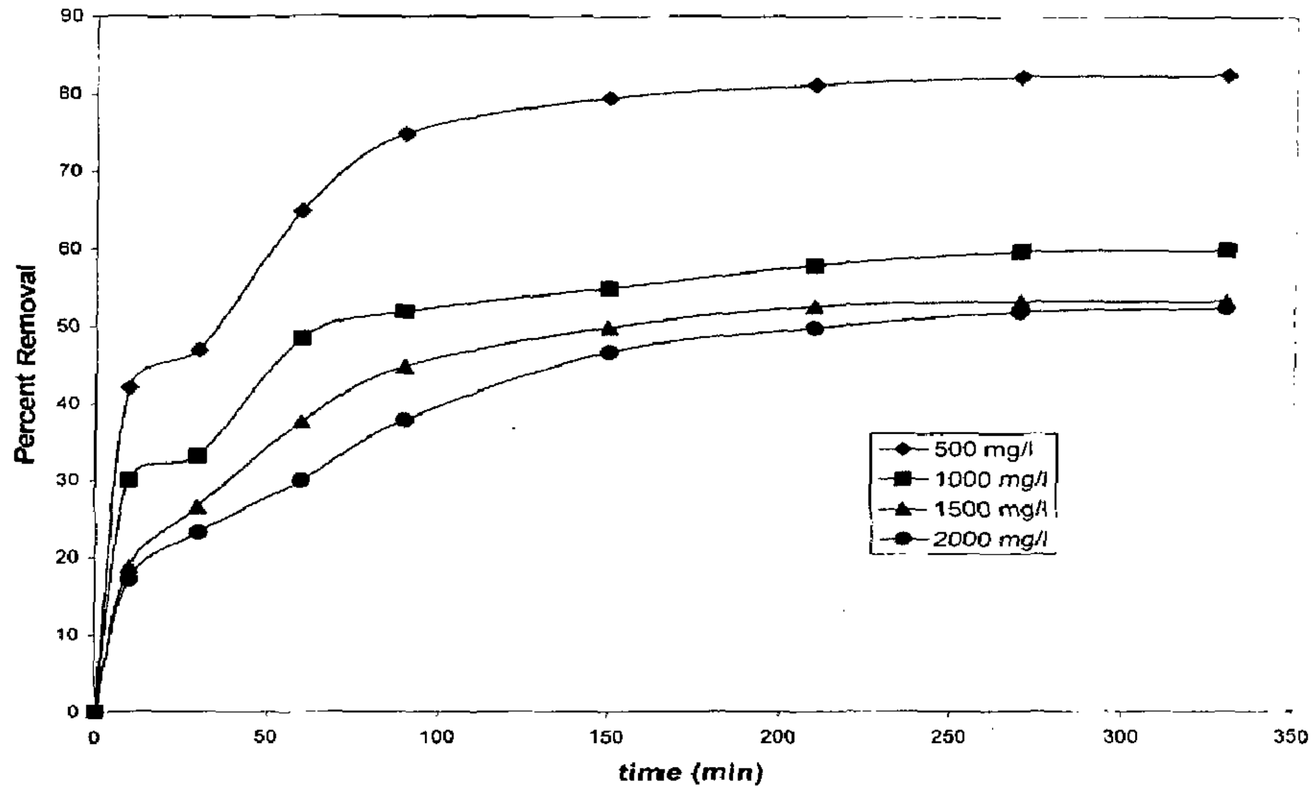

Fig.7.9 Effect of different initial concentration on adsorption of Sn(II) by GAC (pH=4,T=303K, Co-500-2000mg/l, m=8g/l)

7.3.4 Effect of different initial concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is important. From Fig.7.9. It is evident that the percent adsorption was decreased with increase in initial metal concentration. Though the percentage removal decreased with increase in initial metal concentration but the actual amount of Sn(II) adsorbed per unit mass of GAC increased with increase in initial metal concentration in test solution. This was because of the decrease in resistance for the uptake of solute from solution with increase in metal concentration.

7.3.5 Effect of temperature

The adsorption studies were carried out at four different temperatures, 288.15, 303.15, 318.15 and 333.15K. in Fig.7.10. Present the result of the experiments for Sn(II), since the adsorption is increasing at higher temperatures therefore Sn(II) adsorption on GAC are endothermic in nature.

7.4 ADSORPTION KINETICS STUDY

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

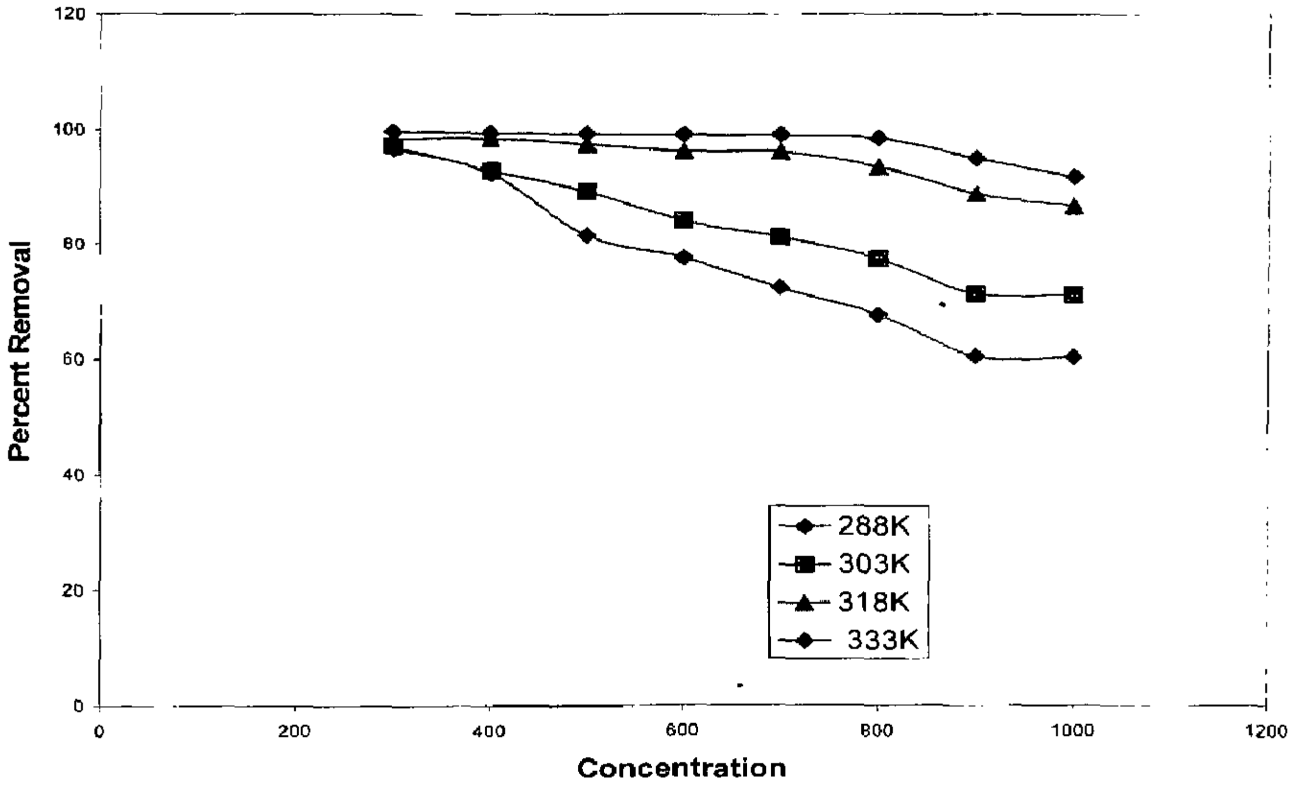

Fig.7.10 Effect of different temperature on adsorption of Sn(II) by GAC (pH=4,T=288K-333K, t=330min, m=8g/l)

7.4.1 Pseudo-First-Order and Pseudo-second-order Model

Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption.

