COMPARATIVE STUDY ON METAL IONS ADSORPTION ON A LOW COST CARBONACEOUS ADSORBENT KINETIC EQUILIBRIUM AND MECHANISTIC STUDIES

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ABSTRACT

A carbonaceous adsorbent prepared from an indigenous waste and treated by acid was tested for its efficiency in removing metal ions of Fe(II), Co(II) and Ni(II). The process parameters studied included agitation time, initial metal ion concentration, carbon dosage, pH, other ions and temperature. The kinetics of adsorption followed first order reaction equation and the rate was mainly controlled by intraparticle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity obtained from the Langmuir isotherm plots was found around 28mg/g for all selected metal ions at an initial pH of 6. The temperature variation study showed that the metal ions adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying pH of the metal ion solutions. The type I and II isotherms obtained, positive $\triangle H^0$ values, pH dependent results and desorption of metal ions in mineral acid suggests that the adsorption of metal ions on this type of adsorbent involves both chemisorption and physical adsorption mechanisms.

Key words: Activated carbon, metal ions, adsorption isotherms, kinetic and thermodynamic parameters, intraparticle diffusion, regeneration pattern

INTRODUCTION

Wastewater generally contains toxic inorganic and organic pollutants. Inorganic pollutants consist of mineral acids, inorganic salts, finely divided metal compounds, trace elements, cyanides, nutrients and organometallic compounds. Some of the trace elements play essential roles in biological processes, but at higher concentrations, they may be toxic to the biota; they disturb the biochemical processes and cause hazards.

Heavy metals contamination exists in aqueous waste streams from many industries such as nickel plating, mining, tanneries, and painting, car radiator manufacturing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used. Cu, Fe, Co, Ni, Zn, Cr, Cd, etc., are harmful wastes produced by industries that pose a risk of contaminating groundwater and other water resources. Heavy metals are not biodegradable

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and tend to accumulate in living organisms, causing various diseases and disorders. For example, chromium causes serious ailments.

The treatment process, for removing heavy metals such as iron, cobalt and nickel comprises of chemical precipitation, coagulation, complexation, solvent extraction, ion-change, sorption, osmosis and electrolysis. Adsorption using plant wastes offers an alternative to the other methods as the treatment is single step and no sludge is produced (Chuah *et al.*, 2005).

The present study was undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated Borassus bark carbon (BBC) for the removal of metal ions in aqueous solutions. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and mass-transfer models for the adsorption of chromium ion onto acid treated activated carbon.

MATERIALS AND METHODS

The activated carbon was prepared by treating air dried Borassus bark carbon with sulfuric acid in a weight ratio of 1:1. The resulting black product was kept in a furnace maintained at 500°C for 12 hours followed by washing with water untill it became free from excess acid and dried at 150 ± 5°C. The carbon product obtained from Borassus bark carbon(BBC) was ground well to fine powder and the portion retained between 30 and 50μm sieves was used in all the adsorption experiments.

Sigma-Aldrich, India, supplied all chemicals used in the study with high purity. The adsorption experiments were carried out by agitating with the fixed amount of carbon with 5, 10, 15, 20, 25 and 30mg/L of selected metal ion solutions such as Fe(II), Co(II) and Ni(II) at pH=6 and at temperatures 30, 40, 50 and 60 ± 0.5°C in a mechanical shaker (120rpm). After the defined time intervals, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual metal ion concentration using a UV-Vis spectrophotometer. Effect of adsorbent dosage was studied by varying the carbon dose from 10 to 100mg/50mL, taking 20 mg/L as initial metal ion concentration. For studies on the effect of pH, the initial 20mg/L metal ion solution was adjusted to a desired value of pH using small amounts of dilute hydrochloric acid or sodium hydroxide and agitated with 50mg of the adsorbent. For temperature variation study, 50 mg of the adsorbent was agitated with 5, 10, 15, 20, 25 and 30mg/L of selected metal ion solutions using a temperature controlled water bath shaker. Langmuir and Freundlich isotherm studies were carried out with metal ions of varying initial concentrations of 5, 10, 15, 20, 25 and 30mg/L with a fixed adsorbent dose (50mg) at temperatures 30, 40, 50 and 60 ± 0.5°C, until the equilibrium was reached.

