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Cobalt 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, by acid treatment was tested for its efficiency in removing metal ion. The process parameters studied include agitation time, initial Cobalt ion concentration, carbon dose, pH and temperature. The adsorption followed first order reaction equation and the rate is mainly controlled by intraparticle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plot were 28.248, 26.954, 27.129, 26.150 mg/g respectively at an initial pH of 6.0 and at 30, 40, 50, 60 ± 0.5^{0}C. The influence of pH on metal ion removal was significant and the adsorption was increased with increase in temperature. A portion of the Cobalt was recovered from the spent carbon using 0.1M HCl.

Key words: Activated carbon, cobalt ion, adsorption isotherm, equilibrium, thermodynamic parameter, Intraparticle diffusion.

INTRODUCTION

Heavy metals contamination exists in aqueous waste streams from many industries such as ferrous plating, mining, tanneries, painting, car radiation manufacturing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used. Cu, Co, Fe, Zn, Cr, Cd, etc., are harmful wastes produced by industry that pose a risk of contaminating groundwater and other water resources. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. For example, chromium causes serious ailments. The treatment process, to remove heavy metals such as Iron, comprises of chemical precipitation, coagulation, complexing, 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.

The treatment process, to remove heavy metals such as Cobalt, comprises of chemical precipitation, coagulation, complexing, 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[1].

MATERIALS AND METHODS

Carbon was prepared by treating air-dried Borassus bark with con sulphuric acid in a weight ratio of 1:1. The resulting black product was kept in an air-oven maintained at 300°C for 12 hours followed by washing with water until free of excess acid and dried at 150 ± 5°C. The carbon product obtained from Borssus bark (BBC) was ground and the portion retained between 30 and 50 mm sieves was used in all the experiments.

All chemicals supplied by S.d. fine chemicals with high purity. The adsorption experiments were carried out by agitating the carbon with 5, 10, 15, 20, 25, 30 mg/L metal solution

of desired concentration at pH 6.0 and at temperatures (30, 40, 50, 60 ± 0.5°C) in a mechanical shaker (120 rpm). After the defined time intervals, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analysed for residual metal ion concentration using a Uv-Visible Spectrophotometer at 620 nm. Effect of adsorbent dosage was studied by varying the carbon dose from 10 to 100 mg, 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 using small amounts of dilute hydrochloric acid or sodium hydroxide and agitated with 50 mg of the carbon. For temperature variation study 50 mg of the carbon was agitated with 5,10,15,20,25,30 mg/L metal ion solution using a temperature controlled water bath-cum-shaker. Freundlich isotherm was derived from the studies on the effect of carbon dosage on the percent Cobalt ion removal. Langmuir isotherm study was carried out with metal ion solutions of different initial concentrations ranging from 5, 10, 15, 20, 25, 30 mg/L and agitating with a fixed carbon dose (50 mg), until equilibrium was reached.

After adsorption of 20 mg/L of metal ion by 50 mg of the carbon, the carbon loaded with metal ion was separated and gently washed with distilled water to remove any unadsorbed metal ion. The metal ion-laden carbons were agitated with 50 mL of neutral pH water, 0.1M sulphuric acid, hydrochloric acid, nitric acid, sodium chloride and sodium chloride with hydrochloric acid separately for 60 min.

RESULTS AND DISCUSSION

Effect of carbon mass

The amount of Cobalt ion adsorption increased with the increase in carbon dose and reached a maximum value after a particular dose (Fig. -1). Taken an initial metal ion concentration of 20 mg/L, complete metal ion removal was obtained at a maximum carbon dose of 100 mg. The increase in the adsorption of metal ion with carbon dose was due to the introduction of more binding sites for adsorption and the availability more surface area[2].

