

Utilization of Activated Carbon Prepared from Industrial Solid Waste for the Removal of Chromium(VI) Ions from Synthetic Solution and Industrial Effluent

N. Vennilamani¹, K. Kadirvelu^{2*}, Y. Sameena¹ and S. Pattabhi² (1) *Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore-641 004, India.* (2) *Department of Environmental Science, PSG College of Arts and Science, Coimbatore-641 014, India.*

(Received 8 April 2004; revised form accepted 6 September 2004)

ABSTRACT: Activated carbon (AC) prepared from sago waste was characterized and used to remove chromium(VI) ions from aqueous solution and industrial effluent by adsorption methods using various conditions of agitation time, metal ion concentration, adsorbent dosage particle size and pH. Surface modification of the carbon adsorbent with a strong oxidizing agent like concentrated H₂SO₄ generates more active adsorption sites on the solid surface and pores for metal ion adsorption.

Adsorption of the metal ion required a very short time and led to quantitative removal. Both the Langmuir and Freundlich isotherm models could describe the adsorption data. The calculated values of Q_0 and b were 5.78 mg/g and 1.75 l/min, respectively. An effective adsorption capacity was noted for particle sizes in the range 125–250 μm at room temperature ($30 \pm 2^\circ\text{C}$) and an initial pH of 2.0 ± 0.2 .

The specific surface area of the activated carbon was determined and its properties studied by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR). These studies revealed that AC prepared from sago waste is suitable for the removal of Cr(VI) ions from both synthetic and industrial effluents.

INTRODUCTION

Heavy metals are of major concern because of their non-degradability and threat to human life and the environment. The heavy metals of most important concern are Hg, Pb, Cd, Cr, Zn, Cu, Ni and Mn (Kadirvelu 1998). The heavy metal contamination of the water system has been identified as responsible for various occupational and corporate diseases, death and destruction of flora and fauna. Among several heavy metals, chromium compounds are used extensively in industrial processes such as metal pickling, electroplating, aluminium anodizing and leather tanning, and also in the manufacture of paints, dyes, paper, explosives and ceramics (Dean *et al.* 1991). Discharge of these wastewaters leads to the presence of chromium in receiving water bodies. Although the salts of trivalent chromium are not harmful physiologically, large doses of hexavalent chromium lead to corrosive effects in the intestinal tract and to nephritis. According to the WHO

*Author to whom all correspondence should be addressed. Present address: Centre for Fir, Explosive & Environment Safety (CFEES), Defence Research & Development Organization (DRDO), Timarpur, Delhi-110 054, India. E-mail: kadirvelu@lycos.com.

International Standard for drinking water, the mandatory limit for hexavalent chromium is 0.05 mg/l (Manivasakam 1997). For this reason, it is necessary to remove chromium ions from industrial effluents before these are discharged into water bodies.

Many conventional methods can be adopted for the removal of heavy metals from wastewater. Most of these methods suffer from drawbacks such as high capital and operational costs, and problems regarding the disposal of the residual metal sludge (Kadirvelu 1998). This has resulted in a search for low-cost non-conventional adsorbents for heavy metal removal. The adsorbents used include wastes such as peanut hull carbon (Namasivayam and Periasamy 1993), coir pith carbon (Namasivayam and Kadirvelu 1997, 1999; Kadirvelu *et al.* 2001), parthenium carbon (Kadirvelu *et al.* 2002), sago carbon (Kadirvelu *et al.* 2004a), waste newsprint (Aoyama *et al.* 2000), coconut sawdust carbon (Selvi *et al.* 2001), *Eichhornia* carbon (Shekinah *et al.* 2002), granular activated carbon (Huang and Blarikship 1984), fly ash (Kapoor and Viraraghavan 1994), rice husk carbon (Bishnoi *et al.* 2004), bagasse and fly ash (Rao *et al.* 2002) and soya cake (Daneshvar *et al.* 2002).

Cassava (*Manihot esculenta* Crantz), an important tropical tuber crop, has diverse uses in the food, feed and industrial sectors. It is cultivated in 13 states in India with a total production of 4.46 metric tonnes. Sago is mainly prepared from the fresh roots of cassava plants. The objective of this work is to investigate the adsorption capacity of the activated carbon prepared from sago waste to remove heavy metal ions such as chromium(VI) from aqueous solution and industrial effluent.

EXPERIMENTAL

Adsorbent

The sago waste collected from the sago industry in Salem district, Tamil Nadu State, India, was used as the source for the preparation of activated carbon. This was dried in sunlight for 3 d, the impurities removed and the resulting material activated chemically by the addition of 50% sulphuric acid and ammonium persulphate (0.5%) with constant stirring (w/w) followed by thermal treatment at $120 \pm 5^\circ\text{C}$. The charred material was maintained in a hot air oven at $100 \pm 5^\circ\text{C}$ for 12 h, cooled to room temperature and washed with doubly distilled water. The material was then soaked in a 5% sodium bicarbonate solution and allowed to stand overnight to eliminate the residual acid from the carbon pores. It was subsequently washed again with doubly distilled water until the pH of the wash water attained a value of 7.0 ± 0.5 . The final material was dried in a hot air oven at $100 \pm 5^\circ\text{C}$ for 3 h, ground and sieved to obtain particle sizes of 125–250, 250–500 and 500–710 μm , respectively. The characteristics of activated sago waste carbon are presented in Table 1. The material exhibited considerable hardness and bulk density, was granular in nature and had a low moisture adsorption capacity.

Batch-mode adsorption studies

For the laboratory studies, a stock 1000 mg/l solution of Cr(VI) ions was prepared in doubly distilled water using potassium dichromate. The working solution was obtained by diluting the above stock solution with distilled water. All the chemicals used were of A.R. grade.

Batch-mode adsorption studies were carried out in 100 ml conical flasks. To each flask was added 100 mg adsorbent and 50 ml of a Cr(VI) ion solution of a desired concentration, the initial pH of each solution being 2.0 ± 0.2 . The flasks were agitated at 170 rpm for predetermined time intervals in a mechanical shaker at room temperature ($30 \pm 2^\circ\text{C}$). After agitation, the adsorbent and

TABLE 1. Properties of Activated Carbon Used in this Study

Parameter	Value
pH of 1% solution	7.1
pH _{PZC}	5.7
Moisture (%)	4.33
Cation-exchange capacity (mequiv/g)	0.75
<u>Composition (%)</u>	
Carbon	65.0
Hydrogen	2.0
Nitrogen	3.0
Oxygen (by difference)	30.0
Yield (%)	78.0
Ash (%)	12.0
Apparent density (g/ml)	0.75
Decolourizing power (mg/g)	55.5
Matter soluble in H ₂ O (%)	5.5
Matter soluble in 1 M HCl (%)	8.0
Porosity (%)	80.0
BET surface area (m ² /g)	625.00 ^a
<u>Surface acid groups (mequiv/g)</u>	
Carboxyl (I)	1.20
Lactonic (II)	1.80
Phenolic (III)	0.90
Carbonyl (IV)	1.60
Total basic groups (mequiv/g)	1.10
Pore volume (ml/g)	0.67

