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Thermodynamics of removal of cadmium by adsorption on an indigenous clay

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ABSTRACT

Equilibrium and thermodynamic studies of the removal of cadmium by adsorption on an indigenous adsorbent, china clay, have been investigated. The results of effect of temperature and thermodynamic parameters confirm the process of removal to be exothermic in nature. The removal decreased from 80.3% to 51.3% by increasing the temperature from 30 to 50 °C at 5.10×10^{-5} M initial concentration of cadmium, 1.0×10^{-2} M $NaClO_4$ ionic strength, 6.5 pH, 100 μm particle size and 100 rpm. Rate was found in decreasing pattern with increasing temperature and value of rate constant of the reaction, k_{ad}, was found to be 5.10×10^{-2} min^{-1} at 30 °C. Values of Langmuir's constants, 'Q^o' and 'b' were also determined. Thermodynamic parameters namely enthalpy of adsorption, isosteric heat of adsorption, change in standard free energy, ΔG°, standard enthalpy, ΔH°, and standard entropy, ΔS° were determined.

1. Introduction

Cadmium is a heavy and toxic metal and has been placed in the category of non-essential substances [1]. Cadmium is relatively a less abundant metallic element. Its harmful effects on fauna, flora and human beings are well documented [2]. It is an important alloying element of a number of alloys. It is extensively used in electroplating, Ni–Cd batteries and paint pigments. Discharge of untreated effluents from various industries into water resources has been one of the major sources of Cd pollution. Cadmium has been reported to be a potent carcinogen and teratogen [2]. It is an enzyme inhibitor and is reported to interact with —SH— groups of a number of enzymes. Cadmium is toxic to plants, animals and to human beings also [1,2]. As cadmium is a well known toxic metal, industrial effluents and wastewaters rich in cadmium must be treated prior to their disposal.

Chemical precipitation is the most common conventional method of treatment for cadmium containing effluents [3] but large amount of sludge produced during the treatment poses disposal problems. Ion exchange, vacuum evaporation, solvent extraction, membrane technologies, etc. are the other well known methods employed for treatment of cadmium containing wastewaters [4,5]. Adsorption offers comparatively a simpler treatment of large volumes of effluents and wastewaters and powdered activated carbon treatment (PACT) has been quite popular especially in developed nations [6–10]. The high cost of activated carbon and its loss in regeneration limits its application at large scale in developing nations like India. Further, the high cost of activated carbon treatment has insisted scientific workers to search its alternates and this has been an important area of research for them. Saeed and Iqbal [11] used gram husk, Kumar and Bandyopadhyay [12] reported rice husk and Pino et al. [13] reported green coconut shell powder for removal of cadmium from aqueous solutions. Other non-conventional and economically viable adsorbents have also been reported for uptake of cadmium [14–20] from water and wastewaters. Mohan et al. [21] have reported removal of cadmium by chars produced from wood and bark and have reported significant removal. A comparative study of 11 adsorbents has been conducted [22] for removal of a number of metallic species including cadmium.

During the removal of pollutants from solutions, the different parameters viz. contact time and concentration, pH, particle size of the adsorbent, etc. play important roles and many workers have reported effect of these parameters on removal of these pollutants from aqueous solutions and wastewaters [23–26]. Objective of the present work is to study adsorption equilibrium of cadmium on an indigenous material, china clay. Thermodynamic studies for the removal of cadmium have been undertaken to understand the process of removal in a better way.

