



## Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies

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### Abstract

The adsorption of mercury from aqueous solutions and chlor-alkali industry effluent on steam activated and sulphurised steam activated carbons prepared from bagasse pith have been studied comparatively. The uptake of mercury(II) (Hg(II)) was maximum by steam activated carbon in presence of SO<sub>2</sub> and H<sub>2</sub>S (SA–SO<sub>2</sub>–H<sub>2</sub>S–C) followed by steam activated carbon in presence of SO<sub>2</sub> (SA–SO<sub>2</sub>–C), steam activated carbon in presence of H<sub>2</sub>S (SA–H<sub>2</sub>S–C) and steam activated carbon (SA–C) at the same concentration, pH and temperature of the solution. Adsorption experiments demonstrate that the adsorption process corresponds to the pseudo-second-order kinetic model and equilibrium results correspond to the Langmuir adsorption isotherm. Kinetic parameters as a function of initial concentration, for all adsorbents were calculated. Batch studies indicated that the optimum pH range for the adsorption of Hg(II) on sulphurised carbons was between 4 and 9 and for sulphur free carbon was between 6 and 9 at 30 °C. The adsorptive behaviour of the activated carbons is explained on the basis of their chemical nature and porous texture. Decrease in ionic strength and increase in temperature of the solution has been found to improve the uptake of Hg(II). Synthetic and chlor-alkali industrial wastewaters were also treated by sulphurised activated carbons to demonstrate their efficiencies in removing Hg(II) from wastewaters. Some feasibility experiments have been carried out with a view to recover the adsorbed Hg(II) and regenerate the spent activated carbons using 0.2 M HCl solution. The data obtained point towards viable adsorbents, which are both effective as well as economically attractive for Hg(II) removal from wastewaters. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Mercury removal; Sulphurised activated carbon; Bagasse pith; Synthetic and chlor-alkali industrial wastewaters; Adsorption isotherm; Regeneration

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## 1. Introduction

Mercury, deriving from chlor-alkali, paper and pulp, oil refinery, paint, pharmaceutical and battery manufacturing industrial wastewater discharges, present an ongoing and serious threat to human health and natural water quality. The necessity to reduce the amount of mercury ions in wastewater streams of industries and subsequent possible reuse of the metal ions, has led to an increasing interest in selective adsorbents [1]. In recent years considerable attention has been devoted to develop the surface-modified adsorbents from locally available materials for the treatment of mercury wastewaters. These materials range from industrial products such as waste tyre rubber, coal, photofilm industrial waste sludge [2–4] and agricultural products and by-products such as waste tea leaves, tree bark, onion skin, sawdust, and coconut husk [5–9]. Recently, Sreedhar and Anirudhan [10] studied the removal of mercury(II) (Hg(II)) from chlor-alkali industrial wastewater using polyacrylamide grafted coconut husk.

Recent studies speculated that the reaction between mercury and sulphur groups present in the adsorbent materials accounted for high adsorption capacity. In this direction, Meng et al. [11] reported the ability of used tyre rubber containing sulphur groups to scavenging the Hg(II) from solutions. Sreedhar et al. [12] performed batch experiments with polysulphide treated coconut husk for Hg(II) binding. Activated carbons prepared from lignocellulosic materials have widely used for recovery of Hg(II) from wastewaters. Since mercury species show a high affinity towards sulphur a method of improving adsorption potential of activated carbon could be based on immobilising sulphur on the material. Serrano et al. [13] utilised commercial activated carbon loaded with sulphur groups for the removal of Hg(II), Pb(II) and Cd(II) ions from aqueous solutions. The primary aim of this work is to present the results of ongoing studies on the adsorption of Hg(II) by sulphurised activated carbons prepared by locally available sugar industry waste materials, bagasse pith. The utility of this adsorbent material in removing Hg(II) from chlor-alkali industry wastewater has also been explored.

## 2. Materials and methods

### 2.1. Sorbent preparation

The raw material (bagasse pith), a waste product from local sugar mill was used as a precursor for preparing activated carbons. Bagasse pith was treated with dilute HCl to remove the adhering materials and washed with distilled water and then dried. The carbonisation of the bagasse pith was performed in a muffle furnace at 200 °C for 2 h (C-200). Steam activation of the carbon was done using the method described in earlier publication [14]. Steam generated by a steam generator, entered in the carbon at a rate of 5 ml/min. The sample was heated at the rate of 10 °C/min to 400 °C and held at this temperature for 1h. Before utilising this steam pyrolysed activated carbon (SA-C) was treated with 1 M HCl solution to remove ash content and then washed with distilled water. The material was dried at 100 °C and sieved to –80 + 230 mesh size.

Sulphurised activated carbons were prepared by steam activation of C-200 at 400 °C in presence of H<sub>2</sub>S (SA-H<sub>2</sub>S-C) or steam activation of C-200 at 400 °C in presence of

SO<sub>2</sub> (SA–SO<sub>2</sub>–C) or steam activation of C-200 at 400 °C in presence of SO<sub>2</sub> and H<sub>2</sub>S for 2 h (SA–SO<sub>2</sub>–H<sub>2</sub>S–C). SO<sub>2</sub> and H<sub>2</sub>S gases were flushed into the reaction tube from SO<sub>2</sub> and H<sub>2</sub>S gas generators. About 5 g of C-200 was placed in a specially made clay tube and flushed with a flow of steam 5 ml/min in the presence of a stream first of SO<sub>2</sub> (10 ml/min) for 90 min and then of H<sub>2</sub>S (15 ml/min) during 120 min from gas generators at a heating rate of 10 °C/min from 30 to 400 °C. The amount of sulphur attached to the carbon surface was determined by using Eschka method (standard analysis). This deals with the transformation into BaSO<sub>4</sub> of the sulphur present in adsorbents by treatment with the Eschka mixture (Na<sub>2</sub>CO<sub>3</sub>, MgO) at 800 °C and then successively with Br<sub>2</sub> and BaCl<sub>2</sub> solution [15]. The FTIR spectra of adsorbents were recorded between 4000 and 400 cm<sup>-1</sup> using a KBr method with a Perkin-Elmer IR-180 spectrophotometer. The surface area and porosity of the adsorbents were measured by a Quantasorb surface area analyser (model QS-7) and micrometrics mercury porosimeter (model 9310), respectively. The pore volumes V<sub>3</sub> (pore volume greater than 50 nm in diameter, macropores), V<sub>2</sub> (pore volume greater than 7.5 nm and less than 50 nm in diameter, mesopores) and V<sub>1</sub>, pores smaller than 7.5 nm (as estimated from  $V_1 = V_T - (V_2 + V_3)$ ) as estimated from mercury porosimetry are also listed in Table 1. Densities of the adsorbents were also calculated from the displacement of water ( $\rho_{\text{water}}$ ) and nitrobenzene ( $\rho_{\text{nitrobenzene}}$ ), according to the pycnometric method. Potentiometric method [16] was carried out to determine the surface charge (pH<sub>ZPC</sub>) of the adsorbents. The total number of acidic groups on the adsorbents was determined by conductometric titrations [17]. The surface and physical properties of the investigated adsorbent samples are given in Table 1.

