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Kinetic and equilibrium modelling of cobalt(II) adsorption onto bagasse pith based sulphurised activated carbon

K. Anoop Krishnan [a,*], T.S. Anirudhan [b]

[a] *Environmental Technology, Regional Research Laboratory (CSIR), Industrial Estate Post, Trivandrum 695019, India*
[b] *Department of Chemistry, University of Kerala, Trivandrum 695581, India*

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Abstract

The applicability of sulphurised activated carbon (SAC) as adsorbent for the effective removal of Co(II) from aqueous solutions was investigated. Bagasse pith, a sugarcane industry waste, was used for the synthesis of SAC. Bench scale batch experiments were performed to study the effects of various parameters such as pH, contact time, initial concentration, temperature, ionic strength and adsorbent dose on the adsorption process. Maximum adsorption was observed at the pH range of 4.5–8.5. With an initial concentration of 50 and 100 mg dm^{-3} of the adsorbate at pH 6.0, the percentage adsorptions were found to be 90.3 and 81.0%, respectively. SAC showed a high adsorption capacity for Co(II) removal compared with laboratory and commercial grade activated carbons. Equilibrium studies were conducted to study the effects of initial concentration and temperature for the adsorption of Co(II) onto SAC. The results indicated that adsorption process obeys Langmuir isotherm model other than Freundlich model. An empirical relationship has been suggested to predict the percentage Co(II) removal at any time for known values of adsorbent dose and initial adsorbate concentration under the investigated conditions.

Keywords: Adsorption; Sulphurised activated carbon; Bagasse pith; Cobalt removal; Isotherm

1. Introduction

The presence of heavy metals in aqueous solution beyond certain limit creates serious threat to the environment due to their non-degradability and toxicity. Cobalt is present in mining, electronics, metallurgical, electroplating and paint industries [1]. Cobalt as a pollutant has many toxic effects such as imparting neurotoxicological disorders, genotoxicity, carcinogenicity, cardiomyopathy and bronchial asthma [2]. Therefore, the removal of cobalt from natural streams and industrial wastewaters has received much importance in the recent years.

Among the several methods to treat metal polluted effluent are precipitation, coagulation, photolysis, electrolysis and adsorption. But the selection of a treatment technology is based on the concentration of waste and the cost of the treatment process [3]. Among the known physico-chemical treatment methods, adsorption seems to be the most promising technique for the removal of metals from chemical process industries [4]. There are many reports on the applicability of adsorption techniques in the removal of heavy metals from aqueous solutions [5–7]. Moreover, activated carbon adsorption has become one of the most useful methods for wastewater treatment [8]. Due to the high cost of commercial activated carbon, it was advisable to think of the utilization of agricultural residues for the production of activated carbons in a cost effective manner. A number of research work dealing with the applicability of activated carbon obtained from used tyres, sawdust, jute fiber, coconut shell, almond husk [9–13] for wastewater treatment have been reported. The adsorption capacity of activated carbon can be increased by activation process (chemical or physical), surface impregnation or functionalization. The utility of surface modified carbons for the effective removal of heavy metals from water and wastewaters has been registered by a number of investigators [14,15]. Only a few studies have been published for the removal of Co(II) from aqueous solution using various adsorbents [16–18]. Recent studies revealed that adsorbents with sulphur groups are very effective for the removal of heavy metal ions from aqueous solutions. In this track, Gomez-Serrano et al. [19] studied the ability of commercial activated carbon loaded with sulphur groups for the removal of Hg(II), Pb(II) and Cd(II) from aqueous solutions. In our laboratory, earlier workers explained the

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* Corresponding author. Tel.: +91 471 2515 262; fax: +91 471 2491 712.
E-mail address: sreeanoop@rediffmail.com (K.A. Krishnan).

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adsorption kinetics of Hg(II) by polysulphide treated coconut husk [20].

The basic material for the preparation of SAC was bagasse pith from a local sugar industry. Being a waste material, it was obtained free of cost. Potential disposal problems with this sugarcane industry waste could be minimized if this material gets some commercial utility. From this point of view, we have decided to explore the possibilities for utilizing bagasse pith for the production of SAC for the removal of Co(II) from water and wastewaters.

2. Experimental

2.1. Materials

Analytical grade chemicals were used through out the study. The precursor material (bagasse pith) for preparing SAC was collected from the Co-operative Sugars Ltd., Palakkad, Kerala, India. Commercial as well as laboratory grade activated carbons were obtained from E-Merck India Limited. Distilled water was used throughout. The pH of the solutions was adjusted using various concentrations of HCl and NaOH. Stock solution of the test reagent (1000 mg dm^{-3}) was prepared by dissolving cobalt chloride in distilled water.