^aBET surface area corresponds to a particle size of 125–250 μm .

adsorbate were separated by centrifugation at 6000 rpm for 20 min and the Cr(VI) ion content estimated spectrophotometrically at 540 nm using diphenylcarbazide. The effect of agitation time on the percentage removal was studied using Cr(VI) ion solutions with concentrations between 5 mg/l and 20 mg/l. Similarly, the effect of carbon dosage was examined using Cr(VI) ion solutions of 10 mg/l and 20 mg/l concentration and varying the dosage from 25 mg to 500 mg. Such studies enabled the Freundlich adsorption isotherm to be applied to the data obtained. The effect of adsorbent particle size on the removal of Cr(VI) ions was also obtained using Cr(VI) ion solutions of 10 mg/l concentration, while the effect of pH on such removal was studied using 10 mg/l and 20 mg/l concentration Cr(VI) ion solutions.

The metal ion concentration in the adsorbent phase (q_e , mg/g), was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and final concentrations of metal ion in solution (mg/l), V is the volume of the solution (ml) and M is the mass of adsorbent (mg).

TABLE 2. Characteristics of Chromium Plating Wastewater

Parameter	Value
pH	2.5
Total solids (mg/l)	9526
Total suspended solids (mg/l)	736
Calcium (mg/l)	170
Sodium (mg/l)	295
Potassium (mg/l)	15
Chloride (mg/l)	430
Sulphate (mg/l)	43
Chromium (mg/l)	30

Studies were also undertaken using the wastewater from Electroplating Industries, Coimbatore, India. In this case, 50 ml samples of a 10% solution of wastewater were adjusted to different pH values and agitated for 75 min with 100 mg adsorbent with particle sizes in the range 125–250 μm . The effect of agitation time on the percentage removal of Cr(VI) ions from the industrial effluent was studied by agitating a 10% solution of wastewater with an initial pH of 2.0 ± 0.2 for 5 h. The effect of carbon dosage on the percentage removal of Cr(VI) ions from the effluent was also studied by agitating 50 ml samples of a 10% solution of wastewater at an initial pH of 2.0 ± 0.2 with various amounts of adsorbent (50–1000 mg) for 75 min. Some of the characteristics of raw wastewater are listed in Table 2.

Desorption studies

After adsorption experiments employing 50 ml of the Cr(VI) ion solution and 100 mg carbon, the metal ion-laden carbon was carefully separated from the aqueous solution. The solid material was then gently washed with doubly distilled water to remove any unadsorbed metal ions. Desorption studies were carried out by agitating the metal-loaded carbon with 50 ml of an aqueous solution of NaOH of various strengths (0.01 N to 0.1 N). The adsorbent was then separated from the aqueous solution by centrifugation and the supernatant analyzed as before.

Control experiments were undertaken to allow for any adsorption of Cr(VI) ions onto the container walls. No such adsorption was observed. All experiments were carried out in duplicate with the maximum deviation observed being 3%.

RESULTS AND DISCUSSION

Adsorbent characterization

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using a JSM-840 microscope (JEOL Techniques Ltd., Japan) at 2500 \times magnification (Figure 1). At such magnification, the activated carbon particles showed rough areas of surface within which micropores were

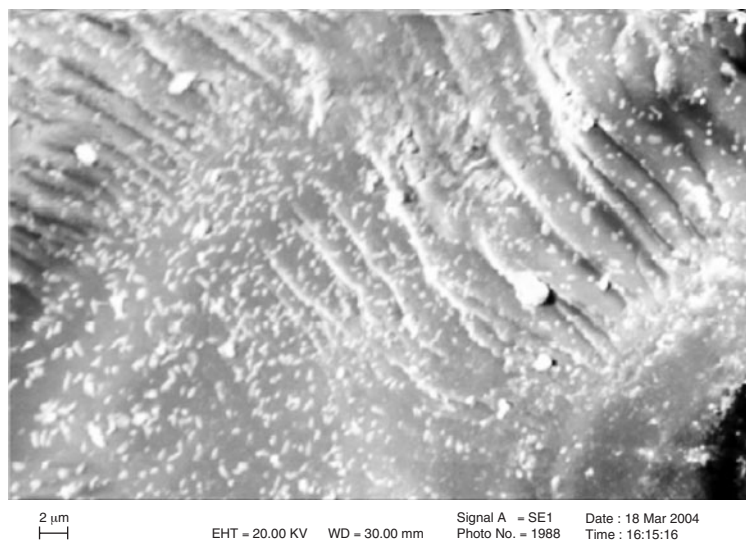


Figure 1. SEM micrograph of the surface of sago waste carbon. Magnification = 2500 \times .

clearly identifiable. The BET surface area ($625 \text{ m}^2/\text{g}$) was higher than those of some other carbons prepared from agricultural wastes such as peanut hull ($208 \text{ m}^2/\text{g}$), coir pith ($595 \text{ m}^2/\text{g}$), *Eichhornia* ($266 \text{ m}^2/\text{g}$), cassava peel ($200 \text{ m}^2/\text{g}$) and coconut tree sawdust ($325 \text{ m}^2/\text{g}$). Such an enhanced surface area is ideal for adsorption processes.

Specific acidic groups were also measured using Boehm's method with the results again being comparable with those for activated carbons prepared from other agricultural wastes (Kadirvelu *et al.* 2004b). Such acidic surface groups are generally located at points where a wide microporosity occurs since their generation depends on the ability of the oxidizing molecule to diffuse into the carbon pores (El-Hendawy 2003). It was found that high concentrations of lactonic groups were present in the activated carbon along with carbonyl, carboxyl basic and phenolic groups. It has been reported that carboxyl groups dissociate within the pH range 3.0–7.0. Heavy metal adsorption onto activated carbons is due to a series of reactions involving the metal ions and the organic functional groups in the carbons (Chen and Wu 2004).

Influence of agitation time and initial metal ion concentration on the removal of Cr(VI) ions

The data depicted in Figure 2 show the effect of agitation time on the percentage removal of Cr(VI) ions from aqueous solution by an activated carbon prepared from sago waste. The removal rate was rapid initially and then gradually diminished to attain an equilibrium value beyond which there was no significant increase in the rate of removal. Such equilibrium was attained within 90 min for all the Cr(VI) ion concentrations studied (5 to 20 mg/l). It should be noted that the contact time required for all metal ion concentrations was very short which is an important parameter for economic wastewater treatment applications.

