

## Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent

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### Abstract

The removal of Cd(II), Pb(II), Hg(II), Cu(II), Ni(II), Mn(II) and Zn(II) by carbon aerogel has been found to be concentration, pH, contact time, adsorbent dose and temperature dependent. The adsorption parameters were determined using both Langmuir and Freundlich isotherm models. Surface complexation and ion exchange are the major removal mechanisms involved. The adsorption isotherm studies clearly indicated that the adsorptive behaviour of metal ions on carbon aerogel satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy.

The applicability of the Lagergren kinetic model has also been investigated. Thermodynamic constant ( $K_{ad}$ ), standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were calculated for predicting the nature of adsorption. The results indicate the potential application of this method for effluent treatment in industries and also provide strong evidence to support the adsorption mechanism proposed.

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### 1. Introduction

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of life. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe), etc.

This problem has received considerable amount of attention in recent years. One primary concern is that marine animals which can readily absorb those heavy metals in wastewater and directly enter the human food chains present a high health risk to consumers.

Wastewater from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery-manufacturing industries, etc. contains one or more of these toxic heavy metals. Industries carries out operations like electroplating, metal/surface finishing and solid-state wafer processing, generate wastewater contaminated with hazardous heavy metals. The concentrations of some of the toxic metals like Cr, Hg, Pb, As, etc. are higher than permissible discharge levels in these effluents. It, therefore, becomes necessary to remove these heavy metals from these wastewaters by an appropriate treatment before releasing them into the environment.

#### 1.1. Lead

Lead is one such heavy metal with specific toxicity and cumulative effects. The chief sources of lead in water are the effluents of lead and lead processing industries. Lead is also used in storage batteries, insecticides, plastic water pipes,

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food, beverages, ointments and medicinal concoctions for flavoring and sweetening [1].

Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnancy. Chronic lead poisoning may cause three general disease syndromes:

- (a) Gastrointestinal disorders, constipation, abdominal pain, etc.
- (b) Neuromuscular effects (lead lapsy) weakness, fatigue muscular atrophy.
- (c) Central nervous system effects or CNS syndrome that may result to coma and death [2].

### 1.2. Cadmium

Cadmium is an irritant to the respiratory tract and prolonged exposure to this pollutant can cause anemia and a yellow stain that gradually appears on the joints of the teeth. Cadmium and their salts are used in electroplating, paint pigments, plastics, silver cadmium batteries [3], smelting, cadmium nickel batteries, stabilizer, phosphate fertilizer, mining and alloy industries [4,5].

### 1.3. Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fibre production, pipe corrosion and metal plating industries [6]. The other major industries discharging copper in their effluents are paper and pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes [7] also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink.

Copper has been reported to cause neurotoxicity commonly known as “Wilson’s disease” due to deposition of copper in the lenticular nucleus of the brain and kidney failure [8]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever [9]. Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers.

### 1.4. Mercury

Mercury is generally considered to be one of the most toxic metals found in the environment [10]. Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in humans and animals. The major sources of mercury pollution in environment are industries like chlor-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer [11], batteries, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals [12].

Methyl mercury causes deformities in the offspring, mainly affecting the nervous system (teratogenic effects). Children suffer from mental retardation, cerebral palsy and convulsions. Mercury also brings about genetic defects causing chromosome breaking and interference in cell division, resulting in abnormal distribution of chromosome. Mercury causes impairment of pulmonary function and kidney, chest pain and dyspnoea [13,14]. The harmful effect of methyl mercury on aquatic life and humans was amply brought out by the Minamata episode in Japan [15].

### 1.5. Manganese

Chronic manganese poisoning has been reported to affect the central nervous system, and manganese pneumonia has often been reported to be resulting in death [16,17]. Manganese compounds are known to catalyze the oxidation of other pollutants, such as SO<sub>2</sub> to more harmful compounds. Manganese toxicity has been found to results in acute effects on lungs, liver, central nerves system and blood system of the body. Manganese and its salts have been reported to be present in the wastewater of the following industries: steel alloy dry cell battery, glass and ceramics, paint and varnish, ink and dyes, match and fire works [18]. Galvanization plant effluents have also been found to contain Mn(II) at significant levels [19].

### 1.6. Nickel

Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni(II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries [20].

Higher concentration of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni(II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [21–23].

### 1.7. Zinc

Due to its remarkable resistant to atmospheric corrosion, zinc is commonly used to protect iron from rusting, in the process called galvanization. Zinc is widely used for the manufacturing of zinc white and several useful alloys such as brass, German silver, delta metal, for the preparation of gold and silver in the cyanide method, for the desilverization of lead in Parks process and as an anode material in galvanic cells.

Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments, steel production and batteries [24]. Zinc toxicity from excessive ingestion is uncommon but causes gastrointestinal distress and diarrhoea.

### 1.8. Treatment techniques

In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment. Conventional methods for the removal of heavy metals include precipitation, coagulation/flocculation, ion exchange, reverse osmosis [25,26], complexation/sequestration, electrochemical operation and biological treatment [27,28]. Application of above-mentioned methods becomes economically unviable for the removal of heavy metals at lower concentrations. Adsorptive treatment using non-conventional adsorbents, such as agricultural and industrial solids wastes, have been used for the removal of heavy metals [29]. A number of other materials have also been used to remove heavy metals from wastewater, such as peat, human hair, wool, silk, and water hyacinth [30]. Many papers have appeared on preparation of activated carbon from cheaper and readily available materials [31]. Tree bark and bottom ash [32] from thermal power plant [33], sawdust [34], cow dung [35], activated rice husk carbon [36], peanut hull, carbon black [37] and activated carbon electrode [38], have been investigated for the adsorption of heavy metals.