The adsorption isotherms frequently employed for single-solute systems are Langmuir isotherm model that obey the correct thermodynamic boundary condition of Henry's law in the range of infinitely dilute concentrations. The Langmuir isotherm model for liquid-phase adsorption is written as follows:

$$Q_e = Q_m b C_e / 1 + b C_e \qquad (1)$$

Where Ce is the equilibrium concentration (mg/L), Qe is the amount adsorbed at equilibrium (mg/g) and Qm and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The Freundlich model is written as follows:

$$Q_e = x/m = K_f C_e^{1/n} \qquad (2)$$

$$\log Q_e = \log K_f + 1/n \log C_e \qquad (3)$$

where x(mg/L) is the amount of solute adsorbed, m(g/L) is the weight of the adsorbent used, C_e (mg/L) is the equilibrium solute concentration in solution and K_f(mg/g) and n are constants incorporating factors affecting the adsorption process such as adsorption capacity and intensity of adsorption, respectively.

RESULTS

Effect of carbon mass, agitation time and initial metal ion concentration

The effects of carbon dosage, agitation time and initial metal ion concentrations for the adsorption process are shown in Figs.1 and 2. The results obtained from the batch adsorption for the adsorption of metal ions are shown in Table 1.

Adsorption isotherms

To identify the regeneration capacity of the adsorbent, the carbon loaded with metal ions were separated and gently washed with distilled water to remove any unadsorbed metal ions. The metal ion-laden carbons were agitated with 50mL of
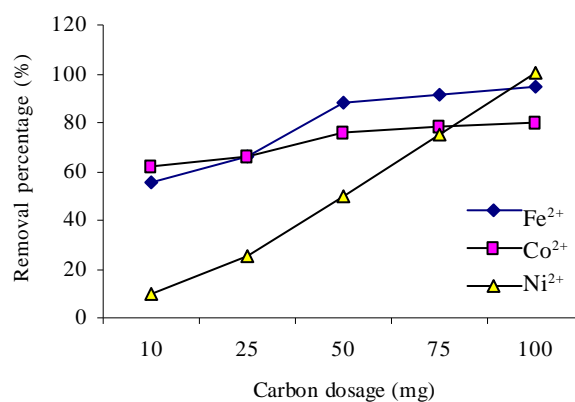

Fig. 1: Effect of carbon dosage on the removal of metal ions with the initial concentration of 20 mg/L

neutral pH water, 0.1M sulfuric acid, hydrochloric acid, nitric acid, sodium chloride and sodium chloride with hydrochloric acid, separately for 60min. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir model (representative Fig. 3). The values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 2.

The equilibrium data obtained at varying initial metal ion concentration with fixed carbon dosage conform to the Freundlich equation (Fig. 4). The correlation coefficient (r), were obtained for the linear plot Fig. 4). The constants K_f and n determined from the intercept and slope of the plots are given in Table 3.

The dimensionless separation factor R_L was calculated from the constant b, obtained from Langmuir isotherm was shown in Table 4.

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process was studied at different concentrations. The ions were added to 20 mg/L of metal ion solutions and the contents were agitated for 60 minutes at 30°C.
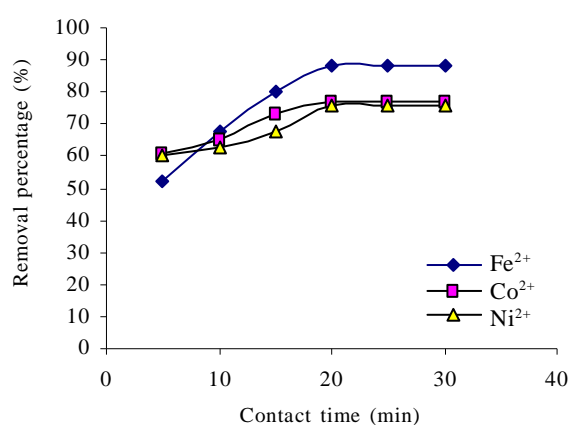