## 2.2. Adsorption and desorption experiments

The kinetic batch experiments examined the uptake of Hg(II) ions from solution. The test solution was prepared by dissolving HgCl<sub>2</sub> in distilled water to give approximately 1000 mg/l. A known amount of adsorbent was placed in a 100 ml stoppered bottle containing

Table 1  
Properties of the investigated activated carbons

Number	Parameter	Value			
		SA–C	SA–H <sub>2</sub> S–C	SA–SO <sub>2</sub> –C	SA–SO <sub>2</sub> –H <sub>2</sub> S–C
1	Surface area (m <sup>2</sup> /g)	536.5	530.2	506.5	500.5
2	Cation-exchange capacity (meq/g)	3.96	4.74	4.82	5.02
3	$\rho_{\text{water}}$ (g/ml)	1.06	1.46	1.49	1.55
4	$\rho_{\text{nitrobenzene}}$ (g/ml)	0.87	0.92	1.06	1.22
5	pH <sub>ZPC</sub>	5.6	5.1	5.0	4.3
6	V <sub>1</sub> (ml/g)	0.13	0.06	0.04	–
7	V <sub>2</sub> (ml/g)	0.20	0.28	0.29	0.33
8	V <sub>3</sub> (ml/g)	0.19	0.14	0.15	0.10
9	V <sub>T</sub> (ml/g)	0.52	0.48	0.48	0.43
10	Sulphur content (wt.%)	–	7.8	8.0	8.9
11	Total acid groups (meq/g)	2.3	2.4	2.6	2.9
12	Particle size (mesh size)	–80 + 230	–80 + 230	–80 + 230	–80 + 230

50 ml solution. The pH and ionic strength of the solution were adjusted to constant values. The samples were shaken in a temperature controlled water bath shaker. Samples were then drawn from the bottle at predetermined time intervals and residual Hg(II) concentration was determined using spectrophotometric method [18].

Adsorption isotherms were determined by the bottle point method. About 0.1 g of the adsorbents were added to the stoppered bottles, which contain 50 ml of varying concentration of Hg(II) solution (50–1000 mg/l). pH of the solution was kept at 6. The sample bottles were shaken continuously in a water bath shaker for 4 h after which samples were taken and filtered. Adsorbent loadings were calculated from the mass balance after initial and residual concentrations had been determined.

The experimental conditions for the desorption of Hg(II) from spent carbons were similar to that of the batch adsorption methods. Four hour agitation of Hg(II) laden carbons was used to desorb Hg(II) ions into solution. For regeneration the same procedure was followed for two cycles. In order to find out whether there is any sulphur leakage from the sulphurised carbon during the adsorption and desorption experiments, the supernatant solution was analysed for sulphur. There was no sulphur leakage in any of the adsorption and desorption media used, indicate that simple washing procedure was sufficient for the removal of unadsorbed sulphur from the surface of the carbons.

### 3. Results and discussion

#### 3.1. Sorbent characterisation

Some fundamental absorption frequencies of SA–C and SA–SO<sub>2</sub>–H<sub>2</sub>S samples are shown in Table 2. The asymmetric absorption band observed at a wave number of 3764 cm<sup>-1</sup> for SA–C and 3762 cm<sup>-1</sup> for SA–SO<sub>2</sub>–H<sub>2</sub>S–C indicates the presence of exchangeable –OH groups on both carbons. Sulphurised and sulphur free carbons contain carboxyl (bands at 1724 cm<sup>-1</sup> for SA–C and 1730 cm<sup>-1</sup> for SA–SO<sub>2</sub>–H<sub>2</sub>S–C) functional groups. The IR spectra shows bands at 1600 and 1608 cm<sup>-1</sup> for SA–C and SA–SO<sub>2</sub>–H<sub>2</sub>S–C, respectively,

Table 2  
Some fundamental IR absorption frequencies of sulphurised and sulphur free activated carbons

Band position (cm <sup>-1</sup> )		Possible assignments
SA–C	SA–SO <sub>2</sub> –H <sub>2</sub> S–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
–	1165	C=S stretching
–	1111	S=O stretching
–	460	S–S stretching

indicating the presence of conjugated hydrogen bonded carbonyl group as suggested by Hallum and Drushell [19]. Additional peaks at 1165, 1111 and  $460\text{ cm}^{-1}$  in the spectra of SA-SO<sub>2</sub>-H<sub>2</sub>S-C represent the C=S, S=O and S-S stretching vibrations are due to the surface sulphur groups bonded to activated carbon [20]. Based on these results, it is assumed that carbon surface is modified with sulphur groups. The  $\text{pH}_{\text{zpc}}$  of the sulphur free SA-C sample was 5.3 and it decreased with increasing amount of sulphur enrichment, which indicate that the surface of the SA-C has been modified after steam activation in presence of SO<sub>2</sub> and H<sub>2</sub>S. Although sulphurised carbons contain sulphur groups or linkage; the surface area and porosity values remain considerably higher with respect to SA-C. Only a small decrease in surface area and porosity was observed for sulphurised carbons. This suggests that most of the functional groups or pores are not reacted or clogged with sulphur atoms.

### 3.2. Effect of pH

Fig. 1 shows the effect of pH on the percentage adsorption of Hg(II) by sulphur free carbons and sulphurised carbons. It is clear that sulphurised carbons are effective for the quantitative removal of Hg(II) over the pH range 4–9. Sulphur free carbon, however, is effective with in a narrow range of 6–8. Perusal of the literature on Hg(II) speciation diagram [2] shows that in the presence of Cl<sup>-</sup>, the dominant mercury species at pH >4 is Hg(OH)<sub>2</sub>. The species such as HgCl<sub>2</sub> or (HgCl<sub>2</sub>)<sub>2</sub>, Hg(OH)<sup>+</sup> and HgOHCl are also present in small concentration. The existence of dimeric HgCl<sub>2</sub> in aqueous solutions has been reported by many authors [21]. The increase in Hg(II) adsorption above pH 6 for both sulphur free and sulphurised carbons may be due to the retention of the Hg(OH)<sub>2</sub> species into pores of the carbon particles. Maximum sorption efficiency in the pH range

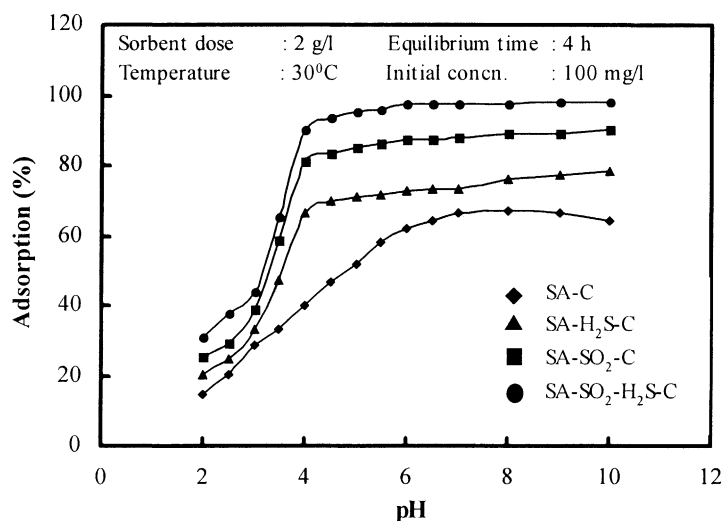


Fig. 1. Effect of pH on the removal of Hg(II) by different activated carbons.

