

Removal of cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies

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Abstract

Removal of cadmium(II) from aqueous solutions was studied using steam activated sulphurised carbon (SA-S-C) prepared from bagasse pith (a sugar-cane industry waste). Batch adsorption experiments were performed as a function of solute concentration, contact time, adsorbent dose, pH, temperature and ionic strength. The maximum removal took place in the pH range of 5.0 to 9.0. The maximum adsorption of 98.8 % (24.70 mg/g) took place by SA-S-C with 8.9 % sulphur content at pH 6.0 from an initial Cd(II) concentration of 50 mg/dm³. The sorption process follows pseudo-second-order kinetics. Kinetic parameters as a function of initial concentration and temperature were determined to predict the adsorption behaviour of Cd(II) onto SA-S-C. Decrease in ionic strength of the solution was found to improve the adsorption capacity of the adsorbent. The equilibrium data could be best fitted by the Langmuir adsorption isotherm equation over the entire concentration range (50 to 1 000 mg/dm³). The effectiveness of the SA-S-C for Cd(II) removal was examined and compared with other adsorbents reported in the literature. At solution pH of 6.0, the maximum adsorption capacity of SA-S-C calculated by the Langmuir isotherm is 149.93 mg/g at 30°C. Acid regeneration was tried for several cycles with a view to recover the sorbed metal ions and also to restore the sorbent to its original state.

Keywords: Adsorption dynamics, Langmuir equation, Cd(II) removal, Sulphurised carbon, Desorption

Introduction

Cadmium (Cd), which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells (Drash, 1993). Because of the toxicity and bioaccumulation, Cd(II) is considered as a priority pollutant by the U S Environmental Protection Agency. The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm³. The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries (Cheremisinoff, 1995). Adsorption of heavy metal ions onto activated carbon has been applied widely as a unit operation in the treatment of industrial wastewater. The use of commercial activated carbon is not suitable for developing countries because of its high cost. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Activated carbons prepared from rice husk, groundnut husk, fertiliser waste slurry, peanut hull, jute stick, *Moringa oleifera* seed husk, coconut husk and sawdust (Manju and Anirudhan, 1997; Raji et al., 1997; Warhurst et al., 1997) have been used for wastewater treatment and the potential of their ultimate usage may be determined by their adsorption capacity, regeneration characteristics and physical properties of the subsequent product.

In recent years considerable attention has been devoted to develop surface modified carbons from locally available materials for the treatment of heavy metal-bearing wastes. Removal of heavy metals from wastewater by adsorption on copper and lanthanum impregnated activated carbons from sawdust and coconut husk has been reported (Manju et al., 1998; Raji and Anirudhan, 1999). Recent studies speculated that the reaction between heavy metal ions and sulphur groups present in the adsorbent materials accounted for high adsorption efficiency. In this direction, Gomez-Serrano et al. (1998) reported the ability of commercial activated carbon loaded with sulphur groups for the removal of Hg(II), Pb(II) and Cd(II). Sreedhar et al. (1999) studied the sorption of Hg(II) by polysulphide-treated coconut husk. Bagasse pith is a sugar industry waste by-product, which is available in large quantities at no cost and can form a good basis for the development of adsorbent materials. Only a limited number of studies, however, have so far been focused on the use of bagasse pith for the removal of heavy metal ions from wastewater (Gupta et al., 1998; Peternele et al., 1999). Earlier workers have successfully used a single-step steam pyrolysis activation to make high-quality carbon from a variety of materials (Warhurst et al., 1997). The purpose of this work is to study the possibility of the utilisation of single-step steam pyrolysis in the presence of H₂S and SO₂ for the production of sulphurised carbon for the reduction of cadmium concentration in the solution, since this material has not been considered previously for this purpose. This study examines the effects of the initial concentration of Cd(II), adsorbent dose, initial pH, contact time, temperature, etc. in metal adsorption with bagasse pith-based sulphurised activated carbon prepared by single-step steam pyrolysis in the presence of H₂S and SO₂ and the results are presented in this paper. Desorption and regeneration studies have also been carried out.

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TABLE 1
Surface and physical properties of the investigated activated carbons

No.	Parameters	Value			
		SA-C	SA-S(2.3)-C	SA-S(6.8)-C	SA-S(8.9)-C
1	Surface area (m ² /g)	536.5	523.6	509.5	500.5
2	Cation exchange capacity (meq/g)	3.96	4.12	4.63	5.02
3	$\rho_{\text{nitrobenzene}}$ (g/cm ³)	0.87	0.80	0.91	1.22
4	pH _{zpc}	5.8	5.5	4.7	4.3
5	V ₁ (cm ³ /g)	0.13	0.10	0.06	–
6	V ₂ (cm ³ /g)	0.20	0.23	0.28	0.33
7	V ₃ (cm ³ /g)	0.19	0.17	0.14	0.10
8	V _T (cm ³ /g)	0.52	0.50	0.48	0.43
9	Sulphur content (%)	–	2.3	6.8	8.9
10	Total acidic groups (meq/g)	2.0	2.6	2.8	2.9
11	Carboxyl groups	0.61	0.67	0.70	0.77
12	Phenolic acidic groups	0.42	0.35	0.33	0.30
13	Particle size (mesh size)	-80+230	-80+230	-80+230	-80+230

Materials and methods

Adsorbent preparation

The bagasse pith collected from a sugar industry, the Co-operative Sugars Ltd., Palakkad, Kerala, India was washed several times with distilled water and left to dry. The carbonisation of the bagasse pith was performed in a Matri-made muffle furnace (India) at 200°C for 2 h (C-200). Steam activation (SA) of the carbon (C-200) was carried out using the method described by the earlier workers (Warhurst et al., 1997). About 50 g of the carbon was placed in a purpose-made graphite tube and positioned at the centre of the furnace. Steam produced by a steam generator, entered the graphite tube at a rate of approximately 5 cm³/min. The sample was heated at a rate of 10°C/min to 400°C and held at this temperature for 1 h. After allowing the furnace to cool to room temperature, the product steam-activated carbon (SA-C) was removed and washed with 1 M HCl and distilled water. The material was dried at 100°C and sieved to -80+230 mesh size.