Activated carbon produced from almond shell [39], sawdust based GAC [40], tree bark treated with formaldehyde and sulphuric acid [41], bone char, tea leaves, wood charcoal [42], coconut shell carbon [43,44], sulphurised activated carbon [45,46], ozonized activated carbon, rice hulls and rice bran [47], pine bark and agricultural waste [48] have been used with and without treatment for adsorption. Adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds [49,50], which have metal binding functional groups, such as carbonyl, hydroxyl, sulphate, phosphate and amino groups [51]. Some of the other adsorbents used for the adsorption of heavy metals are fly ash [52], dispersed iron-oxide, activated carbon fibres [53], waste rubber [54], polymerised onion skin, peat moss [55], polymerised sawdust [56], treated sawdust, mustard husk [57], cellulose [51], aqueous solution of waste Fe(III)/Cr(III) hydroxide, rice husk [49], agricultural waste and by products [58], tree bark, peanut skin, citrus skin, coffee husk [21], coconut shell and peanut hull carbon, ozonized GAC [59], heat treated and sulphurised GAC, steam sulphurised GAC prepared from bagasse pith and activated alumina [50].

Moreover, the removal of metal ions from their solutions in the presence of agricultural materials may be due to the adsorption on surface and pores and also to complexation by these materials.

The main objective of this study was to investigate the feasibility of using carbon aerogel for the maximum removal of above metal ions from aqueous solutions at optimised process parameters such as initial concentration, adsorbent dose, contact time and pH.

## 2. Experimental

### 2.1. Instrumentation

GBC 932 AA atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze the concentration of heavy metals. The minimum detection limit was equal to or less than EPA requirement. Three standard solutions with concentrations of heavy metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for heavy metals concentration, those samples in which the concentration of heavy metals is observed beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and those results in which the standard deviations were found greater than 0.1 mg/l were not accepted.

The pH measurements were performed with a controlled pH analyzer (LAB INDIA). The pH meter was standardized using buffer solutions of pH values: 4, 7, 9 and 12.

Micromeritics ASAP 2010 surface area analyzer and a mechanical shaker of WIDSONS SCIENTIFIC make was used for all the adsorption experiments for agitating the sample for a desired contact time.

### 2.2. Chemicals

Analytical grade reagents were used for heavy metal solution, ACS reagent grade concentrated nitric acid, NaOH and pH buffer solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

### 2.3. Adsorbate solution

Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analar grade salts in the distilled demineralised water. The salts used are cadmium chloride, zinc chloride, manganese chloride, mercury chloride, nickel nitrate, copper nitrate, lead nitrate for Cd(II), Zn(II), Mn(II), Hg(II), Ni(II), Cu(II), Pb(II), respectively, for the preparation of stock solution. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

### 2.4. Adsorbent

Carbon aerogels are new and emerging adsorbent materials composed of covalently bonded nanometer sized

Table 1  
Characteristics of the carbon aerogel

Parameters	Value
pH	8.4
Conductivity ( $\mu\text{S cm}^{-1}$ )	125
Salinity	0.0
Bulk density (g/ml)	0.74
Cation exchange capacity (meq/g)	0.8
Moisture (%)	14
Decolorizing capacity (mg/g)	4.95
Single point surface area ( $\text{m}^2/\text{g}$ )	420
BET surface area ( $\text{m}^2/\text{g}$ )	426
Langmuir surface area ( $\text{m}^2/\text{g}$ )	544
Micropore area ( $\text{m}^2/\text{g}$ )	148
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.0632
Average pore diameter A	0.445
Maximum pore volume ( $\text{cm}^3/\text{g}$ )	0.202
Median pore diameter A	7.625
Carboxylic functional group (meq/(g CA))	0.8
Lactonic functional group (meq/(g CA))	0.07

particles that are arranged in three-dimensional network and have high porosity and high surface area. Thus, maybe produced in solid shapes, powder and sheet forms and provide excellent treatment efficiency in a cost effective manner for the purification of effluents/wastewaters. Stock aerogels are derived from the sol–gel polymerization of selected resorcinol formaldehyde monomers in solution. The sol–gel solution is cast into the desired shape after the formation of a highly cross-linked gel, the solvent is removed from the pores of the gel. The remaining rigid monolithic shape consists of covalently bonded. Resorcinol formaldehyde (Rf) aerogels are carbonized to form pure carbon aerogels. They are mainly prepared by pyrolysis of Rf aerogels in an inert atmosphere.

Carbon aerogel (supplied by Marketech International, USA) was used as an adsorbent material without any pre-treatment. However, it was characterized for relevant parameters before conducting experiments (shown in Table 1).

### 2.5. Batch mode adsorption studies

The adsorption of heavy metals on carbon aerogel was studied by batch technique. The general method used for this study is described as below:

A known weight of adsorbent (e.g. 0.5–1.2 g adsorbent) was equilibrated with 100 ml of the heavy metals solution of known concentration in a stoppered borosil glass flask at a fixed temperature in a thermostatic mechanical shaker (WIDSONS Scientific) for a known period (24–72 h) of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman No. 1 filter paper. The concentration of heavy metal ions remaining in solution was measured by AAS (GBC 932 AA) using flame method. The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using nitric acid, sodium hydroxide and buffer solutions when required. Adsorption of metal ions on the walls of glass flasks

determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution.

The percent heavy metal removal was calculated using Eq. (1)

$$\text{metal ion removal (\%)} = (C_0 - C_e) \times \frac{100}{C_0} \quad (1)$$

where  $C_0$ : initial metal ion concentration of test solution, mg/l;  $C_e$ : final equilibrium concentration of test solution, mg/l.