Separate curves were obtained for each Cr(VI) ion concentration. Each was smooth and continuous up to the saturation point on the activated carbon surface. The results obtained also show

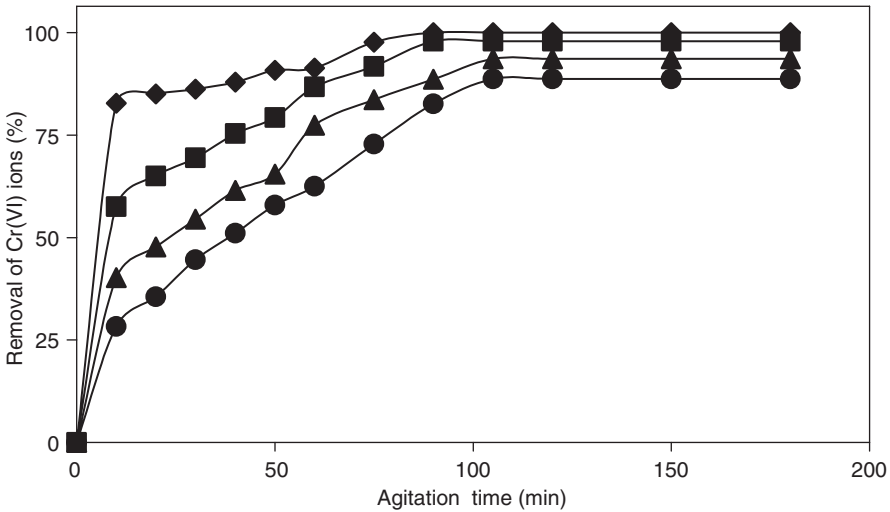


Figure 2. Effect of agitation time and initial Cr(VI) ion concentration on the adsorption of Cr(VI) ions onto sago waste carbon. Data points refer to the following initial Cr(VI) ion concentrations: \blacklozenge , 5 mg/l; \blacksquare , 10 mg/l; \blacktriangle , 15 mg/l; \bullet , 20 mg/l.

that although the equilibrium adsorption increased with increasing metal ion concentration, this increase was not proportional to the initial metal ion concentration, i.e. a two-fold increase in the metal ion concentration did not lead to a doubling of the equilibrium adsorption capacity. This is related to the finite surface area of the substrate on which the competitive adsorption of metal ions occurred. The curves shown in Figure 2 may be sub-divided into two distinct regions: the first corresponds to the initial portion of the curve which increases linearly, while the second corresponds to the curved section following the initial increase which differs for different metal ion concentrations. The plateau portion of the curve corresponds to pore diffusion while the initial linear portion reflects surface layer diffusion (Namasivayam and Kadirvelu 1999).

The effect of agitation time on the percentage removal of Cr(VI) ions from industrial effluent is shown in Figure 3 which indicates that 90% removal required agitation for 200 min.

Adsorption kinetics

The rate of Cr(VI) ion adsorption onto sago waste carbon followed a first-order rate expression of the kind given by Lagergren:

$$\log_{10}(q_e - q) = \log_{10}q_e - \frac{K_{\text{ads}} t}{2.303} \quad (2)$$

where q and q_e are the amounts of metal ion adsorbed by the adsorbent at time 't' and at equilibrium, respectively, while K_{ads} is the adsorption rate constant expressed in 1/min units. The linear plots of $\log_{10}(q_e - q)$ versus t obtained for the various metal ion concentrations studied (Figure 4) indicate the applicability of the above equation to the adsorption of Cr(VI) ions from aqueous solution onto the activated carbon employed. Values of K_{ads} were calculated from the slopes of the linear plots and are listed in Table 3.

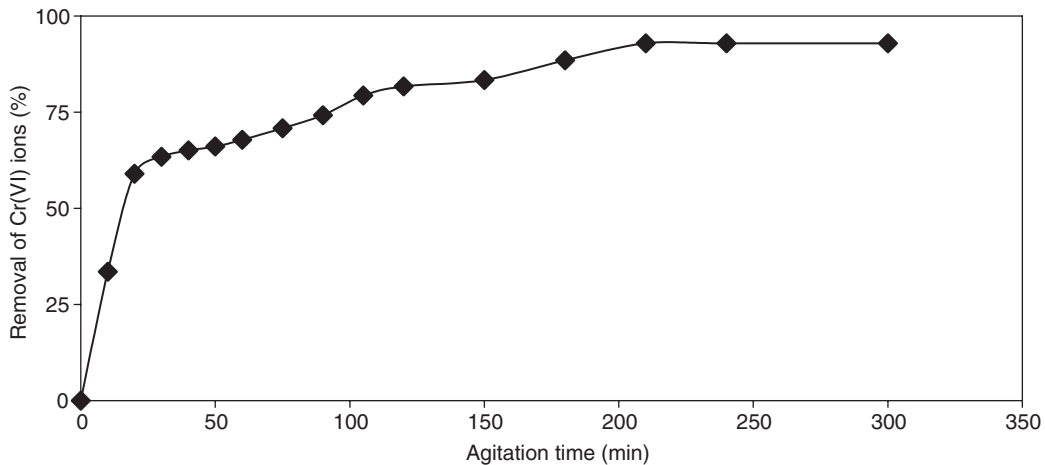


Figure 3. Effect of agitation time on the adsorption of Cr(VI) ions from a 10% solution of wastewater derived from an electroplating process onto sago waste carbon.