4–6 for sulphurised carbons is explained well by the Pearson theory. According to Pearson theory [22], during acid–base reaction, hard acids prefer to co-ordinate with hard bases and soft acids to soft bases. Neutral molecules are softer acids than metal cations and as a rule [22], the interaction of Hg(II) species such as  $\text{HgCl}_2$ ,  $(\text{HgCl}_2)_2$ ,  $\text{Hg}(\text{OH})_2$  and  $\text{HgOHCl}$  with surface sulphur groups (soft bases) is likely favoured at pH range 4–6. The enhancement of Hg(II) adsorption on sulphurised activated carbon is also attributed to the formation of  $\text{Hg}(\text{HS})_2$  and  $\text{Hg}_2(\text{HS})_2$  species and their retention in the meso- and macropores of the carbon particles ( $\text{Hg}^{2+}$  ions formed by the following possible redox reaction:  $2\text{Hg}^{2+} + \text{SO}_3^{2-} + 2\text{OH}^- \rightarrow \text{Hg}_2^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$ ). The experimental results also showed that adsorption capacity of sulphurised carbon for Hg(II) ions decreased in the order  $\text{SA-SO}_2\text{-H}_2\text{S-C} > \text{SA-SO}_2\text{-C} > \text{SA-H}_2\text{S-C}$ . The observed order of adsorption efficiency for different carbons was in the same as that of their increasing sulphur content. The data clearly indicates that steam activation of carbon in presence of  $\text{H}_2\text{S}$  and  $\text{SO}_2/\text{H}_2\text{S}$  is an effective method to improve the adsorption efficiency of the carbon. The sites responsible for the sorption process are not exclusively due to the sulphur groups. Other sites on the carbon surface can also contribute to the adsorption process. In acidic medium particularly below the pH of zero point charge ( $\text{pH}_{\text{zpc}}$ ), the positively charged  $\text{Hg}^{2+}$  or  $\text{Hg}(\text{OH})^+$  species present in the solution may exchange with  $\text{H}^+$  from  $-\text{COOH}$  groups of the carbons. It has been shown that final pH of the solution is always less than the initial pH at pH range between 2 and pH of zero point charge.

### 3.3. Effect of agitation time

Removal of Hg(II) by activated carbons with time was carried out at pH 6 and a temperature of  $30^\circ\text{C}$  (Fig. 2). The amount of Hg(II) adsorbed increases with agitation time and attain equilibrium at about 200 min for sulphurised activated carbons and 240 min

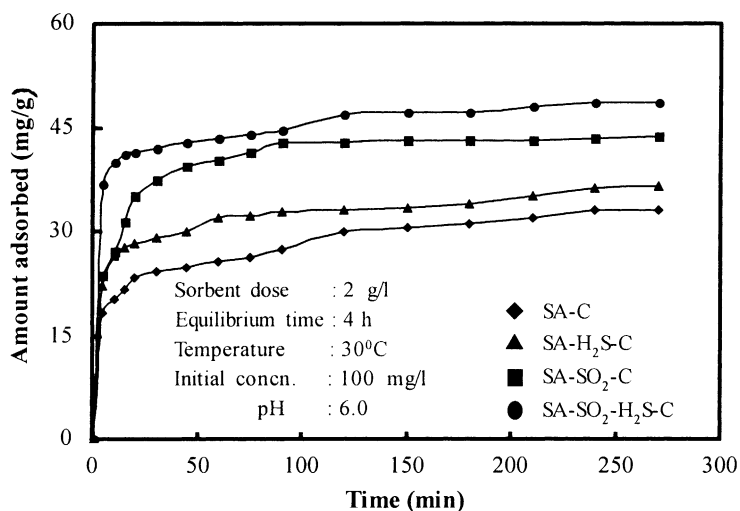


Fig. 2. Effect of agitation time on Hg(II) removal by different activated carbons.

for sulphur free activated carbons for an initial concentration of 100 mg/l. Therefore, an optimum agitation period of 4 h was selected. The curves shown in Fig. 2, present a double nature, the initial portion of the curve rises linearly and is changed into a curve and levels off 4 h of contact time. The plateau portion of the curve corresponds to pore diffusion and the linear portion of the curve reflects surface layer diffusion [23]. It is also evident from the figure that the amount adsorbed on sulphurised activated carbons is greater than that of sulphur free activated carbon.

### 3.4. Adsorption dynamics

The two important aspects for parameter evaluation of the adsorption study are the kinetic and the equilibrium of adsorption. The mechanism involved in the metal removal is assumed basically, to be complexation. The simplest way to describe the kinetics of metal removal, in the absence of stoichiometric data, can be represented as



where  $P$  is the number of active sites occupied on the adsorbent,  $M$  the concentration of free metal in solution and  $PM$  is the concentration of metal bound to sorbent. Parameters  $k$  and  $k^1$  are the adsorption rate and desorption rate constants, respectively.

The rate equation for the adsorption process can be developed by making certain assumptions. In deriving kinetic expression, it was assumed [24] that

- sorption occurs only on localised sites and involves no interaction between sorbed ions;
- the energy of adsorption is independent of surface coverage;
- maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface;
- the process of metal uptake on activated carbons is governed by a pseudo-second-order and is chemical in nature, i.e. chemisorption;
- the rate of desorption,  $k^1$  is negligible in comparison with rate of adsorption,  $k$ .

The reactions involving in pseudo-second-order are greatly influenced by the amount of metal on the surface of the adsorbent and the amount of metal adsorbed at equilibrium. It means that the rate of reaction is directly proportional to the number of active sites on the surface of the adsorbent.

The rate expression for the pseudo-second-order reaction can be written as

$$\frac{d(P)_t}{dt} = k [(P)_0 - (P)_t]^2 \quad (2)$$

where  $(P)_0$  and  $(P)_t$  are the number of active sites occupied on the adsorbent at initial time ( $t = 0$ ) and at time ' $t$ ', respectively. In terms of adsorbed quantity, the Eq. (2) can be rewritten as

$$\frac{dq_t}{dt} = k [q_e - q_t]^2 \quad (3)$$

where  $k$  is the rate constant of sorption (g/mg min),  $q_e$  and  $q_t$  are the amount of metal ion adsorbed (mg/g) at equilibrium and at time ' $t$ ', respectively.

Separating the variables in Eq. (3) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k dt \quad (4)$$

on integrating, taking into consideration that  $q_0 = 0$  when  $t = 0$ , and that  $q_t = q_t$  when  $t = t$ , it is seen that

$$\frac{1}{(q_e - q_t)^2} = \frac{1}{q_e} + kt \quad (5)$$

on rearranging the Eq. (5) can be rewritten as

$$q_t = \frac{t}{(1/kq_e^2) + (t/q_e)} \quad (6)$$

Thus, by plotting  $t/q_t$  versus  $t$ , values for  $k$  could be calculated [24] where

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (7)$$

The product  $kq_e^2$  is actually the initial sorption rate represented as  $h = kq_e^2$ .