Steam-activated sulphurised carbon (SA-S-C) was prepared by steam activation of C-200 at 400°C in the presence of H₂S and SO₂ for 2 h. About 50 g of C-200 was placed in a graphite tube and flushed with a flow of steam (5 cm³/min) in the presence first of a stream of SO₂ (10 cm³/min) for 90 min and then of H₂S (15 cm³/min) for 30 min from a gas generator at a heating rate of 10°C/min from 30 to 400°C. Yield of the finished product was 43.0 % of the original material. The product was washed with distilled water and dried at 100°C. The dried material was then ground and sieved to separate particles of -80+230 mesh size.

Adsorbent characterisation

The amount of sulphur attached to the carbon sample was determined by using the Eschka method (Rump and Krist, 1992). The method deals with the transformation into BaSO₄ of the sulphur present in adsorbents by treatment with the Eschka mixture (Na₂CO₃ and MgO) at 800°C and then successively with Br₂ and BaCl₂ solutions. The infrared spectra of the activated carbons were recorded on a Perkin-Elmer FTIR spectrophotometer (Model IR-180) through a wavelength range of 400 to 4 000 cm⁻¹. The surface

area of the adsorbents was determined using the N₂ gas adsorption method with a Quantasorb Surface Area Analyser, USA (Model Q S-7). The porosity and density ($\rho_{\text{nitrobenzene}}$) of the adsorbent were determined by using the Micrometrics Mercury Porosimeter (Model 9310) and pycnometric methods respectively. The pore volumes V₃ (pore volume greater than 50 nm in diameter, macropores), V₂ (pore volume greater than 7.5 nm and less than 50 nm in diameter, mesopores) and V₁, pores smaller than 7.5 nm [as estimated from V₁=V_T-(V₂+V₃)] as estimated from mercury porosimetry are also listed in Table 1. The zero point charge (pH_{zpc}) is defined as the pH of the suspension at which the surface charge density $\sigma_0 = 0$. The σ_0 as a function of pH on activated carbons was determined using the procedure described by Schawrz et al. (1984). A conductometric method developed by James and Parks (1982) was used to determine the total number of acidic groups (including carboxyl, lactonic, sulphonic and phenolic groups) on the adsorbent surface. The carboxyl and phenolic acid groups were estimated using the methods proposed by Boehm and Voll (1970). The surface and physical properties of the SA-C and SA-S-C are given in Table 1.

Preliminary studies showed that the required sulphur concentration on the carbon surface could be consistently obtained under the following conditions:

- 2.3 % sulphur content in SA-S-C [SA-S(2.3)-C]: flow time, 30 min for SO₂ and 90 min for H₂S; heating rate, 10°C/min from 30 to 400°C.
- 6.8 % sulphur in SA-S-C [SA-S(6.8)-C]: flow time, 60 min for SO₂ and 60 min for H₂S; heating rate, 10°C/min from 30 to 400°C.
- 8.9 % sulphur in SA-S-C [SA-S(8.9)-C]: flow time, 90 min for SO₂ and 30 min for H₂S; heating rate, 10°C/min from 30 to 400°C.

Adsorption studies

Batch adsorption experiments were carried out by shaking 0.1 g of carbon with 50 cm³ aqueous solution of Cd(II) of the desired concentration at various retention times in a temperature-controlled water-bath shaker (Remi, India make). The pH and ionic strength (0.01 M) of the solutions were adjusted to constant values.

Continuous mixing was provided during the experiments with a constant agitation speed of 200 r/min. Kinetic studies were carried out at constant pH with an initial concentration range from 50 to 400 mg/dm³ and adsorbent dose from 2 to 10 g/dm³. After shaking, the samples were withdrawn at suitable time intervals, filtered through a 0.45 µm microporous membrane filter and then analysed for Cd(II) concentration with an atomic absorption spectrophotometer (Perkin Elmer 2380). For the isotherm studies, 0.1 g of activated carbon was put into 50 cm³ solutions of various concentrations of Cd(II) (50 to 1 000 mg/dm³). The flasks were shaken for 5 h to attain equilibrium. A known volume of the solution was removed and filtered for Cd(II) analysis. The amount of Cd(II) adsorbed was determined by the difference between the initial and the equilibrium concentrations. Effect of pH on the adsorption of Cd(II) was studied by varying the pH from 2.0 to 10.0. The effect of temperature on kinetics and adsorption equilibria was studied by varying temperature from 30 to 60°C. All experiments were duplicated and showed differences of less than 5.0%.

Similar batch experiments were carried out using commercial activated carbon (CAC) for comparison, obtained from E.Merck India Ltd. No pretreatment was given to the CAC and it was used as received in the experiments. The surface and physical properties of the CAC were also determined: surface area, 284.0 m²/g; porosity, 0.43 cm³/g; density, 0.92 g/cm³; total acidic groups, 2.3 meq/g; carboxyl groups, 0.57 meq/g; phenolic acidic groups, 0.28 meq/g; cation exchange capacity, 4.02 meq/g and pH_{zpc}, 5.8.

Desorption and regeneration studies

Regeneration of the activated carbon and recovery of the adsorbed Cd(II) were carried out by shaking the spent adsorbent material in 0.2 M HCl for a period of 5 h. After attaining equilibrium, the sorbent was filtered and washed with distilled water. It was further dried at 80°C for 2 h. The sorbent sample thus regenerated was reused for adsorption purposes. The loading and regeneration cycles were repeated three times. After each cycle the sorbent was washed with distilled water and dried.