2. Experimental

2.1. Materials

All the chemicals used in the present studies were of AR grade and were obtained from B.D.H., Mumbai, India. Stock solution of cadmium was prepared following standard methods [27]. China clay, the adsorbent used in the studies, was procured from

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Nomenclature

b	Langmuir's constant related to energy of adsorption ($l\,mg^{-1}$)
C_e	equilibrium concentration of cadmium ($mg\,l^{-1}$)
ΔG°	change in free energy ($kcal\,mol^{-1}$)
ΔH	eenthalpy of adsorption ($kcal\,mol^{-1}$)
ΔH_x	isosteric heat of adsorption ($kcal\,mol^{-1}$)
ΔH°	change in enthalpy ($kcal\,mol^{-1}$)
k	Langmuir's constant ($l\,g^{-1}$)
k_{ad}	rate constant of adsorption (min^{-1})
K	equilibrium constant at temperature T
K_1	equilibrium constant at temperature T_1
K_2	equilibrium constant at temperature T_2
q_e	amount of Cd(II) adsorbed ($mg\,g^{-1}$) at equilibrium
q	amount of Cd(II) adsorbed ($mg\,g^{-1}$) at any time t
Q^o	Langmuir's constant related to capacity of adsorption ($mg\,g^{-1}$)
R	gas constant ($kcal\,mol^{-1}\,K$)
ΔS°	change in entropy ($kcal\,K^{-1}\,mol^{-1}$)
t	time (min)
T	absolute temperature (K)

Patharghatt, Bihar, India. In order to keep the cost of treatment of cadmium low, it was used as such in the experiments without any pretreatment after crushing it to powder. Sieving was done to maintain a uniform particle size.

2.2. Methods

2.2.1. Characterization of the adsorbent

The average particle size of the adsorbent was measured by particle size analyzer, Model HIAC-320 (Royco Instruments Div., NY, USA) and the surface charge of the adsorbent was measured by Lazer Zee Meter, Model- 500 (Penkem Inc., NY, USA). Surface area was measured by a "three point" N_2 gas adsorption method using Quantasorb Surface Area Analyser, Model QS/7 (Quantachrome Corp., USA) and the porosity by a mercury porosimeter. Chemical characterization of the adsorbent was carried out by Indian Standard Methods [28].

2.2.2. Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 1.0 g of the adsorbent of desired particle size with 50 ml aqueous solution of cadmium of desired concentration, temperature, pH, and ionic strength in different polythene bottles on a shaking thermostat at 100 rpm. After predetermined time intervals, the adsorbent was separated from solutions by centrifugation. The progress of adsorption was assessed by determining concentration of cadmium left in the aliquot by atomic absorption spectrophotometer(GBC Australia). pH of the solutions was maintained by adding 1.0 M HCl/NaOH and ionic strength of the solutions was maintained by 1.0×10^{-2} M $NaClO_4$. For equilibrium and thermodynamic studies experiments were carried out at different temperatures with solutions of different concentrations of cadmium.

3. Results and discussion

3.1. Physicochemical characterization of the adsorbent

Physicochemical characterization of the adsorbent was carried out by Indian Standard Methods and has been given in Table 1. This table shows that silica and alumina are the major components of the adsorbent. Oxides of other metals are present in trace amounts. The surface area of china clay was found to be $9.78\,m^2\,g^{-1}$.

Table 1
Physicochemical characterization of the adsorbent

Constituents	Weight (%)
SiO_2	46.22
Al_2O_3	38.40
CaO	0.86
Fe_2O_3	0.68
MgO	0.37
Loss on ignition (%)	13.47
Surface area ($m^2\,g^{-1}$)	9.78
Porosity	0.33
Density ($g\,cm^{-3}$)	2.69
Mean particle diameter (μm)	100.00

3.2. Effect of temperature on the removal

Temperature is an important parameter and has pronounced effect on adsorption. During the present investigations the removal of cadmium decreased from 80.3% to 51.3% by increasing the temperature from 30 to 50 °C (Fig. 1) at an initial cadmium concentration of 5.0×10^{-5} M. The ionic strength of the solutions during the experiments was maintained at 1.0×10^{-2} M $NaClO_4$. The higher ionic strength helps eliminating the effects of change in concentration during the process of removal. The experiments were conducted at 6.5 pH and agitation speed was maintained at 100 rpm. It is clear that like most adsorption processes, removal of cadmium is also an exothermic reaction. It is also clear from this figure that equilibrium was established in 80 min. This variation in removal of cadmium seems due to the enhancement of relative escaping tendencies of the metal ions from aqueous phase to the bulk and consequent reduction in the boundary layer thickness. The decrease in the removal at increasing temperatures can also be attributed to the increased solubility of metal at relatively higher temperatures.