## 3. Results and discussion

### 3.1. Effect of initial concentration of heavy metal

The effect of initial concentration on the percentage removal of heavy metals by carbon aerogel is shown in Fig. 1. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration. For Hg(II) is seen the percentage removal is almost complete (nearly 100%) throughout the initial metal ions concentration range 1–5 mg/l for 10 g/l adsorbent dose, at pH 6 and a contact time of 48 h. For Mn(II), Zn(II) and Pb(II) at same adsorbent dose and contact time, there are slight drop in percentage removal at higher initial concentration, whereas for Ni(II), Cd(II) and Cu(II), the percentage removal is highly effective upto 1 mg/l initial concentration after which percentage removal decreases gradually to below 80%. At higher initial concentrations, Cu(II) shows greater percentage removal than Cd(II) and Ni(II). At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percent-

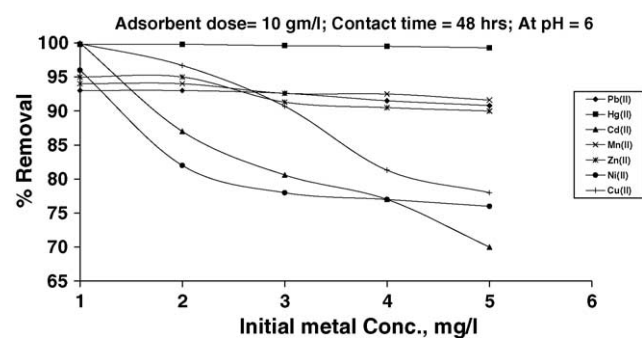


Fig. 1. Effect of initial metal concentration on percent removal of heavy metals by carbon aerogel.

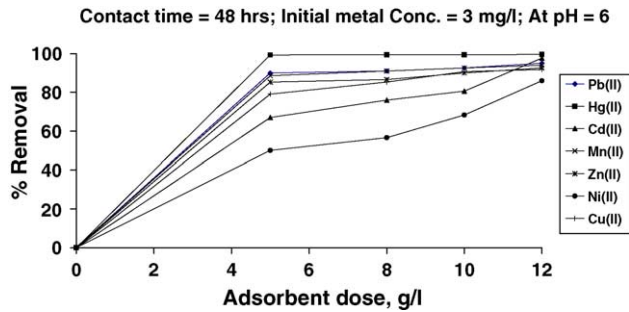


Fig. 2. Effect of adsorbent dosage on percent removal of heavy metals by carbon aerogel.

age removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent.

### 3.2. Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Fig. 2 over the range 5–12 g/l, at pH 6 the percentage removal of heavy metals is seen to increase with adsorbent dose. From Fig. 2, the percentage removal of Hg(II) ions show 100% removal throughout the range of concentrations studied (1–5 mg/l). It is observed that there is a sharp increase in percentage removal with adsorbent dose for Ni(II) and Cd(II) ions, Pb(II) and Mn(II) ions but in case of Cu(II) and Zn(II) ions, there is slight and gradual increase in percentage removal with increasing dose.

It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

### 3.3. Effect of contact time

Fig. 3 shows the variation in the percentage removal of heavy metals with contact time using 10 g/l of carbon aerogel at pH 6 for varying initial metal ions concentration ranging from 1 to 5 mg/l. It is observed that for Hg(II) ions, the percentage removal is nearly 100% even throughout the all contact times.

It is observed that in all cases the percentage removal is comparatively lower for 24 h contact time, with increasing removal efficiencies at higher contact time. In case of Ni(II) and Cd(II) ions rise sharp rise in percentage removal with increasing contact time. On other hand, percentage removal of Mn(II), Zn(II) and Cu (II) increases gradually with contact time, reaching nearly 100% removal only at around 72 h.

It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration

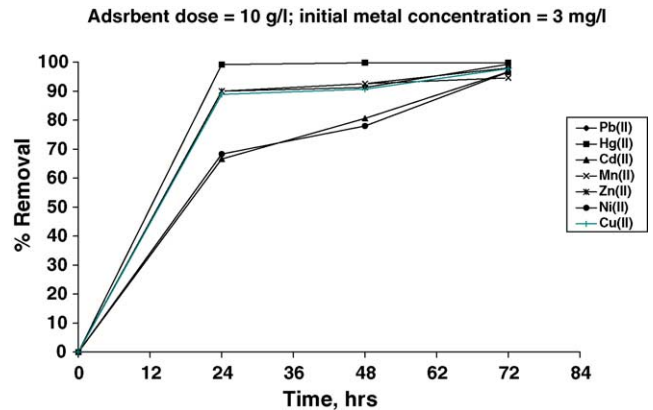


Fig. 3. Effect of contact time on percent removal of heavy metals by carbon aerogel.

of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with carbon aerogel was experimentally found to be about 48 h.

### 3.4. Effect of pH

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 4 shows the effect of pH on heavy metals removal efficiencies of carbon aerogel. These studies were conducted at a constant initial metal ions concentration of 3 mg/l, adsorbent dose 10 g/l solution and agitation period of 48 h for all heavy metal ions at varying the pH on carbon aerogel.

The percentage adsorption increases with pH to attain a maximum at pH 6 and thereafter it decreases with further increase in pH. The maximum removal of Hg(II), Mn(II), Cu(II), Zn(II) and Ni(II) at pH 6 were found to be nearly 99.2, 92.6, 88.8, 93.3 and 69%, respectively, whereas, for Pb(II) 93% removal at pH 7 and for Cd(II) 91.3% removal at pH 4.