The kinetic plots as per Eq. (7) were made for all adsorbents and the results for different concentrations are shown in Fig. 3. A linear straight line plot in all cases was observed with correlation coefficients of more than 0.98, and indicated that the adsorption reaction can be approximated to pseudo-second-order as suggested by Ho and McKay [24]. The kinetic parameters  $k$ ,  $h$  and  $q_e$  were calculated from the slope and intercepts of the plots and presented in Table 3. It can be showed that initial adsorption rate ( $h$ ) is increased with an increase in initial metal concentration. The values of  $h$  are higher for SA–SO<sub>2</sub>–H<sub>2</sub>S–C than other adsorbents. The values of  $h$  increased from 1.74 to 6.85 mg/g min for SA–C, 2.68 to 12.04 mg/g min for SA–H<sub>2</sub>S–C, 3.89 to 16.61 mg/g min for SA–SO<sub>2</sub>–C and 4.76 to 19.95 mg/g min for SA–SO<sub>2</sub>–H<sub>2</sub>S–C with the increase of initial concentration from 50 to 250 mg/l. For a decrease in the initial concentration of Hg(II) from 250 to 50 mg/l, the values of  $k$  were found to increase from  $1.54 \times 10^{-3}$  to  $4.38 \times 10^{-3}$ ,  $1.82 \times 10^{-3}$  to  $5.21 \times 10^{-3}$ ,  $2.01 \times 10^{-3}$  to  $6.82 \times 10^{-3}$  and  $2.27 \times 10^{-3}$  to  $7.73 \times 10^{-3}$  g/mg min for SA–C, SA–H<sub>2</sub>S–C, SA–SO<sub>2</sub>–C and SA–SO<sub>2</sub>–H<sub>2</sub>S–C, respectively. Observations of similar kind, i.e. the variations in  $h$  and  $k$  values with the initial concentrations have been reported also by the earlier workers [25] who studied the adsorption characteristics of Cu(II) ions on chitosin. The decrease in  $k$  values with an increase in metal concentration is a common phenomena observed with a variety of adsorbents such as chitosan, moss peat and activated carbon used for the adsorption of Hg(II), Ni(II) and Cr(VI), respectively [26–28]. There are many factors which can contribute to this sorbate concentration effect on rate of adsorption. 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. The second cause can be due to the progressive decrease in covalent interactions, relative to electrostatic interaction of the sites with lower affinity for Hg<sup>2+</sup> with an increase of initial Hg(II) concentration. The perusal of data in Table 3 reveals that for the equilibrium time, the metal ion adsorbed ( $q_e$ ) is higher for greater values of initial metal ion concentration. This is obvious because more efficient utilisation of the adsorptive capacities of the adsorbent is expected due to a greater driving



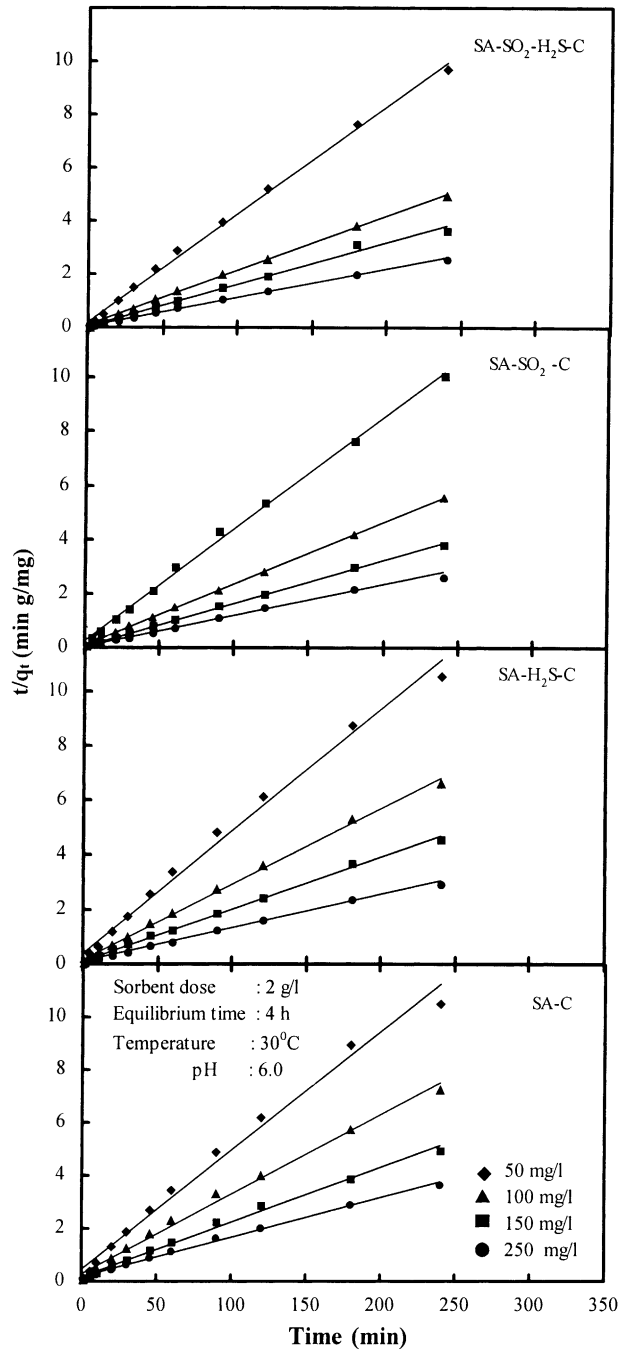


Fig. 3. Pseudo-second-order kinetic plots for the adsorption of Hg(II) on different activated carbons at various initial concentrations.

Table 3  
Kinetic parameters for the adsorption of Hg(II) on activated carbons

Sample	50 mg/l			100 mg/l			150 mg/l			250 mg/l		
	$k$ (g/mg min)	$q_e$ (mg/g)	$h$ (mg/g min)	$k$ (g/mg min)	$q_e$ (mg/g)	$h$ (mg/g min)	$k$ (g/mg min)	$q_e$ (mg/g)	$h$ (mg/g min)	$k$ (g/mg min)	$q_e$ (mg/g)	$h$ (mg/g min)
SA-C	$4.38 \times 10^{-3}$	19.96	1.74	$3.03 \times 10^{-3}$	33.22	3.34	$2.48 \times 10^{-3}$	48.31	5.79	$1.54 \times 10^{-3}$	66.67	6.85
SA-H <sub>2</sub> S-C	$5.21 \times 10^{-3}$	22.68	2.68	$4.79 \times 10^{-3}$	36.36	6.33	$2.75 \times 10^{-3}$	52.33	7.52	$1.82 \times 10^{-3}$	81.35	12.04
SA-SO <sub>2</sub> -C	$6.82 \times 10^{-3}$	23.87	3.89	$4.85 \times 10^{-3}$	43.48	9.21	$3.68 \times 10^{-3}$	63.29	14.74	$2.01 \times 10^{-3}$	90.91	16.61
SA-SO <sub>2</sub> -H <sub>2</sub> S-C	$7.73 \times 10^{-3}$	24.81	4.76	$5.23 \times 10^{-3}$	48.61	12.36	$4.06 \times 10^{-3}$	66.00	17.69	$2.27 \times 10^{-3}$	93.75	19.95

force by a higher concentration gradient pressure. The linearised  $k$  and  $C_0$  values as a log–log plots showed correlation coefficients  $>0.98$  and the following relationship between these two parameters were obtained for SA–C, SA–H<sub>2</sub>S–C, SA–SO<sub>2</sub>–C and SA–SO<sub>2</sub>–H<sub>2</sub>S–C, respectively.

$$k = 1.2631C_0^{-0.6340} \quad (8)$$

$$k = 1.0650C_0^{-0.6823} \quad (9)$$

$$k = 0.8712C_0^{-0.7404} \quad (10)$$

$$k = 0.8207C_0^{-0.7430} \quad (11)$$

### 3.5. Effect of particle size

The experimental data for the adsorption of Hg(II) ions at different size of carbons (75, 100, 150 and 300  $\mu\text{m}$ ) at a fixed adsorbent dose and an initial concentration of 100 mg/l are shown in Fig. 4. The results show that the metal ion adsorbed is higher for smaller adsorbent size. As the particle size increases from 75 to 300  $\mu\text{m}$ , the percentage Hg(II) adsorption decreases from 70.8 to 44.3% for SA–C, 80.8 to 51% for SA–H<sub>2</sub>S–C, 90.5 to 67% for SA–SO<sub>2</sub>–C and 99.9 to 85.1% for SA–SO<sub>2</sub>–H<sub>2</sub>S–C. This is because adsorption being a surface phenomenon, the smaller adsorbent sizes offered comparatively large surface area and, hence, higher adsorption occurs at equilibrium. According to Weber Jr. [29], breaking of larger particles tends to open tiny cracks and channels on the particle surface, providing added surface area which can be employed in the adsorption process. The study also reveals that the size of the adsorbent particle is playing an important role in the adsorption process.