2.2. Preparation of the adsorbent-SAC

The precursor material, say bagasse pith of sugar cane, was thoroughly washed with water for removing the adhered and soluble impurities. The production of SAC involved two stages of treatment. In the first stage, the material was broken into pieces, dried, ground and introduced into Matri made muffle furnace (India) at 200 °C for 2 h for carbonization. Steam activation of the carbon thus obtained was carried out using the method described by earlier workers [21]. About 50 g of the carbon was placed in a purpose made graphite bowl and positioned at the centre of the furnace. Steam from a steam generator was allowed to enter into the graphite bowl at a rate of approximately 5 cm^3 min^{-1}. The carbon was heated at a rate of 10 °C min^{-1} to 400 °C and held at this temperature for 1 h. After cooling, the steam activated carbon was removed from the furnace and washed with 1 M HCl followed by distilled water and dried at 100 °C for 2 h. This carbon was used for the production of SAC. In the second stage sulphurised activated carbon (SAC) was prepared by steam activation of first stage carbon (FSC) at 400 °C in the presence of H_2S and SO_2. The required quantities of SO_2 and H_2S gases were flushed into the furnace, respectively from SO_2 and H_2S gas-generators. For the preparation of SAC about 50 g of FSC was placed in a graphite bowl and flushed with a flow of steam (5 cm^3 min^{-1}) in the presence of a stream of SO_2 (10 cm^3 min^{-1}) for 90 min followed by a stream of H_2S (15 cm^3 min^{-1}) for 30 min at a heating rate of 10 °C min^{-1} from 30 to 400 °C. The flow rates of gases were determined using a gas flow meter. The product was washed with distilled water and dried at 100 °C for 1 h. The dried material was then ground and sieved to separate particles of −80 + 230 mesh size and as stored in an airtight polypropylene container.

2.3. Analytical methods

The amount of sulphur attached to the carbon sample was determined using Eschka method [22]. The functional groups present in the adsorbent material were identified using IR spectra recorded on a Shimadzu FTIR spectrophotometer (model 1801). The Quantasorb surface area analyzer (model Q S-7) was used for the determination of surface area of the adsorbent by N_2 gas adsorption method. The surface charge density, σ_o as a function of pH and ionic strength on activated carbon was determined using the procedure described by earlier workers [23]. A conductometric method [24] was carried out to determine the total number of acidic groups on the adsorbent surface. The Co(II) content in the aqueous solution was analysed using atomic absorption spectrophotometer (GBC Aventa, model-A4001, Australia).

2.4. Procedure

Batch adsorption experiments were carried out by shaking 0.1 g of SAC with 50 cm^3 aqueous solution of Co(II) having the desired concentration in a temperature controlled water bath shaker (Remi, India make). The pH and ionic strength (0.001 M) of the solutions were adjusted to constant values. Continuous mixing was provided during the experiments with a constant agitation speed of 200 rpm. Effect of pH on the adsorption of Co(II) was studied by varying pH from 2.0 to 10.0. The kinetic curves were drawn by following the evaluation of Co(II) residual concentration at different time intervals. The amount of Co(II) adsorbed onto carbon surface was calculated as

$$q = \frac{(C_O - C_A)V}{m} \tag{1}$$

where q is the amount of Co(II) adsorbed onto unit amount of the adsorbent (mg g^{-1}); C_O and C_A, the concentrations of Co(II) (mg dm^{-3}) in the aqueous phase, respectively before and after adsorption; V, the volume of the aqueous phase (cm^3); m is the weight of the adsorbent (g). Kinetic studies were carried out at constant pH with an initial concentration ranging from 50 to 400 mg dm^{-3} and adsorbent dose from 2 to 10 g dm^{-3}. Isotherm studies were performed using various concentrations of Co(II) ranging from 25 to 1000 mg dm^{-3}. The contents of the flasks were shaken for 4 h to attain equilibrium. Known volume of the solution was removed and filtered for Co(II) analysis. Langmuir and Freundlich isotherms were studied using the above equilibrium data. The effect of temperature on kinetics and adsorption equilibria was studied by varying temperature from 30 to 60 °C. All experiments were carried out in duplicate and showed differences less than 3%.