The pseudo-first-order equation is

$$\frac{dq_t}{dt} = k_f\,(q_e - q_t) \tag{7.1}$$

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

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \tag{7.2}$$

The plot of log $(q_e - q_t)$ against t for Sn(II) is shown in Fig.7.11. The straight-line plot shows the validity of this model. Table 7.5 gives the value of adsorption rate constant (k_f) of Sn (II) with GAC.

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

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{7.3}$$

Where, k_s is the rate constant of pseudo-second-order model (in g/mg min). After integrating eq. (7.3) for boundary conditions at t=0, q_t =0 and at t=t, $q_t = q_t$, the following form of equation can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_s q_{e^2}} + \frac{1}{q_e}t \tag{7.4}$$

The initial sorption rate, h (mg/g min), as t → 0 can be defined as

$$h = k_s q_e^{\,2} \tag{7.5}$$

The initial sorption rate (h), the equilibrium adsorption capacity (q_e), and the pseudo-second order constant k_s can be determined from the plot of t/q versus t. Fig.7.121 to shows the results obtained for tin. Calculated correlation coefficients both linear and for pseudo-first-order model and pseudo-second order model by using regression procedure for Sn(II) adsorption on GAC are shown in Table.7.5.

Since correlations coefficients were found to be more close to unity for pseudo second order model than first order, therefore sorption reaction was better approximated by pseudo-second-order kinetics model. The k_s and h values as calculated from the figure are also listed in Table7.5.

7.4.2 Intra-particle Diffusion Model

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.

$$q_t = k_{id} t^{1/2} + C \tag{7.6}$$

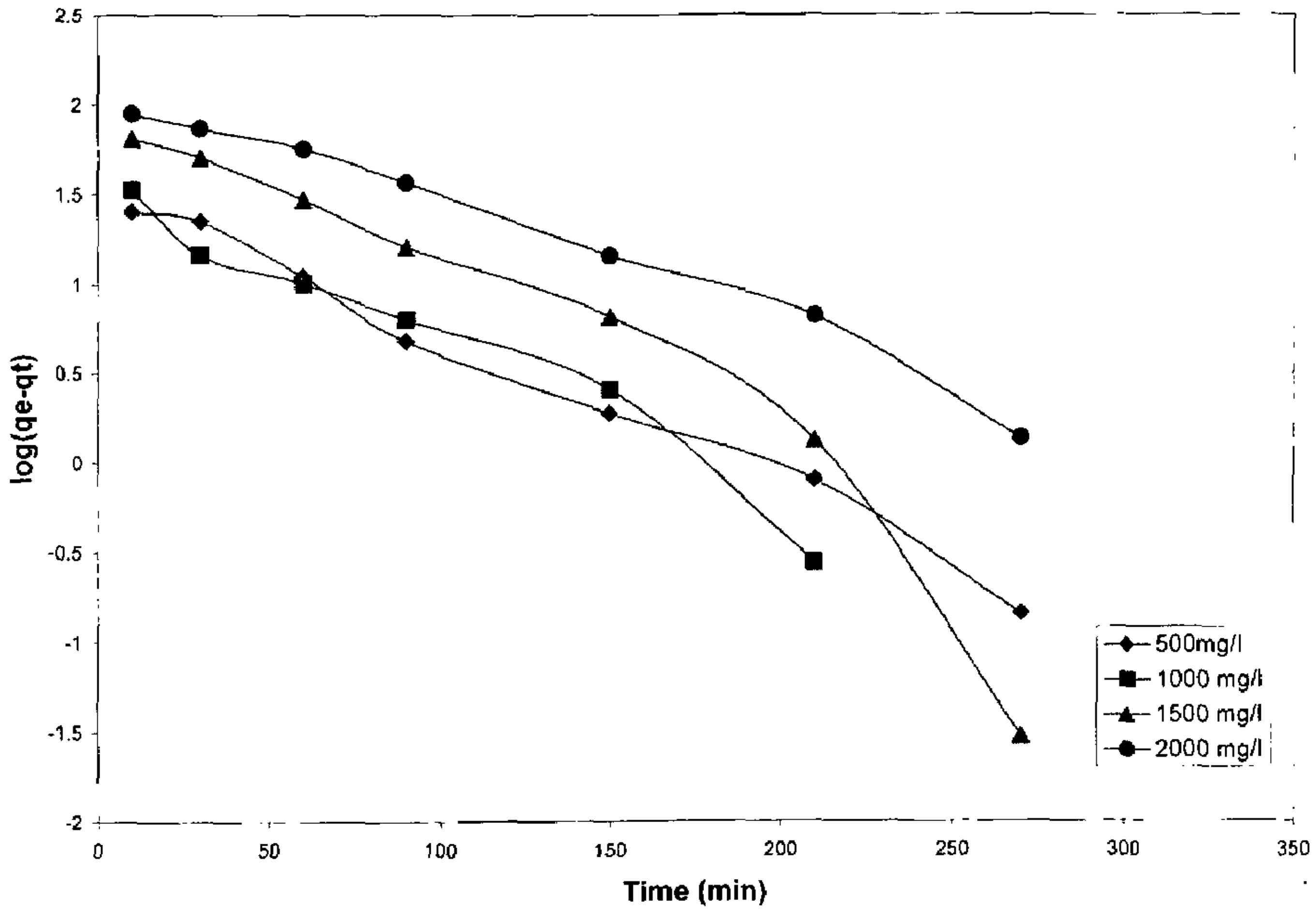

Fig.7.11 Pseudo First- order kinetics for the removal of Sn(II) by GAC (pH=4, T=303K, Co-500 -2000 mg/l, m=8g/l)