Results and discussion

Adsorbent characterisation

The possible assignments of the observed peaks in the FTIR spectra of SA-C and SA-S(8.9)-C samples are furnished in Table 2. The asymmetric absorption bands observed at 3 764 cm⁻¹ for SA-C and at 3 762 cm⁻¹ for SA-S(8.9)-C indicate the presence of exchangeable OH⁻ groups on both carbons. The IR spectra show bands at 1 600 and 1 608 cm⁻¹ for SA-C and SA-S(8.9)-C, respectively, indicating the presence of conjugated hydrogen bonded carbonyl groups as suggested by Hallum and Drushell (1958). The carbons also contain carboxyl [bands at 1 724 cm⁻¹ for SA-C and 1 730 cm⁻¹ for SA-S(8.9)-C] functional groups. Additional peaks at 1 167, 1 111 and 460 cm⁻¹ in the spectrum of SA-S(8.9)-C represent the C=S, S=O and S-S stretching vibrations due to the sulphur groups bonded to activated carbon (Nakanishi and Solamon, 1977).

The experimental results of surface titrations in 0.01 M NaCl on steam-activated and steam-activated sulphurised carbons with 2.3, 6.8 and 8.9 % sulphur content are compared in Fig.1. The SA-C displays a zero point charge at pH_{zpc} = 5.8; at pH above that value the surface of the carbon has a negative charge, below that pH the carbon has a positive charge. The pH_{zpc} of SA-C (5.8) was decreased to 5.5, 4.7 and 4.3 respectively by the loading of 2.3, 6.8 and 8.9 % of sulphur content, which indicates that the surface of

TABLE 2
Some fundamental IR absorption frequencies of sulphurised [SA-S(8.9)-C] and sulphur-free activated carbons

Band position (cm ⁻¹)		Possible assignments
SA-C	SA-S(8.9)-C	
3764	3762	O-H stretching of hydroxyl group
2925	2925	C=C-H stretching
2854	2854	C=C-H stretching
1724	1730	C=O stretching of -COOH group
1600	1608	C=O stretching of carbonyl group
1357	1360	C-H deforming
-	1167	C=S stretching
-	1111	S=O stretching
-	460	S-S stretching

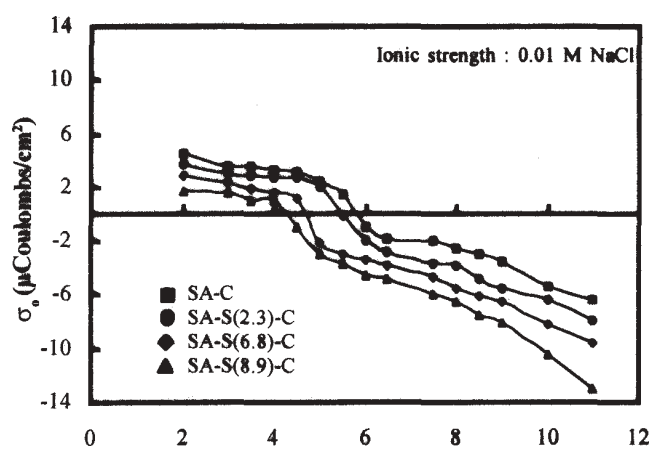


Figure 1
Effect of pH on the surface charge density of different activated carbons

SA-C has been modified after steam activation in the presence of SO₂ and H₂S. At any pH higher than the pH_{zpc} the charge on the sulphurised carbons is lower than on the sulphur-free carbons. Increasing sulphur content resulted in an increase of sulphonic acid groups (-SO₃H) on the activated carbons. The sulphonic acid groups have a lower pK_a than normal carboxylic acids and hence the pH_{zpc} decreases in the same way as samples with higher sulphur content. As shown in the figure, the increased negative charge caused by sulphur enrichment is significant and would be expected to alter the adsorption properties of the carbons due to electrostatic effects. Although sulphurised carbons contain sulphur groups or linkages only, the surface area and porosity values remain considerably higher with respect to SA-C. This suggests that most of the functional groups or pores are not reacted or clogged with sulphur atoms.

Effect of pH on Cd(II) adsorption

Figure 2 shows the percentage of adsorbed Cd(II) vs. pH over the range of 2.0 to 10.0 for SA-S-C, SA-C and CAC. The percentage adsorption of metal ions increased with an increase in pH up to a certain value and then decreased with further increase of pH. It is