3.3. Effect of temperature on reaction rate

The rate constant of the process decides the speed of the transfer of metallic species from bulk to the surface of the adsorbent. In

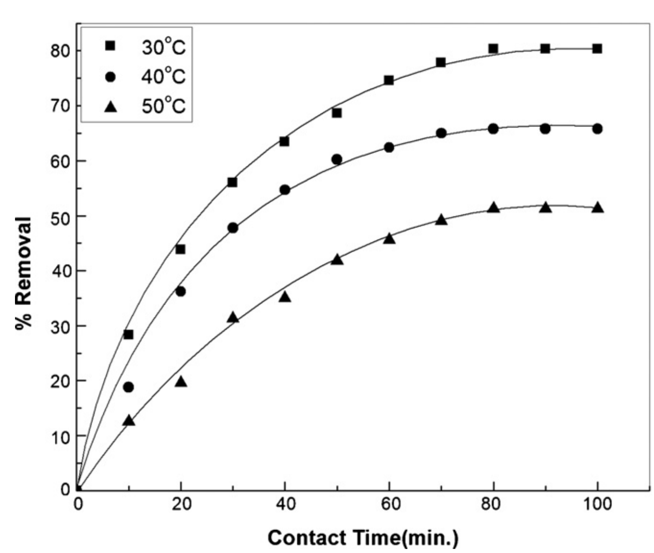

Fig. 1. Variation of removal (%) of cadmium at different temperature.

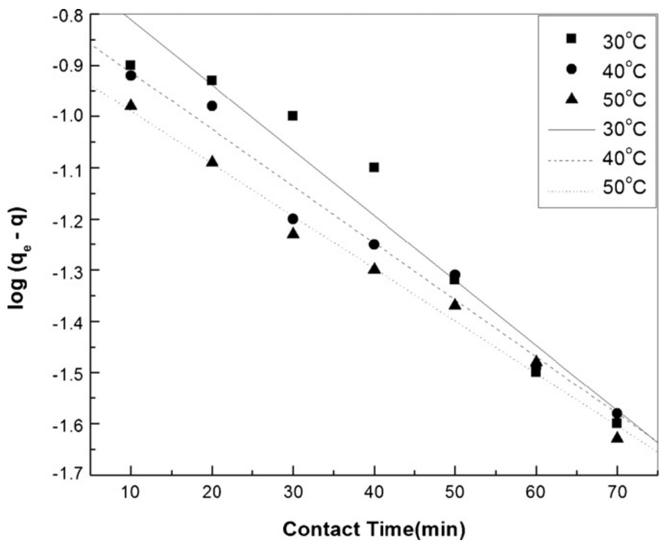

Fig. 2. Effect of temperature on reaction rate.

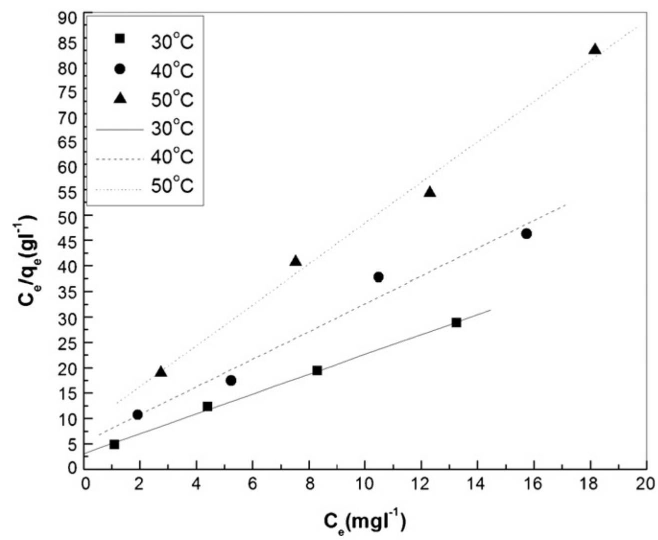

Fig. 3. Langmuir's plot for equilibrium modeling of the process of cadmium removal.