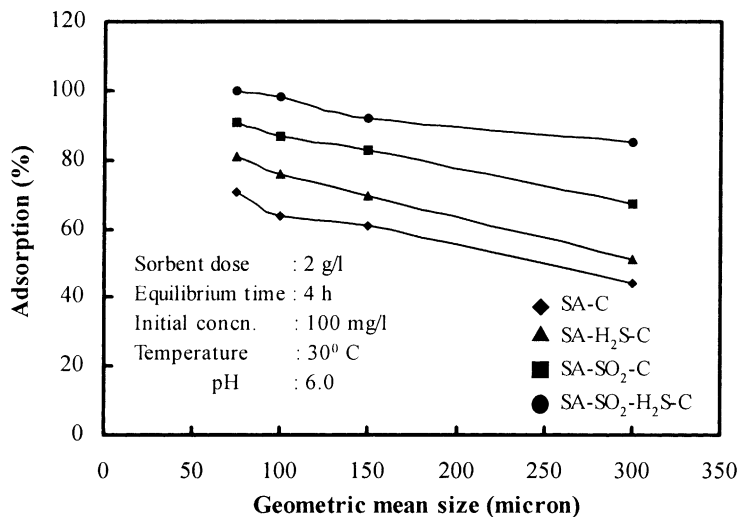


Fig. 4. Effect of particle size on the adsorption of Hg(II) on different activated carbons.

The sorption mechanism could be controlled by reaction kinetics or by diffusion such as film or pore diffusion. In the present investigation, we have selected an agitation speed of 300 rpm, so that the shear on the particle surface is high. Therefore, the thickness of the boundary layer surrounding the particles should be minimal. It appears that film diffusion is not the rate controlling step in the removal of Hg(II) by activated carbon.

In order to assess the nature of the diffusion process responsible for the adsorption of Hg(II) on carbon, attempts were made to calculate coefficients of the process. Assuming spherical geometry for the carbons, film diffusion ( $D_f$ ) and pore diffusion ( $D_p$ ) coefficients were calculated using the following equations [30]:

$$D_f = 0.23 \frac{r_0 \delta \bar{c}}{t_{1/2} c} \quad (12)$$

$$D_p = 0.03 \frac{r_0^2}{t_{1/2}} \quad (13)$$

where  $r_0$  is the radius of the adsorbent,  $\delta$  the film thickness,  $\bar{c}/c$  is the equilibrium loading of the adsorbent. According to earlier workers [31] for film diffusion to be rate limiting, the values of  $D_f$  should be in the range of  $10^{-6}$  to  $10^{-8}$  cm<sup>2</sup>/s. For pore diffusion to be rate limiting, the value of  $D_p$  should be in the range of  $10^{-11}$  to  $10^{-13}$  cm<sup>2</sup>/s. However, earlier workers [26,32] in this direction reported the  $D_p$  values in the order of  $10^{-10}$  cm<sup>2</sup>/s for pore diffusion to be rate limiting step for the adsorption of metals onto different adsorbents. The kinetic data ( $q_t$  versus  $t$ ) obtained for different particle sizes of activated carbon were used to calculate diffusion coefficients for the adsorption of Hg(II). The results are present in the Table 4. It is evident that the rate limiting step appears to be pore diffusion process since the coefficient values are in the range of  $10^{-10}$  to  $10^{-11}$  cm<sup>2</sup>/s. The values of  $D_p$  increased with increasing the particle size of the carbon. A similar variation in  $D_p$  values with increasing particle size was also observed for the adsorption of vanadium on chitosan [32] and mercury on humous-kaolin complex [33]. Based on porosimeter studies it was found that the pore size within the sulphurised carbons is greater than 7.5 nm. Thus, in the absence of micropores (<7.5 nm), the adsorption of Hg(II) ions might be due to the reaction within the mesopores and macropores. Thus, the variation in adsorption capacity on carbon particles might be due to their variation in  $V_2$  and  $V_3$  values, which suggests that these carbons have big fractions of their surface accessible to Hg(II) ions. Hg(II) ions react with surface, internal and external, sites.

### 3.6. Effect of ionic strength

The amount of Hg(II) removal from solution is influenced by the presence of electrolyte like NaCl (Fig. 5). It was found that adsorption of Hg(II) from solution decreased with increase in NaCl. This effect may be imparted to changes in mercury activity or in the properties of the electric double layer. In view of the charge shield action of electrolyte [34], it might be expected that electrostatic interactions also determine the amount of adsorption. The cation competition and modification of mercury speciation are less important factors since NaCl was used to the adjustment of the ionic strength.

Table 4  
The values of  $t_{1/2}$  and diffusion coefficients ( $D_f$  and  $D_p$ ) for the adsorption of Hg(II) on activated carbons

Sample	Particle size											
	75 $\mu\text{m}$			100 $\mu\text{m}$			150 $\mu\text{m}$			300 $\mu\text{m}$		
	$t_{1/2}$ (s)	$D_f$ ( $\text{cm}^2/\text{s}$ )	$D_p$ ( $\text{cm}^2/\text{s}$ )	$t_{1/2}$ (s)	$D_f$ ( $\text{cm}^2/\text{s}$ )	$D_p$ ( $\text{cm}^2/\text{s}$ )	$t_{1/2}$ (s)	$D_f$ ( $\text{cm}^2/\text{s}$ )	$D_p$ ( $\text{cm}^2/\text{s}$ )	$t_{1/2}$ (s)	$D_f$ ( $\text{cm}^2/\text{s}$ )	$D_p$ ( $\text{cm}^2/\text{s}$ )
SA-C	5400	$4.67 \times 10^{-11}$	$7.81 \times 10^{-11}$	6348	$6.59 \times 10^{-11}$	$1.18 \times 10^{-10}$	6612	$1.02 \times 10^{-10}$	$2.55 \times 10^{-10}$	8746	$2.20 \times 10^{-10}$	$7.72 \times 10^{-10}$
SA-H <sub>2</sub> S-C	5100	$3.25 \times 10^{-11}$	$8.27 \times 10^{-11}$	5978	$4.48 \times 10^{-11}$	$1.26 \times 10^{-10}$	6235	$5.36 \times 10^{-11}$	$2.71 \times 10^{-10}$	8265	$6.59 \times 10^{-11}$	$8.17 \times 10^{-10}$
SA-SO <sub>2</sub> -C	4800	$1.71 \times 10^{-11}$	$8.79 \times 10^{-11}$	5782	$2.69 \times 10^{-11}$	$1.30 \times 10^{-10}$	5900	$5.12 \times 10^{-11}$	$2.86 \times 10^{-10}$	7562	$6.91 \times 10^{-11}$	$8.93 \times 10^{-10}$
SA-SO <sub>2</sub> - H <sub>2</sub> S-C	4700	$1.01 \times 10^{-11}$	$8.97 \times 10^{-11}$	5120	$1.13 \times 10^{-11}$	$1.47 \times 10^{-10}$	5600	$2.46 \times 10^{-11}$	$3.01 \times 10^{-10}$	7000	$7.35 \times 10^{-11}$	$9.64 \times 10^{-10}$

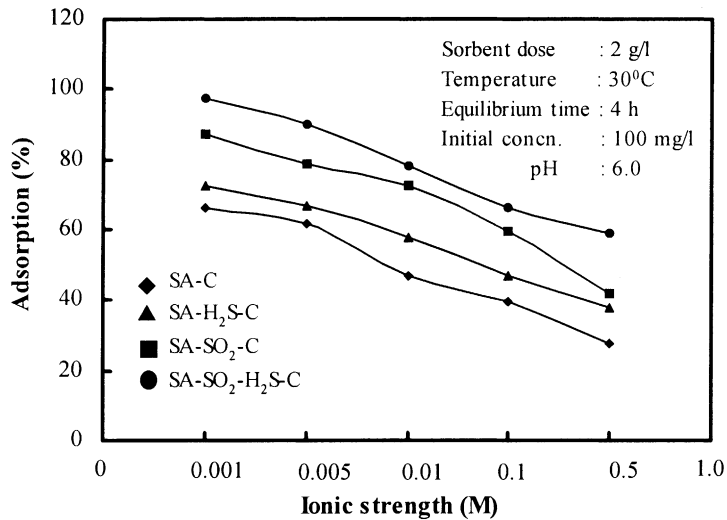


Fig. 5. Effect of ionic strength on the adsorption of Hg(II) on different activated carbons.