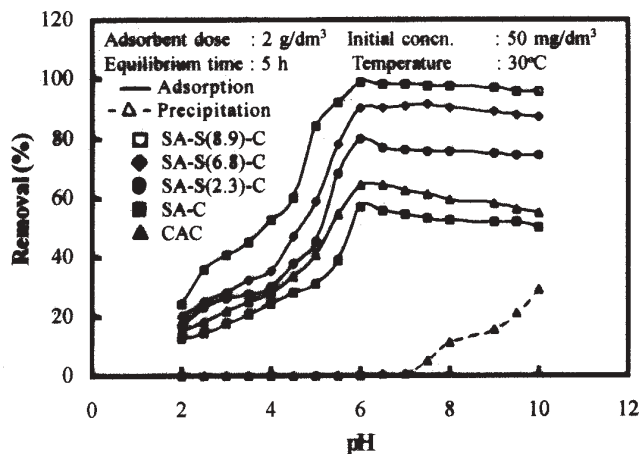


Figure 2

Effect of pH on the removal of Cd(II) by activated carbons

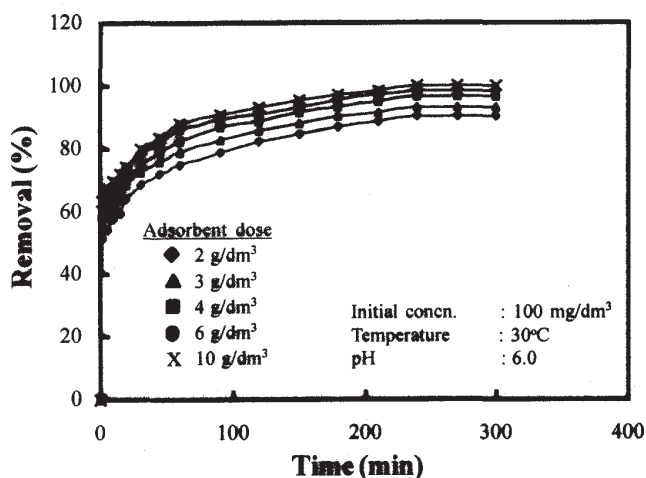


Figure 3

Variation of Cd(II) removal versus time at different SA-S(8.9)-C doses

clear that sulphurised activated carbons are effective for the quantitative removal of Cd(II) over the pH range 5.0 to 9.0. Sulphur-free carbon, however, is effective within a narrow range of 6.0 to 8.0. The maximum adsorption of 98.8 % (24.70 mg/g), 90.6 % (22.65 mg/g), 79.6 % (19.90 mg/g), 64.2 % (16.05 mg/g) and 56.8 % (14.20 mg/g) took place by SA-S(8.9)-C, SA-S(6.8)-C, SA-S(2.3)-C, CAC and SA-C, respectively at pH 6.0 from an initial concentration of 50 mg/dm³. The data clearly show that sulphurised carbons are 1.4 to 1.7 times more effective than sulphur-free carbon for the removal of Cd(II). For comparison, Cd(II) removal by hydroxide precipitation as a function of pH with no adsorbent is also given. The experimental precipitation curves which show a sharp decrease in concentration of Cd(II) ions in solution, suggest that Cd(II) is precipitating from the solution at this concentration, well before adsorption is complete. However, at any pH metal removal by adsorption is very much greater than hydroxide precipitation.

The effect of pH can be explained in terms of pH_{zpc} of the adsorbent and species of Cd(II) formed in the solution. The surface charge is a function of pH. The pH with which the charge of the solid surface is zero is referred to as the zero point of charge (pH_{zpc}). Above pH_{zpc} the surface charge of the adsorbent is negative. Perusal

of the literature on Cd(II) speciation diagram (Ramos et al., 1997) shows that the dominant Cd(II) species at $pH > 8.0$ is $Cd(OH)_2$ and at $pH < 8.0$ is Cd^{2+} and $Cd(OH)^+$. The maximum sorption efficiency in the pH range of 5.0 to 8.0 may be due to the interaction of Cd^{2+} and $Cd(OH)^+$ with surface sulphur groups present in sulphurised carbon. According to the Pearson theory (Pearson, 1988) during acid base reaction, hard acids prefer to interact with hard bases and soft acids with soft bases. Positively charged Cd(II) species are soft acids and as a rule the interaction of Cd^{2+} and $Cd(OH)^+$ with surface sulphur groups (soft bases) is likely favoured at the pH range of 5.0-8.0. In addition to sulphur groups, the carbon containing carboxyl and hydroxyl groups are also responsible for the sorption of Cd(II) ions. At low pH particularly below pH_{zpc} the positively charged Cd^{2+} and $Cd(OH)^+$ species present in the solution may exchange with H^+ from peripheral $-COOH$ or hydroxyl groups of carbon. It was shown that final pH of the solution is always less than the initial pH at pH range between 2.0 and pH of zero point charge.

Decrease in removal of Cd(II) ions at very low pH is apparently due to the higher concentrations of H^+ ions present in the mixture which compete with the Cd^{2+} for the adsorption sites of carbon. A decreasing trend in adsorption was also observed at very high pH and this may be due to the formation of soluble hydroxy complexes (Raji et al., 1997).

The lowest pH_{zpc} shown by SA-S(8.9)-C, indicates that it has more acidic functional groups (Table 1) than the rest of carbons, or in other words, it is less basic, which is advantageous for the removal of metal cations. Even though sulphurised activated carbons of various sulphur content were effective for the removal of Cd(II), SA-S(8.9)-C appeared to be more efficient. As such subsequent experiments were carried out using sulphurised carbon having 8.9 % of sulphur content.

The extent of Cd(II) adsorption onto CAC as a function of pH for an initial concentration of 50 mg/dm³ is also shown in Fig. 2. The percentage adsorption increased with increasing pH up to a certain value and then decreased with further increasing pH. The maximum adsorption of 64.2 % was observed at pH 6.0. Above and below this pH the adsorption was found to be considerably lower.

Effect of initial concentration and adsorbent dose

Several experiments were conducted in order to normalise the procedure for the determination of the adsorption isotherm and to study the kinetic behaviour. The kinetic data for the removal of Cd(II) by adsorption vs. contact time for a fixed initial concentration of 100 mg/dm³ (C_0) with five different doses (W_s) of SA-S-C varying between 2 g/dm³ and 10 g/dm³ are presented in Fig. 3. The rate of Cd(II) sorption was very high initially and decreased markedly after 1 h. A quasi-stationary state was obtained within 5 h of shaking and is independent of adsorbent dose. Based on the experimental results an equilibrium contact time of 5 h was used in all further experiments. The Cd(II) removal from its solution is influenced by W_s . It was noted that at any time for a given C_0 value the Cd(II) removal increased with increase in W_s values. This is because at higher dose of adsorbent due to increased surface area, more adsorption sites are available causing higher removal of Cd(II). Removal of Cd(II) on SA-S(8.9)-C as a function of time at different initial concentrations and adsorbent doses was also studied and in all cases the shape of the removal vs. time curves was similar to that observed in Fig. 3. Based on studies conducted on the effect of contact time for the removal Cd(II) with different initial concentrations and adsorbent doses showed that an equilibrium time of 5 h is sufficient to reach equilibrium. The saturation period of the adsorption is entirely independent of the initial concentra-

tion. The effect of variation in these parameters on Cd(II) removal was quantified in terms of their plateau (5 h) values. The dependence of the process of Cd(II) removal from different initial concentrations (50 to 400 mg/dm³) with different adsorbent doses is illustrated in Fig. 4. The increase in initial Cd(II) concentration decreased the percentage removal and increased the amount of Cd(II) uptake per unit mass of the adsorbent (mg/g). The removal of Cd(II) ions decreased from 98.8% (24.70 mg/g) to 48.2% (96.38 mg/g) by increasing the concentrations from 50 to 400 mg/dm³ at an adsorbent dose of 2 g/dm³. This is because at higher initial concentrations the ratio of initial number of moles of Cd(II) to the available surface area is high, hence fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase in initial sorbate concentration.