the present studies the rate constant of the process of removal is determined by using Lagergren's equation [19]:

$$\log(q_e - q) = \log q_e - \left(\frac{k_{ad}}{2.303}\right) t \quad (1)$$

where 'q_e' and 'q' (both mg g^{-1}) are the amounts of cadmium adsorbed onto surface of china clay at equilibrium and at any time, and 'k_{ad}' (min^{-1}) is the rate constant of adsorption. The plots of '$\log(q_e - q)$ vs t' (Fig. 2) are straight and indicate validity of the equation for the studies carried out. It also shows that the process involved in the removal of cadmium is governed by first order rate kinetics [29–31]. The values of 'k_{ad}' were determined at 30, 40, and 50 °C and have been given in Table 2. The values of 'k_{ad}' decreased from 5.1×10^{-2} min^{-1} to 3.7×10^{-2} min^{-1} by increasing the temperature from 30 to 50 °C. This decrease in the values of 'k_{ad}' further confirms exothermic nature of the process of removal.

3.4. Equilibrium modeling

In the state of equilibrium, there is a defined distribution of adsorbate at the solid solution interface and also in the bulk at constant temperature. The data generated on equilibrium modeling gives an insight for suitability of the adsorbent for the adsorbate–adsorbent system. Equilibrium modeling for the present system has been carried out by using Langmuir's adsorption isotherm equation [32]:

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \quad (2)$$

where C_e (mg l^{-1}) is the concentration and q_e (mg g^{-1}) is the amount of cadmium adsorbed by solid phase at equilibrium, Q^o (mg g^{-1}) and b (l mg^{-1}) are the terms related to capacity and energy of adsorption and are known as Langmuir's constants. Their product is usually expressed as '$k = Q^o b$'. The linear plots 'C_e/q_e vs C_e' (Fig. 3) indicate that the data fits the Langmuir's isotherm model.

Table 2
Values of k_{ad}, the rate constant for adsorption at different temperatures

Temperature (±0.5 °C)	k_{ad} ($\times 10^{-2}$ min^{-1})
30	5.1
40	4.2
50	3.7

It also indicates a monolayer coverage of adsorbate onto the surface of the adsorbent. The values of Langmuir's constants 'Q^o' and 'b' were determined at the three temperatures by using slopes and intercepts of the plots of Fig. 3. Their values are given in Table 3. Further, the small variation in the graphical and regression values suggests the validity of our data. It can be seen from this table that the values of Q^o decrease with increasing temperature. Similar trend has been reflected in the values of 'b' also. This trend supports the exothermic nature of the process of cadmium removal. The results are supported by earlier workers [33,34].

3.5. Thermodynamics of removal

3.5.1. Enthalpy of adsorption

In the Langmuir treatment, the maximum adsorption corresponds to a saturated monolayer of adsorbate phase on the surface of the adsorbent and the energy of adsorption on whole of the surface remains constant. ΔH, the change in apparent heat or net enthalpy of adsorption is related to Langmuir's constant 'b' as follows [35]:$b = b' e^{-\Delta H/RT}$ or

$$\ln b = \ln b' - \Delta H/RT \quad (3)$$

where b' is a constant. The values of ΔH were calculated from the straight line plots of '$\ln b$ vs $1/T$' (Fig. 4). The values of ΔH for the present system are found to be -4.40 kcal mol^{-1}. The negative value of ΔH is indicative of exothermic nature of the process of removal of Cd(II).