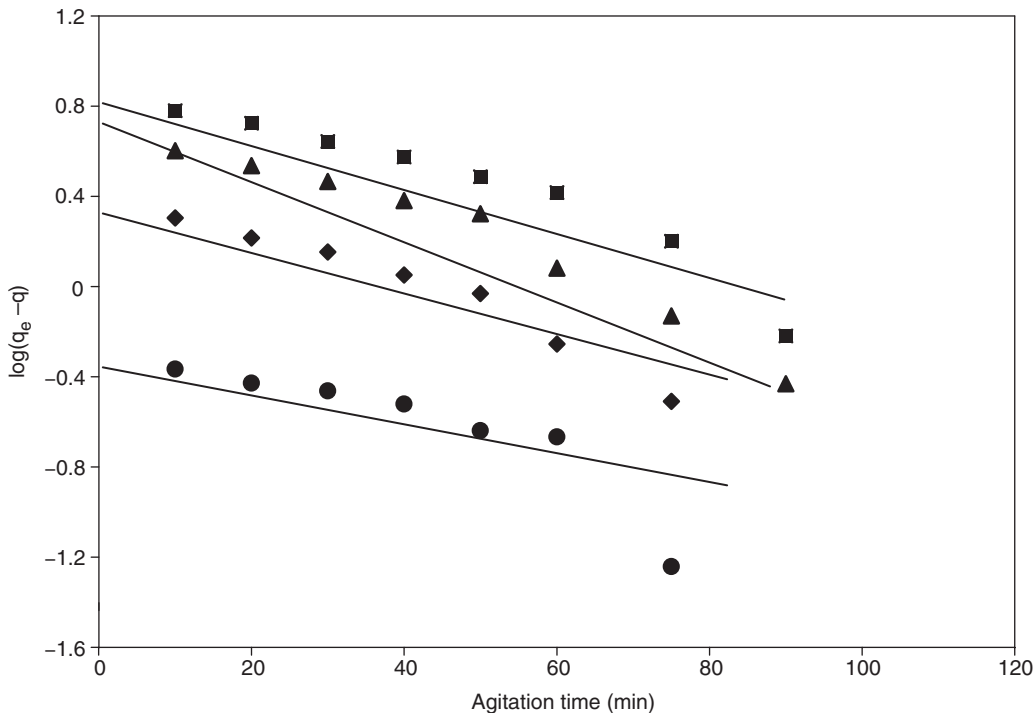


Figure 4. First-order Lagergren plots for the adsorption of Cr(VI) ions from aqueous solution onto sago waste carbon. Data points refer to the following initial Cr(VI) ion concentrations: ●, 5 mg/l; ◆, 10 mg/l; ▲, 15 mg/l; ■, 20 mg/l.

TABLE 3. Adsorption Rate Constant for Cr(VI) Ion Adsorption

Cr(VI) ion conc.(mg/l)	K_{ads} (1/min)
5	0.026
10	0.028
15	0.029
20	0.026

If intraparticle mass transfer is the rate-limiting step for adsorption, the plot of metal ion uptake q_c (mg/g) versus $t^{1/2}$ would be linear. If the line passes through the origin, intraparticle diffusion is the controlling step (Kadirvelu *et al.* 2000). The kinetic plots were modelled to allow the initial adsorption coefficients γ [l/(mg min)] (Kadirvelu *et al.* 2000) to be computed. These were found to be 3.75, 4.85, 7.10 and 8.85 mg/g for 5, 10, 15 and 20 mg/l Cr(VI) ion concentrations, respectively. The initial adsorption coefficient was calculated using the following equation:

$$\gamma = \left(\frac{dC}{dt} \right)_{t \rightarrow 0} \frac{V}{mC_0} \quad (3)$$

where t is the time (min), C is the metal ion concentration at time t (mg/l), V is the volume (ml) and m is the mass of carbon (mg) employed.

Influence of sago waste carbon dosage on the removal of Cr(VI) ions

Figure 5 shows the effect of carbon dosage on the percentage removal of Cr(VI) ions. It will be seen that when the carbon dosage increased, the percentage removal also increased. Thus, it was found that the removal of 10 and 20 mg/l Cr(VI) ions from 1000 ml of aqueous solution required 4.4 g and 8.0 g carbon, respectively. The effect of carbon dosage on the percentage removal of Cr(VI) ions from industrial effluent is shown in Figure 6. In this case, it was found that a 10% solution of wastewater required 500 mg adsorbent for the complete removal of Cr(VI) ions. The increase in sago waste carbon dosage necessary to achieve an increase in the percentage removal of metal ions is due to the availability of more active functional groups at higher carbon doses. Similar results have been reported by several other authors (Kadirvelu *et al.* 2004a).

Increasing percentage removal of Cr(VI) ions with increasing adsorbent dose may be due to the availability of more and more surface for solute adsorption. The removal efficiency of metal ions is affected by the initial metal ion concentration, with such removal decreasing with increasing concentration at a constant pH value of 4.5. This can be explained in terms of a low metal/carbon ratio. Since metal ion adsorption involves high-energy sites, such sites become saturated as the metal/carbon ratio increases so that adsorption can only proceed at lower energy sites. This, in turn, leads to a decrease in adsorption efficiency (Kadirvelu *et al.* 2000, 2001, 2004a). However, the very slow increase in removal beyond the optimum dose may be attributed to the attainment of equilibrium between the adsorbate and adsorbent under the operating conditions employed. This effect has been termed the "solid concentration effect", i.e. the overcrowding of particles (Sharma and Forster 1993).

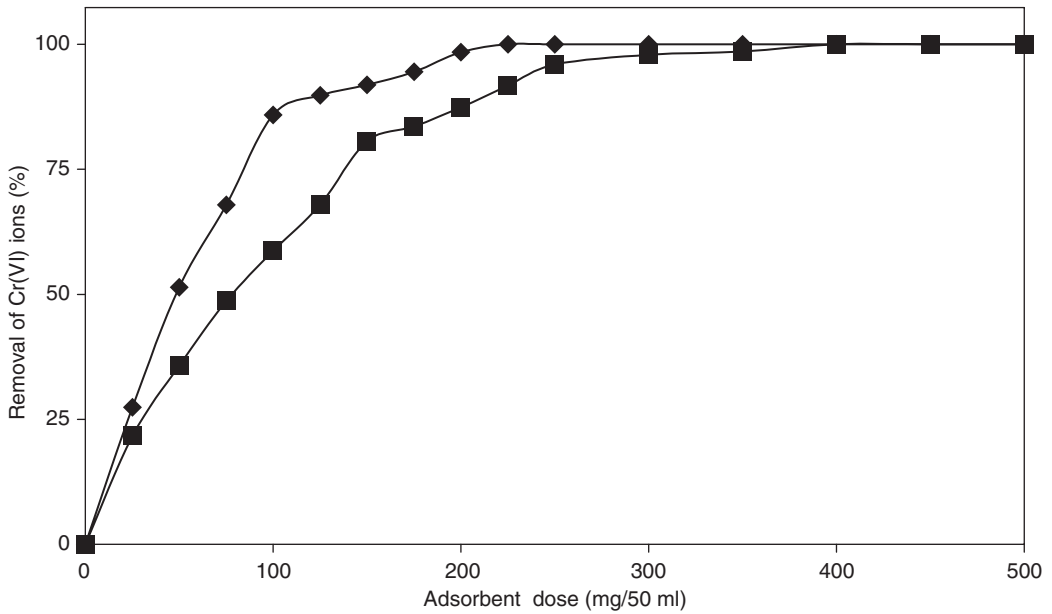


Figure 5. Effect of sago waste carbon dose on the adsorption of Cr(VI) ions. Data points correspond to the following initial Cr(VI) ion concentrations: \blacklozenge , 10 mg/l; \blacksquare , 20 mg/l.