Adsorption dynamics

Kinetics of adsorption, in terms of solute uptake rate, which governs the residence time, is one of the important characteristics defining the efficiency of adsorption. Earlier workers proposed a surface complexation mechanism for heavy metal adsorption onto activated carbon. By virtue of its surface composition, sulphurised activated carbon is assumed to have C=S, S=O, S-S, C=O, C-OH and C-O⁻ groups. The kinetic model that was used in the present study to describe the reaction rate was based on the assumption that the adsorption of Cd(II) onto carbon is a surface complexation reaction and can be represented as:



where:

P is the active site occupied on the adsorbent,
M is the concentration of free metal in solution,
PM is the concentration of metal bound to adsorbent
k and k' are the adsorption rate and desorption rate constants, respectively.

The rate equation for the reaction can be written as:

$$\frac{d(P)_t}{dt} = k[(P)_o - (P)_t]^2 \quad (2)$$

where:

(P)_t and (P)_o are the number of active sites occupied on the sorbent at any time t and the number of equilibrium sites available on the adsorbent.

The rate constant k of the adsorption of Cd(II) on activated carbon was determined using the following equation developed by Ho and McKay (2000).

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

where:

q_e is the amount adsorbed at equilibrium (mg/g) and
q_t is the amount adsorbed at time t (mg/g).

The kinetic plots of t/q_t vs. t for Cd(II) removal at different concentrations and temperatures are presented in Fig. 5. The relationship is linear, and the correlation coefficient (Table 3), suggests a strong relationship between the parameters and also

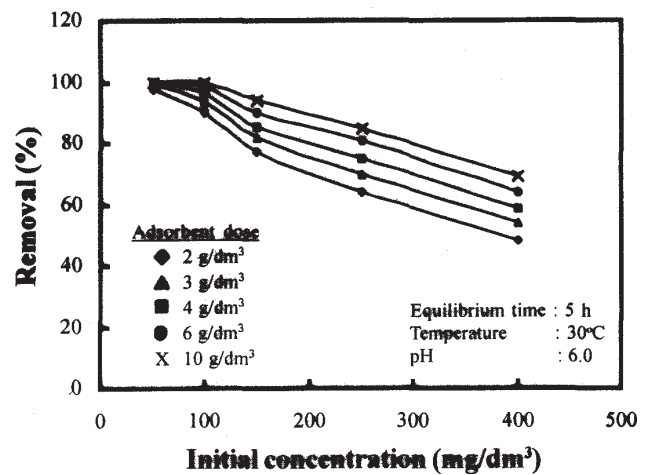


Figure 4
Variation of Cd(II) removal vs. initial concentration at different SA-S(8.9)-C doses

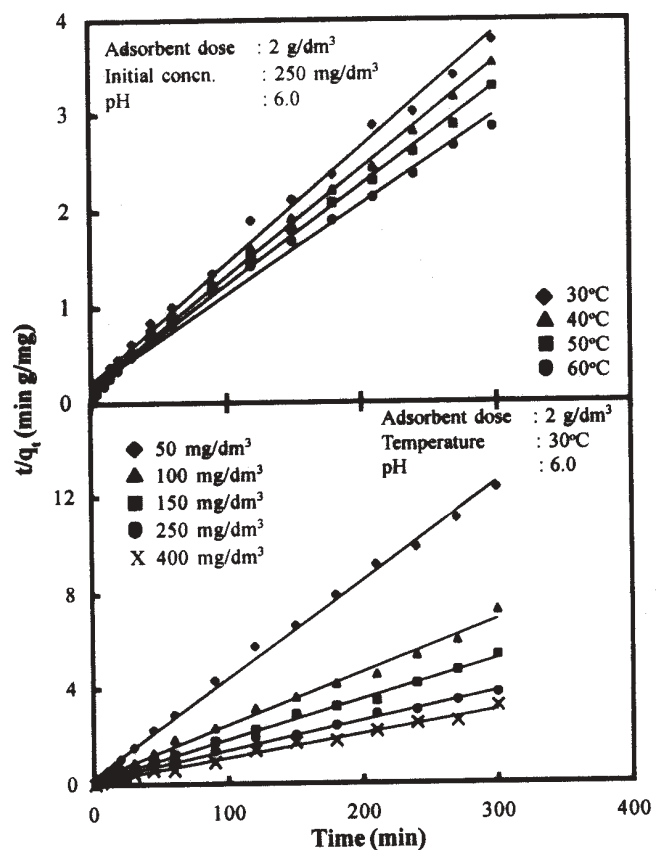


Figure 5
Pseudo-second-order kinetic plots for the adsorption of Cd(II) on SA-S(8.9)-C at different initial concentrations and temperatures

explains that the process of adsorption follows pseudo-second-order kinetics. The product kq_e² is the initial sorption rate represented as h = kq_e². From Table 3, it can be shown that the initial adsorption rate 'h' is increased with increase in metal concentration. Table 3 shows that the equilibrium sorption capacity, q_e, increased from 24.39 to 96.15 mg/g as the initial concentration varied from 50 to 400 mg/dm³. The values of k, however, were

Variable	k (g/mg·min)	q _e (mg/g)	h (mg/g·min)	R ²
Concentration (mg/dm ³)				
50	7.88x10 ⁻³	24.39	4.69	0.998
100	4.74x10 ⁻³	45.25	9.71	0.998
150	3.40x10 ⁻³	57.47	11.24	0.999
250	2.33x10 ⁻³	79.37	14.71	0.997
400	1.64x10 ⁻³	96.15	15.15	0.999
Temperature (°C)				
30	2.33x10 ⁻³	79.37	14.71	0.997
40	2.80x10 ⁻³	86.21	20.83	0.997
50	3.58x10 ⁻³	93.46	31.25	0.995
60	4.46x10 ⁻³	101.01	45.45	0.991