Fig. 2: Effect of contact time on the removal of metal ions with the initial concentration of 20 mg/L
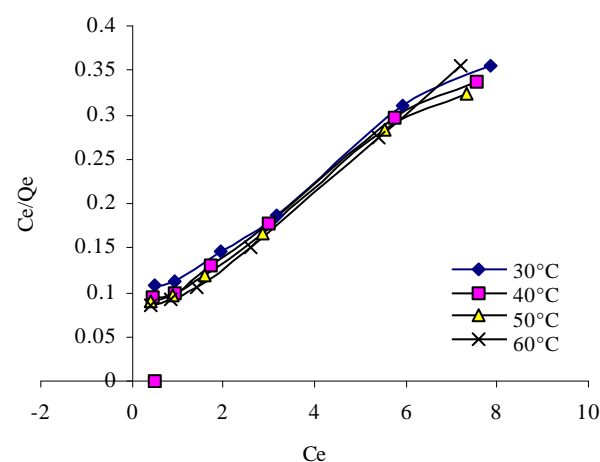

Fig. 3: Langmuir isotherm for the adsorption of ferrous ion

Table 1: Equilibrium parameters for the adsorption metal ions onto BBC

Metal ion	C_e (mg/L)				Q_e (mg/g)				Metal ions removed (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Ferrous ion adsorption												
5	0.4896	0.4526	0.4134	0.3957	4.5104	4.5404	4.5866	4.6083	90.20	90.94	91.73	92.08
10	0.9257	0.9028	0.8842	0.8459	9.0743	9.0972	9.1158	9.1541	90.74	90.97	91.15	91.54
15	1.9256	1.7428	1.6017	1.4224	13.0744	13.2572	13.3983	13.5776	87.16	88.38	89.32	90.51
20	3.1492	3.0146	2.8422	2.6156	16.8508	16.9854	17.1578	17.3844	84.25	84.92	85.78	86.90
25	5.9252	5.7349	5.5125	5.3926	19.0748	19.2651	19.4875	19.6074	76.29	77.06	77.95	78.42
30	7.8523	7.5511	7.3425	7.1926	22.1477	22.4489	22.6575	22.8074	73.02	74.82	75.52	76.08
Cobalt ion adsorption												
5	0.7564	0.6085	0.5795	0.4296	4.2436	4.3915	4.4205	4.5704	84.87	87.83	88.41	91.40
10	1.6896	1.3528	1.1799	0.9924	8.3104	8.6472	8.8201	9.0076	83.10	86.47	88.20	90.07
15	2.6785	2.1235	1.8245	1.5446	12.3215	12.8765	13.1755	13.4554	82.14	85.84	87.83	89.70
20	4.3522	3.9459	3.5998	3.2527	15.6478	16.0541	16.4002	16.7473	78.23	80.27	82.00	83.72
25	7.1586	6.8959	6.3728	6.0142	17.8414	18.1041	18.6272	18.9858	71.36	72.41	74.50	75.94
30	9.8496	8.9928	8.4224	8.1256	20.1504	21.0072	21.5776	21.8744	67.16	70.02	71.92	72.91
Nickel ion adsorption												
5	0.9856	0.8123	0.7256	0.6012	4.0144	4.1877	4.2744	4.3988	80.28	83.74	85.48	87.97
10	1.8598	1.7122	1.4829	1.2526	8.1402	8.2878	8.5171	8.7474	81.40	82.87	85.51	87.47
15	3.1246	2.9452	2.7158	2.4112	11.8754	12.0548	12.2842	12.5888	79.16	8.36	81.89	83.92
20	4.7592	4.4125	4.1925	3.8852	15.2408	15.5875	15.8075	16.1148	76.20	77.93	79.03	80.57
25	8.3123	8.1123	7.8712	7.5546	16.6877	16.8877	17.1288	17.4454	66.75	67.55	68.51	69.78
30	10.5128	10.2528	9.8928	9.4926	19.4877	19.7472	20.1072	20.5074	64.95	65.82	67.02	68.85