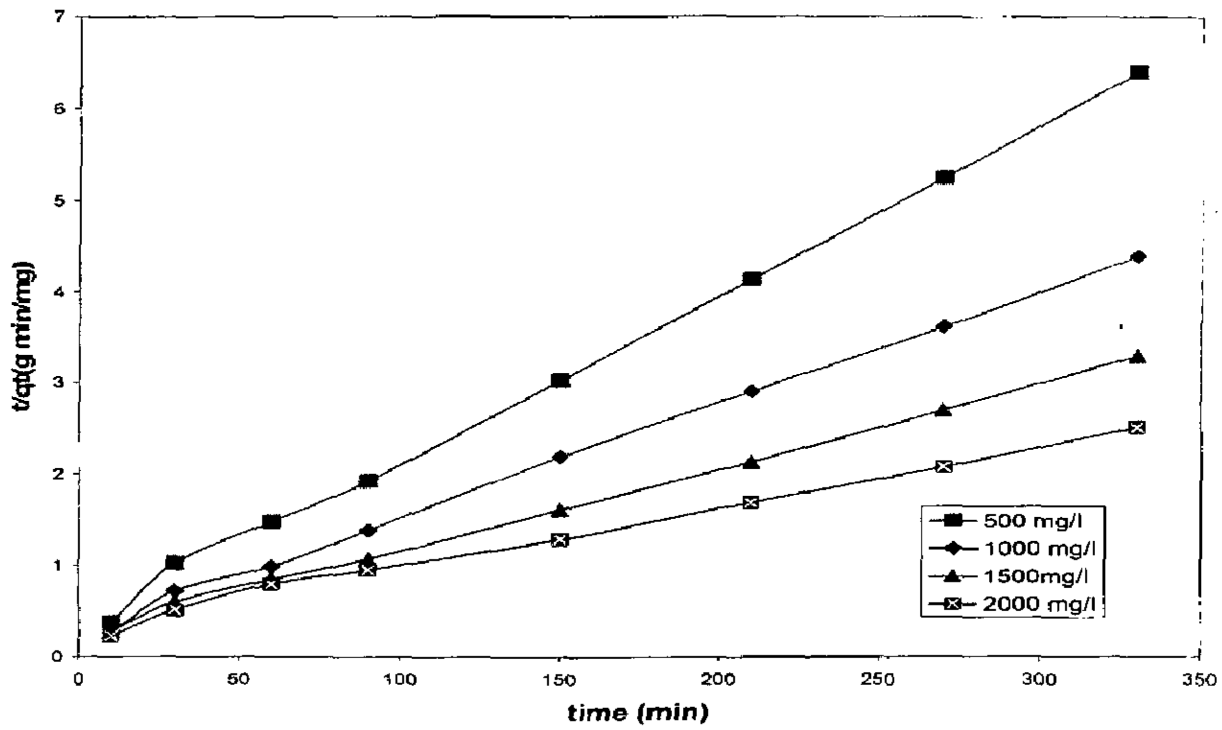

Fig.7.12 Pseudo second-order kinetics plots for the removal of Sn(II) by GAC(pH=4,T=303K,Co=500- 2000mg/l, m=8g/l)

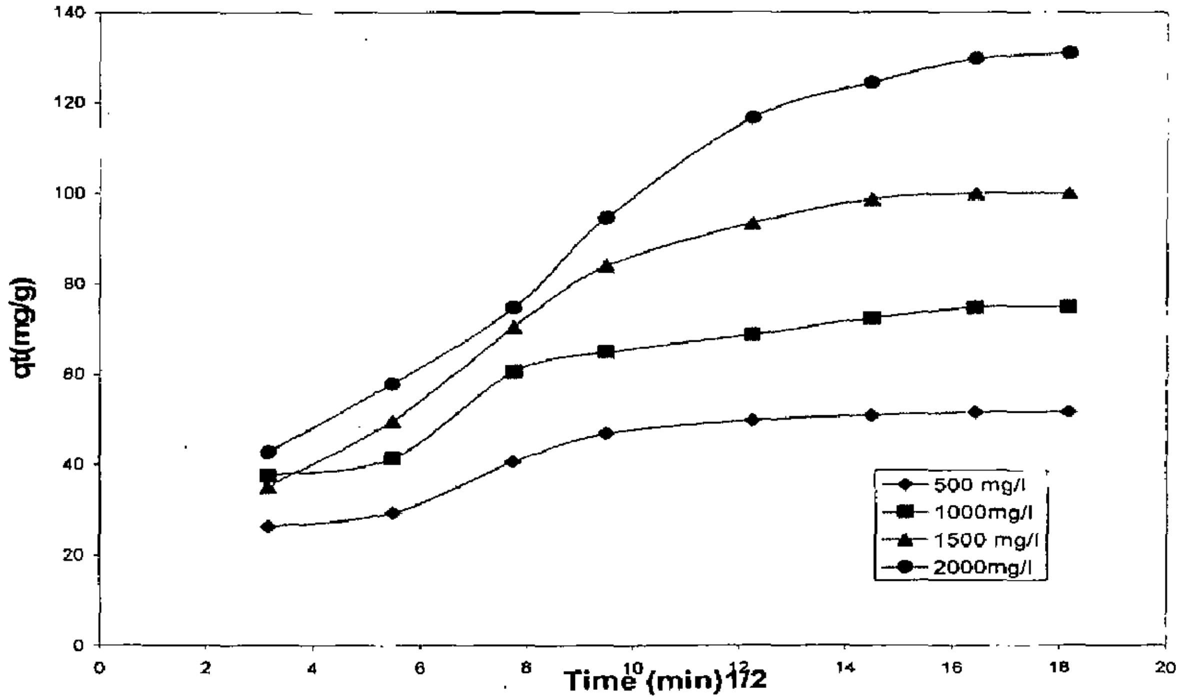

Fig.7.13 Weber and Morris intra particle diffusion plots for the removal of Sn(II) by GAC (pH=4,T=303K,Co-500-2000mg/l, m=8g/l)

Where k_{id} is the intra-particle diffusion rate constant (Fig.7.13) shows the results obtained for Sn(II). Values of intercept C give the idea about the thickness of boundary layer. The deviation of straight line from the origin (Fig7.13) may be due to difference 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.

From Fig 7.13, It may be seen that there are two separate regions-the initial portion is attributed to bulk diffusion and liner portion to intra-particle diffusion. The values of $K_{id,1}$ and $K_{id,2}$ as obtained from the intercepts of straight lines are listed in Table7.5. Again it may be that both film and pore diffusion was involved in the removal process to different extent. The values of intra-particle diffusion rate parameters are given in Table7.5.

Table 7.5 Kinetic parameter of the removal of tin by GAC (pH=4, T=303K, C_0=500-2000mg/l and m = 8g/l)

Pseudo -First -Order

C_0 mg/l	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	$K_f(min^{-1})$	R^2
500	51.532	34.127	0.0195	0.989
1000	74.943	51.558	0.01704	0.9412
1500	99.97	146.049	0.0382	0.9164
2000	131.0525	135.831	0.01566	0.9719

Pseudo-Second -Order

C_0mg/l	$q_{e,calc}$ (mg/g)	h (mg/g.min^{-1})	k_s	R^2
500	53.475	4.1788	0.0046	0.9968
1000	77.519	5.3966	0.00695	0.9963
1500	106.3829	5.1308	0.00453	0.9935
2000	144.927	4.0048	0.001906	0.9703

Intra Particle diffusion

C_o(mg/l)	K_{id1}(mg/g $min^{-1/2}$)	C_1	R_1^2
500	3.4132	13.628	0.9519
1000	4.785	20.113	0.9266
1500	7.8806	8.7861	0.9945
2000	7.3659	16.76	0.86
C_o (mg/l)	K_{id2}(mg/g $min^{-1/2}$)	C_2	R_2^2
500	0.3223	45.89	0.9321
1000	1.089	55.968	0.9164
1500	1.098	81.143	0.8026
2000	2.5047	87.036	0.9461

7.5 ADSORPTION EQUILIBRIUM STUDY

To optimize the design of an 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 used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, Redlich-Peterson, Dubinin-Radushkevich (D-R) and Temkin isotherm equations. Out of these Freundlich and Langmuir isotherm equations are widely used by researchers in the field of environmental engineering.