### 3.7. Adsorption isotherm

The study of adsorption isotherm is helpful in determining the maximum adsorption capacity of adsorbate for the given adsorbent. Adsorption isotherms are regular, positive and concave to the concentration axis for all carbon system (Fig. 6). Initially the adsorption is quite rapid, which is followed by a slow approach to equilibrium at high concentrations. As can be seen from Fig. 6 and according to the slope of the initial portion of the curve, these isotherms were classified as L type of Giles et al.'s classification [35]. This indicates that Hg(II) is strongly sorbed on the sorbent samples, and that there is no competition from the solvent for sorption sites. The adsorption data exhibit a Langmuir type isotherm, which can be described by the following equation:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (14)$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/l) and  $Q^0$  and  $b$  are the Langmuir constants related to the adsorption capacity and energy of adsorption. The equilibrium adsorption data was fitted to the linear form of the Langmuir equation and the adsorption parameters of the adsorbents were determined as shown in Table 5. In all cases, the correlation coefficients ( $r^2$ ) for the linear regression fits were found to be  $>0.98$ . Solid lines in Fig. 6 represent the Langmuir isotherm (Eq. (14)) using  $Q^0$  and  $b$  values from Table 5. It can be sure that the  $Q^0$  of the sulphurised carbons for Hg(II) is much higher than the capacity of the sulphur free activated carbon. This suggests that the surface modification approach used in this study has significantly increased the adsorption capacity of the bagasse pith based activated carbon through the binding mechanism of the metal to the surface sulphur groups on the sulphurised activated carbons. The maximum capacity

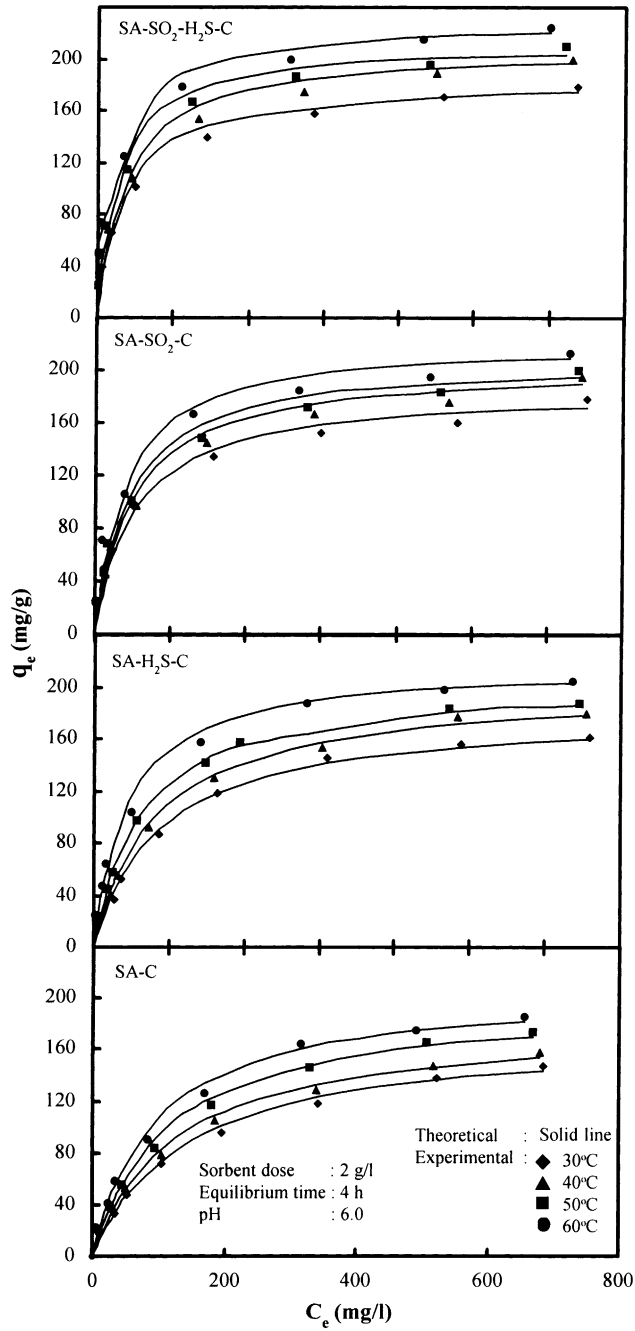


Fig. 6. Adsorption isotherm of Hg(II) on different activated carbons at different temperatures.

Table 5  
Langmuir constants for the adsorption of Hg(II) on different activated carbons

Sample	30 °C		40 °C		50 °C		60 °C	
	$Q^0$ (mg/g)	$b$ (l/mg)	$Q^0$ (mg/g)	$b$ (l/mg)	$Q^0$ (mg/g)	$b$ (l/mg)	$Q^0$ (mg/g)	$b$ (l/mg)
SA-C	172.4	0.0072	181.8	0.0080	200.0	0.0086	208.3	0.0106
SA-H <sub>2</sub> S-C	181.8	0.0113	200.0	0.0123	204.1	0.0164	217.4	0.0229
SA-SO <sub>2</sub> -C	185.2	0.0195	204.1	0.0202	208.3	0.0229	222.2	0.0262
SA-SO <sub>2</sub> -H <sub>2</sub> S-C	188.7	0.0281	208.3	0.0273	212.8	0.0367	227.3	0.0480

of SA-SO<sub>2</sub>-H<sub>2</sub>S-C was found to be 188.7 mg/g, which was very much higher than values reported. The  $Q^0$  values for the adsorption of Hg(II) on 2-mercaptobenzothiazole treated clay [36], photofilm industrial waste [4], used tyre rubber [11], formaldehyde polymerized sawdust [37], activated carbon from Merck [13], polysulphide treated coconut husk [12], bicarbonate treated peanut husk carbon [38] and amino functionalised chitosan [39] were found to be 2.81, 11.76, 14.65, 38.8, 74.21, 88.17, 109.7 and 124.46 mg/g, respectively.