The maximum adsorption at pH 6 may be attributed to the partial hydrolysis of  $M^+$ , resulting in the formation of  $MOH^+$  and  $M(OH)_2$ .  $M(OH)_2$  would be adsorbed to a greater extend on the non-polar adsorbent surface compare to  $MOH^+$ . With increase of pH from 2 to 6, the metal exists as  $M(OH)_2$  in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption. At

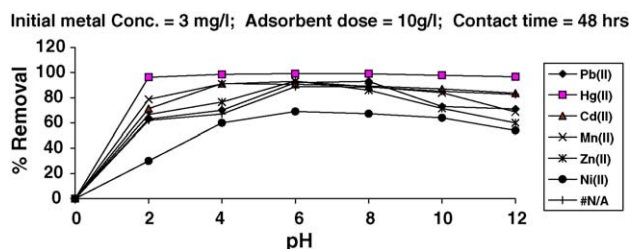
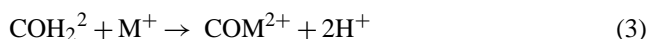
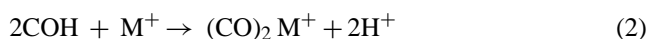


Fig. 4. Effect of pH on percent removal of heavy metals by carbon aerogel.

higher pH, that is, above optimum pH of 6, increase in  $\text{OH}^-$  ions cause a decrease in adsorption of metal ions at adsorbent–adsorbate interface [60].

Lower solubilities of hydrolysed metal ions species may be another reason for the maximum adsorption at pH 6. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between  $\text{H}^+$  and  $\text{M}^+$  ions for adsorption at the ion-exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH, may be another reason for decrease in adsorption of metal in lower pH range.

The mechanism of metal ion adsorption may also be explained based on ion exchange model. In carbon aerogel, carbon–oxygen complexes are present. The surface oxygen complexes hydrolysed water molecules are shown below:



The above mechanism has been confirmed by an increasing initial metal ion concentration in aqueous solution as the final pH of solution decrease. This clearly indicates that uptake of more metal ions causes release of more  $\text{H}^+$  ions.

The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above pH 6) is due to the formation of soluble hydroxy complexes [61]. The difference in adsorption behaviour of different heavy metal ions may be because of difference in their ion exchange capacity on the surface depending on their charge density, extent of hydrolysis and solubility of hydrolysed metal ions in solution under present experimental condition.

### 3.5. Effect of temperature

Fig. 5 shows the experimental results obtained from a series of contact time studies for metal ions adsorption with an

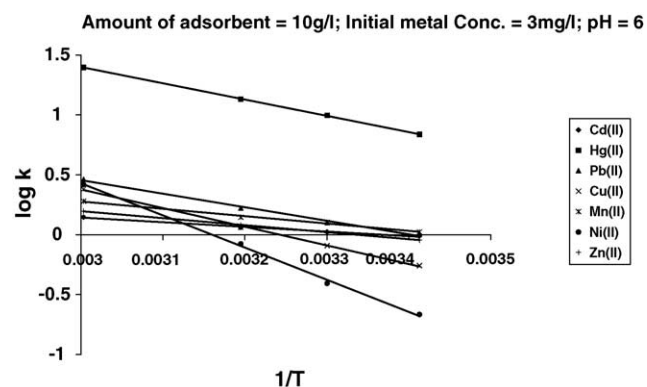


Fig. 5. Plot of  $\log K$  vs.  $1/T$  for heavy metals on carbon aerogel.

initial metal ions concentration of 3 mg/l at pH 6 in which temperature was varied from 20 to 60 °C. The adsorption of metal ions has been found to increase with an increase in temperature from 20 to 60 °C. The increase in adsorption capacity of carbon aerogel with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. At higher temperatures the possibility of diffusion of solute within the pores of the adsorbent may not be ruled out as reported by earlier workers for the adsorption of cations on GAC. Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperatures. The above results were further substantiated by the various thermodynamic parameters evaluated of adsorption.

The thermodynamic parameters, such as free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) were determined using the following equations and presented in Table 2

$$K_c = \frac{C_{Ac}}{C_e} \quad (4)$$

where,  $K_c$  is the equilibrium constant,  $C_{Ac}$  and  $C_e$  are the equilibrium concentration (mg/l) of the metal ion on adsorbent and in the solution, respectively. The free energy change ( $\Delta G$ ) was calculated from the relation:

$$\Delta G = -RT \ln K_c \quad (5)$$

where,  $T$  is temperature in Kelvin (273 K) and  $R$  is gas constant ( $8.314 \times 10^{-3}$  kJ/mol K). Enthalpy change ( $\Delta H$ ) was calculated from the following equation

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (7)$$

$\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of Vant Hoff plots of  $\log K_c$  versus  $1/T$  (Fig. 5). Positive values of  $\Delta H$  thermodynamically substantiate the assumption that the adsorption of metal ions on the carbon aerogel is endothermic. The negative values of  $\Delta G$  indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent.  $\Delta S$  is estimated to be very small in the experimental conditions. Therefore, the entropic change occurring from adsorption is thought to be negligible.

### 3.6. Adsorption kinetics

Kinetics is another important aspect in any evaluation of sorption as a unit operation. The kinetic constants of metal adsorption, which could be used to optimize the residence

Table 2  
Equilibrium constants and thermodynamic parameters for the adsorption of heavy metal ions on carbon aerogel

Metal	Temperature (°C)	$K_e$	$\Delta G$ (kJ/mol)	$\Delta S$ (kJ/mol K)	$\Delta H$ (kJ/mol)
Cd(II)	20	0.9714	0.0706	0.02522	7.4612
	30	1.0538	-0.1321	0.02506	
	40	1.1500	-0.3637	0.02500	
	60	1.400	-0.9317	0.02520	
Hg(II)	20	6.8767	-4.6978	0.1047	26.0054
	30	9.9000	-5.7762	0.1048	
	40	13.5363	-6.7811	0.1047	
	60	24.9000	-8.9021	0.1048	
Pb(II)	20	1.0111	-0.0269	0.0739	21.6265
	30	1.2636	-0.5895	0.0733	
	40	1.6647	-1.3264	0.0733	
	60	2.9000	-2.9482	0.0737	
Cu(II)	20	0.5521	1.4469	0.0967	29.7927
	30	0.8090	0.5337	0.0965	
	40	1.1500	-0.3637	0.0963	
	60	2.400	-2.4242	0.0967	
Mn(II)	20	1.0538	-0.1277	0.0404	11.7367
	30	1.2636	-0.5895	0.0406	
	40	1.4000	-0.8757	0.0402	
	60	1.9000	-1.7773	0.0465	
Ni(II)	20	0.2157	3.7361	0.1625	51.3733
	30	0.3918	2.3608	0.1617	
	40	0.8375	0.4615	0.1626	
	60	2.6272	-2.6747	0.1623	
Zn(II)	20	0.9000	0.2567	0.0373	11.1960
	30	1.0538	-0.1321	0.0373	
	40	1.2043	-0.4839	0.0373	
	60	1.5666	-1.2431	0.0373	