7.5.1 Freundlich and Langmuir Isotherm

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7.7}$$

$$\frac{C_e}{q_e} = \frac{1}{K_A q_m} + \frac{C_e}{q_m} \tag{7.8}$$

Fig7.14. to shows the Freundlich isotherm plots ($\ln q_e$ vs $\ln C_e$) for Sn(II) at 288.15, 303.15, 318.15K and 333.15K. Langmuir isotherm plot ($\frac{C_e}{q_e}$ vs C_e) are shown in Fig.7.15 to for Sn(II) adsorption on GAC.

Freundlich and Langmuir isotherm parameter along with linear correlation coefficients are given in Table7.6. At all temperatures, Langmuir isotherm represents a better fit of the experimental data then Freundlich isotherm equation. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, which describes the type of pattern and is defined as $R_L = 1/(1 + K_A C_o)$ (where Co is initial concentration and K_A is Langmuir constant) indicates the nature of adsorption .

If $R_L > 1$	unfavorable
$R_L = 1$	linear
$0 < R_L < 1$	favorable
$R_L = 0$	irreversible

The values of R_L for Sn(II) are also given in Table7.6. The value of R_L is found to be less than 1 for both the metals, so adsorption using GAC is favorable. The values of $\frac{1}{n}$ were also found to be less than 1. So, it again proves adsorption to be favorable.

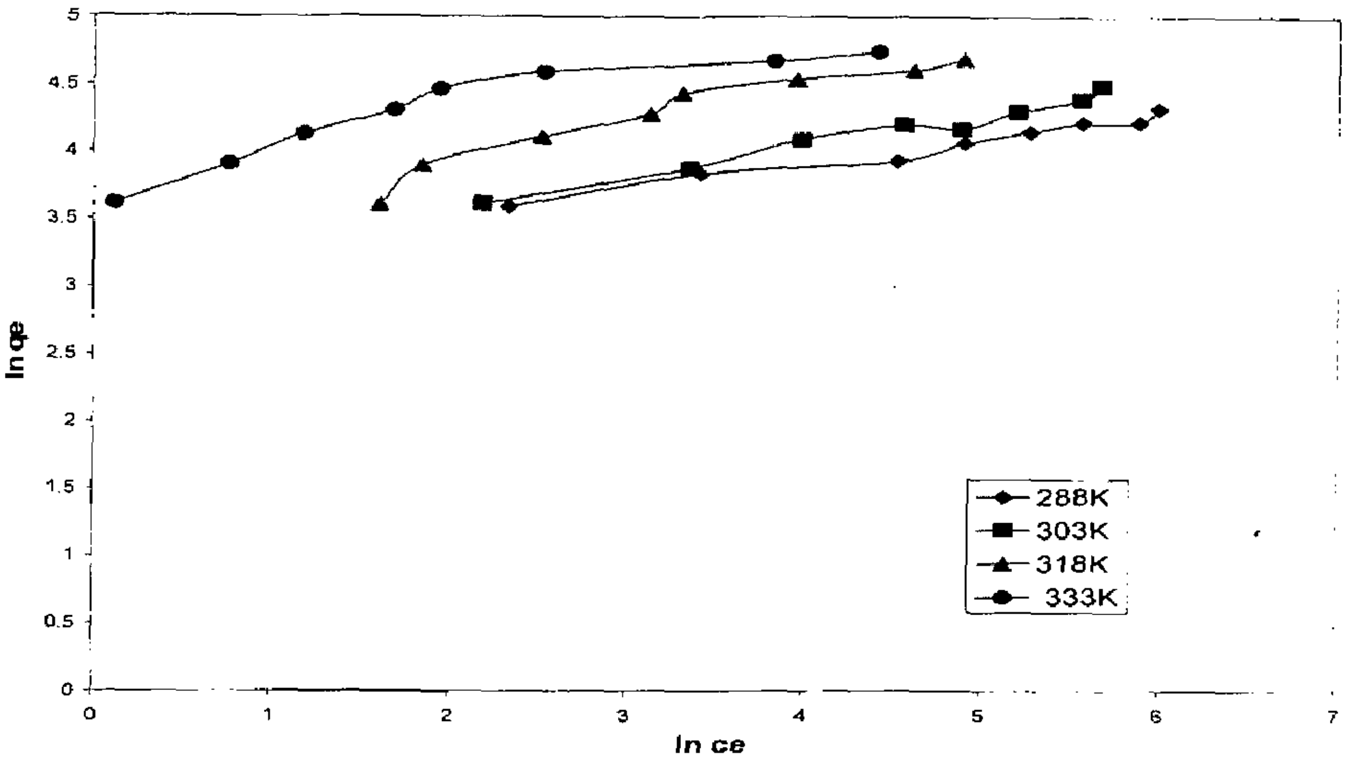

Fig.7.14 Freundlich isotherm plots for the removal of Sn(II)by GAC(pH=4, T=288K- 333K, t=330 min,Co= 300-1000 mg/l, m= 8g/l)