Table 2: Langmuir isotherm results

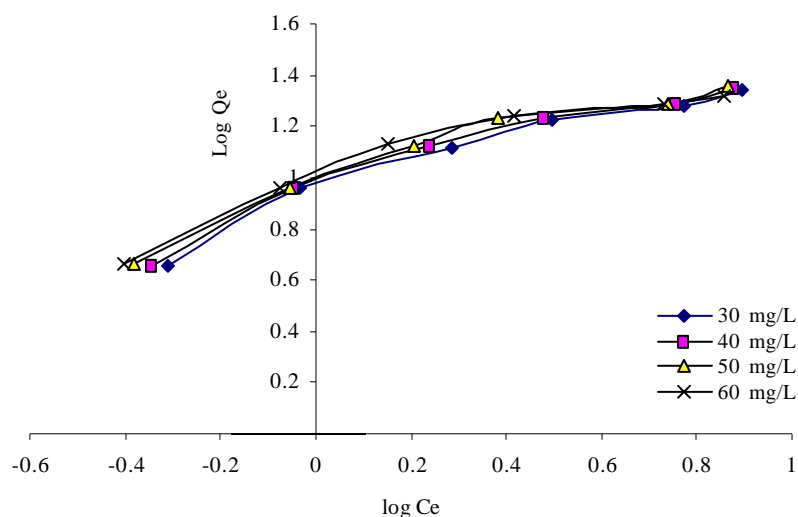| Metal ions	Temperature (°C)	R^2	Q_m	B
Ferrous^{2+}	30°	0.9940	27.9300	0.4601
	40°	0.9944	28.5714	0.4796
	50°	0.9940	28.1690	0.5268
	60°	0.9975	25.1319	0.6657
Cobalt^{2+}	30°	0.9951	28.2480	0.2565
	40°	0.9933	26.9541	0.3553
	50°	0.9902	27.1296	0.3757
	60°	0.9954	26.1506	0.5437
Nickel^{2+}	30°	0.9754	28.2480	0.2090
	40°	0.9899	26.5900	0.2631
	50°	0.9899	25.8390	0.3152
	60°	0.9919	25.0000	0.4048

Fig. 4: Freundlich isotherm for the adsorption of ferrous ion

Table 3: Freundlich isotherm results

Metal ions	Temperature (°C)	R^2	k_f	n
Ferrous^{2+}	30°	0.9835	1.4197	2.8530
	40°	0.9794	1.3973	2.9886
	50°	0.9574	1.3512	3.3222
	60°	0.9790	1.3338	3.4698
Cobalt^{2+}	30°	0.9759	1.8204	1.6691
	40°	0.9681	1.7342	1.8162
	50°	0.9582	1.7311	1.8221
	60°	0.9614	1.6485	2.0004
Nickel^{2+}	30°	0.9613	1.8790	1.5840
	40°	0.9690	1.7920	1.7129
	50°	0.9662	1.7431	1.7997
	60°	0.9649	1.6796	1.9282

Table 4: Dimensionless separation factor (R_L)

Metal ion (mg/L)	Temperature (°C)			
	30	40	50	60
Ferrous ion				
5	0.303	0.294	0.277	0.232
10	0.178	0.172	0.161	0.131
15	0.126	0.121	0.113	0.091
20	0.098	0.094	0.087	0.070
25	0.080	0.076	0.071	0.057
30	0.067	0.064	0.059	0.048
Cobalt ion				
5	0.438	0.370	0.344	0.270
10	0.280	0.219	0.208	0.156
15	0.206	0.156	0.149	0.109
20	0.163	0.123	0.116	0.084
25	0.135	0.101	0.095	0.068
30	0.115	0.085	0.080	0.057
Nickel ion				
5	0.487	0.434	0.384	0.198
10	0.322	0.277	0.238	0.200
15	0.240	0.200	0.172	0.142
20	0.192	0.161	0.135	0.111
25	0.160	0.133	0.111	0.090
30	0.136	0.113	0.094	0.076

Temperature studies

The adsorption capacity of BBC increased with increase in the temperature of the system from 30 to 60°C. Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (H^0) and entropy (ΔS^0) were determined using the following equations.

$$K_0 = C_{solid}/C_{liquid} \qquad (4)$$

$$\Delta G^0 = -RT \ln K_0 \qquad (5)$$

$$\log K_0 = \Delta S^0/(2.303R) - \Delta H^0/(2.303RT) \qquad (6)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in kelvin and R is the gas constant. ΔH^0 and ΔS^0 were obtained from the slope and intercept of Van't Hoff plots and are presented in Table 5.