Adsorbent concentration = 10 g/l; contact time = 24 h; initial metal concentration = 3 mg/l.

time of an industrial wastewater carbon aerogel, were computed using the above experimental data. Earlier workers proposed a surface complexation mechanism for heavy metal removal onto carbon aerogel [62]. By virtue of its surface composition, is assumed to have C=O, C-OH and C-O groups.

The adsorption kinetics of heavy metal ion adsorption on carbon aerogel follows first order rate expression given by Lagergren and Svenka [63].

$$\log_{10}(q_e - q) = \log_{10}q_e - \frac{K_{ad} t}{2.303} \quad (8)$$

$$Q_e = (C_0 - C_e) \frac{V}{m} \quad (9)$$

where,  $K_{ad}$  (1/h) is the rate constant of adsorbent,  $q$  and  $q_e$  are the amount of heavy metal ions adsorbed (mg/l) at time  $t$  (h) and equilibrium time. Linear plots of  $\log_{10}(q_e - q)$  versus  $t$  (Fig. 6) show the applicability of above equation for carbon aerogel. The  $K_{ad}$  values at a metal ion concentrations were calculated from the slop of linear plots and presented in Table 3 the  $K_{ad}$  values were comparable with recently reported values for heavy metal ions removal by carbon aerogel [5].

The initial adsorption kinetic coefficients  $\gamma$  (1/mg h) is also computed as per [45] and are presented in Table 3

$$\gamma = \left( \frac{dC}{dt} \right)_{t=0} \frac{V}{mC_0} \quad (10)$$

where  $t$  is the time (h),  $C$  the metal ion concentration at time ( $t$ ),  $V$  the solution volume (l),  $m$  the carbon aerogel weight (mg),  $C_0$  is the initial concentration (mg/l).

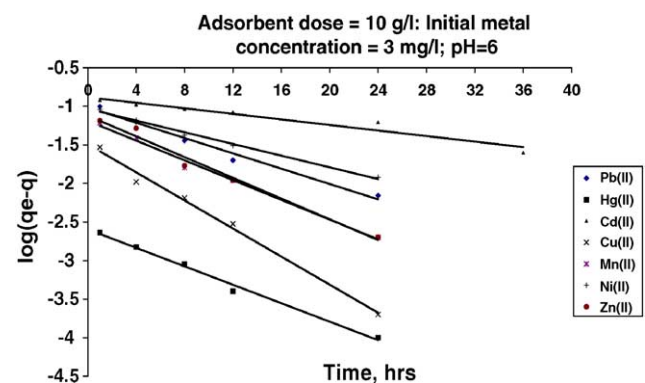


Fig. 6. Plot for Lagergren rate constant for adsorption of heavy metal ions by carbon aerogel.

Table 3  
Kinetics constants for heavy metal ions adsorption

Metal ions	Adsorption rate constant ( $K_{ad}$ ) (1/h) $\times 10^{-2}$	Initial adsorption coefficient ( $\gamma$ ) (l/mg min)
Cd(II)	2.740	0.06783
Hg(II)	13.77	1.2753
Pb(II)	11.44	0.04721
Cu(II)	20.95	0.01943
Mn(II)	14.73	0.0296
Ni(II)	8.72	0.05814
Zn(II)	15.47	0.03328

Adsorbent concentration = 10 g/l; initial metal ion concentration = 3 mg/l; temperature = 30 °C.

### 3.7. Adsorption isotherms

The adsorption studies were conducted at fixed initial concentration of heavy metals by varying adsorbent dosage. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation is given by [64].

$$\frac{x}{m} = K_e C_e^{1/n} \quad (11)$$

Taking the logarithmic form of the equation

$$\log\left(\frac{x}{m}\right) = \log K_e + \frac{1}{n} \log C_e \quad (12)$$

Langmuir equation is given by [65].

$$\frac{x}{m} = \frac{abC_e}{(1 + bC_e)} \quad (13)$$

or,

$$\frac{x}{m} = \left(\frac{1}{ab}\right) \cdot \left(\frac{1}{C_e}\right) + \frac{1}{a} \quad (14)$$

where  $x/m$  is the amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/gm,  $C_e$  the equilibrium concentration of heavy metal ions in mg/l,  $K_e$  and  $n$  are Freundlich constants, 'a' is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g, 'b' is also Langmuir constant which is a measure of energy of adsorption expressed in l/mg. The parameters 'a' and 'b' have been calculated from the slope and the intercept of the plots.

Fig. 7 gives the Freundlich adsorption isotherm plot of  $\log x/m$  versus  $\log C_e$ . The values of  $K_e$  and  $1/n$  obtained from intercept and slope of the plot are given in Table 4.