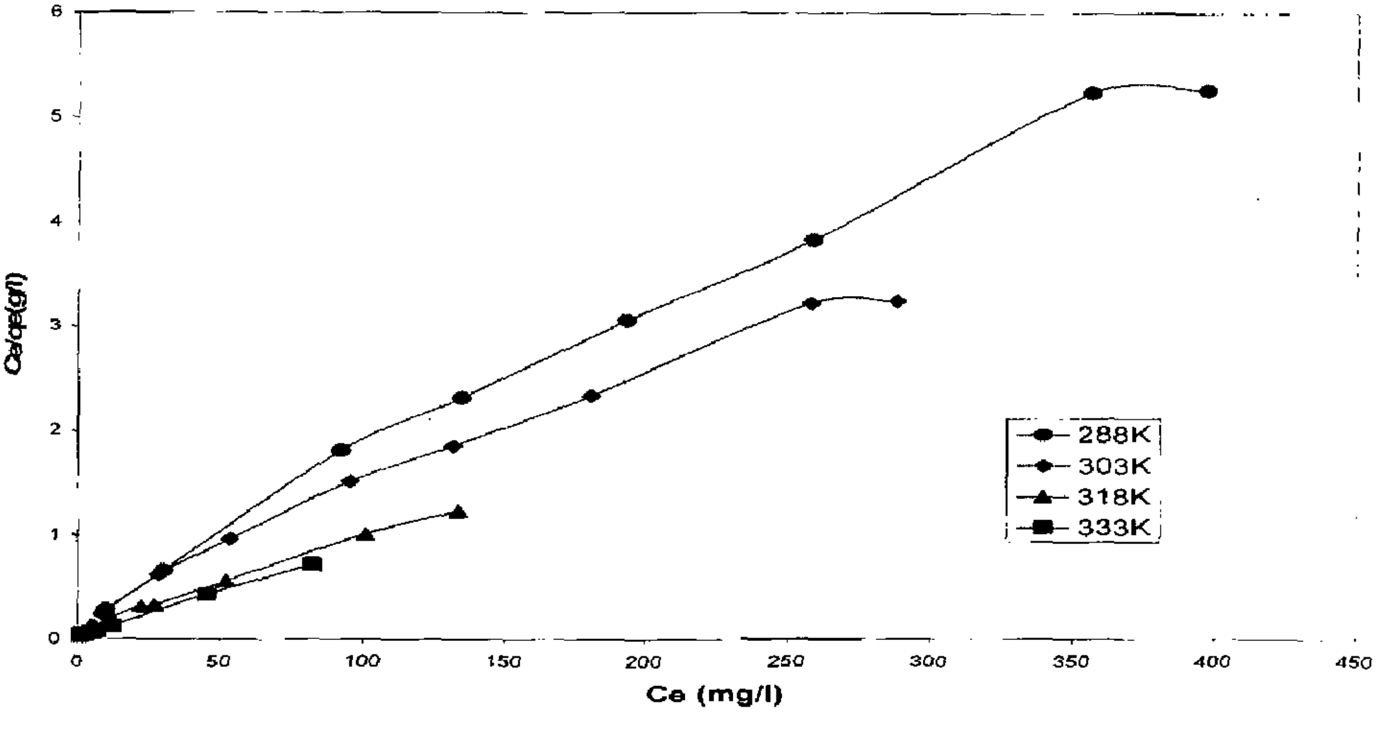

Fig.7.15 Langmuir isotherm plots for the removal of Sn(II) by GAC(pH=4,T=288K-333K, t= 330 min,Co=300-1000mg/l, m=8g/l)

7.5.2 Redlich-Peterson isotherm

Redlich and Peterson (1959) model has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{7.9}$$

Where K_R is R–P isotherm constant (l/g), a_R is R–P isotherm constant (l/mg) and β is the exponent which lies between 1 and 0, where $\beta = 1$

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{7.10}$$

It becomes a Langmuir equation. Where $\beta = 0$

$$q_e = \frac{K_R C_e}{1 + a_R} \tag{7.11}$$

i.e. the Henry's Law equation

Eq. (7.11) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1 \right) = \ln a_R + \beta \ln C_e \tag{7.12}$$

Plotting the left-hand side of equation (7.12) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure was adopted to solve equation (7.12) by maximizing the correlation coefficient between the theoretical data for q_e predicted from Eq. (7.12) and experimental data. Therefore, the parameters of the Eqs. were determined by minimizing the distance between the experimental data points and the theoretical model predictions with the solver add-in function of the Microsoft excel. Fig.7.16 to show the R-P isotherm plot. The R-P isotherm parameters and the correlation coefficients, R^2 for the R-P isotherms are listed in Table7.6. The correlation coefficients are significantly higher than both the Langmuir and Freundlich values for Sn(II) adsorption on GAC. The Redlich Peterson is certainly the best-fit isotherm equation of the three isotherm studied so far.

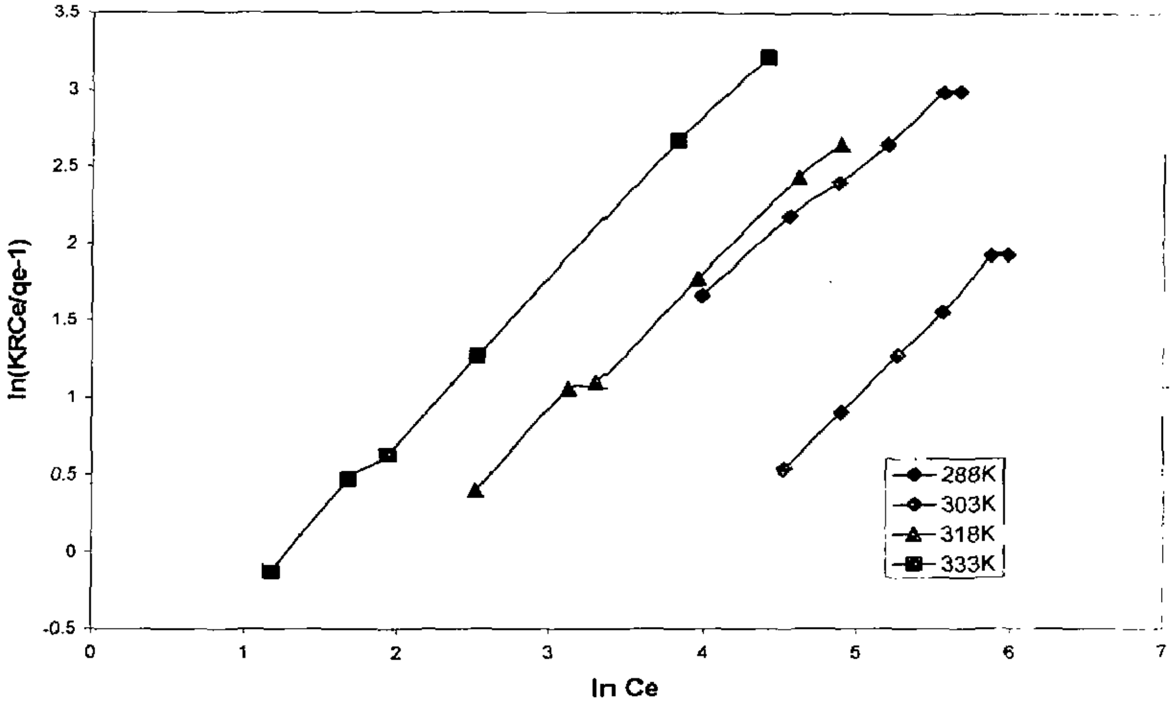

Fig.7.16 Redlich Peterson isotherm plots for removal of Sn(II) by GAC (pH=4,T=288-333K,t=330 min, Co=300-1000mg/l, m=8g/l)

7.5.3 Temkin Isotherm

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. The Temkin isotherm is represented by following equation:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad (7.13)$$

Eq. 7.13 can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{7.14}$$

Where $$B_1 = \frac{RT}{b} \tag{7.15}$$

The adsorption data can be analyzed according to Eq. 7.14. A plot of q_e versus lnCe enables the determination of the isotherm constants K_T and B_1. K is the equilibrium binding constant (l/mg) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. This isotherm for Sn(II) is plotted in Fig.7.17 to Compared to Langmuir the Temkin isotherm yields more negative values.