Table 5: Equilibrium constants and thermodynamic parameters for the adsorption of metal ions onto BBC

Ferrous ion (mg/L)	K_o				$\Delta G°$				$\Delta H°$	$\Delta S°$
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C		
5	9.21	10.03	11.09	11.63	-5.59	-5.98	-6.44	-6.78	1.81	11.12
10	9.80	10.07	10.30	10.82	-5.74	-6.01	-6.25	-6.58	1.69	7.67
15	6.78	7.60	8.36	9.54	-4.81	-5.25	-5.69	-6.22	2.57	12.90
20	5.35	5.63	6.03	6.64	-4.20	-4.47	-4.80	-5.23	1.68	9.36
25	3.21	3.35	3.53	3.63	-2.92	-3.14	-3.38	-3.53	1.01	6.02
30	2.82	2.97	3.08	3.17	-2.59	-2.81	-3.00	-3.18	0.92	5.42
Cobalt ion										
5	5.610	7.216	7.628	10.638		-5.12	-5.45	-6.53	4.55	19.01
10	4.918	6.392	6.950	9.076	-4.00	-4.83	-5.20	-6.11	4.39	18.21
15	4.600	6.063	7.221	8.711	-3.85	-4.68	-5.31	-5.97	4.74	19.22
20	3.595	4.068	4.555	5.148	-3.22	-3.64	-4.08	-4.53	2.74	11.97
25	2.492	2.625	2.927	3.156	-2.29	-2.51	-2.87	-3.15	1.84	8.15
30	2.045	2.336	2.561	2.692	-1.80	-2.21	-2.52	-2.74	2.16	8.82
Nickel ion										
5	4.073	5.155	5.890	7.316	-1.404	-1.639	-1.773	-1.989	2.70	12.27
10	4.376	4.840	5.743	6.983	-1.476	-1.576	-1.747	-1.943	3.63	15.35
15	3.800	4.093	4.523	5.220	-1.335	-1.408	-1.508	-1.652	2.37	10.87
20	3.202	3.532	3.770	4.147	-1.163	-1.261	-1.327	-1.420	1.95	9.14
25	2.007	2.081	2.176	2.309	-0.693	-0.732	-0.774	-0.832	1.05	5.07
30	1.853	1.926	2.032	2.166	-0.615	-0.655	-0.708	-0.770	1.15	5.21

$\Delta G°$(kJ/mol); $\Delta H°$ (kJ/mol); $\Delta S°$ (J/k/mol)

Effect of initial pH and other ions

Figs. 5, 6 and 7 shows the effect of initial pH and the presence of other ions on the adsorption of metal ions by BBC.

Adsorption kinetics

The rate constant of adsorption of metal ions onto BBC was determined using the following rate expression given by Lagergren (Khare *et al*., 1987).

$$\log(Q_e-Q)=\log Q_e-(K_{ad}/2.303)t \qquad (7)$$

Where Q_e is the amount of solute adsorbed per unit weight of the adsorbent (mg/g) at equilibrium time, Q is the amount adsorbed (mg/g) at time t (min) and K_{ad} is the rate constant (1/min). The linear plots of log (Q_e–Q) versus t suggest the applicability of the Lagergren equation. The rate constants (K_{ad}, k_1, k_2) were calculated from the slope and are presented in Table 6.
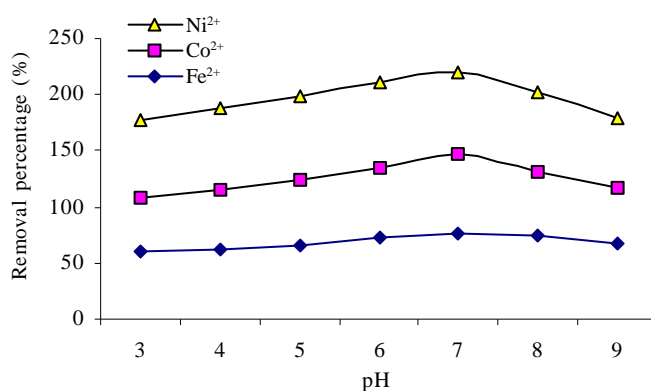