3. Results and discussion

3.1. Characterization of SAC

The IR spectrum of the carbon showed a strong asymmetric absorption band at 3762 cm^{-1} indicating the presence of hydroxyl groups. The peaks at 1167, 1111 and 460 cm^{-1} in

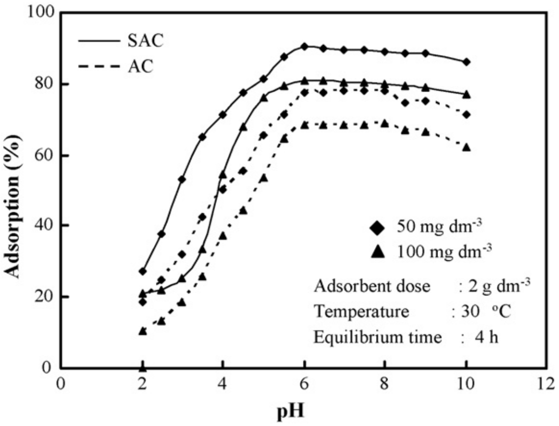

Fig. 1. Influence of pH on the adsorption of Co(II) on SAC.

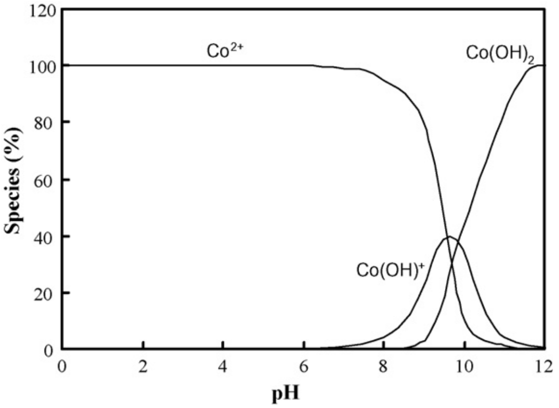

Fig. 2. Speciation diagram for Co(II) in aqueous solution.

the spectrum of activated carbon represented the C=S, S=O and S–S stretching vibrations, respectively, and were strong indicative of the presence of sulphur groups bonded to activated carbon [25]. An additional peak at 1606 $\mathrm{cm^{-1}}$ indicated the presence of conjugated hydrogen bonded carboxyl groups [26]. The carbon also contained free carboxyl (absorption band at 1730 $\mathrm{cm^{-1}}$) groups. The peaks at 690 and 608 $\mathrm{cm^{-1}}$ indicate the stretching vibration of C–S and sulphonate group, respectively. The surface and physical properties of the sulphurised activated carbon were as follows: surface area, 500.5 $\mathrm{m^2\,g^{-1}}$; porosity, 0.43 $\mathrm{cm^3\,g^{-1}}$; density 1.39 $\mathrm{g\,cm^{-3}}$; sulphur content, 8.9%; total acid groups, 0.32 mequiv. $\mathrm{g^{-1}}$; cation exchange capacity, 1.57 mequiv. $\mathrm{g^{-1}}$ and $\mathrm{pH_{zpc}}$, 4.3.

3.2. *Influence of pH on Co(II) adsorption*

The influence of pH on the adsorption of Co(II) using SAC and commercial grade activated carbon (AC) over a pH range 2.0–10.0 is depicted in Fig. 1. From the figure it is clear that SAC is effective for the quantitative removal of Co(II) over the pH range 4.5–8.5, where as sulphur free carbon is effective only in a narrow pH range of 6.0–8.0. At lower and higher pH values the adsorption was bare minimum. As the pH increases from 2.0 to 6.0, there is a sharp increase in the amount of adsorption and at pH 6.0, both carbons show maximum adsorption of Co(II). After pH 6.0, there is a slight decrease in the amount of adsorption with further increase in pH due to precipitation. A maximum amount of 22.58 $\mathrm{mg\,g^{-1}}$ (90.3%) and 40.50 $\mathrm{mg\,g^{-1}}$ (81.0%) of Co(II) was adsorbed on SAC from initial concentrations of 50 and 100 $\mathrm{mg\,dm^{-3}}$, respectively at pH 6.0. Under the same conditions, the sulphur free activated carbon showed a maximum amount of 19.40 $\mathrm{mg\,g^{-1}}$ (77.6%) and 34.20 $\mathrm{mg\,g^{-1}}$ (68.4%) of Co(II) adsorption. From this, it is obvious that Co(II) is effectively adsorbed on SAC than on AC.

The effect of pH can be explained in terms of 'pH at zero point of charge' ($\mathrm{pH_{zpc}}$) and Co(II) speciation (Fig. 2) in solution. The pH at which the charge of the solid surface is zero is referred to as the $\mathrm{pH_{zpc}}$. Above $\mathrm{pH_{zpc}}$, the surface charge of the adsorbent is negative and below the particular pH it will be positive. The amount of adsorption above the $\mathrm{pH_{zpc}}$ was maximum due to the interaction of $\mathrm{Co^{2+}}$ and $\mathrm{Co(OH)^+}$ with the negatively charged carbon surface. At low pH, particularly below $\mathrm{pH_{zpc}}$, the positively charged $\mathrm{Co^{2+}}$ and $\mathrm{Co(OH)^+}$ species may repel with carbon surface carrying equal charge and thereby decreases the Co(II) adsorption. Earlier workers have reported a similar pattern for the influence of pH on the adsorption of heavy metals onto activated carbons [27,28].