Effect of agitation time and initial Cobalt ion concentration

The kinetics of adsorption of Cobalt ion by BBC is shown in Fig. - 2, with smooth and single plots indicating monolayer adsorption of metal ion

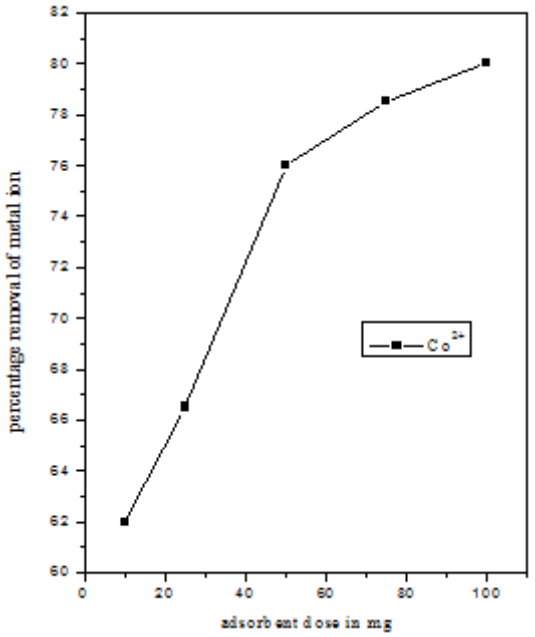

Fig. - 1: Effect of dosage on the removal of metal ion

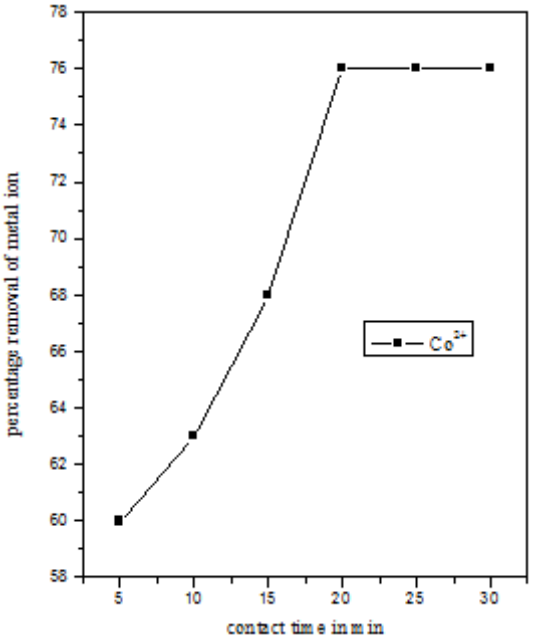

Fig. - 2: Effect of contact time on the removal of metal ion

Table - 1: Equilibrium Parameters for the adsorption of Cobalt ion on to acid activated Carbon

[Cobalt ion] (mg/L)	Ce (mg / L)				Qe (mg / g)				Metal ion Removed (%)			
	30°	40°	50°	60°	30°	40°	50°	60°	30°	40°	50°	60°
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

on the carbon[3]. The removal of metal ion increased with the lapse time and attains equilibrium in 20 min for 20 mg/ L. With increase in metal ion concentration from 5 to 30 mg/L, the amount of metal ion adsorbed increased while the percent removal decreased, indicating that the metal ion removal by adsorption on BBC concentration dependent.

Adsorption isotherms

The distribution of metal ion between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can be generally expressed by the most popular isotherm theories viz., Langmuir[9] and the Freundlich[10] isotherms.

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[11]. The Langmuir isotherm model for liquid-phase adsorption is written as follows.

$$Q_e=Q_m bC_e/ 1+bC_e \quad \ldots(1)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg /g) and Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (representative Fig. - 3). Values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table -2. From the results, it is clear that the value of adsorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. From the values we can conclude 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 shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism. Further, it confirms 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 constant separation factor or equilibrium parameter R_L[5], which is defined as $R_L=1/(1+bC_0)$, where b is the Langmuir constant and C_0 is the initial metal ion concentration. R_L values obtained (Table 4) were between 0 and 1, which indicate favourable adsorption[4] of metal ion on BBC for the concentration range studied.

