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Removal of Lead Ion from Industrial Wastewaters by Activated Carbon Prepared from Periwinkle Shells (*Typanotonus fuscatus*)

M. A. O. BADMUS, T. O. K. AUDU and B. U. ANYATA
Department of Chemical Engineering, University of Benin, Benin-City-NIGERIA
e-mail: badmusolalekan@yahoo.com

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Abstract

Lead adsorption from industrial wastewater was studied with the aim of detoxifying industrial effluents before their safe disposal onto land or into river waters. Activated periwinkle shell carbon (PSC) was prepared and characterised for various physiochemical properties. To determine lead(II) removal capacity, the performance of PSC was compared with that of commercial activated carbon (CAC) and a mixture of PSC and CAC (PSC: CAC) in a ratio 1:1. The effect of various parameters such as adsorbent dose, contact time, pH, agitation speed, and particle size of the adsorbent was studied to optimise the conditions for maximum adsorption. Batch adsorption kinetic experiments revealed that the adsorption of Pb(II) onto PSC involved fast and slow processes. The mechanisms of the rate of adsorption were analysed using the Elovich equation and a pseudo-second-order model. It was found that the adsorption mechanisms in the lead/adsorbent system follow pseudo-second-order kinetics with a significant contribution from film diffusion. The adsorption isotherms were described by means of the Langmuir and Freundlich isotherms and both models represent the adsorption process. The percentage removal of lead onto PSC, PSC:CAC, and CAC was 82.78%, 92.68%, and 88.44%, respectively.

Key words: Lead, Adsorption, Kinetics, Periwinkle shell, Wastewater.

Introduction

Metals and their compounds are indispensable to the industrial, agricultural, and technological advancement of any nation. The numbers of applications of metals for commercial uses continue to grow with the developments in modern science and technology.

Industrial processes and spent commercial (metallic) products generate large quantity of metallic waste products, which are discharged into the water or land-dump sites. It has been estimated that the toxicity due to metallic discharge annually into the environment far exceeds the combined total toxicity of all radioactive and organic wastes as measured by the quantity of waste required to dilute such wastes to the drinking water standard (Nriagu, 1981; Bready and Weil, 1999; Abdus-Salam and Adekola, 2005).

Lead contamination of the environment is primarily due to anthropogenic activities, making it the most ubiquitous toxic metal in the environment (Amdur et al., 1991; WHO and ILO, 1995). Research on Pb has become a dominant topic for environmental and medical scientists for 2 obvious reasons: (i) it has no known biological use, and (ii) it is toxic to most living things (Abdus-Salam and Adekola, 2005).

Lead is a metal ion toxic to the human biosystem, and is among the common global pollutants arising from increasing industrialisation. The assimilation of relatively small amounts of lead over a long period of time in the human body can lead to the malfunctioning of the organs and chronic toxicity. The toxic effects of lead ions on humans, when present above the threshold level in the hydrosphere, are well documented (Khurshid and Qureshi, 1984). Previously, various researchers have studied the adsorption of heavy metal ions from solution using naturally occurring minerals. Pyrolusite has been used for adsorption of lead and magnesium ions from their aqueous solution (Ajmal et al., 1995). Zeolites have been used for the removal of heavy metals from wastewater (Yuan et al., 1999). Sigworth and Smith (1972), and Muscas (1995) have also used adsorption techniques for the removal of heavy metals from polluted water. Other adsorbents that have been used for the removal of heavy metals solution include soils (Campbell and Davies, 1995) and carbonaceous material developed from fertiliser waste slurry (Srivestava et al., 1989). Adsorption of heavy metal ions from polluted water by activated carbons from date pits (Girgis and Hendawy, 1997) and by ferrite and chelating resin method (Tokunaga and Uthium, 1997) has also been studied. Other researchers reported the adsorption of lead on oxide of silicon, manganese, aluminium (Bilinshi et al., 1977), bentonite (Kozar et al., 1992), hydrated titanium dioxide (Abe et al., 1989), modified silica gel (Volkan et al., 1987; Mareira et al., 1990), dithizone-anchored poly (EDGMA-HEMA) micro beads (Salih et al., 1998), anionic micro gel (Morris et al., 1997), ZnS surface (Pattrick et al., 1998), magnetite (Georgeaud et al., 1998), pedogenic oxides, ferrihydrite and leaf compost (Sebastein et al., 2000), sawdust (Yu et al., 2001), lateritic minerals (Ahmad et al., 2002), and carbon (Akhtar and Qadeer, 1997; Qadeer and Akhtar, 2005).