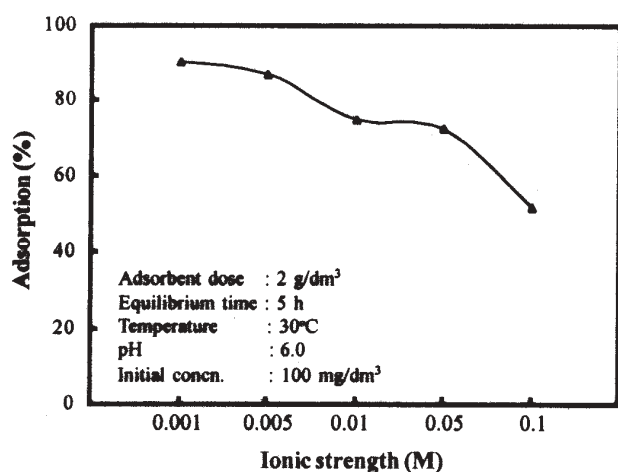


Figure 6
Effect of ionic strength on the adsorption of Cd(II) on SA-S(8.9)-C

found to decrease with increase of initial concentration. Earlier workers also presented similar results for the adsorption of Hg(II), Ni(II) and Cr(VI) onto chitosan (McKay et al., 1986) moss peat (Ho et al., 1995) and activated carbon (Raji and Anirudhan, 1997) respectively. Increasing the metal concentration in solution seems to reduce the diffusion of metal ions in the boundary layer and to enhance the diffusion in the solid. Another cause could be due to the progressive decrease in covalent interactions, relative to electrostatic interactions of the sites with lower affinity for Cd²⁺ with an increase in initial Cd(II) concentration. The linearised k and C_o values as a double logarithmic plot showed a correlation coefficient of 0.98, the relationship between k and C_o being of the type:

(4)

This equation can be used to predict the k values for any concentration within the test limits.

The perusal of data on Table 3 reveals that for the equilibrium time, the metal ion adsorbed q_e is higher for higher temperature and greater values of initial metal ion concentration. The values of h and k increase with increase in temperature. The increase in rate of

adsorption with increasing temperature is described by the Arrhenius equation:

$$\ln k = \ln A_0 - \frac{E_a}{RT} \quad (5)$$

where:

A₀ is the temperature independent factor called "frequency factor",

k is the rate constant and

E_a is the activation energy.

A linear relationship was obtained between ln k and 1/T. The values of A₀ and E_a were calculated from the intercept and slope of the ln k versus 1/T plot (Figure not shown) and were found to be 3.24 g/mg min and 18.28 kJ/mol respectively. The value 18.28 kJ/mol in the present study indicates a chemical sorption process involving weak interactions between sorbent and sorbate (Ho et al., 2001). The relatively low E_a value suggests that the adsorption has a low potential energy barrier.

Effect of ionic strength

Figure 6 shows the influence of ionic strength on the adsorption of Cd by sulphurised activated carbon. It is evident that the adsorption of Cd(II) decreased in the presence of NaCl. The percentage of adsorption decreased from 90.1 to 51.8 % with an increase in ionic strength from 0.001 to 0.1 M NaCl. Adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism. Thus the results indicate that electrostatic attraction plays an important role in the adsorption of Cd(II) onto activated carbon (Das and Bandyopadhyay, 1991). At high ionic strength, the increased amount of NaCl can help to swamp the surface of the carbon, which decreases Cd(II) ion's access to the carbon surface for adsorption. According to the Surface Chemistry Theory developed by Guoy and Chapman (Osipow, 1972), when solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and Cd(II) species from approaching each other more closely and, through the decreased electrostatic attraction, leads to the decreased uptake of Cd(II) ions.

The modification of the Cd(II) species is another important factor leading to a decrease in adsorption with increase in ionic strength. It has been reported by earlier workers (Benjamin and Leckie, 1982) that an increase in chloride concentration reduced the Cd²⁺ and Cd(OH)⁺ species due to the formation of chloro-complexes. Cadmium forms some stable chloro-complexes, namely CdCl⁺, CdCl₂ and CdCl₃⁻, which do not appear to be adsorbed to the same extent as Cd²⁺ and Cd(OH)⁺ ions.

Effect of co-ions

The effect of Cu(II), Hg(II) and Pb(II) on the uptake of Cd(II) by the SA-S(8.9)-C was investigated. Batch experiments were conducted using 50 cm³ of Cd(II) solution having co-ions in the molar ratio of 1:1 and 1:2. The percentage adsorption of Cd(II) from solution was 98.8 % in the absence of any co-ions. The adsorption decreases to 83.8, 79.1 and 72.1 % respectively; when Cu(II), Hg(II) and Pb(II) ions are present in the 1:1 ratio. As the molar ratio

TABLE 4
Langmuir constants and thermodynamic parameters for the adsorption of Cd(II) onto SA-S(8.9)-C