The equilibrium data obtained at varying initial metal ion concentration with fixed carbon dosage conform to the Freundlich equation (Fig. 4), which has the following forms

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

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

Here 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

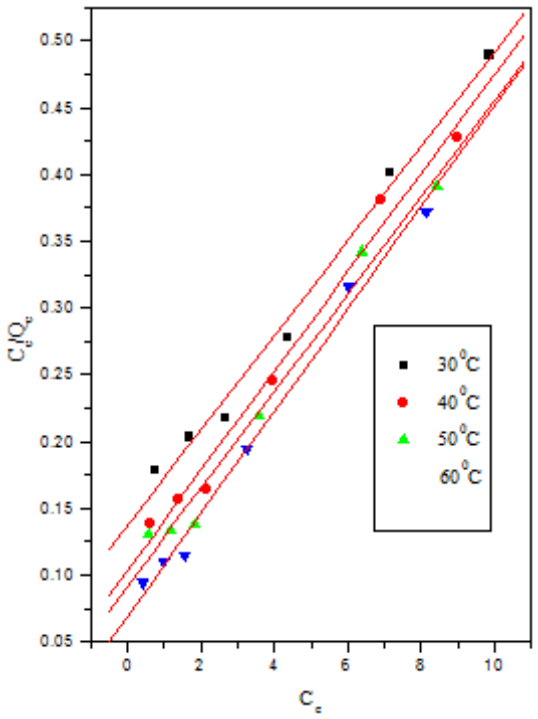

Fig. - 3: Langmuir isotherm for the adsorption of Cobalt ion

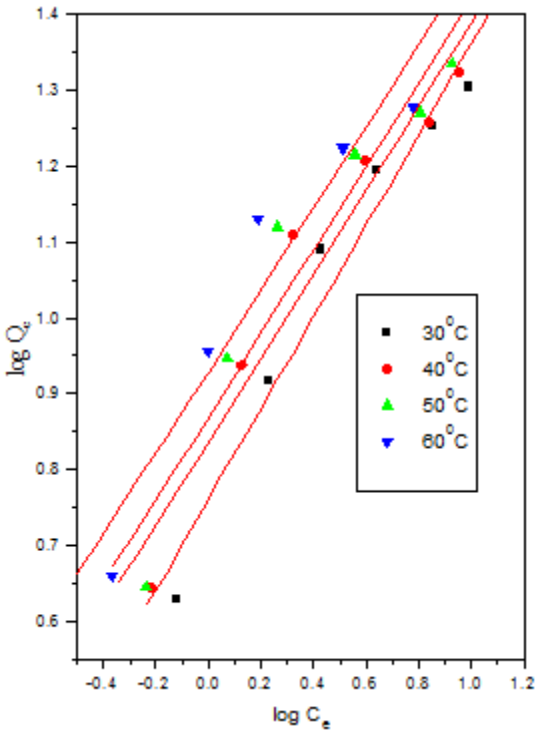

Fig. - 4: Freundlich isotherm for the adsorption of Cobalt ion

Table - 2: Langmuir isotherm results

(Cobalt ion)	Temp (°C)	Statistical parameters R^2	Q_m	Constants b
	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

concentration is 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. The correlation coefficient (r), obtained for the linear plot (Fig. - 4). The constants K_f and n obtained from the intercept and slope of the plot are given Table -3. According to Treybal, it has been shown using mathematical calculation that n values between 1 and 10 represent 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.

Table - 3: Freundlich isotherm results

(Cobalt ion)	Temp (°C)	Statistical parameters R^2	k_f	Constants n
	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

Effect of temperature

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

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

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

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

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 plot and are presented in Table 5. Positive value of ΔH^0 shows the endothermic nature of adsoption. 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[12]. As chemisorption is mainly an irreversible process, the low positive êH^0 value depicts that cobalt ion is both physically as well as chemically adsorbed onto BBC. This is in agreement with the type I and II isotherm obtained, which is close to irreversible adsorption[13].

Table - 4 Dimensionless Separation Factor (R_L)

(Cobalt ion) (mg/L)	Temperature (°C)			
	30°	40°	50°	60°
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

The negative values of ΔG^0 (Table 5) indicate that the metal ion adsorption is spontaneous. The positive value of ΔS^0 shows increased randomness at the solid-solution interface during the adsorption of metal ion on BBC. The adsorbed water molecules, which are displaced by the adsorbate species, gain more

Table - 5: Equilibrium constant and thermodynamic parameters for the adsorption of Cobalt ion onto acid activated carbon.
Temperature (°C)

[Cobalt ion] (mg/L)	K_o 30°	40°	50°	60°	ΔG° 30°	40°	50°	60°	ΔH°	ΔS°
5	5.610	7.216	7.628	10.638	-4.33	-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

Table - 6: Rate constants for the adsorption of Cobalt ion (10^3 k_{ad}, min^{-1}) and the constants for forward (10^3 K_1, min^{-1}) and reverse (10^3 K_2, min^{-1}) process
Temperature (°C)

(Cobalt ion) (mg/L)	K_{ad} 30°	40°	50°	60°	K_1 30°	K_2 30°	K_1 40°	K_2 40°	K_1 50°	K_2 50°	K_1 60°	K_2 60°
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

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[14].