7.5.4 Dubinin-Radushkevich (D-R) isotherm

D-R (Dubinin and Radushkevich, 1947) is given as

$$q_e = q_s \exp(-B\varepsilon^2) \tag{7.16}$$

Where, q_s is the D-R constant and ε can be correlated as

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7.17}$$

The constant B gives the mean free energy E of sorption per molecule of sorbet when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship:

$$E = 1/\sqrt{2B} \tag{7.18}$$

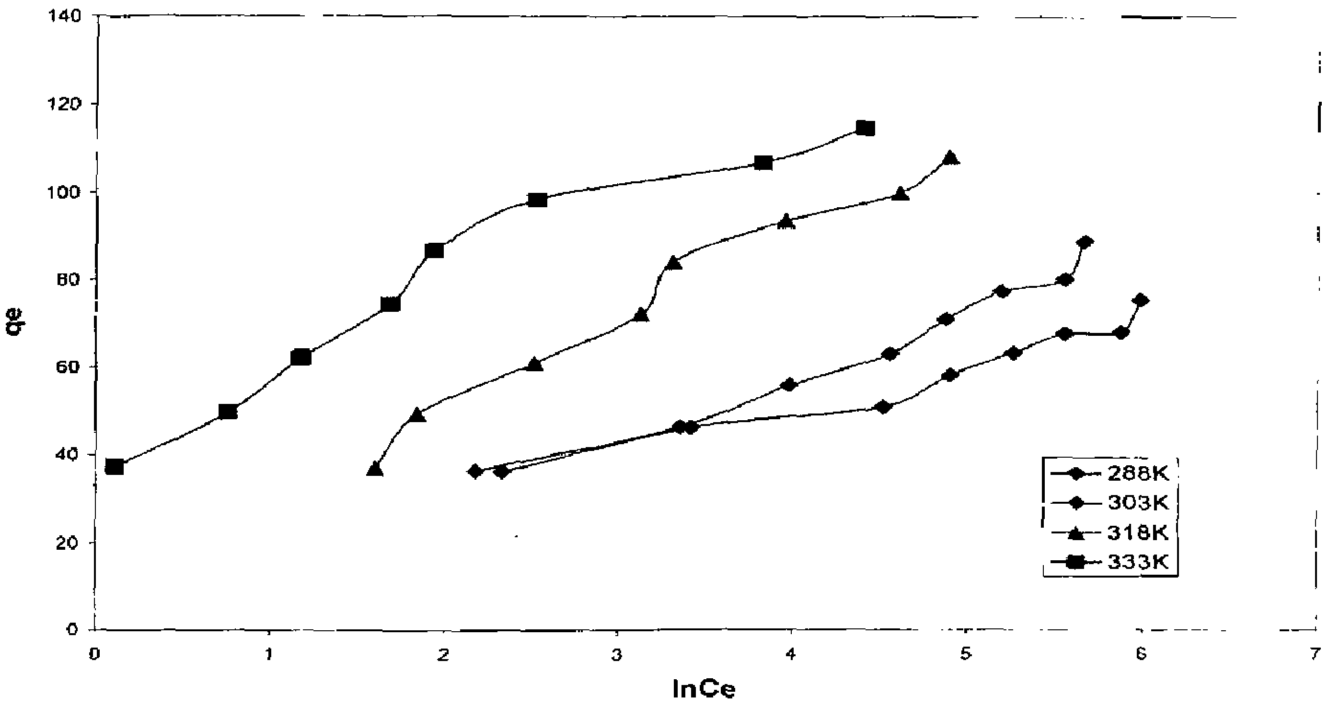

Fig.7.17 Temkin isotherm plots for removal of Sn(II) by GAC (pH=4,T=288K-333K,t=330min,Co=300-1000mg/l, m=8g/l)

Table 7.6 Isotherm Parameters for Removal of Tin by GAC (pH=4, T=288-330 K, t=330 min, C_0(500-2000mg/l) and m=8g/l)

Freundlich constants

T(K)	K_f(mg/g)(mg/l)$^{-1/2}$	1/n	R_f^2
288.15K	23.392	0.1876	0.9745
303.15K	22.340	0.2338	0.9756
318.15K	27.3249	0.2974	0.927
330.15K	17.416	0.3056	0.9798

Langmuir Constants

T(K)	K_L(1/g)	q_m(mg/g)	R_1^2
288.15	0.03335	76.3358	0.988
303.15	0.03189	92.5925	0.9862
318.15	0.09186	114.9425	0.9975
330.15	0.3512	117.647	0.9993

Tamkin constants

T(K)	K_T(mg/g)	B_1	R_1^2
288.15	3.1066	9.9299	0.9484
303.15	0.997	14.682	0.9614
318.15	1.5649	20.55	0.9755
330.15	0.3865	20.829	0.921

Redlich-Peterson constant

T(K)	K_R(1/g)	$a_R(1/mg)^{1/B}$	β	R^2
288.15	1.5	0.01974	0.9867	0.9967
303.15	6.5	0.2134	0.8094	0.9962
318.15	12.3	0.138	0.95	0.9973
333.15	36.0	0.2647	1.0355	0.9991

7.6 THERMODYNAMIC STUDY

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation

$$\Delta G^0 = -RT\ln K \qquad (7.19)$$

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (7.20)$$

Combining above two equations, we get

$$\ln K = \frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R}\frac{1}{T} \tag{7.21}$$

where ΔG^0 is the free energy change (kJ/mol), ΔH^0 is the change in enthalpy (kJ/mol), ΔS^0 is the entropy change (kJ/mol K), T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). Thus ΔH^0 can be determined by the slope of the linear Van't Hoff plot i.e. as ln K versus (1/ T), using equation:

$$\Delta H^0 = \left[R \frac{d \ln K}{d(1/T)} \right] \tag{7.22}$$

The negative ΔH^0 value confirms the endothermic nature of the overall sorption process. The adsorption process in the solid-liquid system is a combination of two processes: (a) The desorption of the molecules of solvent (water) previously adsorbed and (b) the adsorption of adsorbate species. ΔG^0 Values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative ΔG^0 indicates the feasibility and spontaneity of the adsorption process. The Gibbs free energy of adsorption of tin on GAC for temperatures 288.15, 303.15, 318.15 and 333.15K as calculated given in Table-7.7

Table7.7 Thermodynamic parameter for the removal of Tin by GAC

Δ G(kJ/mole K^{-1})				Δ H(kJ/moleK^{-1})	Δ S(J/mole K^{-1})
288K	303K	318K	333K	39.301	201.5978
-58.020	-61.044	-64.068	-67.092		

7.7 ERROR ANALYSIS

Due to the inherent bias resulting from linearization, five different error functions of non-linear regression basin were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data.

7.7.1 The sum of the squares of the errors (SSE)

This error function, SSE is given as

$$SSE = \sum_{i=1}^{n} \left(q_{e,cal} - q_{e,\exp}\right)_i^2 \tag{7.23}$$

Here, $q_{e,cal}$ and $q_{e,\exp}$ are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g) and n is the number of data points. This most commonly used error function; SSE has one major drawback in that it will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because of the magnitude of the errors, which increase as the concentration increases.