The Langmuir adsorption isotherm plot for  $m/x$  versus  $1/C_e$  is shown in Fig. 8 and the plots show two distinct regions, one for low  $1/C_e$  values up to about 25 l/mg and another for higher  $1/C_e$  values. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant  $R_L$ , which is defined as,

$$R_L = \frac{1}{(1 + bC_i)} \quad (15)$$

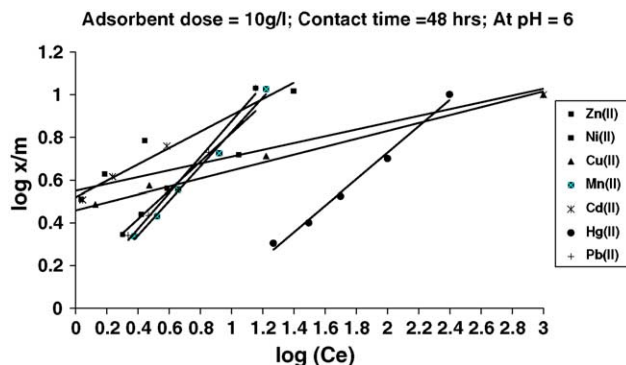


Fig. 7. Freundlich isotherms of heavy metals for carbon aerogel.

Table 4  
Values of Langmuir and Freundlich isotherm constants for the adsorption of heavy metal ions on carbon aerogel

Langmuir constants				
Metal ions	a (mg/gm)	b (l/mg)	$R^2$	$R_L$
Pb(II)	0.75	1.880	0.9977	0.1503
Hg(II)	45.62	0.6389	0.9989	0.3428
Cd(II)	400.8	0.2513	0.8554	0.5701
Cu(II)	561.7	0.2780	0.9038	0.5450
Mn(II)	1.275	1.3352	0.9968	0.1997
Zn(II)	1.843	0.9494	0.8478	0.2598
Ni(II)	12.875	0.2787	0.8747	0.5446
Freundlich constants				
Metal ions	$K_e$	n	$R^2$	
Pb(II)	1.0381	1.1930	0.9905	
Hg(II)	0.6004	1.6142	0.9905	
Cd(II)	1.7341	6.2770	0.8864	
Cu(II)	1.5828	5.4054	0.9834	
Mn(II)	1.0195	1.2405	0.9926	
Zn(II)	1.1616	1.4912	0.8980	
Ni(II)	1.6830	2.6109	0.9230	

Adsorbent concentration = 10 g/l; contact time = 48 h, pH 6.

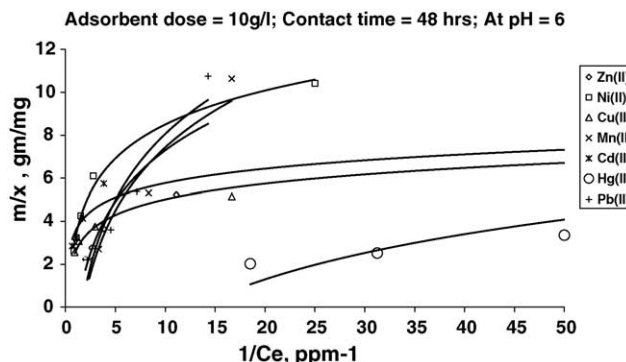


Fig. 8. Langmuir isotherms of heavy metals by carbon aerogel.

where  $C_i$  is the initial concentration of heavy metal ions (mg/l) and  $b$  is Langmuir constant which indicates the nature of adsorption. The separation factor  $R_L$  indicates the isotherm shape and whether the adsorption is favourable or not, as per the criteria given below.



$R_L$ values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of Langmuir constants 'a', 'b' and  $R_L$  are presented in Table 4. Since  $R_L$  values lie between 0 and 1 for all three adsorbents studied, it is seen that the adsorption of heavy metal ions is favourable [66].

Adsorption capacity as indicated by value of 'a' is seen to be maximum for carbon aerogel, i.e. Cd(II) (400.8 mg/g), Cu(II) (561.71 mg/g), Hg(II) (45.62 mg/g), and Ni(II) (12.85 mg/g), Zn(II) (1.84 mg/g), Mn(II) (1.27 mg/g) and Pb(II) (0.70 mg/g) with a much lower capacities. The energies of adsorption, as indicated by 'b' are seen to be highest for Pb(II) (1.88 l/mg), Mn(II) (1.33 l/mg), Zn(II) (0.94 l/mg), Hg(II) (0.64 l/mg), Ni(II) (0.27 l/mg), Cu(II) (0.27 l/mg) and Cd(II) (0.25 l/mg) in that order. A comparison of the Freundlich adsorption isotherms for the metal ions show that  $n$  in that order Cd(II) > Cu(II) > Ni(II) > Hg(II) > Zn(II) > Mn(II) and Pb(II). The values of  $n$  lie between 1 and 10 indicating favourable adsorption [67].  $K_e$  seen to be Cd(II) > Ni(II) > Cu(II) > Zn(II) > Pb(II) > Mn(II) and Hg(II). This gives a similar inference as that obtained from Langmuir isotherms.

On the basis of regression analysis of the experimental data on the adsorptive behaviour of metal ions on carbon aerogel, it may be inferred that the adsorption behaviour of metal ions on carbon aerogel is in good agreement with Langmuir model. These can be attributed to three main causes (i) the formation of monolayer coverage on the surface of carbon aerogel with minimal interaction among molecules of substrate (ii) immobile and localized adsorption and (iii) all sites having equal adsorption energies. The shapes of isotherms suggest that there are high-energy adsorption sites to favour strong adsorption at low equilibrium concentrations for the carbon aerogel.