Marine snails in general are part of the family Gastropoda and vary in size. They are found in oceans all over the world. The common periwinkle (Littorina littorea) is one of the most abundant marine gastropods in the North Atlantic but T. fuscatus is commonly found in the Niger Delta, Nigeria. Periwinkles distribute themselves in different positions on the shore. They are usually 1.3 to 2.5 cm in height, and colouration is grey to black. The shell is fairly heavy and solid. They live in the intertidal zone (the area of the shore that has alternating periods of exposure to air and then water). One of the main advantages of lead ion removal using activated carbon prepared from periwinkle shells (PSC) over the other chemical treatment methods and commercial activated carbon (CAC) is that it is in abundance and its easy availability makes it a strong choice in the investigation of an economical way of lead removal.

In this study, PSC as an alternative to CAC was used for the removal of lead ion from industrial wastewater. Parameters affecting adsorption like contact time between the wastewater and the adsorbent, adsorbent dose, pH of the sample, agitation speed, and size of the adsorbent particles were investigated, and data on adsorption isotherm were obtained and fitted to common isotherm models, Langmuir and Freundlich.

In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. The use of periwinkle shell with surface modification to improve its metal removal performance would add to its economic value, help reduce the cost of waste disposal, and, most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon.

Materials and Methods

Three types of adsorbents, PSC, CAC, and ratio 1:1 mixture of PSC and CAC (PSC:CAC), were used as the media (precipitating agent and/or adsorbent) to remove lead ion from industrial wastewater. Industrial effluent was collected from a stream carrying wastewater from an industrial plant. Materials used for sample collection were pretreated by washing the container with dilute hydrochloric acid and later rinsed with distilled water. The containers were later dried in an oven for 1 h at 110 ± 5 °C and allowed to cool to ambient temperature. At the collection point, containers were rinsed with samples 3 times and then filled with sample, corked tightly, and taken to the laboratory for treatment and analysis. The method of analysis was consistent with the standard methods (Goltermann, 1978; APHA, 1985). The pH of the sample was measured at the site and other parameters were measured in the laboratory. Samples were stored at below 3 °C to avoid any change in physico-chemical characteristics. An atomic absorption spectrophotometer was used: model Phillip PU 9100 × with a hollow cathode lamp and a fuel rich flame (air acetylene). Each sample was aspirated and the mean signal response recorded at the metal ion's wavelength. This was used to compute the concentrations of metal ions absorbed by the adsorbents. Batch experiments were carried out in different sets by taking PSC in the range of 20-70 g/100 ml of wastewater sample. The steps of the experiments are described below:

Effect of adsorbent dose: The experiments were individually set up for each adsorbent. For each 100 ml of wastewater sample, the amounts of PSC used were 20, 30, 40, 50, 60, and 70 g. Samples were withdrawn regularly after a fixed time interval, filtered, and analysed for residual lead. The experiment was repeated for CAC and PSC:CAC.

Effect of mixing time: The experiments were performed by varying mixing time from 30 to 300 min. The adsorbent dose used was obtained from the best value received from previous experiments.

Effect of pH: pH plays an important role in the precipitation and adsorption mechanisms. The experiments were performed by varying pH level of the samples wastewater ranging from pH 2 to 12 before adding adsorbents. The amount of adsorbents and time used were obtained from the best values received from the previous experiments. The experiment was carried out using PSC, CAC, and PSC:CAC, in that order.

Effect of mixing speed: Studies on mixing speed was performed by comparing the removal efficiency of lead at various mixing speeds from 100 to 700 rpm. The best treatment conditions for time, pH, and adsorbent dose were obtained from the 3 sets of experiment described above.

Effect of particle size: The experiments were performed by varying particle sizes from 0.5 to 3.0 mm. The best conditions for mixing speed, time, pH, and dosage were obtained from the 4 sets of experiments described above.