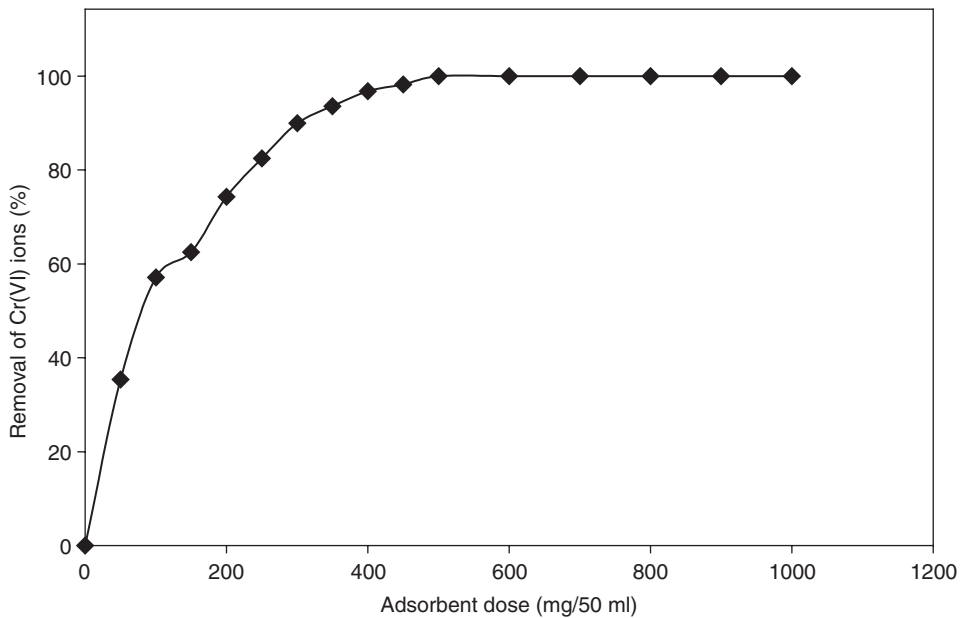


Figure 6. Effect of sago waste carbon dose on the adsorption of Cr(VI) ions from a 10% solution of wastewater derived from an electroplating process.

Adsorption isotherms

Several mathematical models, such as those derived by Langmuir and Freundlich, are capable of describing the distribution of metal ions between the liquid phase and the solid phase. It is very important to have a satisfactory description of the equilibrium state between the two phases in order to successfully represent the dynamic behaviour of any adsorbate from solution to the solid (carbon) phase. The adsorption isotherm may be defined as a functional expression at constant temperature for the variation in adsorption by an adsorbent as the concentration of adsorbate in the bulk solution is varied (Kadirvelu *et al.* 2004b; Namasivayam and Kadirvelu 1999).

The Langmuir model (Langmuir 1918) assumes that the uptake of metal ions onto a homogeneous surface occurs via the formation of a monolayer without any interaction between the adsorbed ions. Thus, the Langmuir isotherm can be applied to the adsorption equilibrium of Cr(VI) ions onto sago waste carbon:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount of Cr(VI) ions adsorbed (mg/g), and Q_0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e versus C_e depicted in Figure 7 shows that the adsorption followed the Langmuir isotherm model. The corresponding values of Q_0 and b obtained from the plot were 5.78 mg/g and 1.75 l/min, respectively. The Langmuir isotherm can also be expressed in terms of a dimensionless separation factor or equilibrium parameter (McKay *et al.* 1982) that can be written as:

$$R_L = 1/(1 + bC_0) \quad (5)$$

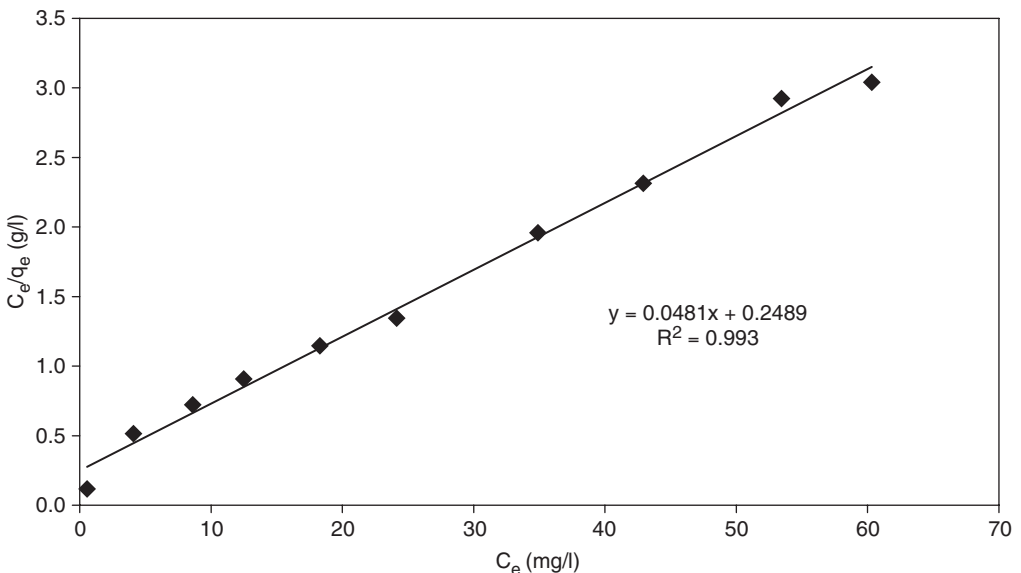


Figure 7. Application of the Langmuir equation to the adsorption of Cr(VI) ions onto sago waste carbon.

where C_0 is the initial Cr(VI) ion concentration in mg/l and b is the Langmuir constant (l/mg). The magnitude of the R_L value may be related to the type of isotherm obtained as given in the following table:

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The Freundlich model (Freundlich and Heller 1939) assumes that the uptake of metal ions onto a homogeneous surface occurs by monolayer adsorption. The linear form of this equation may be written as:

$$\log_{10} \left(\frac{x}{m} \right) = \log_{10} K_f + 1/n \log_{10} C_e \quad (6)$$

where x is the amount of Cr(VI) ions adsorbed at equilibrium (mg), m is the weight of adsorbent used (mg), C_e is the equilibrium concentration of Cr(VI) ions in solution (mg/l), and K_f and n are constants. The linear plot of $\log_{10}(x/m)$ versus $\log_{10} C_e$ depicted in Figure 8 shows that the adsorption also obeyed the Freundlich isotherm. The Freundlich constants K_f and n were found to be 4.3516 and 1.6974, respectively, at a Cr(VI) ion concentration of 10 mg/l. According to Treybal (1980), mathematical calculations have shown that n values between 1 and 10 represent a beneficial adsorption process.

From the correlation coefficients (R^2) for the plots depicted in Figures 7 and 8, the experimental data showed a closer fit to the Langmuir isotherm ($R^2 = 0.9930$) than to the Freundlich isotherm ($R^2 = 0.9294$). This suggests that the adsorbent was homogeneous and leads to the conclusion that the surface of the adsorbent was composed of small particles.