7.7.2 The sum of the absolute errors (SAE)

SAE is given as $SAE = \sum_{i=1}^{n} \left|q_{e,cal} - q_{e,\exp}\right|_i$ (7.24)

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data.

7.7.3 The average relative error (ARE)

ARE (Kapoor and Yang, 1989) is given as

$$ARE = \frac{100}{n} \sum_{i}^{n} \left| \frac{\left(q_{e,\exp} - q_{e,calc} \right)}{q_{e,\exp}} \right|_i \tag{7.25}$$

This error function attempts to minimize the fractional error distribution across the entire concentration range.

7.7.4 The hybrid fractional error function (HYBRID)

HYBRID is given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{\left(q_{e,\exp} - q_{e,calc}\right)}{q_{e,\exp}} \right] \tag{7.26}$$

This error function was developed [Porter and McKay 1999] to improve the fit of the ARE method at low concentration values. Instead of n as used in ARE, the sum of the fractional errors is divided by (n-p) where p is the number of parameters in the isotherm equation.

7.7.5 Marquardt's percent standard deviation (MPSD)

MPSD [Marquardt, 1963] has been used by a number of researchers in the field to test the adequacy and accuracy of the model fit with the experimental data. It has somewhat similarity to the geometric mean error distribution, but modified by incorporating the number of degrees of freedom. The values of all the error functions are given in table 7.8 for GAC

MPSD is given as

$$MPSD = 100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{\left(q_{e,mean} - q_{e,calc}\right)}{q_{e,mean}}\right)^2_i} \qquad (7.27)$$

Table 7.8 Values of Five different error analysis of isotherm models for adsorption of Tin by GAC (pH=4, T=288k-330K and t=330 min, Co=300-1000mg/l and m=8g/l)

288K					
	SSE	**SAE**	**ARE**	**HYBRID**	**MPSD**
Freundlich	32.1973	12.1626	2.5761	-0.33816	4.1002
Langmuir	124.8624	45.7571	12.2735	6.5658	21.2463
Tamkin	61.4188	17.5898	3.9047	-0.11166	5.68052
R-P	28.6911	47.8923	13.9215	16.633	3.5535
303K					
	SSE	**SAE**	**ARE**	**HYBRID**	**MPSD**
Freundlich	43.9733	15.4193	2.9272	-0.55216	3.8624
Langmuir	136.5858	40.6176	9.4560	4.9335	19.0652
Tamkin	86.6549	22.6629	4.9557	0.1046	6.9928
R-P	38.9843	23.7211	6.8854	26.2144	13.8277
318K					
	SSE	**SAE**	**ARE**	**HYBRID**	**MPSD**
Freundlich	157.9343	47.8508	8.3830	-0.61516	11.2588
Langmuir	81.2371	20.8282	3.1926	0.4336	5.6293
Tamkin	109.4052	24.3661	4.6916	-0.9115	7.3277
R-P	28.9157	26.9157	4.9055	0.12616	7.2097
333K					
	SSE	**SAE**	**ARE**	**HYBRID**	**MPSD**
Freundlich	169.1269	43.7542	55.3346	73.7734	64.4423
Langmuir	60.8535	19.3852	3.5717	1.4113	5.3828
Tamkin	186.6549	47.0159	8.1285	-0.2166	11.0453
R-P	46.8533	54.2377	7.9967	5.1726	11.7212

CHAPTER 8
CONCULUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The following major conclusions drawn from the present work and study are given below:

1. Adsorption of Sn(II) was maximum at pH 4.0 and decreased with the in increase pH.
2. Percent removal of Sn(II) increased with the increase in adsorbent dose upto 8 g/l after that removal remains constant.
3. Adsorption of Sn(II) onto GAC always increased with time and reached equilibrium in 330 min. Rate of adsorption of Sn(II) was fast initially and decreased gradually with increase in time.
4. Adsorption of Sn(II) onto GAC increased with increase in temperature indicating endothermic nature of the adsorption process.
5. Kinetic study shows that Sn(II) adsorption on GAC followed the Pseudo-second order kinetics.
6. Weber-Morris plot revealed that the intraparticle transport (pore diffusion) was not the only rate-controlling step.
7. Langmuir and Redlich-Peterson isotherms follow the equilibrium adsorption data very well.
8. GAC showed excellent adsorptive characteristics for the removal of Sn(II) from synthetic solution

8.2 RECOMMENDATIONS

1. GAC from other sources should be characterized for physicochemical parameters and surface characteristics to arrive at average values for use in design.
2. GAC which showed good adsorptive characteristic for removal of Sn(II) from synthetic solution and should further be tested for the treatment of Sn(II) bearing industrial wastewater.

3. Column study should be performed, utilizing GAC as adsorbent for the removal of Sn(II) from both synthetic and industrial effluents.
4. GAC should be further be tested for the removal of other heavy metals.
5. Costing of the industrial scale treatment system utilizing GAC as adsorbent, should be carried out to popularize its usage, as it is easily available (almost free of cost) in developing countries.

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Table A-1: Calibration Curve for Tin

S.No.	Concentration	Absorbance
1.	0	0.0
2.	35	0.0474
3.	40	0.0542
4.	50	0.0719
5.	60	0.0814
6.	75	0.1005
7.	80	0.1071
8.	100	0.1389
9.	120	0.1679
10.	135	0.1886

Table A-2: Effect of pH for removal of Tin on *initial concentration* of 500 mg/l at 303.15K with GAC dose (8g/l)

S.No.	pH	% Tin removal
1.	2	98.0
2.	4	99.4
3.	6	99.0
4.	8	83.1064
5.	10	70.651
6.	12	34.822
7.	14	39.537

Table A-3 Effect of contact time on removal of Tin on various initial concentrations using GAC dose (8g/l)

S.No.	Time (min)	500 (mg/l)	1000(mg/l)	1500(mg/l)	2000(mg/l)
		%Removal	%Removal	%Removal	%Removal
1.	10	41.954	29.972	18.685	17.071
2.	30	46.844	33.092	26.472	23.161
3.	60	64.87	48.425	37.603	24.977
4.	90	74.844	51.915	44.748	37.855
5.	150	79.466	54.94	49.81	46.636
6.	210	81.182	57.9125	52.6097	49.771
7.	270	82.22	59.733	53.301	51.8825
8.	330	82.452	59.955	53.31	52.421

Table A-4 Effect of initial concentration on removal of Tin on various temperatures using GAC (8g/l)

S.No.	Initial Conc.(mg/l)	288.15K	303.15K	318.15K	333.15K
		%Removal	%Removal	%Removal	%Removal
1.	300	96.5786	97.058	98.345	99.6257
2.	400	92.384	92.844	98.42875	99.46525
3.	500	81.5482	89.2698	97.5324	99.351
4.	600	77.5662	84.0738	96.1986	99.10367
5.	700	72.38214	81.1851	96.087	99.007
6.	800	67.6335	77.4265	93.472	98.4415
7.	900	60.4335	71.297	88.79044	94.9075
8.	1000	60.3217	71.1609	86.6414	91.7343