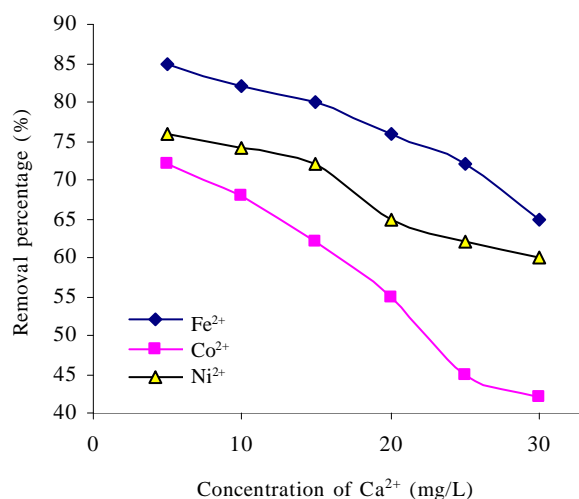Fig. 5: Effect of pH on the removal of metal ions

Fig. 6: Effect of calcium ion on the removal of metal ions with the initial concentration of 20 mg/L
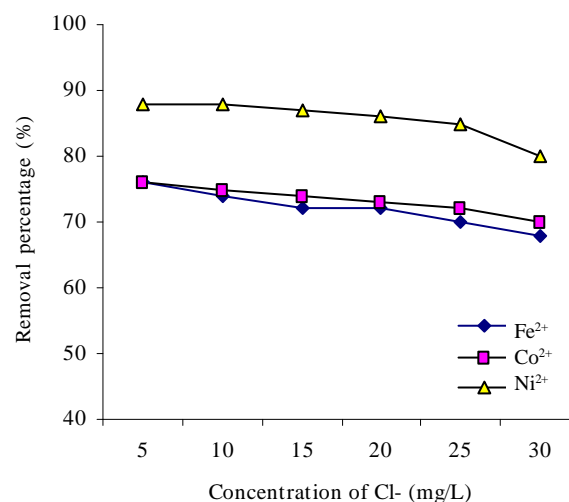

Fig. 7: Effect of chloride ion on the removal of metal ions with the initial concentration of 20 mg/L

Table 6: Rate constants for the adsorption of metal ions ($10^3 k_{ad}$, 1/min) and the constants for forward ($10^3 K_1$, 1/min) and reverse ($10^3 K_2$, 1/min) process

Metal ion (mg/L)	Temperature (°C)											
	30	40	50	60	30		40		50		60	
	K_{ad}				K_1	K_2	K_1	K_2	K_1	K_2	K_1	K_2
Ferrous ion												
5	68.49	75.99	79.68	84.28	61.78	6.70	69.10	6.88	73.09	6.59	77.61	6.67
10	42.83	43.29	23.03	23.95	38.87	3.95	39.38	3.90	20.93	2.09	21.92	2.02
15	9.21	9.21	13.81	15.19	8.03	1.18	8.14	1.07	12.42	1.47	13.74	1.44
20	13.81	13.81	11.97	13.81	11.64	2.17	11.73	2.08	10.27	1.70	12.01	1.80
25	11.51	13.35	11.28	6.44	8.76	2.74	10.28	3.07	8.79	2.49	4.67	1.77
30	5.52	8.75	4.14	18.42	4.08	1.44	6.55	2.20	3.13	1.01	14.01	4.41
Cobalt ion												
5	23.09	32.90	31.52	39.15	19.59	3.49	34.90	4.00	27.87	3.65	35.78	3.36
10	20.72	25.33	30.10	97.87	17.22	3.50	21.90	3.42	26.31	3.78	88.15	9.71
15	11.51	18.42	25.33	23.49	9.46	2.05	15.81	2.60	22.24	3.08	21.08	2.41
20	11.51	13.81	16.12	13.81	9.01	2.50	11.09	2.72	13.21	2.90	11.56	2.25
25	4.60	4.60	6.90	9.21	3.28	1.31	3.31	1.28	5.14	1.76	6.72	2.49
30	4.60	6.21	6.90	6.90	3.08	1.51	4.33	1.88	4.97	1.93	5.03	1.86
Nickel ion												
5	6.54	20.17	18.42	20.72	5.26	1.28	16.90	3.27	15.74	2.67	18.23	2.49
10	7.64	13.15	20.26	27.17	6.23	1.42	10.90	2.25	17.26	3.00	23.77	3.40
15	11.51	13.81	14.04	11.97	9.12	2.39	11.09	2.72	11.49	2.55	9.99	1.92
20	6.90	10.82	9.21	11.51	5.26	1.64	8.44	2.38	7.28	1.93	9.27	2.24
25	3.91	5.29	4.60	5.75	2.61	1.30	2.75	2.54	3.15	1.45	1.02	1.74
30	4.72	5.98	5.98	6.90	3.07	1.65	3.93	2.04	4.01	1.97	4.72	2.18