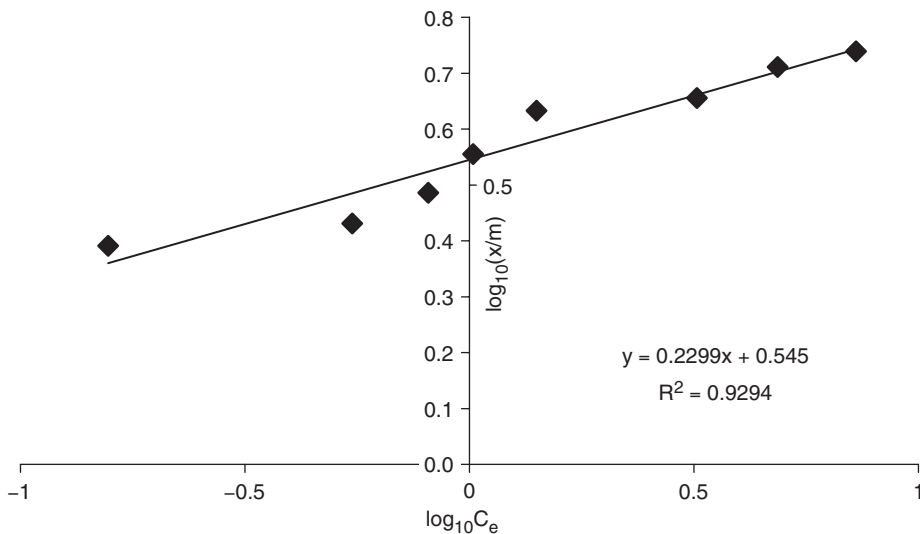


Figure 8. Application of the Freundlich equation to the adsorption of Cr(VI) ions onto sago waste carbon.

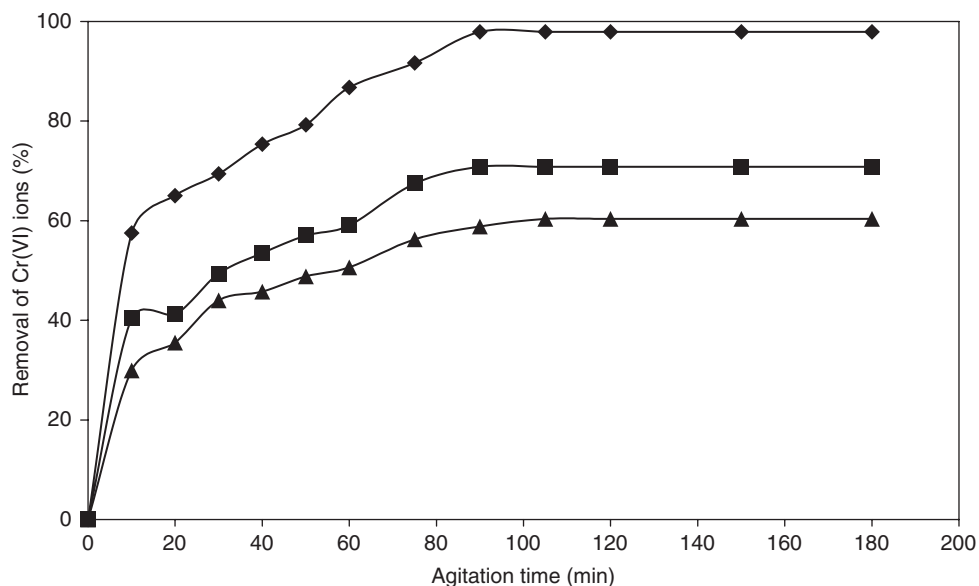


Figure 9. Influence of adsorbent particle size on the removal of Cr(VI) ions from aqueous solution by sago waste carbon. Data points relate to the following particle size ranges: ◆, 125–250 μm ; ■, 250–500 μm ; ▲, 500–710 μm .

Influence of adsorbent particle size on the removal of Cr(VI) ions

Figure 9 shows that the percentage removal of Cr(VI) ions decreased with increasing particle size of the adsorbent, with the percentage removal for particle sizes within the ranges 125–250, 250–500 and 500–710 μm being 97.92%, 70.84% and 60.36%, respectively. The equilibrium times attained for these particle size ranges were 90, 90 and 105 min, respectively. A higher percentage removal with lower particle sizes is due to the availability of more surface area for adsorption (Anoop and Anirudhan 2002). Because adsorption is a surface phenomenon, smaller adsorbent particles offer a comparatively larger and more accessible surface area; hence, greater adsorption occurs at equilibrium. According to Asfour *et al.* (1985), disruption of a larger particle tends to open tiny cracks and channels on the particle surface, thereby providing added surface area that can be employed in the adsorption process. The present study therefore reveals that the size of the adsorbent played an important role in the adsorption of Cr(VI) ions onto sago waste carbon.

Influence of pH on the removal of Cr(VI) ions

The effect of pH on the removal of Cr(VI) ions from aqueous solution is depicted in Figure 10. The data depicted show that, when the pH value was decreased from 9.0 to 2.0, the amount adsorbed increased from 30% to 89.97% at an initial Cr(VI) ion concentration of 10 mg/l and from 28.81% to 81.16% at an initial Cr(VI) ion concentration of 20 mg/l. This indicates that the adsorption capacity of the adsorbent was clearly pH-dependent. It is clear that the pH generates a favourable surface charge on the adsorbent surface to facilitate the removal of Cr(VI) ions.

In aqueous solution, chromium mainly exists in two oxidation states, i.e. Cr(VI) and Cr(III), whose stability is dependent on the pH of the system (Kobyta 2004). Although potassium

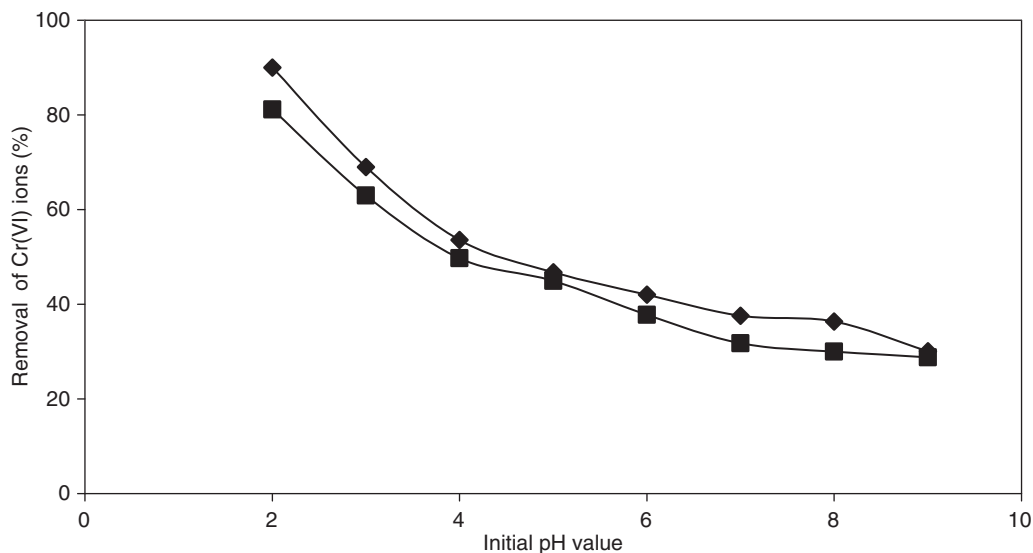
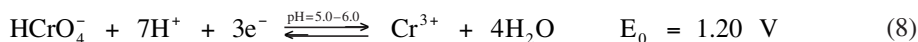