Table A-5 Lagergen plot for removal of Tin for differential initial concentration at 303Kusing GAC dose (8g/l)

S.No.	Time (min)	Log(q_e-q_t)	Log(q_e-q_t)	Log(q_e-q_t)	Log(q_e-q_t)
		500(mg/l)	1000(mg/l)	1500(mg/l)	2000 (mg/l)
1.	10	1.403314	1.5737	1.812479	1.9463
2.	30	1.3474	1.526065	1.7018	1.8642
3.	60	1.0409	1.1587	1.4692	1.8363
4.	90	0.67715	1.00216	1.2034	1.5618
5.	150	0.27097	0.797181	0.81787	1.16024
6.	210	-0.10032	0.407072	0.122789	.821186
7.	270	-0.84239	-0.55674	-1.52288	.129216
8.	330	-	-	-	-

Table A-6 Pseudo second order kinetics plot for Removal of Tin for different initial concentration at 303K using GAC dose (8g/l)

S.No.	Time (min)	t/q_t	t/q_t	t/q_t	t/q_t
		500mg/l	1000mg/l	1500mg/l	2000mg/l
1.	0	0	0	0	0
2.	10	0.3817	0.2669	0.285429	0.234316
3.	30	1.02467	0.7252	0.604412	0.518112
4.	60	1.479883	0.991224	0.850988	0.96088
5.	90	1.92400	1.3868	1.071476	0.951487
6.	150	3.02016	2.1868	1.6060	1.28656
7.	210	4.138869	2.9009	2.1288	1.6877
8.	270	5.2540	3.616	2.7016	2.0816
9.	330	6.4037	4.4033	3.300	2.5180

Table A-7 Weber Morris plot for Removal of Tin for different initial concentration at 303K using dose (8g/l)

S.No.	(Time)$^{0.5}$ (min)$^{0.5}$	q_t(mg/g)	q_t(mg/g)	q_t(mg/g)	q_t(mg/g)
		500 mg/l	1000mg/l	1500mg/l	2000mg/l
1.	0	0	0	0	0
2.	3.1622	26.2212	37.465	35.035	42.6775
3.	5.477	29.2775	41.365	49.635	57.9024
4.	7.7459	40.5437	60.5312	70.5062	62.4425
5.	9.4868	46.7775	64.89375	83.9962	94.58875
6.	12.2474	49.6625	68.6750	93.3953	116.5921
7.	16.414.4913	50.7385	72.3906	98.6432	124.4275
8.	16.4316	51.3887	74.6661	99.9921	129.4275
9.	18.1659	51.5325	74.9437	99.9704	131.0525

Table A-8 Freundlich Isotherm for removal of Tin at different temperature with GAC dose (8g/l)

S.No.	288.15K		303.15K		318.15K		330.15K	
	lnq_e	lnC_e	lnq_e	lnC_e	lnq_e	lnC_e	lnq_e	lnc_e
1.	3.5895	2.3286	3.6115	2.1777	3.6076	1.60221	3.6205	0.1160
2.	3.8328	3.4165	3.8773	3.3542	3.8961	1.83811	3.9066	0.7603
3.	3.9311	4.5246	4.090	3.9825	4.1101	2.5126	4.1286	1.1771
4.	4.634	4.9023	4.200	4.5597	4.2787	3.2271	4.3084	1.6823
5.	4.1484	5.2643	4.1711	4.8805	4.4317	3.3101	4.4616	1.9380
6.	4.2141	5.5565	4.2996	5.1962	4.5376	3.9554	4.5894	2.5239
7.	4.2192	5.8752	4.3846	5.5542	4.6040	4.61391	4.6706	3.8249
8.	4.3228	5.9833	4.4880	5.6643	4.6849	4.8947	4.7420	4.4146

Table A-9 Langmuir Isotherm for Removal of Tin at different temperature with GAC dose (8g/l)

S.No.	288.15K		303.15k		318.15K		330.15K	
	C_e/q_e	C_e	C_e/q_e	C_e	C_e/q_e	C_e	C_e/q_e	C_e
1.	0.2834	10.264	0.2429	8.826	0.1346	4.964	0.03009	1.123
2.	0.6594	30.463	0.6166	28.624	0.1277	6.285	0.04301	2.139
3.	1.8101	92.259	0.9615	53.651	0.2024	12.338	0.0522	3.245
4.	2.313	134.600	1.5154	95.557	0.3161	22.808	0.07235	5.378
5.	3.05245	193.325	1.8540	131.704	0.3257	27.388	0.08167	6.945
6.	3.82845	258.932	2.3323	180.588	0.5586	52.219	0.12665	12.468
7.	5.2383	356.932	3.2206	258.325	1.0099	100.886	0.4262	45.832
8.	5.2622	396.783	3.2421	288.3904	1.2330	133.586	0.7208	82.657

Table A-10 Tamkin Isotherm for Removal of Tin at different Temperature with GAC dose (8g/l)

S.No.	288.15 K		303.15K		318.15k		330.15k	
	q_e	$\ln C_e$	q_e	$\ln C_e$	q_e	$\ln C_e$	q_e	$\ln C_e$
1.	36.217	2.3286	36.3967	2.1777	36.8795	1.60221	37.35963	0.1160
2.	46.19213	3.4165	46.422	3.3542	49.2143	1.83811	49.73263	0.7603
3.	50.96763	4.5246	55.7936	3.9825	60.95775	2.5126	62.0943	1.1771
4.	58.175	4.9023	63.05537	4.5597	72.149	3.2271	74.3277	1.6823
5.	63.334	5.2643	71.037	4.8805	84.0765	3.3101	86.63188	1.9380
6.	67.6335	5.5565	77.4265	5.1962	93.4726	3.9554	98.4414	2.5239
7.	67.9842	5.8752	80.2093	5.5542	99.88925	4.61391	106.771	3.8249
8.	75.4021	5.9833	88.9512	5.6643	108.3018	4.8947	114.6679	4.4146

Table A-11 Redlich–Peterson adsorption isotherm for removal of Tin at different temperatures with DAC dose (8g/l)

S.No	288K		303K		318K		333K	
	ln(K_R*Ce/qe-1)	lnCe	ln(K_R*Ce/qe-1)	lnCe	ln(K_R*Ce/qe-1)`	lnCe	ln(K_RCe/qe-1)	lnCe
1.	0.5395	4.5246	1.6584	3.9825	0.3984	2.5123	-0.1263	1.1771
2.	0.9044	4.9023	2.1804	4.5597	1.0606	3.1276	0.47299	1.6823
3.	1.2749	5.26437	2.4025	4.8801	1.10085	3.3105	0.6344	1.9380
4.	1.5566	5.5565	2.6504	5.1962	1.7701	3.9554	1.2696	2.5231
5.	1.9253	5.8752	2.9924	5.5542	2.4356	4.613	2.6709	3.8249
6.	1.9305	5.9833	2.9994	5.6643	2.6512	4.8947	3.2168	4.4146