The rate constant for intraparticle diffusion was obtained using the equation

$$Q = K_p t^{1/2} + C \qquad (8)$$

Where K_p (mg/g/min) is the intraparticle diffusion rate constant. The nature of the plots in Fig. 8 suggests that the initial curved portion is attributed to the film or boundary layer diffusion effect and the subsequent linear portion to the intraparticle diffusion effect. Furthermore, Fig. 8 also depicts that the intra-particle diffusion is the slow and the rate determining step. The K_p values were obtained from the slope of the linear portions of the curves for all selected metal ion concentrations (Table 7).

Table 7: Intraparticle diffusion coefficient (K_p)

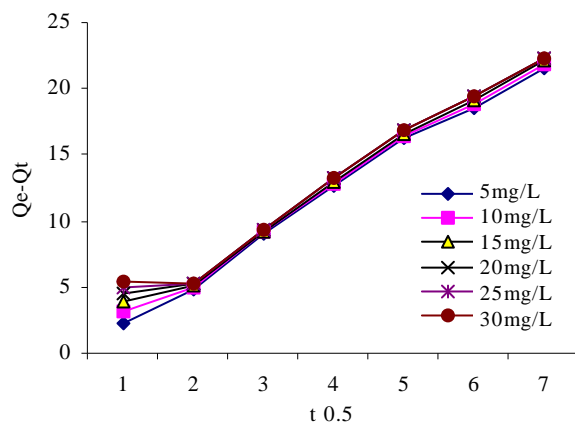| Concentration (mg/L)	Ferrous ion	Cobalt ion	Nickel ion
5	4.5289	3.7480	3.5907
10	8.8207	7.8042	7.3299
15	12.1814	11.9185	11.0860
20	15.7814	15.4408	14.0814
25	17.8781	17.0781	14.5814
30	20.6423	19..0725	18.3720

Fig. 8: Intraparticle diffusion of ferrous ion onto BBC

DISCUSSION

Effect of carbon mass

The amount of metal adsorption increased with the increase in carbon dosage and reached a maximum value after a particular dose (Fig. 1). The optimum metal ions removal was observed at 100mg of carbon mass. The increase in the adsorption of metal ions with carbon dosage was due to the introduction of more binding sites for adsorption and the availability of more surface area (Senthilkumar *et al.*, 2005).

Effect of agitation time and initial metal ion concentration

The kinetics of adsorption of metal ions by BBC shown in Fig. 2, presents smooth and single plots

indicating monolayer adsorption of metal ions onto the adsorbent (Namasivayam and Kanchana, 1992). The removal of metal ion increased with the lapse time and attained equilibrium in 20 minutes. With increase in metal ions concentration from 5 to 30mg/L, the amount of metal ion adsorbed onto the adsorbent was increased, while the removal percentage was decreased indicating that the metal ions removal by adsorption onto BBC is a concentration dependent process.