Figure 10. Influence of initial pH value on the removal of Cr(VI) ions from aqueous solution by sago waste carbon. Data points refer to the following initial Cr(VI) ion concentrations: \blacklozenge , 10 mg/l; \blacksquare , 20 mg/l.

dichromate was used as the source of Cr(VI) ions in the synthetic wastewater, under neutral pH conditions (pH = 6.0) the predominant form of Cr(VI) is HCrO_4^- which arises from the hydrolysis reaction of the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) according to the equation:



In acid solution and when there is intimate contact between the adsorbent and adsorbate, Cr(VI) demonstrates a very high positive redox potential (E_0) which lies within the range 1.33–1.38 V. This shows that Cr(VI) is unstable in the presence of electron donors and is strongly oxidizing. The surface of the activated carbon contains carboxylic, phenolic, carbonyl and lactonic groups that can act as electron donors in solution. In the presence of such electron donors, the Cr(VI) oxyanion is readily reduced to Cr(III) ions via the following electron-transfer process:



This equation indicates that the reduction of the Cr(VI) oxyanion is accompanied by a considerable consumption of protons from the acidic solution, thus confirming the decisive role played by the H^+ ion in the removal of Cr(VI) ions (Babel and Kurniawan 2004). As the pH increases, the degree of surface protonation is gradually reduced leading to a reduction in adsorption (Kobya 2004).

The adsorption of heavy metal ions such as Cr^{3+} , Pb^{2+} , Cu^{2+} onto activated carbons occurs via a series of reactions between the metal ions and the organic functional groups on the carbon surface. Thus, in the adsorption of Cu^{2+} ions onto a sulphuric acid-modified carbon, the concentration of acidic surface oxides on the carbon surface increased and this led to the occurrence of cation-exchange reactions (Chen and Wu 2004).

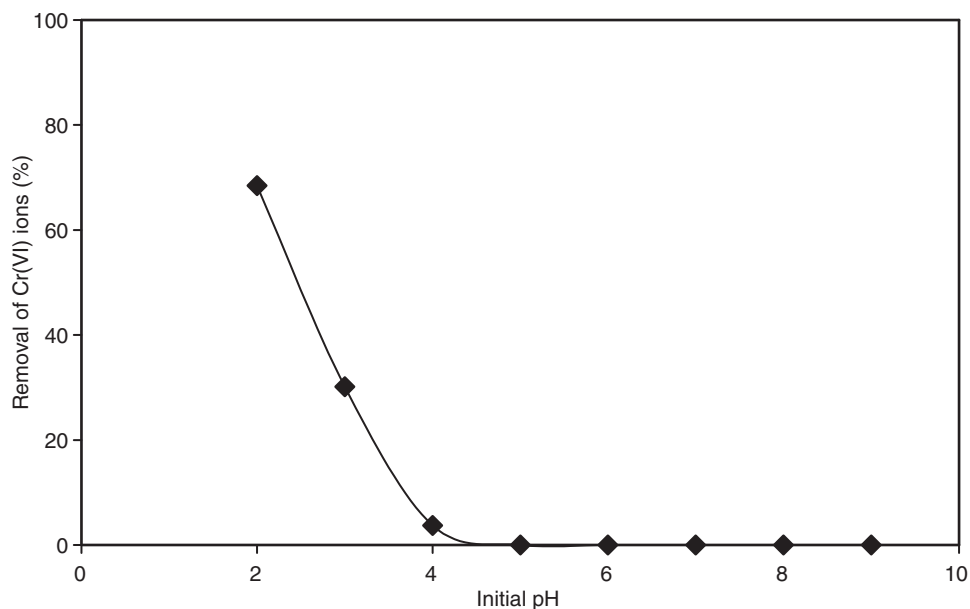


Figure 11. Influence of pH value on the removal of Cr(VI) ions from a 10% solution of wastewater derived from an electroplating process.

The influence of pH on the removal of Cr(VI) ions from wastewater derived from an electroplating process is depicted in Figure 11. The increased removal at lower pH values may be attributed to the increased number of negatively charged groups on the sago waste carbon surface under these circumstances leading to a higher uptake. The low removal efficiency at higher pH may be due to covalent coordinate bonding between Cr(III) ions and surface functional groups of the activated carbon, such as carboxylic and hydroxyl which are very weak under basic conditions (Babel and Kurniawan 2004).

Desorption studies

Desorption studies were conducted in an attempt to regenerate the metal ion from the metal ion-laden carbon using aqueous NaOH solutions of various strengths in the range 0.01–0.2 N. The results obtained are depicted in Figure 12 which shows that this desorption method gave quite poor results. This may be a reflection of the strong electrostatic interaction between the Cr(VI) ion and the functional groups on the surface of the sago waste carbon.

FT-IR spectroscopic studies

Several absorption peaks appearing in the FT-IR spectra of both the sago waste carbon and its chromium ion-laden form indicate the complex natures of the materials examined. Thus, a broad band at ca. $3200\text{--}3600\text{ cm}^{-1}$ in the spectrum of the initial sago waste carbon may be assigned to --OH stretching vibrations possibly associated with the interaction between physically adsorbed water and the hydroxyl groups on the carbon surface (Chen and Wu 2004). It should be noted that

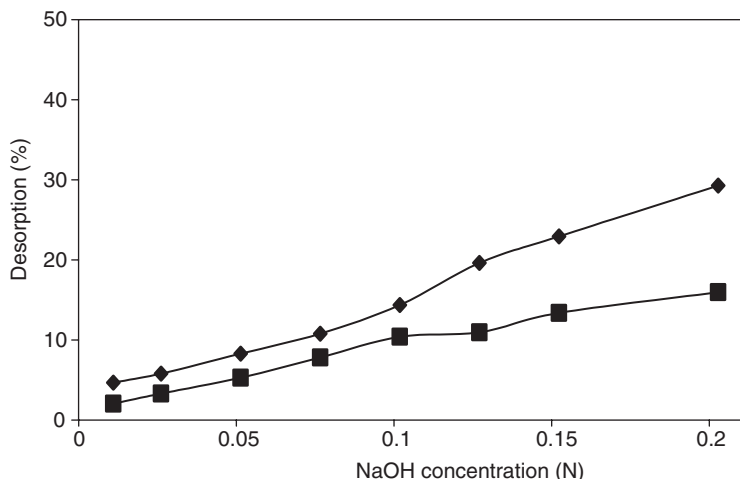


Figure 12. Desorption of Cr(VI) ions from sago waste carbon. The data points relate to the following initial concentrations from which Cr(VI) ions were adsorbed: ◆, 10 mg/l; ■, 20 mg/l.