Effect of pH

The experience carried out at different pH show that there was a change in the percent removal of Cobalt ion over the entire pH range (Fig. 5). This indicates the strong force of interaction between the metal ion and BBC that either H^+ or

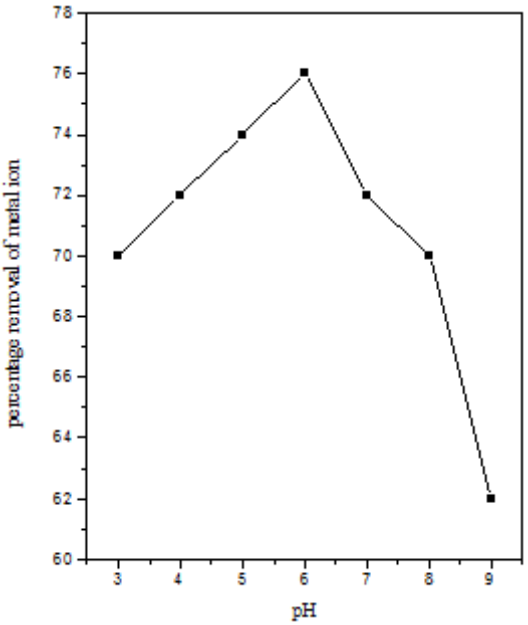

Fig. - 5: Effect of pH on the removal of Cobalt ion

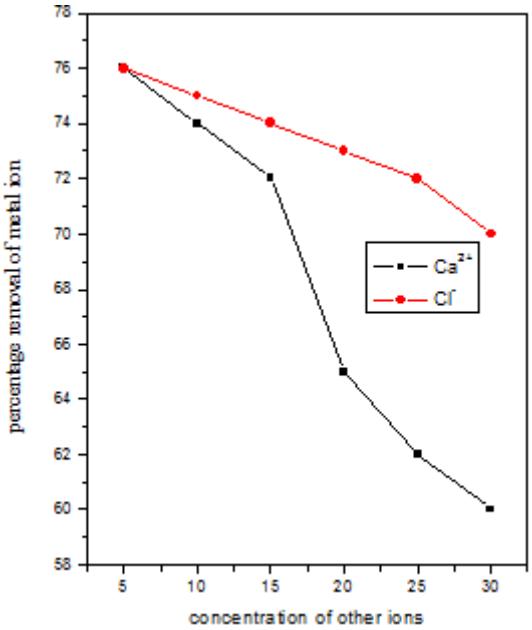

Fig. - 6: Effect other ions on the removal of Cobalt ion

OH^- ions could influence the adsorption capacity. In other words, the adsorption of metal ion on BBC does involve ion exchange mechanism that have been an influence on the metal ion adsorption while varying the pH[15] This observation is in line with the type I and II isotherm and positive ΔH^0 value obtained, which indicates irreversible adsorption probably due to polar interactions.

Effect of other ions

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process studied at different concentrations. The ions added to 20mg/L of Cobalt ion solutions and the contents were agitated for 60 min at 30 C. The results had shown in the Fig. 6 reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion 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+} increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. The interference was more in the presence of Ca^{2+} compared with Cl^- ion. This is so because ions with smaller hydrated radii decrease the swelling pressure with in the sorbent and increase the affinity of the sorbent for such ions[16]

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. If the adsorbed Cobalt ions can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. The effect of various reagents used for desorption studies is shown in Figure 7. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through physisorption as well as by chemisorption mechanisms[16]

Adsorption rate constant

The rate constant of adsorption of Cobalt ion on BBC was determined using the following

rate expression given by Lagergren[4].