Periwinkle shell

Periwinkle shell was collected from a large dumpsite in Port Harcourt, Nigeria. The samples were transported to the laboratory for immediate use.

The periwinkle shell was washed to remove dirt and sorted out by removing unwanted ones. The samples were charred by carbonising them in a furnace at 300 °C for about 2 h, after which it was ground using a hammer mill (Scotmec model) and later sifted with 180 μm Standard Tyler Sieve No. 80. The ground sample was later kept in a plastic container and stored at room temperature.

Periwinkle carbon activation

Activation of the charred periwinkle was carried out using the method recommended by Mansfield (1998) with slight modifications as follows: 200 g of the charred sample was mixed with 250 ml of 5.5 M HCl and refluxed by boiling for 2 h. After slight cooling, the slurry was filtered, washed free of acid, and dried at 110 °C for 3 h, ground using a mortar and pestle, and sifted using mesh of different sizes to obtain various particle sizes. The charred periwinkle was characterised for its bulk density as described by Okaka and Potter (1979). The SiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, K_2O, and MgO were determined according to Jackson (1998). The major compositions of the sample are alumina, silica, iron oxide, and calcium oxide. Physical properties such as density and surface area were also determined.

Commercial activated carbon

The commercial carbon, Calgon carbon (F-300), was obtained from Calgon Carbon Inc., Pittsburgh, PA, USA.

Results and Discussion

Table 1 shows the physico-chemical analysis of the wastewater sample, depicting the level of lead in the wastewater sample.

Table 1. Characterisation of the effluent wastewater.

Parameter	Value
pH	8.7
TSS (mg/l)	42
Lead (mg/l)	19.1
Temperature (°C)	31
Turbidity (NTU)	22.5

The composition of typical Niger Delta (Nigeria) periwinkle shell carbon is shown in Table 2. The analysis showed that the periwinkle shell carbon is predominantly siliceous, followed by the insoluble oxides of aluminium, iron, calcium, magnesium, titanium, alkali oxides, and negligible amounts of phosphorus pentoxide and sulphur oxides.

In the case of periwinkle shell carbon as an adsorbent, the metal salt hydrolyses in the presence of natural alkalinity to form metal hydroxides. The multivalent cations present in periwinkle shell carbon can reduce the zeta potential while the metal hydroxides are good adsorbents.

Calculation of Pb^{2+} adsorbed

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the

Table 2. Characterisation of activated carbon and ash obtained from periwinkle shell.

Chemical composition (%)		Proximate analysis (%)		General characteristics	
Silicon dioxide (SiO_2)	60.2	Ash	4.6	Surface area, m^2/g	840
Aluminium oxide (Al_2O_3)	20.5	Loss on ignition	20.8	Bulk density, kg/m^3	0.147
Iron oxide (Fe_2O_3)	7.0	Volatile matter	1.7	Mean particle size, mm	1.75
Calcium oxide (CaO)	3.7	Fixed carbon	54.9		
Magnesium oxide (MgO)	1.12	Moisture	18.0		
Phosphorus pentoxide (P_2O_5)	1.82				
Titanium oxide (TiO_2)	2.1				
Alkali oxide (Na_2O/K_2O)	2.3				
Sulphur trioxide (SO_3)	1.37				

adsorbent (Ho et al., 1995). The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between amount of solute adsorbed per unit amount of adsorbent (solid phase concentration) and concentration of solute in solution at a fixed temperature at equilibrium.

The amount of metal ion adsorbed during the series of batch investigations was determined using a mass balance equation:

$$q = \frac{v}{m}\left(C_o - C_f\right) \qquad (1)$$

where q is the metal uptake (mg/g); C_o and C_f are the initial and equilibrium metal concentrations in the wastewater sample (mg/l), respectively; v is the wastewater sample volume (l); and m is the mass of adsorbent used (g).

The definition of removal efficiency is as follows:

$$Removalefficiency(\%) = \left(\frac{C_0 - C_f}{C_o}\right) \times 100 \qquad (2)$$

where C_o and C_f are the metal concentrations in the wastewater sample before and after treatment, respectively.