after the adsorption of Cr(VI) ions onto the carbon surface this broad band narrowed as a result of the electrostatic binding of Cr(III) ions with the surface functional groups. The peak at 2923.9 cm^{-1} in the spectrum of the original sago waste carbon may be assigned to a C–H stretch while the peaks at 2360.7 cm^{-1} are associated with double-bonded C=O groups. In turn, the broad band at 616.2 cm^{-1} may be assigned to overlapping of the aromatic ring stretching vibrations with the bands of the carboxylate moieties, while the broad band at ca. $1000\text{--}1200\text{ cm}^{-1}$ may be due to the presence of functional groups containing single-bonded oxygen atoms such as phenols, ethers and lactones (Chen and Wu 2004). Many of these bands experienced a shift in frequency when Cr(III) ions were adsorbed onto the sago waste carbon surface. This may be due to coordinate covalent bonding between the Cr(III) ion and the surface functional groups of the sago waste activated carbon.

CONCLUSIONS

The following conclusions may be drawn from the studies undertaken:

1. Activated carbon prepared from sago waste can be used for the effective removal of Cr(VI) ions from both aqueous solution and industrial effluent.
2. Such adsorption depends on the solution pH, the initial Cr(VI) ion concentration, the carbon dose employed and the particle size of the adsorbent.
3. The adsorption process followed both the Langmuir and Freundlich isotherm models.
4. The adsorption capacity of sago waste carbon was found to be 5.78 mg/g at an initial pH of 2.0 ± 0.2 at room temperature ($30 \pm 2^\circ\text{C}$) for a particle size in the range $125\text{--}250\text{ }\mu\text{m}$.
5. The adsorption of Cr(VI) ions onto sago waste carbon follows the usual kinetic models.
6. The use of NaOH for the desorption of Cr(VI) ions from the sago waste carbon surface was not satisfactory.
7. FT-IR studies confirmed the presence of coordinate covalent bonding between Cr(III) ions and the donor atoms associated with surface functional groups.

8. Analysis of SEM images showed that the sago waste surface was rough and possessed micropores.

ACKNOWLEDGEMENTS

One of the authors (K.K.) expresses his thanks to the Council of Scientific and Industrial Research (C.S.I.R.) for the award of a research associate fellowship. The authors are also grateful to Dr. B. Sampathkumar, Principal and Secretary of PSG College of Arts and Science, for his constant encouragement and support.

REFERENCES

- Anoop, K.K. and Anirudhan, T.S. (2002) *J. Hazard. Mater.* **B92**, 161.
- Aoyama, M., Seki, K., Kasai, A., Kurimoto, Y., Chen, K. and Doi, S. (2000) *Environ. Technol.* **21**, 1013.
- Asfour, H.M., Nazar, M.M., Fadoli, O.A. and Geundi, M.S.E. (1985) *J. Chem. Technol. Biotechnol.* **35**, 28.
- Babel, S. and Kurniawan, T.A. (2004) *Chemosphere* **54**, 951.
- Bishnoi, N.R., Bajaj, M., Sharma, N. and Gupta, A. (2004) *Bioresource Technol.* **91**, 305.
- Chen, J.P. and Wu, S. (2004) *Langmuir* **24**, 2233.
- Daneshvar, N., Salari, D. and Aber, S. (2002) *J. Hazard. Mater.* **B94**, 49.
- Dean, J.B., Bosqui, F.L. and Lanouette, K.H. (1991) *Environ. Sci. Health A* **54**, 29.
- El-Hendawy, A.A. (2003) *Carbon* **41**, 713.
- Freundlich, H. and Heller, W. (1939) *J. Am. Chem. Soc.* **61**, 28.
- Huang, C.P. and Blarickenship, D.W. (1984) *Water Res.* **18**, 37.
- Kadirvelu, K. (1998) *PhD Thesis*, Bharathiar University, Coimbatore, India.
- Kadirvelu, K., Faur-Brasquet, C. and Le Cloirec, P. (2000) *Langmuir* **16**, 8404.
- Kadirvelu, K., Thamaraiselvi, K. and Namasivayam, C. (2001) *Sep. Purif. Technol.* **24**, 495.
- Kadirvelu, K., Kanmani, P., Senthilkumar, P. and Subburam, V. (2004) *Adsorp. Sci. Technol.* **22**, 207.
- Kadirvelu, K., Sivasankari, C., Jambuligam, M. and Pattabhi, S. (2002) *Indian J. Chem. Technol.* **9**, 499.
- Kadirvelu, K., Kavipriya, M., Karthika, C., Vennilamani, N. and Pattabi, S. (2004) *Carbon* **42**, 745.
- Kapoor, A. and Viraraghavan, T. (1994) *Adsorp. Sci. Technol.* **11**, 130.
- Knocke, W.R. and Hemphill, L.H. (1991) *Water Res.* **25**, 225.
- Koby, M. (2004) *Bioresource Technol.* **91**, 321.
- Kumar, P. and Dara, S.S. (1991) *J. Polym. Sci., Polym. Chem.* **19**, 397.
- Lagergren, S. (1898) *K. Sven. Vetenskapsakad. Handl.* **24**, 1.
- Langmuir, I. (1918) *J. Am. Chem. Soc.* **40**, 1361.
- Manivasakam, N. (1997) *Physico-Chemical Examination of Water, Sewage and Industrial Effluents*, Coimbatore, India, pp. 142–143.
- McKay, G., Blair, M.S. and Gardner, T.K. (1982) *J. Appl. Polym. Sci.* **27**, 3043.
- Namasivayam, C. and Kadirvelu, K. (1997) *Chemosphere* **34**, 377.
- Namasivayam, C. and Kadirvelu, K. (1999) *Carbon* **37**, 79.
- Namasivayam, C. and Periasamy, K. (1993) *Water Res.* **27**, 1663.
- Rao, M., Parwate, A.V. and Bhole, A.G. (2002) *Waste Manage.* **22**, 821.
- Selvi, K., Pattabi, S. and Kadirvelu, K. (2001) *Bioresource Technol.* **80**, 87.
- Sharma, D.C. and Forster, C.F. (1993) *Water Res.* **27**, 1201.
- Shekinah, P., Kadirvelu, K., Kanmani, P., Senthilkumar, P. and Subburam, V. (2002) *J. Chem. Technol. Biotechnol.* **77**, 458.
- Treybal, R.E. (1980) *Mass Transfer Operations*, 3rd Edn, McGraw-Hill, New York.
- Waics, A.C., Willey, M.E., Kohnle, J.A., Potter, A.L. and McCready, R.M. (1993) *Environ. J. Qual.* **2**, 369.