Adsorption isotherms
From the results, it is clear that the value of adsorption efficiency Q_m remained almost stable and the adsorption energy (b) of the carbon increased with increase in temperature. It may be concluded that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The trend showed that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism. Furthermore, it confirmed the endothermic nature of the processes involved in the system. The influence of isotherm shape has been considered with a view to predicting if an adsorption system is "favourable" or "unfavourable". The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter R_L, which is defined as $R_L=1/(1+bC_o)$, where b is the Langmuir constant and C_o is the initial metal ion concentration. The R_L values obtained (Table 4) were between 0 and 1, which indicate the favourable adsorption (Senthilkumar *et al*., 2005) of metal ions onto BBC for the concentration range studied.

According to Treybal, it has been shown using mathematical calculation that n values between 1 and 10 represent the beneficial adsorption. The sorption equation arrived (x/m) can be employed to determine the volume of wastewater that could be treated. Substituting the concentration of metal ion to be treated for C_e, the respective sorption capacity can be calculated, which on dividing by the actual amount of metal ion to be removed gives the volume of wastewater, containing the metal

ion under study (Ozacar and Sengil, 2005).

Effect of temperature
The positive value of $\triangle H^0$ shows the endothermic nature of adsorption. This rules the possibility of both physical as well as chemical adsorption. Because in the case of physical adsorption alone, while increasing the temperature of the system the extent of metal ion adsorption decreases, as desorption increases with temperature. As chemisorption is mainly an irreversible process, the low positive $\triangle H^0$ value depicts that metal ions is both physically as well as chemically adsorbed onto BBC. This is in agreement with the type Langmuir and Freundlich isotherms obtained, which is close to irreversible adsorption (Namasivayam *et al*., 1994). The negative values of $\triangle G^0$ (Table 5) indicated that the metal ions adsorption is spontaneous. The positive value of $\triangle S^0$ showed increased randomness at the solid-solution interface during the adsorption of metal ions onto BBC. In this conditions the adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity of BBC at higher temperatures may be attributed the enlargement of pore size and/or activation of the adsorbent surface (Syed Shabudeen *et al*., 2006).

Effect of pH
The experience carried out at different pH of medium showed that there was a change in the removal percentage of metal ions over the entire pH range shown in Fig. 5. This indicated the strong force of interaction between the metal ions and BBC that either H^+ or OH^- ions could influence the adsorption capacity. In other words, the adsorption of metal ions on BBC does involve ion exchange mechanism that has an influence on the metal ions adsorption while varying the pH (Namasivayam *et al*., 1994). This observation is in line with the type Langmuir and Freundlich isotherms and positive $\triangle H^0$ value obtained, which indicate irreversible adsorption probably due to polar interactions.

Effect of other ions
Based on the results shown in Figs. 6 and 7 it was

concluded that low concentration of Cl⁻ does not affect the percentage of adsorption of metal ions on activated carbon, because the interaction of Cl⁻ at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion (Ca^{2+}) increased, the interference of these ions at available surface sites of the sorbent through competitive adsorption increased, leading to the decrease adsorption percentage. The interference was more in the presence of (Ca^{2+}) compared with Cl⁻ ion, because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions (Selvarani, 2000).

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. If the adsorbed metal ions can be desorbed using neutral pH water, then the attachment of the metal ions onto the adsorbent is by weak bonds. The effect of various reagents used for desorption was studied. Results indicated that hydrochloric acid was a better reagent for desorption, because we could get more than 90% removal of adsorbed metal ions. The reversibility of adsorbed metal ion in mineral acid or base was in agreement with the pH dependent results obtained. The desorption of metal ions by mineral acids and alkaline medium indicated that the metal ions are adsorbed onto the activated carbon through physical adsorption as well as by chemisorption mechanisms (Stephen and Sulochana, 2002).

Adsorption rate constants

K_{ad} was found to decrease with the increase in the initial concentration from 5 to 30mg/L. The examination of the effect of metal ions concentration on the rate constant (K_{ad}) helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of reaction will not be linear. It shows that a direct linear relationship does not exist in the adsorption of metal ions onto BBC. It seems likely that pore diffusion limits the overall rate of adsorption. The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as shown by Weber and Morris. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that mass transfer from the bulk liquid to the particle external surface does not limit the rate. One might then postulate that the rate-limiting step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step. The K_p values increased with increase in the metal ions concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed metal ions within the pores of the adsorbent (Syed Shabudeen *et al.*, 2006).

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