3.5.2. Isosteric heat of adsorption

The heat of adsorption is a function of surface coverage 'x'. The isosteric heat of adsorption, ΔH_x, has been calculated by using integrated form of Clasius–Clapeyron equation [35]. It was observed that the values of isosteric heat of adsorption for the present system at a surface coverage of 7.50×10^{-2} mg g^{-1} and

Table 3
Values of Langmuir's constants at different temperatures

Temperature (±0.5 °C)	Graphical values		Regression values	
	Q^o (mg g^{-1})	b (l mg^{-1})	Q^o (mg g^{-1})	b (l mg^{-1})
30	0.50	0.67	0.50	0.69
40	0.40	0.42	0.38	0.41
50	0.28	0.27	0.28	0.25

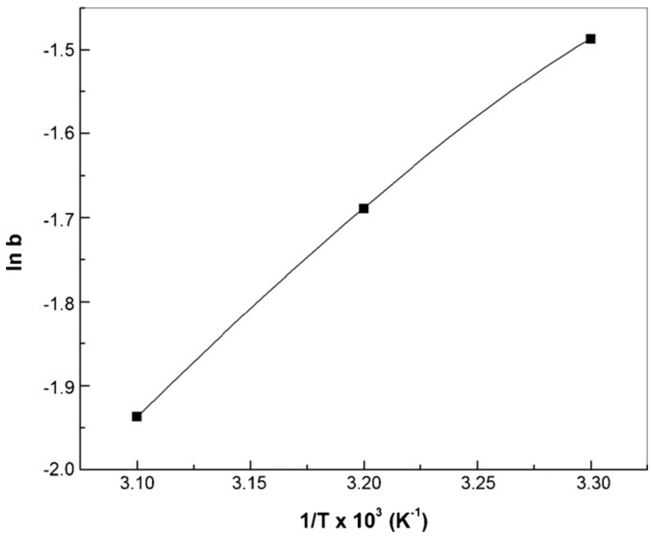

Fig. 4. Adsorption isoster for cadmium removal.

Table 4
Values of isosteric heat of adsorption at different surface coverage for the removal of cadmium by china clay

Surface coverage ($\times 10^{-2}$ mg g^{-1})	$-\Delta H_x$ (kcal mol^{-1})
7.50	24.96
2.50	22.07
1.87	21.15

30 °C was found to be −24.96 kcal mol^{-1} (Table 4). It is clear from this table that the absolute value of ΔH_x decreases from −24.96 to 21.15 kcal mol^{-1} with a decrease in the surface coverage from 7.50×10^{-2} to 1.87×10^{-2} mg g^{-1} at 30 °C. This decrease in the isosteric heat of adsorption may be attributed to surface heterogeneity and adsorbate–adsorbate interactions. The results of the present findings are supported by earlier workers [35]. A perusal of ΔH and ΔH_x values also suggests the possibility of physical and chemical adsorption in the studies undertaken.

The other thermodynamic parameters of concern are change in standard free energy, ΔG°, change in standard enthalpy, ΔH°, and the change in standard entropy, ΔS°. Values of these parameters were calculated at 30, 40, and 50 °C respectively. For the present investigations, values of these parameters were determined using following standard equations [31]:

$$\Delta G^\circ = -RT \ln K \tag{4}$$

$$\Delta H^\circ = R(T_2T_1/(T_2 - T_1)\ln\left(\frac{K_2}{K_1}\right) \tag{5}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{6}$$

where 'R' is gas constant, K, K_1, and K_2 are equilibrium constants at temperatures T, T_1, and T_2, respectively. 'K' is related to Langmuir's constant 'b' [31]. The values of ΔG°, ΔH° and ΔS° calculated for the present studies have been given in Table 5. Table 5 also shows that the values of all the parameters are negative and further confirm exothermic nature of the process of cadmium removal. The values of the parameters of ΔG°, ΔH° and ΔS° were found to be −3.20, 9.24 kcal mol^{-1} and 22.15 kcal K^{-1} mol^{-1} at 30 °C. The negative values of ΔG° are important and indicate spontaneity of the reaction. Larger is the negative value of ΔG°, more spontaneous is the process. Negative values of ΔS° suggest the possibility of adsorption [20].