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

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 (min^{-1}). Linear plots of log (Q_e – Q) versus t suggest the applicability of the Lagergren equation. The rate constants (K_{ad}) were calculated from the slope and are presented in Table 6. K_{ad} was found to decrease with the increase in the initial concentration from 5 to 30 mg/L. An examination of the effect of metal ion concentration on the rate constant (K_{ad}, K_1, K_2) 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[6]. It shows that a direct linear relationship does not exist in the adsorption of metal ion 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[7]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. 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 rate constant for intraparticle diffusion is obtained using the equation

$$Q = K_p t^{1/2} \quad ...(8)$$

Here, 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[8]. Fig. 8 also depicts that the intraparticle diffusion is the slow and the rate-determining step. K_p values were obtained from the

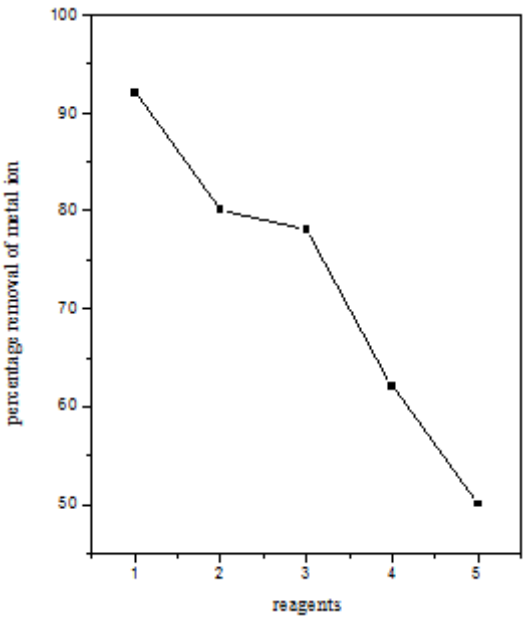

Fig. - 7: Regeneration pattern (1.HCl, $2H_2SO_4$, $3HNO_3$, 4.NaCl, 5.NaCl+H_2O

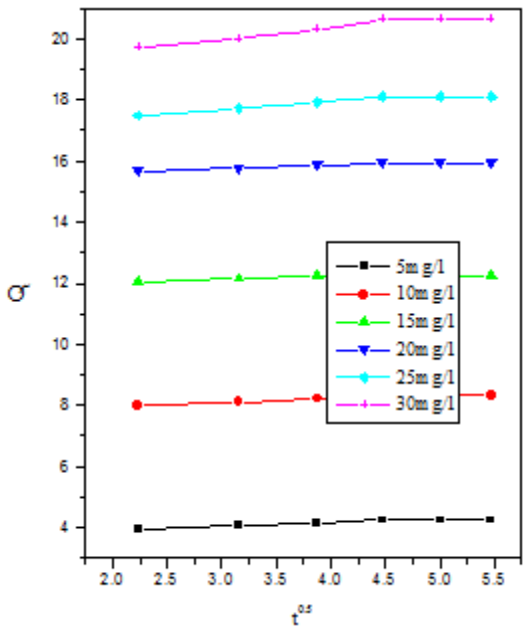

Fig. - 8: Intraparticle diffusion of Cobalt ion at 30°C

Table - 7: Intraparticle diffusion (K_p)

(Cobalt ion) (mg/L)	Temperature (30°C)	
	R^2	K_p
5	0.9625	3.7480
10	0.9616	7.8042
15	0.9085	11.9185
20	0.9625	15.4408
25	0.9619	17.0781
30	0.9625	19..0725

slope of the linear portions of the curves at each metal ion concentration (Table 7). The K_p values increased with increase in the metal ion concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed metal ion within the pores of the adsorbent.

Conclusions

Carbon prepared from waste Borassus bark was found effective in removing Cobalt ion from aqueous solution. The adsorption is faster and the rate is mainly controlled by intraparticle diffusion. Using the sorption equation obtained from the Langmuir and Freundlich isotherms, it was found that BBC is an effective one for the removal of Cobalt ion. The equilibrium data conformed well with the Langmuir and Freundlich isotherm models. The temperature variation study showed that the metal ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the metal ion solution. The type I and II isotherm obtained, positive ΔH^0 value, pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of Cobalt ion on BBC involves chemisorption as well as physisorption mechanism.

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