Comparison of different adsorbents for $^{2+}$ removal

Equilibrium studies were performed for analysing the performance of all the adsorbents. The data were generated by varying the adsorbent doses (20 to 70 g/l) at room temperature with PSC, CAC, and a ratio 1:1 of PSC:CAC (Figure 1). The influence of adsorbent dose on adsorption of lead at constant adsorbate concentration was studied for the purpose of determining the right adsorbent mass that will bring about a better decontamination of Pb-contaminated effluent. The result suggests that after a certain dose of adsorbent the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remain constant even with further addition of the dose of adsorbent. About 47.86% of Pb(II) can be removed with PSC and PSC:CAC, and about 26.42% can be removed with CAC.

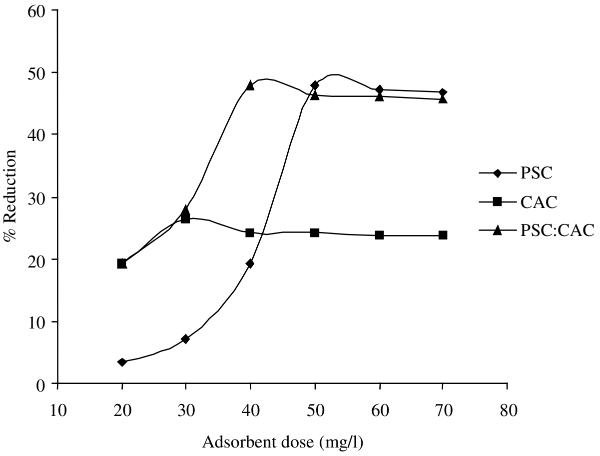

Figure 1. Effect of adsorbent dose on the adsorption of lead.

The distribution of lead between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the most popular isotherm models — Langmuir and Freundlich adsorption isotherms.

Effect of reaction time: Figure 2 shows removal of lead ion from water sample using different adsorbents as a function of time. The result shows that for PSC the removal rate was rapid within the first 30 min, sharply increased for 90 min, slowing down between 150 and 180 min, and then gradually approaching equilibrium after 180 min. For CAC, the removal rate was rapid within the first 60 min, sharply increased for 30 min, slowing down between 120 and 180 min, and then gradually approaching equilibrium after 180 min, whilst for PSC:CAC the adsorption process was rapid, being complete in 90 min.

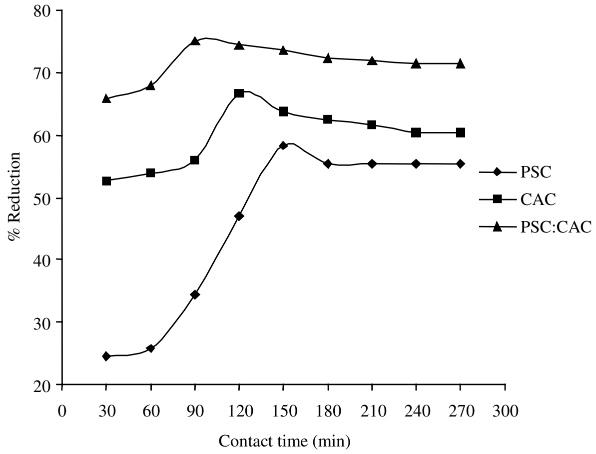

Figure 2. Effect of reaction time on the adsorption of lead.

The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depend on the surface area of the adsorbents. The lead adsorption takes place at the more reactive sites. As these sites are progressively filled the more difficult the sorption becomes, as the sorption process tends to be more unfavourable. This is the general characteristic of adsorption of this metal ion (Smith, 1970; Johnson, 1990; Appel and Lena, 2002; Abdus-Salam and Adekola, 2005; Qadeer and Akhtar, 2005).

These changes and differences in metal ion uptake rate could be attributed to 2 different adsorption processes, namely a fast ion exchange followed by chemisorption (Low, 1993).

Effect of pH: pH is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionisation of the adsorbate during reaction.