Temperature (°C)	Langmuir constants				R ²	Thermodynamic parameters	
	Q ⁰ (mg/g)	95 % confidence limit	b (dm ³ /mg)	95 % confidence limit		ΔG(kJ/mol)	ΔS(J/mol/K)
30	149.93 ± 5.44	146.00-156.88	0.161 ± 0.015	0.154-0.181	0.988	-0.89	93.77
40	163.32 ± 7.16	158.30-172.62	0.213 ± 0.017	0.199-0.241	0.992	-1.81	93.71
50	172.81 ± 4.17	172.03-180.37	0.317 ± 0.028	0.284-0.350	0.991	-2.73	93.64
60	190.48 ± 12.07	184.52-206.66	0.421 ± 0.046	0.380-0.463	0.987	-3.65	93.61

increases to 1:2 even more reduction of Cd(II) removal yield was noticed. The experimental results show that a 72.2, 70.5 and 60.6 % reduction in Cd(II) removal was observed when Cu(II), Hg(II) and Pb(II) ions present at a molar ratio of 1:2. This reduction in Cd(II) adsorption might be due to a competitive ion effect between Cd(II) and co-ions for the adsorption sites on the carbon. Based on these experimental results, the Pb(II) ion may be a stronger competitive ion than Hg(II) and Cu(II) ions for Cd(II) removal by SA-S-C. The results can also be explained by the selectivity sequence of the most common cations on the adsorbent surface. It was observed that amongst the cations used, interference of Pb(II) ion is highest, followed by Hg(II) and Cu(II). The observed order of interference was the same as that of their increasing ionic radii, i.e. their decreasing hydrated ionic radii. The smaller the hydrated ionic radius, the greater its efficiency to active groups of the adsorbent. This suggests that the energy required in the dehydration of the metal ions, in order that they could occupy a site in the adsorbent, plays an important role in determining the selectivity series for the metal ions.

Analysis of adsorption capacities by the Langmuir equation

Sorption equilibrium is established when the concentration of metal in a bulk solution (C_e) is in dynamic balance with that of the interface (q_e). Figure 7 shows the experimental sorption isotherms for the Cd(II)-activated carbon system. It is seen that the adsorption density increases with increasing solution temperature. To determine the adsorption capacity of the activated carbon, a study of the adsorption isotherm was attempted by analysing adsorption data by a computer simulation technique to fit the Langmuir isotherm model. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is given by:

$$q_e = \frac{bC_eQ^0}{1 + bC_e} \quad (6)$$

where:

- q_e is the amount of solute adsorbed per unit mass of adsorbent (mg/g),
- C_e is the equilibrium solution-phase concentration (mg/dm³),
- Q^0 and b are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites (mg/g) and energy/intensity of adsorption respectively.

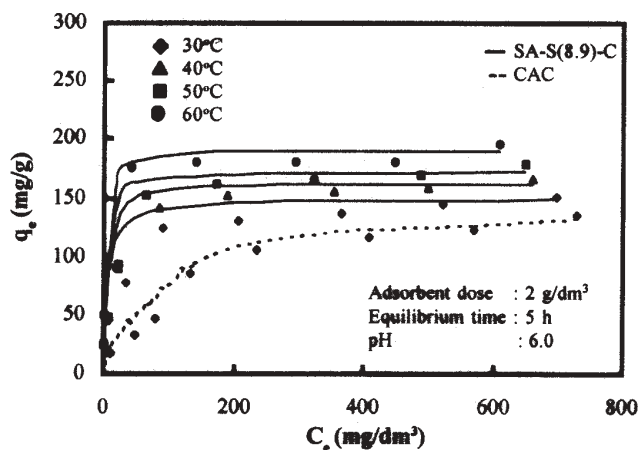


Figure 7
Plots of q_e vs. C_e for the adsorption of Cd(II) on SA-S(8.9)-C and CAC. Lines are Langmuir model curves

The Langmuir parameters were obtained by fitting the experimental data to the linearised equation derived from Eq. (6):

$$\frac{1}{q_e} = \frac{1}{Q^0 b C_e} + \frac{1}{Q^0} \quad (7)$$

The values of Q^0 and b were calculated from the intercept and slope of the linear plots of $1/q_e$ vs. $1/C_e$ for different temperatures and are listed in Table 4 along with standard deviations, 95 % confidence limiting values and their coefficients of correlation (R^2). From the values obtained for the parameters the theoretical Langmuir curves were calculated and are plotted in Fig. 7. The good fit of the experimental data and the correlation coefficients (R^2) higher than 0.987 indicated the applicability of the Langmuir isotherm model. The Langmuir constants Q^0 and b increased with temperature showing that adsorption capacity and intensity of adsorption are enhanced at higher temperatures and indicating the endothermic nature of adsorption. The increase in adsorption capacity with temperature suggested that the active, surface centres available for adsorption have increased with temperature. Another reason may be due to the change in pore size and enhanced rate of intraparticle diffusion of solute as diffusion is an endothermic process.

The change in apparent enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) of adsorption were calculated from the variations of the Langmuir constant, b (dm³/mol) with change in temperature using the following equations:

TABLE 5
Langmuir constants for the adsorption of Cd(II) onto different adsorbents

Adsorbent	Langmuir constants		References
	Q° (mg/g)	b (dm ³ /mg)	
Geothite	2.89	0.456	Johnson (1990)
Straw-based activated carbon	11.10	-	Larsen and Schierup (1981)
Groundnut husk	42.71	0.027	Okieimen et al. (1991)
Activated bentonite	16.50	1.860	Pradas et al. (1994)
Coconut shell-based activated carbon	124.76	0.020	Budinova et al. (1994)
Apricot stone-based activated carbon	134.88	0.044	Budinova et al. (1994)
Bituminous coal	6.47	0.015	Singh and Rawat (1994)
Kimberlite tailings	7.22	0.461	Srinivasa Rao and Bandyopadhyay (1995)
Sphagnum peat moss	198.80	0.010	Allen et al. (1992)
Fe(III)/Cr(III) hydroxide waste	40.49	0.231	Namasivayam and Ranganathan (1995)
Commercial activated carbon (F-400)	8.21	0.380	Ramos et al. (1997)
Commercial activated carbon (E. Merck)	130.21	0.120	Present study
SA-S(8.9)-C	149.93	0.161	Present study

TABLE 6
Desorption and regeneration data

Cycle	Adsorption, mg/g (%)	Desorption, mg/g (%)
1	24.38 (97.5)	23.02 (94.4)
2	23.35 (93.4)	21.30 (91.2)
3	22.03 (88.1)	19.12 (86.8)