Sulphur groups present in the SAC played an important role in the Co(II) adsorption process. Pearson stated that hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases [29]. Because the sulphur groups present in SAC are soft bases, one would expect the coordination of it with positively charged species such as $\mathrm{Co^{2+}}$ and $\mathrm{Co(OH)^+}$ in the aqueous solution at the pH range of 4.5–8.5. In addition to sulphur groups, carboxyl and hydroxyl groups present in the carbon are also responsible for the sorption of Co(II) ions. It has also been shown that the final pH of the solution is always less than the initial pH due to the exchange of $\mathrm{Co^{2+}}$ or $\mathrm{Co(OH)^+}$ species present in the solution with $\mathrm{H^+}$ ions of the carbon. A surface complexation model has been proposed by Corapcioglu and Huang [30] for metal adsorption on activated carbon. Based on the above model the following reactions are proposed for the adsorption of Co(II) on SAC.

$$2\underline{\mathrm{C}}-\mathrm{SO_3H} + \mathrm{Co^{2+}} \rightleftharpoons (\underline{\mathrm{C}}-\mathrm{SO_3}^-)_2\mathrm{Co^{2+}} + 2\mathrm{H^+}$$

$$2\underline{\mathrm{C}}-\mathrm{SO_3}^- + \mathrm{Co^{2+}} \rightleftharpoons (\underline{\mathrm{C}}-\mathrm{SO_3}^-)_2\mathrm{Co^{2+}}$$

$$2\underline{\mathrm{C}}-\mathrm{SO_3H} + \mathrm{Co(OH)^+} \rightleftharpoons (\underline{\mathrm{C}}-\mathrm{SO_3}^-)_2\mathrm{Co(OH)^+} + 2\mathrm{H^+}$$

$$2\underline{\mathrm{C}}-\mathrm{SO_3}^- + \mathrm{Co(OH)^+} \rightleftharpoons (\underline{\mathrm{C}}-\mathrm{SO_3}^-)_2\mathrm{Co(OH)^+}$$

$$2(\underline{\mathrm{C}}\mathrm{OH}) + \mathrm{Co^{2+}} \rightleftharpoons (\underline{\mathrm{C}}\mathrm{O}^-)_2\mathrm{Co^{2+}} + 2\mathrm{H^+}$$

$$2\underline{\mathrm{C}}\mathrm{O}^- + \mathrm{Co^{2+}} \rightleftharpoons (\underline{\mathrm{C}}\mathrm{O}^-)_2\mathrm{Co^{2+}}$$

$$\underline{\mathrm{C}}\mathrm{OH} + \mathrm{Co(OH)^+} \rightleftharpoons (\underline{\mathrm{C}}\mathrm{O}^-)\mathrm{Co(OH)^+} + \mathrm{H^+}$$

$$(\underline{\mathrm{C}}\mathrm{O}^-) + \mathrm{Co(OH)^+} \rightleftharpoons (\underline{\mathrm{C}}\mathrm{O}^-)\mathrm{Co(OH)^+}$$

$\underline{\mathrm{C}}$ represents solid surface.

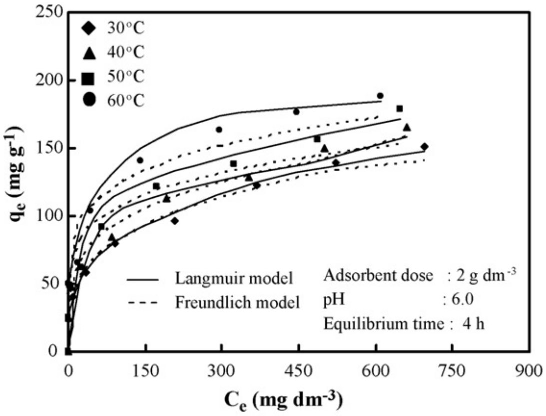

Fig. 3. Plots of q_e vs. C_e on the adsorption of Co(II) on SAC. Legends represent experimental data.

Since SAC was more effective than AC, further experiments were carried out using SAC only. The pH 6.0 was selected as optimum pH for further adsorption studies.