#### 4. Conclusions

- Carbon aerogel showed nearly 100% adsorptive removal of heavy metal ions under optimized conditions of dosage 10 g/l for aqueous solutions containing 3 mg/l metal ions in 48 h.
  - The Langmuir model is found to be in good agreement with experimental data on adsorptive behaviour of all metal ions, on carbon aerogel follows both Freundlich model and Langmuir models.
  - The adsorption follows first order kinetics. pH has been found to be a most effective variable, controlling the adsorption of metal ions on carbon aerogel surface.
  - The applicability of Lagergren kinetic model had been investigated. Adsorption rate constant ( $K_{ad}$ ) and initial adsorption coefficient ( $\gamma$ ) were determined.
- Thermodynamic parameters such as standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were calculated for predicting the nature of adsorption.
  - These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

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#### References

- S. Ponangi, R.A. Shyam, S.G. Joshi, Trace pollutants in drinking water, J. Indian Assoc. Environ. Manage. 27 (2000) 16–24.
- S. Manahan, Environmental Chemistry, Book/colei California, USA, 1984.
- M. Sittig, Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, NJ, 1981, pp. 119–120, 185–186.
- B. Volesky, Biosorption of Heavy Metals, vol. 24, CRC press, Boca Raton, FL, 1992, pp. 13–14.
- A.K. Meena, G.K. Mishra, K. Satish, C. Rajagopal, P.N. Nagar, Adsorption of cadmium ions from aqueous solution using different adsorbents, Indian J. Sci Ind. Res. 63 (2004) 410–416.
- D.C. Barrell, Atomic Spectrophotometer Analysis of Heavy Metals Pollutants in Water, Ann Arbor Science Publishers Inc., Ann Arbor, MI, 1975, p. 25.
- A. Kabata-Pendias, H. Pendias, Trace Metals in Soil and Plants, CRC press, Boca Raton, FL, 1992, pp. 75–86.
- S.J. Banum, Introduction to Organic and Biological Chemistry, third ed., Macmillan Publishing Co., New York, NY, 1982, p. 541.
- U. Soffiotti, J.K. Wagoner, Occupational Carcinogenesis, New York Academy of Science, 1976, p. 271.
- N. Serpone, E. Borgarello, E. Pelizzetti, Photoreduction and photodegradation of inorganic pollutants, in: M. Schiavello (Ed.), Photocatalysis and Environment, Kluwer Academic, Dordrecht, 1988, p. 527.
- C. Namasivayam, K. Periasamy, Bicarbonate treated peanut hull carbon for Hg(II) removal from aqueous solution, Water Res. 27 (1993) 1663–1668.
- A.K. Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies, J. Hazard. Mater. 92 (2002) 161.
- F. Berglund, M. Bertin, Chemical Fallout, Thomas, Springfield, IL, 1969.
- WHO Environmental Health Criteria 101, Methyl Mercury, Geneva, World Health Organization (1990) 68.
- WHO Environmental Health Criteria 118, Inorganic Mercury, Geneva, World Health Organization (1991) 68.
- T.D. Luckey, B. Venugopal, D. Hutcheson, Heavy Metal Toxicity and Harmonology, Academic press, New York, 1975.
- R.J. Sullivan, Air Pollution Aspects of Manganese and its Compounds. Natural Tech. Information Service, Springfield, Va. Report PB (1969).
- J.E. Mckee, H.W. Wolf. Water Quality Criteria California State Water Quality Control Board, Publication No. 3-A (1963).