Table 5
Values of ΔG°, ΔH°, and ΔS° at different temperatures

Temperature (±0.5 °C)	$-\Delta G^\circ$ (kcal mol^{-1})	$-\Delta H^\circ$ (kcal mol^{-1})	$-\Delta S^\circ$ (kcal K^{-1} mol^{-1})
30	3.20	9.24	22.15
40	3.00	5.57	7.50
50	2.94		

4. Conclusions

China clay, a mineral has been successfully used as an economically viable material for the removal of cadmium from aqueous solutions. Unlike many adsorbents this is a non-toxic and naturally occurring material. During the experiments china clay has displayed good efficiency of removal and a high reoval viz. 80.3% was achieved at 30 °C and 6.5 pH. Lagergren's equation fits well the data obtained. Langmuir's model was used for equilibrium modeling of the pracess and the values of Langmuir's constants were calculated. Thermodynamic studies of the removal of cadmium by china clay were carried out and the values of the thermodynamic parameters namely ΔG°, ΔH° and ΔS° were determined. The values of isosteric heat of adsorption, ΔH_x were also calculated and its values were in decreasing pattern with decreasing values of surface coverage. The data obtained could be used for designing treatment plants for the treatment of cadmium containing wastewaters.

References

[1] K. Kannan, Fundamentals of Environmentals of Environmental Pollution, S. Chand & Co. Ltd., New Delhi, India, 1995.
[2] U. Forstner, G.T.W. Wittmann, Metal Pollution in Aquatic Environment, Springer-Verlag, NY, 1979.
[3] G. McKay, F.P. Reinhard, Waste minimization and recovery technologies, Metal Finishing 98 (2000) 817–850.
[4] A.B.P. Martin, V.M. Zapata, O.M. Aguilar, J. Saez, M.L. Lorens, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. 139 (2007) 122–131.
[5] Y. Bulut, Z. Tez, Adsorptio studies on ground shells of hazelnut and almond, J. Hazard. Mater. 149 (2007) 35–41.
[6] A. Gelabert, O.S. Pokrovsky, J. Schott, A. Boudou, A.F. Mazel, Cadmium and lead interaction with diatom surfaces: a combined thermodynamic and kinetic approach, Geochim. Cosmochim. Acta 71 (2007) 3698–3716.
[7] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by $ZnCl_2$ activation, Bioresour. Res. 99 (2008) 492–501.
[8] H.A. Aziz, M.A. Adlan, K.S. Arifin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(VI)) removal from water in Malaysia: post treatment by high quality limestone, Bioresour. Tech. 99 (2008) 1578–1583.
[9] Z.S. Liu, Control of heavy metals during incineration using activated carbon fibers, J. Hazard. Mater. 142 (2007) 506–511.
[10] A. Jusoh, L.S. Shiung, N. Ali, M.J.M. Noor, Simultaneous removal of As, Cd, Cu, Ni and Zn from stormwater: experimental comparison of 11 different adsorbents, Desalination 206 (2007) 9–16.
[11] A. Saeed, M. Iqbal, Bioremoval of cadmium from aqueous solutions by black gram husk, Water Res. 37 (2003) 3472–3480.
[12] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solutions using pretreated rice husk, Biores. Tech. 97 (2006) 104–109.
[13] G.H. Pino, M.L.M.S. de, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Mineral Eng. 19 (2006) 380–387.
[14] J.T. Matheikal, Q. Yu, G.M. Woodburn, Biosorption of cadmium from aqueous solutions by pretreated biomass of marine alga D potatorum, Water Res. 33 (1999) 335–342.
[15] A. Papandreou, C.J. Stournaras, D. Panias, Copper and cadmium adsorption on pellets made from fired coal fly ash, J. Hazard. Mater. 148 (2007) 538–547.
[16] M. Mohapatra, S. Anand, Studies on sorpion of Cd(II) on Tata Chromite mine overburden, J. Hazard. Mater. 148 (2007) 553–559.
[17] P.K. Pandey, Y. Verma, S. Choubey, M. Pandey, K. Chandrashekhar, Biores. Tech., 2007 (online).
[18] E.I. El-Shafey, Sorption of Cd(II) and Se(IV) from aqueous solutions using modified rice husk, J. Hazard. Mater. 147 (2007) 546–555.
[19] V.C.T. Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. 105 (2003) 121–142.