3.3. Equilibrium modelling

The results from the adsorption studies were analysed by the Langmuir and Freundlich adsorption isotherms over a wide range of Co(II) concentration (50–1000 mg dm^{-3}). The adsorption of Co(II) was found to be endothermic. Therefore, the extent of adsorption increased with the temperature in the range 30–60 °C (Fig. 3). From the figure it is clear that as temperature increases from 30 to 60 °C, the amount of adsorption increases from 79.44 mg g^{-1} (63.6%) to 103.25 mg g^{-1} (82.6%) for an initial concentration of 250 mg dm^{-3}. The similar type of increase in adsorption was found in all cases for various initial concentrations under the same conditions. The increase in adsorption capacity with temperature suggested that the active surface centers available for adsorption increased with temperature. This could also be attributed to the change in pore size and enhanced rate of intraparticle diffusion of the solute as diffusion is an endothermic process. The linear form of the Langmuir equation can be represented as

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \tag{2}$$

where q_e is the amount of adsorbate retained per unit weight of the adsorbent (mg g^{-1}) at equilibrium, C_e the equilibrium solution phase concentration (mg dm^{-3}), and Q^o and b are Langmuir constants related to adsorption capacity (mg g^{-1}) and energy of adsorption (dm^3 mg^{-1}), respectively.

Table 2
Comparison of adsorption capacity of SAC with other potential adsorbents for Co(II) removal

Adsorbent	Q^o (mg g^{-1})	Reference
Cation exchange resin, IRN77	86.2	[17]
Cation exchange resin, SKN1	69.4	[17]
SAC	153.6	Present work
Zeolite	85.0	[31]
Clinoptilolite	14.4	[32]
Grafted poly(ethylene terephthalate) fiber	27.2	[33]
Alginate–chitosan hybrid gel	3.2	[34]

The Freundlich isotherm is empirical and used for heterogeneous surface energies in which the energy term, b, in the Langmuir equation varies as a function of the surface coverage, q_e, due to the variation in the heat of adsorption. The linear representation of the Freundlich adsorption equation is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F and $1/n$ are the Freundlich constants related to adsorptive capacity and intensity of adsorption, respectively.

The Langmuir constants (Q^o and b) were calculated from the plots of C_e/q_e versus C_e and Freundlich constants (K_F and $1/n$) were obtained from $\log q_e$ versus $\log C_e$ plots using linear least-squares fitting. The values of the constants of these models together with correlation coefficients (r^2) and normalized standard deviation ($\Delta q(\%)$) are given in Table 1. The adsorption capacities of several potential adsorbents for the removal of Co(II) along with that for SAC is given in Table 2. From the data it could be easily understood that SAC has much higher adsorption capacity among the reported adsorbents. The increase in Langmuir constants as the temperature increases from 30 to 60 °C also explains the endothermic nature of the adsorption process. The values of $\Delta q(\%)$ were calculated using the following equation

$$\Delta q\,(\%) = 100 \times \sqrt{\frac{\sum [(q_t^{\exp} - q_t^{\mathrm{cal}})/q_t^{\exp}]^2}{N-1}} \tag{4}$$

where $q_t^{\exp}$ and q_t^{cal} are experimental and calculated amount of Co(II) adsorbed on SAC at time 't' and N is the number of measurements made. The fitted isotherm plots for the adsorption of Co(II) on SAC at various temperatures ranging from 30 to 60 °C along with the experimental data are given in Fig. 3 for

Table 1
Langmuir and Freundlich constants for the adsorption of Co(II) onto SAC

Temperature (°C)	Langmuir				Freundlich			
	Q^o (mg g^{-1})	b (dm^3 mg^{-1})	r^2	$\Delta q(\%)$	K_F	n	r^2	$\Delta q(\%)$
30	153.85	1.84×10^{-2}	0.978	3.26	21.90	3.46	0.980	4.66
40	166.67	1.98×10^{-2}	0.975	6.02	30.91	4.09	0.971	9.62
50	175.44	2.41×10^{-2}	0.987	4.22	45.35	5.35	0.952	10.97
60	192.31	3.11×10^{-2}	0.981	10.12	53.68	5.50	0.948	17.62

comparison. The values of $\Delta q(\%)$ were compared to determine the appropriate type of isotherm model for Co(II) adsorption, since the r^2 values obtained were close to 1 for both the models. The $\Delta q(\%)$ values at all temperatures for the adsorption of Co(II) show much lower values for Langmuir isotherm than those for Freundlich isotherm (Table 1). Hence the adsorption of Co(II) on SAC can be best described by the Langmuir model. It is also assumed that the adsorption sites have equal energy, but still, the percentage adsorption versus pH plots clearly suggested a range of site energies. Earlier studies [35] in this direction have clearly demonstrated that the Langmuir equation gives adequate results in many cases where surface heterogeneity is known to be present.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter R_L [36]

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where b is the Langmuir constant and C_o is the initial Co(II) concentration. R_L values indicate the type of isotherm. An R_L value between 0 and 1 indicates favourable adsorption. From the experimental data, the values of R_L were found to be between 0 and 1 for all initial Co(II) concentrations and there by obeying the Langmuir isotherm model (table presented in supplementary material).

Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated using the following equation

$$\Delta G^\circ = -RT \ln K_o \tag{6}$$

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

where K_o is the equilibrium constant. The values of K_o were determined from the intercepts obtained by plotting $\ln q_e/C_e$ versus q_e (figure in supplementary material) as suggested by Khan and Singh [37] and extrapolating to zero q_e at various temperatures ranging from 30 to 60 °C. The values of K_o were found to be 2.92, 3.91, 5.69 and 6.72 for 30, 40, 50 and 60 °C, respectively. The plots of $\ln K_o$ versus $1/T$ for Co(II) was found to be linear (figure in supplementary material). The values of ΔH° and ΔS° were obtained from the slope and intercept of the plots and were found to be 24.17 kJ mol^{-1} and 88.73 J mol^{-1} K^{-1}, respectively. The positive value of ΔH° indicates that the adsorption process is endothermic and temperature dependant. The values of ΔG° were found to be −2.70, −3.55, −4.67 and −5.27 kJ mol^{-1} for the adsorption of Co(II) from aqueous solution at 30, 40, 50 and 60 °C, respectively. The negative values of ΔG° show the spontaneous adsorption of metal ions on the adsorbent. The value of ΔG° decreases with increasing temperature, demonstrating an increase in the feasibility of adsorption at higher temperatures. The positive value of ΔS° suggested some structural changes in adsorbent and adsorbate and also reflects the affinity of the adsorbent material under consideration towards Co(II) ions.

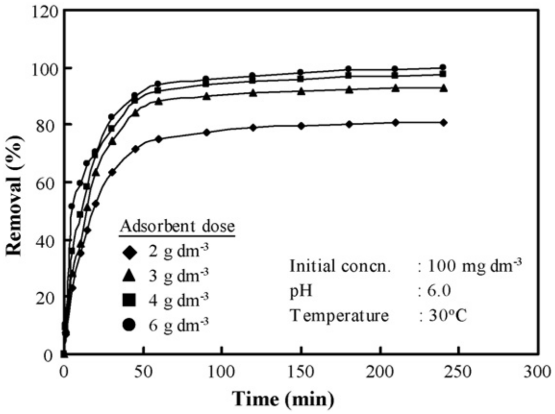

Fig. 4. Variation of Co(II) removal vs. time at various SAC doses.

3.4. Influence of initial concentration and adsorbent dose

Series of experiments were conducted in order to normalize the procedure for the determination of the adsorption isotherm and to study the kinetic behaviour. The kinetic data for the removal of Co(II) by adsorption versus contact time for a fixed initial concentration of 100 mg dm^{-3} (C_o) with four different doses (W_s) of SAC varying between 2 g dm^{-3} and 6 g dm^{-3} is presented in Fig. 4. The rate of Co(II) sorption was initially very rapid and decreased markedly after 1 h. A quasi-stationary was obtained within 4 h of shaking and was independent of adsorbent dose. Based on the experimental results an equilibrium contact time of 4 h was selected for all further experiments. The Co(II) removal from its solution is influenced by W_s. It was noted that at any time for a given C_o value, the Co(II) removal increased with increase in W_s values. This is because at higher dose of the adsorbent, due to increased surface area, more adsorption sites are available causing higher removal of Co(II).

Removal of Co(II) on SAC as a function of time at different initial concentrations and adsorbent doses was also studied and in all cases the shape of the percentage removal versus time curves were similar to that observed in Fig. 4. Based on the studies conducted on the effect of contact time for the removal Co(II) with different initial concentrations and adsorbent doses, it was concluded that a contact time of 4 h was sufficient to reach equilibrium. The saturation period of the adsorption is entirely independent of the initial concentration. The effect of variation in these parameters on Co(II) removal was quantified in terms of their plateau (4 h) values. The dependence of the process of Co(II) removal from different initial concentrations (50–250 mg dm^{-3}) with different adsorbent doses is illustrated in Fig. 5. The percentage removal of Co(II) decreased with an increase in initial Co(II) concentration where as the amount of Co(II) uptake per unit weight of the adsorbent (mg g^{-1}) was found to increase. For example, the percentage removal of Co(II) ions decreased from 90.3% (22.57 mg g^{-1}) to 71.8% (89.75 mg g^{-1}) by increasing the concentrations from 50 to 250 mg dm^{-3} at an adsorbent dose of 2 g dm^{-3}. This is because at higher initial concentrations the ratio of initial number of moles of Co(II) to the available surface area is high, hence fractional adsorption becomes dependent on initial concentration.