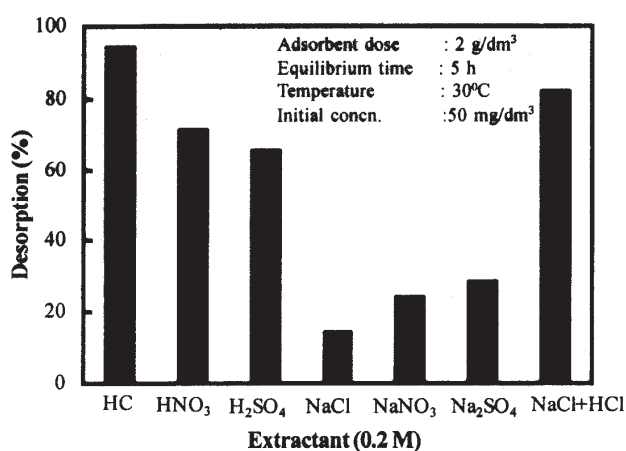


Figure 8

Effect of various extractants on the desorption of Cd(II) from spent SA-S(8.9)-C

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (8)$$

$$\ln b = -\frac{\Delta G}{RT} \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (10)$$

where:

R is the gas law constant, and
b' is equal to $\Delta S/R$.

The plot of $\ln b$ vs. $1/T$ was found to be linear (figure not shown) and H was computed from the slope. The positive value of H (27.52 kJ/mol) reflects the endothermic nature of the process. The negative values of ΔG (Table 4) indicate the process to be feasible and spontaneous. The amount adsorbed at equilibrium must increase with increasing temperature, because ΔG decreases with increasing temperature of the solution. This explains why the negative values increase with increasing temperature. The positive values of ΔS reflect the affinity of the carbon for Cd(II) and also suggest some structural changes in the adsorbate and adsorbent.

The specific surface area occupied by Cd(II) was calculated by the following equation (Viladkar et al., 1996):

$$S_{Cd^{2+}} = 6.023 \times 10^{-2} M_r A_m \quad (11)$$

where:

M_r is the amount of Cd(II) (mmol) adsorbed per 100 g of carbon when the surface is completely occupied by a monolayer of Cd(II).

A_m is the cross-sectional area per molecule in \AA^2 on the surface.

The monolayer adsorption capacity (Q^0) for Cd(II) is 1.33 mmol/g. It can be calculated, assuming the radius of a hydrated Cd(II) ion to be 0.426 nm, that 1.33 mmol/g of Cd(II) would cover 456.5 m²/g for SA-S-C. This value is nearer to the total available surface area (as determined from BET/nitrogen adsorption experiments) of 500.5 m²/g. It is known that carbon is almost entirely composed of mesopores with pore volumes greater than 7.5 nm. Thus, the adsorption of Cd(II) would account for the occupation of the entire activated carbon surface including meso- and macropores.

Comparison with other adsorbents

In order to justify the validity of sulphurised activated carbon as an adsorbent for Cd(II) adsorption, its adsorption potential must be compared with other adsorbents used for this purpose. The values of Q^0 and b for the adsorption of Cd(II) on different adsorbents

reported in the literature compared with the adsorbent of the present study are summarised in Table 5. It may be observed that the uptake of Cd(II) on sulphurised activated carbon is very much greater than other adsorbent materials reported in the literature. However, it is clear from Table 5 that sphagnum moss peat shows much greater (1.33 times) adsorption potential. The high adsorption capacity for this material is probably related to the sorption mechanism including both ion exchange and complexation.

An adsorption isotherm study was also conducted to determine the adsorption capacity of a commercial activated carbon (CAC). For this, a CAC, E. Merck carbon, supplied by E. Merck India Ltd was used. Equilibrium isotherm data at a controlled pH of 6.0 and a temperature of 30°C were correlated using the Langmuir isotherm model. The maximum adsorption capacity, Q^0 and binding constant, b of CAC were calculated from the Langmuir plot (Fig. 7) and were 130.21 mg/g and 0.12 dm³/mg, respectively; which are considerably lower than those of the newly developed activated carbon.

Desorption and regeneration

Desorption studies assist in the recycling of the adsorbent and recovery of metal. For this purpose, different reagents as extractants were tested. The results of the experiments are shown in Fig. 8. The relatively inexpensive HCl eluted almost all the bound Cd(II) from carbon. In contrast NaNO₃, NaCl, Na₂SO₄, HNO₃, H₂SO₄ and NaCl+HCl were not efficient in the desorption of Cd(II) ions. An efficiency of 94.4% was obtained by using 0.2 M HCl solution and is therefore suitable for the extraction of Cd(II) into the aqueous phase. Regeneration studies were also carried out for three cycles. Table 6 summarises the results of desorption and regeneration of activated carbon for Cd(II). After two cycles, the adsorption capacity of activated carbon was reduced by 9.4% and on the other hand recovery of Cd(II) ions in 0.2 M HCl was decreased from 94.4% in the first cycle to 86.8% in the third cycle. The small portion of adsorbed Cd(II) not recoverable by regeneration presumably represents the metal ions which are bound through stronger interactions and, as a result, the sorption efficiency is reduced in subsequent cycles.

Conclusions

The study indicated that sulphurised steam activated carbon prepared from sugar cane bagasse pith could be used as an effective adsorbent material for the treatment of Cd-bearing aqueous waste streams. The adsorption of Cd(II) onto activated carbon is found to be time, concentration, pH and temperature dependent. The maximum percentage removal occurs between the pH range of 5.0 to 9.0. Adsorption data indicate the applicability of pseudo-second-order kinetics. The removal of Cd(II) by this activated carbon is an endothermic process. The calculated E_a for the adsorption is 18.28 kJ/mol, indicating that the adsorption has a low potential energy barrier. The isotherm study indicates that sorption data can be adequately modelled by the Langmuir adsorption isotherm. Spent adsorbent can be regenerated using 0.2 M HCl.

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