[20] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modeling f single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chem. Eng. J. 117 (2006) 79–91.

[21] D. Mohan, D.C.U. Pittman Jr., M. Bricka, F. Smith, B. Yancey, J. Mohammad, P.H. Steele, M.F.A. Franco, V.G. Serrano, H. Gong, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, J. Colloid Interface Sci. 310 (2007) 57–73.

[22] H.G. Fuhrman, P.S. Mikkelsen, A. Ledin, Simultaneous removal of As, Cd, Cu, Ni and Zn from stormwater: experimental comparison of 11 different adsorbents, Water Res. 41 (2007) 591–602.

[23] W. Zheng, X.M. Li, Q. Yang, G.M. Zang, X. Shen, Y. Zhang, J. Liu, Adsorption of Cd(II) and Cu(II) from aqueous solutions by carbonate hydroxylapatite derived from eggshell waste, J. Hazard. Mater. 147 (2007) 534–539.

[24] E.A. Ayuso, G. Sanchez, Removal of cadmium from aqueous solutions by palygorrskite, J. Hazard. Mater. 147 (2007) 594–600.

[25] S. Pacheco, J. Tapia, M. Medina, R. Rodriguez, Cadmium ions adsorption in simulated wastewater using structured alumina–silica nanoparticles, J. Non-Cryst. Solids 352 (2006) 5475–5481.

[26] E.W. Shin, R.M. Rowell, Cadmium ions sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement, Chemosphere 60 (2005) 1054–1061.

[27] Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 15th ed., NY, USA, 1985.

[28] Indian Standard Methods for the Analysis of Fire Clay and Silica Refractory materials, IS:1527, 1960.

[29] H.C. Trivedi, V.M. Patel, R.D. Patel, Adsorption of cellulose triacetate on calcium silicate, Eur. Polym. J. 9 (1973) 525–537.

[30] S.P. Mishra, Vijaya, Radiotracer technique in adsorption studies Part XVIII: uptake of Ce(III) from aqueous solutions by hydrous manganese and stannic oxides, J. Radioanal. Nucl. Chem. 274 (2007) 265–269.

[31] G.S. Gupta, S.P. Shukla, G. Prasad, V.N. Singh, China clay as a n adsorbent for dyehouse wastewaters, Environ. Tech. 1 (1992) 925–936.

[32] G. McKay, M.S. Otterburn, A.G. Sweeny, Surface mass transfer process during colour removal from effluents using silica, Water Res. 15 (1981) 327–331.

[33] V.R. Chaudary, S.N. Sansare, G.N. Thite, Adsorption of reaction species from dehydrogenation of nitrobenzene on copper chromite at catalytic conditions, J. Chem. Tech. Biotech. 42 (1988) 249–260.

[34] C.O. Ania, T.J. Bandosz, Metal loaded polystyrene-based activated carbons as dibenzothiphene removal media via reactive adsorption, Carbon 44 (2006) 2404–2412.

[35] D.B. Singh, G. Prasad, D.C. Rupainwar, As(III) removal from aqueous solutions by adsorption, Water Air Soil Pollut. 42 (1988) 373–386.