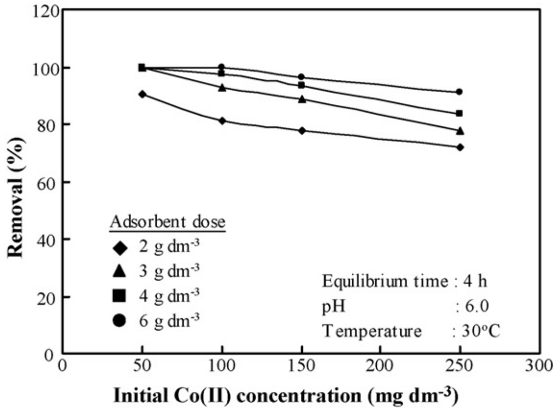

Fig. 5. Variation of Co(II) removal vs. initial concentration at various SAC doses.

For a fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of adsorbate. This will intern result in a decrease in the percentage removal of the adsorbate corresponding to an increase initial adsorbate concentration.

The experimental kinetic data can very well be represented by the following expression

$$\frac{t}{R} = a + bt \tag{8}$$

where R is the percentage removal, t the contact time and 'a' and 'b' are empirical constants. The constants 'a' and 'b' were calculated for each C_o and W_s by fitting Eq. (8) to the experimental data using regressional analysis (Table 3). The values of 'a' at varying amounts of W_s clearly show a decreasing trend in 'a' values with increasing W_s for all values of C_o. The average values of 'a' and W_s can be related by

$$a = \frac{1}{c + dW_s} \tag{9}$$

where 'c' and 'd' are constants. The validity of fitting the data to the above equation was tested by estimating standard error of regression line and the figure is presented in supplementary material. The values of 'c' and 'd' were found to be 3.942 and 1.427, respectively. From Table 3, it can be noted that values of 'b' are increasing with C_o values for all values of W_s. The linearalised form of the data (b versus C_o) showed a fairly high correlation coefficient exhibiting a relationship of the type

Table 4
Values of coefficients of e and f with respect to correlation coefficients (r) for different values of W_s

Adsorbent dose, W_s (g dm^{-3})	e	f	r
2	1262.4	72.41	0.9988
3	1932.5	76.14	0.9967
4	1611.0	82.55	0.9991
6	885.8	92.27	0.9983

$$b = \frac{C_o}{e + fC_o} \tag{10}$$

where 'e' and 'f', are respectively the intercepts and gradients of the regression lines. Table 4 shows the calculated values of 'e' and 'f' along with correlation coefficients. From Table 4 it can be observed that 'e' showed a decreasing trend with the increasing W_s values, whereas 'f' showed an increasing trend.

The values of e and f correlate well with W_s through the relationship

$$e = \frac{W_s}{g + hW_s} \tag{11}$$

$$f = \frac{W_s}{i + jW_s} \tag{12}$$

The constants g, h, i and j were calculated through the regressional analysis and found to be -2.01×10^{-3}, 1.36×10^{-3}, 1.06×10^{-2} and 9.21×10^{-3}, respectively. Substitution of Eqs. (9)–(12) in Eq. (8) yield a relationship of the type

$$\frac{t}{R} = \frac{1}{3.942 + 1.427W_s} + \frac{C_o}{[(W_s/(-2.01 \times 10^{-3} + 1.36 \times 10^{-3}W_s)) + (W_s/(1.06 \times 10^{-2} + 9.21 \times 10^{-3}W_s))C_o]}t \tag{13}$$

with the above equation it is possible to determine the percentage Co(II) removal at any time t as a function of C_o and W_s.

3.5. Testing of the model

In order to confirm the goodness of fit of the model, the values of R (percentage Co(II) removal) under various opera-

Table 3
Values of coefficients of a and b with respect to coefficients of correlation (r) for different values of W_s and C_o

Initial concn. (mg dm^{-3})	Adsorbent dose, W_s (g dm^{-3})			
	2	3	4	6
50	$a = 0.1264$; $b = 0.0105$; $r = 0.9993$	$a = 0.0997$; $b = 0.0096$; $r = 0.9994$	$a = 0.0821$; $b = 0.0096$; $r = 0.9981$	$a = 0.0740$; $b = 0.0095$; $r = 0.9997$
100	$a = 0.1356$; $b = 0.0117$; $r = 0.9983$	$a = 0.1081$; $b = 0.0102$; $r = 0.9997$	$a = 0.0880$; $b = 0.0990$; $r = 0.9964$	$a = 0.0721$; $b = 0.0097$; $r = 0.9984$
150	$a = 0.1604$; $b = 0.0122$; $r = 0.9988$	$a = 0.1259$; $b = 0.0107$; $r = 0.9975$	$a = 0.1019$; $b = 0.0102$; $r = 0.9993$	$a = 0.0846$; $b = 0.0100$; $r = 0.9992$
250	$a = 0.1952$; $b = 0.0130$; $r = 0.9996$	$a = 0.1524$; $b = 0.0121$; $r = 0.9983$	$a = 0.1172$; $b = 0.0114$; $r = 0.9994$	$a = 0.0955$; $b = 0.0105$; $r = 0.9974$