The behaviour of the investigated carbons on Hg(II) adsorption process should be explained on the basis of their chemical nature as well as of their textural characteristics. The observed order of the adsorption capacity of carbons (SA-C < SA-H<sub>2</sub>S-C < SA-SO<sub>2</sub>-C < SA-SO<sub>2</sub>-H<sub>2</sub>S-C) was the same as that of their increasing sulphur content and pore volumes ( $V_2$ ) and decreasing zero point charge. The decrease in  $\text{pH}_{\text{zpc}}$  of the carbons after sulphurisation provide more negative charge on the surface which will helps to adsorb positively charged cations. The lowest  $\text{pH}_{\text{zpc}}$  shown by SA-SO<sub>2</sub>-H<sub>2</sub>S-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 advantages to remove metal cations [40]. The adsorption capacity of the activated carbons ( $Q^0$ ) with relation to Hg<sup>2+</sup> ranges from 172.4 mg/g (SA-C) to 188.7 mg/g (SA-SO<sub>2</sub>-H<sub>2</sub>S-C). The specific surface area occupied by Hg(II) was calculated by the following equation [41]:

$$S_{\text{Hg}^{2+}} = 6.023 \times 10^{-2} M_f A_m \quad (15)$$

where  $M_f$  is the amount of Hg(II) (mmol) adsorbed per 100 g of carbon when surface is completely covered with a monolayer of Hg(II).  $A_m$  is the cross-sectional area per molecule in Å<sup>2</sup> on the surface. The saturation adsorption capacity ( $Q^0$ ) for Hg(II) is 0.862, 0.909, 0.926 and 0.944 mmol/g for SA-C, SA-H<sub>2</sub>S-C, SA-SO<sub>2</sub>-C and SA-SO<sub>2</sub>-H<sub>2</sub>S-C, respectively. It can be calculated, assuming the radius of a Hg(II) ion 0.112 nm, that 0.862, 0.909, 0.926 and 0.944 mmol/g of Hg(II) would cover 20.5, 21.6, 22 and 22.4 m<sup>2</sup>/g for SA-C, SA-H<sub>2</sub>S-C, SA-SO<sub>2</sub>-C and SA-SO<sub>2</sub>-H<sub>2</sub>S-C, respectively. These values are very low compared to the total available surface area (as determined from BET/nitrogen adsorption experiments) of 536.5, 530.2, 506.5 and 500.5 m<sup>2</sup>/g, suggests that only the external surface of the carbon is being utilised for Hg(II) adsorption. It is known that carbons are almost entirely mesopores with pore volume greater than 7.5 nm. However, if the Hg(II) ions in aqueous solution is hydrated, then the true radius of the adsorbed species would increase to 0.56 nm (or greater if other species such as HgCl<sub>2</sub>, (HgCl<sub>2</sub>)<sub>2</sub>, HgOHCl, etc. should consider) which for 0.862, 0.909, 0.926 and 0.944 mmol/g of SA-C, SA-H<sub>2</sub>S-C, SA-SO<sub>2</sub>-C and SA-SO<sub>2</sub>-H<sub>2</sub>S-C



would result in the covering of 511.2, 539.1, 549.2 and 559.6 m<sup>2</sup>/g of carbon, respectively; values much nearer to/or greater than that obtained from nitrogen adsorption experiments. Thus, the adsorption of Hg(II) would account for the occupation of the whole activated carbon surface including meso- and macropores. It is important to note that the adsorption capacity of activated carbons for Hg(II) ions may be enlarged either by creating acidic groups on their surface or by developing their meso- and macroporosities. It is clear from the results that large carbon surface occupied by Hg(II), which indicates the large number of surface centres available to adsorb Hg(II).

### 3.8. Effect of temperature

Temperature has a direct influence on the amount of the sorbed substance. In the present investigation, the adsorption experiments were performed in the temperature range of 30–60 °C. It was found that, according to the adsorption isotherm, the amount of Hg(II) adsorbed on all carbons increase with the solution temperature. The Langmuir parameters for the adsorption isotherms obtained from different temperatures were calculated from the  $C_e/q_e$  versus  $C_e$  plots (Fig. 7), and the results are given in the Table 5. It is observed that the values of  $Q^0$  increases with increase of temperature. The results also show that  $b$  is an increasing function of the solution temperature for different carbons. The increase of  $b$  with temperature indicates that the affinity for Hg(II) ions is favoured by high temperature, and therefore, this adsorption process is endothermic in nature. The increase in capacity with respect to temperature indicates that some kind of chemical interaction may be take place during adsorption process. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in increased adsorption capacity. The results of the present investigation on temperature effect also support the conclusion that Hg(II) sorption is controlled by pore diffusion.

### 3.9. Test with synthetic and industrial wastewaters

The utility of the materials has been demonstrated by treating synthetic and industrial wastewaters. The composition of synthetic and chlor-alkali industrial wastewaters is given in Table 6. Industrial wastewater was collected from a chlor-alkali industry located in Cochin city (India) and was characterised using standard methods [42]. The amount of Hg(II) in industrial wastewater was found to be very low (1.6 mg/l) and it was spiked with a Hg(II) solution so that final concentration of Hg(II) was 20 mg/l. Fig. 8 shows the effect of the mass of activated carbon on the adsorption of Hg(II) from synthetic and industrial wastewaters.

Table 6  
Composition of synthetic and industrial wastewaters

Wastewater	Composition (mg/l)
Synthetic	Hg: 50.0; Na: 25.0; K: 25.0; Mg: 10.0; Ca: 10.0; NH <sub>4</sub> : 10.0; Cl: 40.25; NO <sub>2</sub> : 50.0; SO <sub>4</sub> : 40.; NO <sub>3</sub> : 31.0; CH <sub>3</sub> -COO: 33.0
Industrial	Hg: 1.6; Pb: 2.7; Cd: 0.5; Mg: 25.6; Ca: 41.2; Na: 280.8; PO <sub>4</sub> : 10.9; NO <sub>3</sub> : 16.5; NH <sub>4</sub> : 20.7; Cl: 398.39; BOD: 58.4; COD: 138.6; SS: 358.7

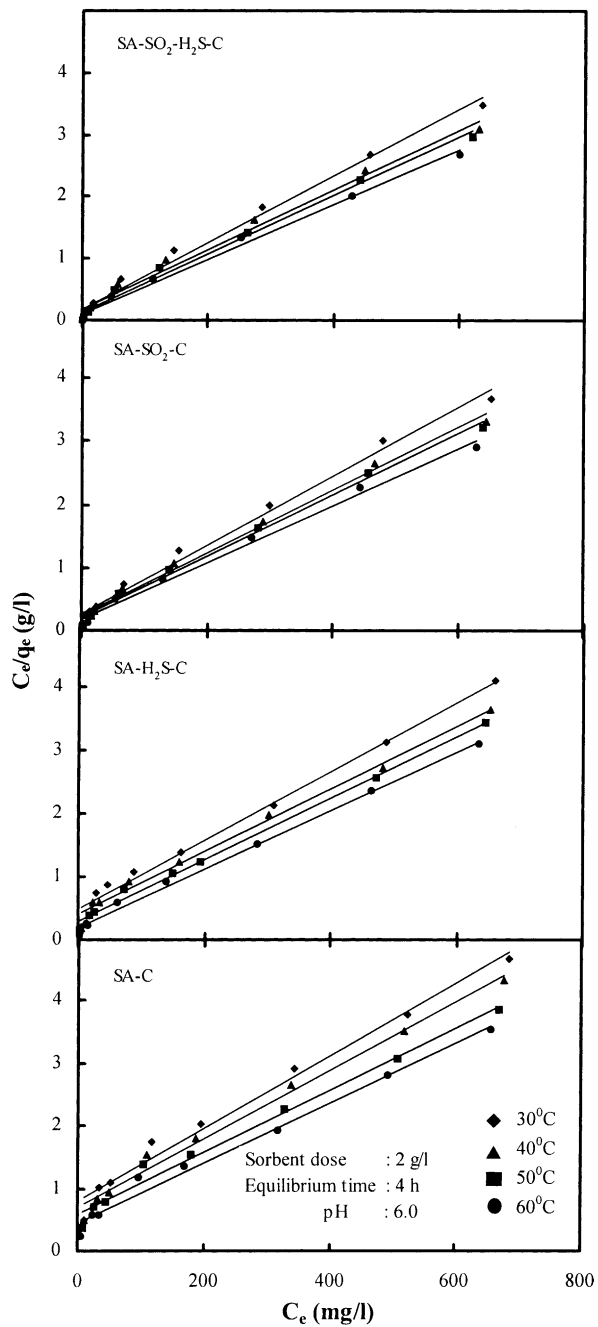


Fig. 7. Langmuir plots for the adsorption of Hg(II) on different activated carbons at different temperatures.