The removal of metal ions from wastewater sample by adsorption is related to the pH of the sample, as the latter affects the surface charge of adsorbents, the degree of ionisation, and the species of adsorbate. The pH of the aqueous solution is an important controlling parameter in the adsorption process (Baes and Mesmer, 1976) and thus the role of H^+ concentration was examined from samples at different pH covering a range of 2-12 (Figure 3). The result shows that adsorption of Pb(II) increased at a steady rate as pH increased up to about 8, attaining a maximum value of around 78.53%, 88.44%, and 88.44% for PSC, CAC, and PSC:CAC, respectively. However, after pH 8, there was a decrease in the adsorption. This decrease may be due to the formation of soluble hydroxyl complexes. According to Low et al. (1995), at low pH values the surface of the adsorbent would be closely associated with hydroxonium ions (H_3O^-), by repulsive forces, to the surface functional groups, consequently decreasing the percentage removal of metal. As the solution pH increase, the onset of the metal hydrolysis and the precipitation began at pH $>$ 8 and the onset of adsorption therefore occurs before the beginning of hydrolysis (Baes Mesmer, 1976). When the pH of the adsorbing medium was increased from 2 to 8, there was a corresponding increase in deprotonation of the adsorbent surface, leading to a decrease in H^+ ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favours adsorption of positively charge species and the positive sites on the adsorbent surface (Ghanem and Mikkelsen, 1988; Kadirvelu and Namasivayam, 2003; Abdus-Salam and Adekola, 2005).

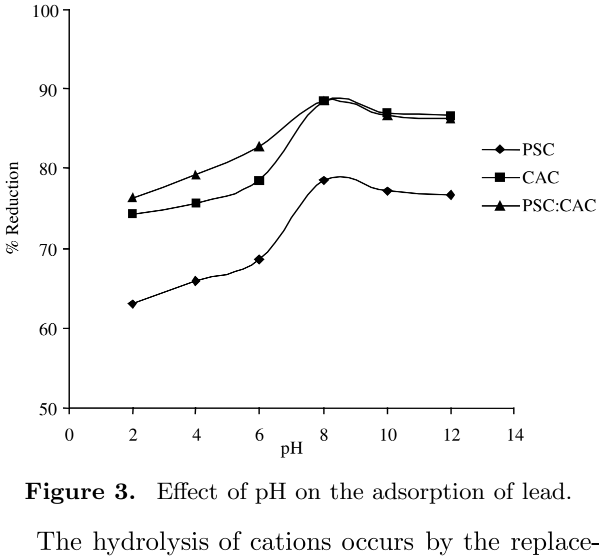

Figure 3. Effect of pH on the adsorption of lead.

The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups (Badmus et al., 2007). This replacement occurs after the removal of the outer hydration sphere of metal cations. In addition, the results obtained agreed with the findings of some researchers showing that the dependence of metal ion adsorption on pH over a wider range of pH (3-12) has an S-like adsorption curve (Johnson, 1990; Bruce, 2000; Glover II et al., 2002). The solubility of metals is known to be lowered at higher pH (at pH > 8) values (Inbaraj and Sulochana, 2002; Abdus-Salam and Adekola, 2005) due to the likelihood of precipitation of the hydroxide forms of the adsorbate species. Thus, results that gave the S-like curve were a reflection of adsorption and precipitation processes on adsorbents rather than adsorption only.

Adsorption may not be related directly to the hydrolysis of the metal ion, but instead of the outer hydration sphere that precedes hydrolysis. Most probably, the removal of Pb(II) from wastewater samples by adsorbents involves a complex mechanism that is partly controlled by adsorption and partly by chemical precipitation at the solid wastewater sample interface and also by the pore filling mechanism.

Effect of agitation speed: The effect of agitation of the sorbent/sorbate system in lead adsorption was monitored at low, medium, and high speed of agitation as shown in Figure 4.

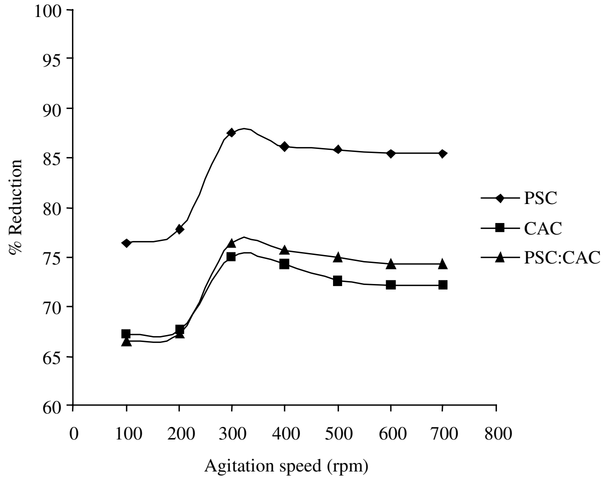

Figure 4. Effect of agitation speed on the adsorption of lead.