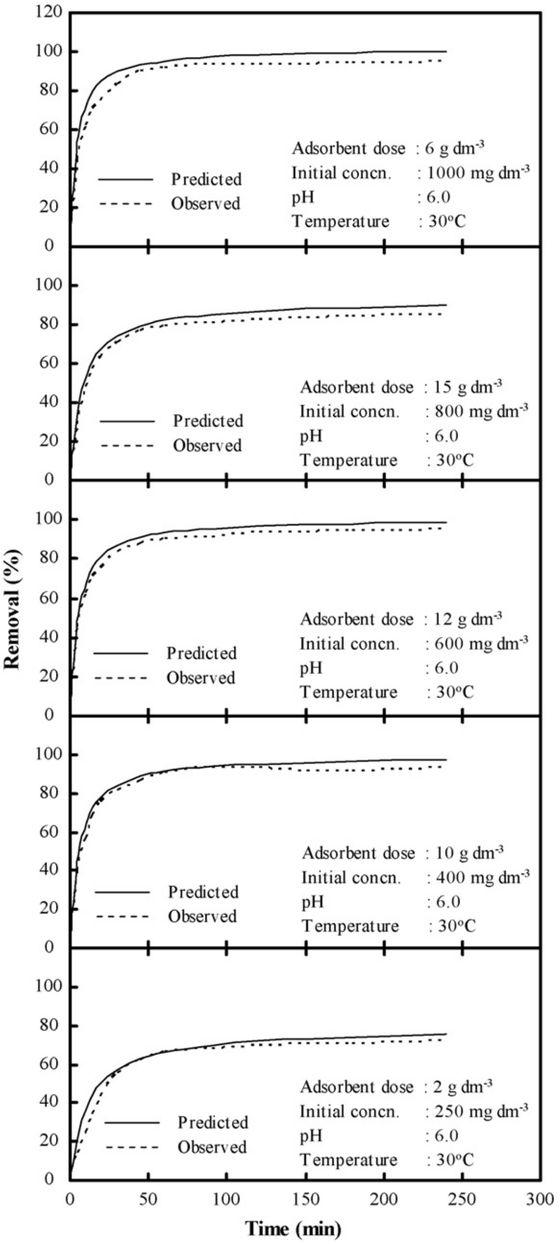

Fig. 6. Comparison of predicted and observed values of Co(II) removal by SAC at different operational conditions.

tional conditions were calculated using Eq. (13). Theoretical plots of Eq. (13) along with the observed data points for different values of C_0 and W_s are shown in Fig. 6. The Fig. 6 clearly shows that the agreement, in general, is good, the difference between experimental and calculated data being insignificant. The relationship given in Eq. (13) can be used to calculate the dose of adsorbent required to get the required Co(II) removal at any given time and initial solute concentration. The required removal efficiency can be obtained by controlling variables such as contact time and dose of the adsorbent in batch reactors. Additional research is warranted to test the practical applicability of the model with respect to real industrial wastewaters and other varying experimental conditions.

3.6. Cost estimation

The economic viability of the adsorption process for the removal of Co(II) from water and wastewater depends on the cost effectiveness as well as the availability of adsorbents. The precursor used in the present study, bagasse pith, was collected free of cost from the sugar cane industry. After considering the expenses for transport, chemicals, electrical energy and man power, the final developed carbon would cost approximately $70/tonne. The cheapest variety of laboratory and commercial grade activated carbons available in India cost approximately $1100/tonne and $750/tonne, respectively. The adsorption capacity of SAC, laboratory grade carbon and commercial grade carbon in the removal of Co(II) from aqueous solution were 153.85, 117.14 and 102.32 mg g^{-1}, respectively. This confirms the viable application of SAC as a low cost adsorbent.

4. Conclusion

It has been indicated that sulphurised activated carbon developed from bagasse pith can be effectively used for the removal of Co(II) from aqueous solutions. The investigated adsorbent was cost effective as well as eco-friendly. The adsorption process was highly pH dependent and was more effective with in the pH range of 4.5–8.5. Equilibrium studies were conducted to evaluate the adsorption parameters. The increase in percentage adsorption with increase in temperature demonstrated the endothermic nature of adsorption. The isotherm data was fitted for Langmuir model. The adsorption capacity and energy of adsorption were found to be very high for SAC. An empirical relationship has been developed to predict the percentage removal of Co(II) at any time for a given adsorbent dose and given initial concentration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2007.04.029.

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