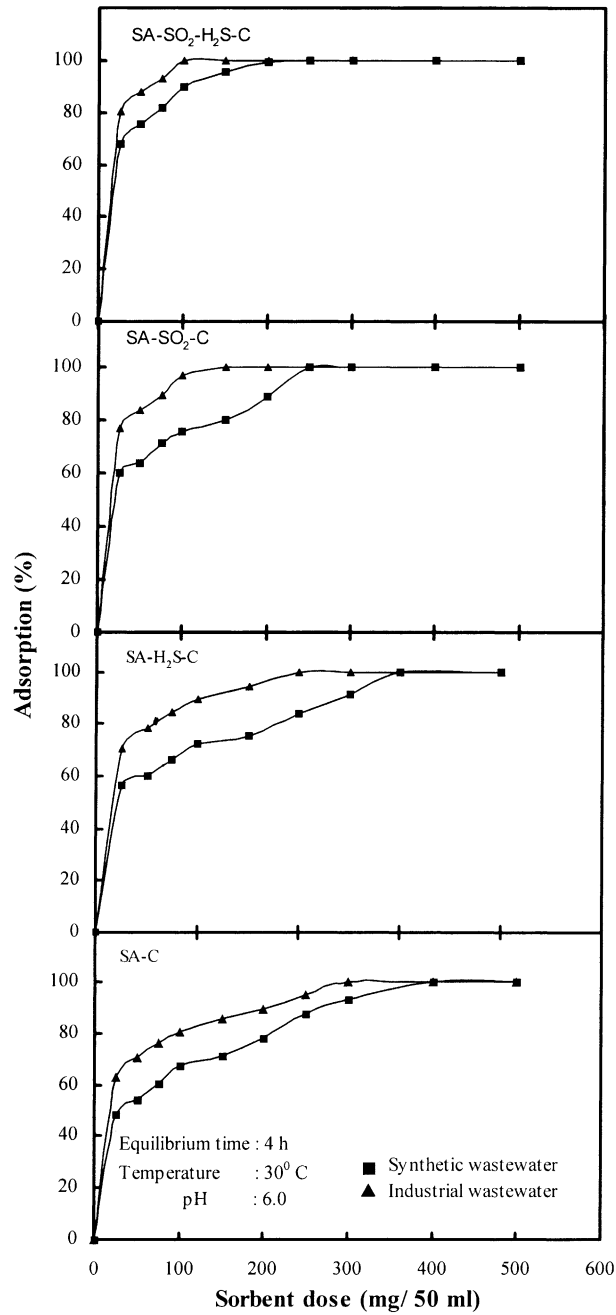


Fig. 8. Effect of sorbent dose for the removal of Hg(II) from synthetic and industrial wastewaters by different activated carbons.

Table 7  
Desorption and regeneration data<sup>a</sup>

Cycle	Adsorption (mg/g)				Desorption at 0.2 M HCl (mg/g)			
	SA-C	SA-H <sub>2</sub> S-C	SA-SO <sub>2</sub> -C	SA-SO <sub>2</sub> -H <sub>2</sub> S-C	SA-C	SA-H <sub>2</sub> S-C	SA-SO <sub>2</sub> -C	SA-SO <sub>2</sub> -H <sub>2</sub> S-C
1	33.27 (66.5)	36.42 (72.8)	43.48 (86.9)	48.50 (97.0)	29.23 (87.9)	32.46 (89.2)	40.34 (90.8)	46.92 (96.7)
2	28.21 (56.4)	33.11 (66.2)	41.21 (82.4)	47.89 (95.8)	23.22 (82.3)	28.51 (86.1)	36.26 (88.0)	45.60 (95.3)
3	24.21 (48.4)	31.01 (62.0)	39.78 (79.6)	47.02 (94.0)	19.44 (80.3)	25.81 (83.2)	33.99 (85.5)	44.44 (94.5)

<sup>a</sup> Values shown in the parenthesis are in percent.

The removal of Hg(II) was found to increase with increase in mass of carbon equilibrated with Hg(II) wastewaters. This may be due to increased adsorbent surface area with the increase of mass of adsorbent. The complete removal of Hg(II) from 50 ml of synthetic and industrial wastewaters was achieved at 200 and 100 mg of SA-SO<sub>2</sub>-H<sub>2</sub>S-C, 250 and 150 mg of SA-SO<sub>2</sub>-C, 300 and 200 mg of SA-H<sub>2</sub>S-C and 400 and 300 mg of SA-C, respectively. From these experimental results, it may be demonstrated that the sulphurised activated carbons can be successfully utilised as adsorbents for treating wastewaters rich in Hg(II) ions.

### 3.10. Desorption and regeneration

Desorption of the adsorbed Hg(II) from the spent adsorbent was also studied. The carbon loaded with the maximum amount of Hg(II) were placed into desorption medium containing 0.2 M HCl and the amount of metal ions desorbed in 4 h was measured. Table 7 shows the results of the adsorption and desorption of mercury on all activated carbons. It can be seen that bound Hg(II) is quantitatively desorbed from the sulphurised carbons to the suspending medium and nearly all sorbed Hg (>95%) on the SA-SO<sub>2</sub>-H<sub>2</sub>S-C. The second and third adsorption cycles reveal that sulphurised carbons can be reused with very small loss in efficiency. Approximately 91–97% of the initial desorption capacity is obtained in the third cycle.

The relative cost of the materials used in the present study is very much lower than commercial activated carbons. The bagasse pith is available almost free of cost and after considering the expenses for transport, chemicals and electrical energy; the cost of final adsorbent materials would be approximately US\$ 40 t<sup>-1</sup>. The cost of cheapest variety carbons used for water treatment in India is ≈US\$ 300 t<sup>-1</sup>. Due to the high heating value of bagasse pith village people may use it for making fire briquettes. This is an alternative method of disposal of bagasse pith.

## 4. Conclusions

The present study clearly establishes that sulphurised activated carbons prepared from bagasse pith are very effective adsorbents for Hg(II) removal from aqueous and chlor-alkali industry wastewaters. The adsorption was found to dependent on Hg(II) concentration, pH, particle size, and temperature of the system. The removal of Hg(II) follows a pseudo-second-order kinetics and a monolayer coverage of adsorbent is involved in the adsorption process. Surface complexation and ion-exchange are the major removal mechanisms involved. The adsorption of Hg(II) increased with increasing pH and reached a plateau value at the pH range 4–9 for sulphurised activated carbons and 6–8 for sulphur free carbon. The equilibrium data fit for Langmuir adsorption isotherm and maximum monolayer adsorption capacities of the activated carbons have been calculated. The adsorption process is found to be endothermic in nature and decreases with increase in ionic strength. Complete removal of Hg(II) from synthetic and chlor-alkali industry wastewaters containing 50 and 20 mg/l metal ions, respectively could be achieved. The spent adsorbent can be regenerated and reused by acid treatment.

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