- [19] G.S. Pandey, P.C. Seth, Galvanizing Plant Effluent: Appraisal of Pollution Load Current Pollution Research in India, Environmental Publication, Karad, 1985, p. 209.
- [20] M. Sittig, Toxic Metals—Pollution Control and Worker Protection, Noyes Data Corporation, New Jersey, 1976.
- [21] S. Al-Asheh, Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, *Adv. Environ. Res.* 1 (1997) 194.
- [22] K. Kadirvelu, Preparation and characterization of activated carbon, from coir pith and its application to metal bearing wastewater, Ph.D. Thesis, Bharathiar University, Coimbatore, India, 1998.
- [23] R.P. Beliles, The lesser metals, in: F.W. Oehme (Ed.), Toxicity of Heavy Metals in the Environment, Part 2, Marcel Dekker, New York, 1979, p. 383.
- [24] P. Parker, Encyclopaedia of Environmental Science, second ed., McGraw Hill, New York, 1980.
- [25] P. Bingau, H. Lonsdale, M. Pinho (Eds.), Synthetic Membranes: Science, Engineering and Application, NATO ASI Series, Series C: Mathematical and Physical Science, vol. 181, D. Ridelo Publishing Company, Dordrecht, 1986.
- [26] Hartiger L. hand buch der Abwasser—und Recycling technichs Munchen, Carl Hanser Verlag, Wien (1991).
- [27] R.J. Kiffs, General inorganic effluents, in: D. Barnes, C.F. Forster, S.E. Hrudehy (Eds.), Surveys in Industrial Wastewater Treatment—Manufacturing and Chemical Industries, vol. 3, Lonngman, New York, NY, 1987 (Chapter 1).
- [28] C. Namasivayam, K. Ranganathan, Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III)/Cr(III) hydroxide and fixed bed studies, *Environ. Technol.* 16 (1995) 851–860.
- [29] K. Perisamy, C. Namasivayam, Removal of copper(II) by adsorption onto peanut hull carbon from water and copper plating industries wastewater, *Chemosphere* 32 (1996) 769–789.
- [30] B.C. Wolverton, R.C. Medonald, J. Gordan, Bioconversion of water hyacinth into methan gas, NASA technical memorandum X-72721 (1975).
- [31] J.W. Hassler, Purification with Activated Carbon, Chemical Publishing Co., New York, NY, 1974, p. 169.
- [32] K.K. Pandey, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, *Water Res.* 19 (1985) 869–873.
- [33] Amrit Kumar, Removal of copper and lead from wastewater by adsorption on bottom ash, *Indian J. Environ. Prot.* 11 (6) (1991) 433–437.
- [34] R.C. Vaishya, Adsorption of copper(II) on sawdust, *Indian J. Environ. Prot.* 2 (4) (1991) 284–489.
- [35] S. Hemesh, M. Mahadeva, Sorption potential of biosorbent for the removal of copper, *Indian J. Environ. Health* 36 (3) (1994) 165–169.
- [36] A.M. Youssef, M.R. Mostafa, Removal of copper ions by modified activated carbons, *Indian J. Technol.* 30 (1992) 413–416.
- [37] M. Arsalakhan, Y.I. Khattal, Adsorption of copper from copper sulphate solution by carbon black, *Carbon* 30 (1992) 957–960.
- [38] K.S. Seshadry, P.K. Sinha, C.A. Anadababu, K.B. Cal, R.V. Amalris, Removal of copper from effluents on activated carbon electrode, *Indian J. Environ. Health* 34 (1992) 59–62.
- [39] C. Namasivayam, K. Kadirvelu, Uptake of Hg(II) from wastewater by activated carbon from an unwanted agricultural solid by product: coir pith, *Carbon* 37 (1999) 79–84.
- [40] W.R. Knocke, L.H. Homphil, Mercury sorption by waste rubber, *Water Res.* 15 (1981) 275–282.
- [41] P. Kumar, S.S. Dara, Binding heavy metal ions with polymerized onion skin, *J. Polym. Sci.* 19 (1981) 397.
- [42] B. Coupal, J.M. lalacette, The treatment of wastewaters with peat moss, *Water Res.* 10 (1976) 1071.
- [43] C. Raji, T.S. Anirudhan, Removal of Hg(II) from aqueous solution by sorption on polymerized sawdust, *Indian J. Chem. Technol.* 3 (1996) 49.
- [44] Ajay Meena, D. Chauhan, P.K. Rai, C. Rajagopal, Treatment of heavy metals contaminated groundwater using GAC National conference on carbon (Indo-carbon 2001). Proceedings, Anand, Gujarat, 2001, pp. 15–19.
- [45] A.K. Meena, G.K. Mishra, Satish Kumar, Chitra Rajagopal, P.N. Nagar, Adsorption of Ni(II) and Zn(II) from aqueous solution by chemically treated activated carbon, in: National Conference on Carbon (Indo-carbon 2003) DMSRDE. Proceedings, Kanpur, 2003, pp. 131–140.
- [46] R.R. Navarvo, K. Sumi, N. Fugir, M. Matsumuru, Mercury removal from wastewater using porous cellulose carrier modified with polyethylene amine, *Water Res.* 30 (1996) 2488.
- [47] D.V. Jahagirdar, J.N. Nigal, Adsorption of Cd(II) and Pb(II) on agricultural by products, *Asian J. Chem.* 9 (1997) 122.
- [48] J. Ravi, M.L. Narwade, M.S. Usha, Studies in adsorption of some toxic metal ions on citrus sinensis skin and Coffea arabica husk: agricultural byproduct, *Asian J. Chem.* 14 (2002) 1257.
- [49] M. Sanchez Polo, Revera Utrilla, Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons, *Environ. Sci. Technol.* 36 (2002) 3850–3854.
- [50] Ajay Meena, Chitra Rajagopal, Comparative studies on adsorptive removal of chromium from contaminated water using different adsorbents, *Indian J. Chem. Technol.* 10 (2003) 72–78.
- [51] V. Gomez-serrane, A. Macia, S. Garcia, A.E. Mansilla, Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurised activated carbon, *Water Res.* 32 (1998) 1.
- [52] K.A. Krishanan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluents by steam activated and sulphurised activated carbons prepared by bagasse pith: kinetics and equilibrium studies, *J. Hazard. Mater.* 92 (2002) 161.
- [53] M.A. Ferror Garcia, J. Rivera-Ultrill, Adsorption of zinc, cadmium and copper on activated carbons obtained from agricultural byproducts, *Carbon* 26 (1988) 363–373.
- [54] C. Raji, G.N. Manju, T.S. Anirudhan, removal of heavy metal ions from water using sawdust based activated carbon, *Indian J. Eng. Mater. Sci.* 4 (1997) 254–260.
- [55] S.K. Nath, A. Jena, S.P. Mishra, Removal of cadmium by wood charcoal, *Trans. India Inst. Met.* 50 (4) (1997) 235.
- [56] P. Siuasamy, R. Muthumari, EDTA assisted removal of heavy metal ions by adsorption on activated charcoal and coconut shell carbon, *Indian J. Environ. Prot.* 20 (10) (1999) 761–771.
- [57] A.K. Meena, G.K. Mishra, C. Rajagopal, P.N. Nagar, Comparative studies on adsorptive removal of lead from contaminated water using different adsorbents, *Indian J. Environ. Prot.* 22 (11) (2002) 1257–1266.
- [58] W.E. Marshall, E.T. Champagne, W.J. Evans, The use of rice milling by products to remove metal ions from solution, *Indian J. Environ. Health* A28 (1993) 1977.
- [59] Y. Orhan, H. Buyuk Yungar, The removal of heavy metals by using agricultural wasters, *Water Sci. Technol.* 28 (1993) 247.
- [60] K. Periasamy, C. Namasivayam, Removal of Ni(II) from aqueous solution and nickel industry wastewater using an agricultural waste: peanut hull, *Waste Manage.* 15 (1995) 63.
- [61] M.O. Corupcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, *J. Water Res.* 21 (1987) 1031.
- [62] P. Rana, N. Mohan, C. Rajagopal, Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes, *Water Res.* 38 (12) (2004) 2811–2820.
- [63] B. Lagergren, V.P. Svenka, Handl, 24, Ascited by Trivedyetal, Adsorption of Cellulose Triacetate on Calcium Silicate, 5 *Environ. Poly.*, 1973, p. 525.
- [64] H. Freundlich, W. Heller, Rubber die adsorption in lusungen, *J. Am. Chem. Soc.* 61 (1939) 2228.
- [65] Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361.
- [66] G. Mckay, H.S. Blair, J.R. Garden, Adsorption of dyes on chitin, equilibrium studies, *J. Appl. Poly. Sci.* 27 (1982) 3045–3057.
- [67] F. Slejko, Adsorption Technology: A Step by Step Approach to Process Evaluation and Application, Marcell Dekker, New York, 1985.