The slight increase in adsorption is primarily due to the fact that agitation facilitates proper contact between the metal ions in solution and the adsorbent binding sites and consequently promoting effective transfer of sorbate ions to the sorbent sites. This also indicates that a shaking rate in the range 300-700 rpm is sufficient to assure that all the surface binding sites are made readily available for lead uptake. Then the effect of external film diffusion on adsorption rate can be assumed to be not significant.

Effect of adsorbents' particle size: The effect of altering adsorbents' particle size on % removal showed that, between 0.5 and 2 μm, there was a more rapid removal of Pb(II) by small particles (Figure 5). This was most probably due to the increase in the total surface area, which provided more adsorption sites for the metal ion. The breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material, resulting in more accessibility to better diffusion, owing to the smaller particle size (Weber and Morris, 1963; Karthikeyan et al., 2004). The enhanced removal of sorbate by smaller particles has been noted previously during a study into the removal of colour by silica (McKay et al., 1980) and during study on the use of sago waste for the sorption of lead and copper (Quek et al., 1998).

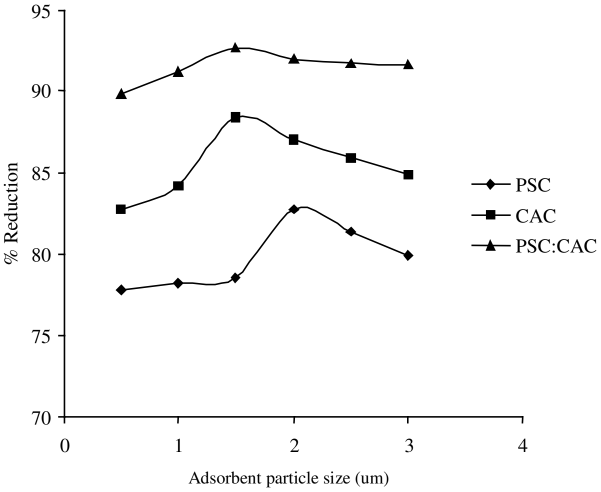

Figure 5. Effect of adsorbent particle size on adsorption of lead.

Adsorption studies

All the experiments were carried out at ambient temperature in batch mode. Batch mode was selected because of its relative simplicity. The batch experiments were run in different glass flasks of 250 ml capacity using a mechanical shaker. Prior to each experiment, a pre-determined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment, ensuring equal mixing. The desired pH was maintained using dilute NaOH/HCl solutions. Each flask was filled with a known volume of sample having the desired pH before the stirring commenced. The flask containing the sample was withdrawn from the shaker at the predetermined time interval and filtered through Whatman No. 44 filter paper. The experiments were carried out under different experimental conditions.

Adsorption model: The result of batch equilibrium was used to obtain metal adsorption isotherms as illustrated in Figure 6. The adsorption isotherm was used to characterise the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate. In this study, the experimental isotherm data set obtained was fitted using adsorption models including the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm and the Freundlich isotherm are 2 common isotherms used to describe equilibria (Domenico and Schwartz, 1990; Reddi and Inyang, 2001; Nitzsche and Vereecken, 2004). The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place.

The equation is described by

$$q_e = \frac{x}{m} = \frac{q_o k C_e}{k C_e + 1} \tag{3}$$

where x is the amount of metal adsorbed, m is the unit mass of adsorbent, and q_e is the amount of metal ion adsorbed per unit mass of adsorbent; q_o and k are empirical constants, and C_e is the equilibrium concentration of adsorbate in wastewater sample after adsorption; q_o is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of adsorbate per g of adsorbent).

Equation (3) can be re-arranged to yield

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o k} \tag{4}$$

The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants.

C_e is the equilibrium concentration of adsorbate (mg/l);

q_o and k are the Langmuir constants and are the significance of adsorption capacity (mg/g) and energy of adsorption (l/mg) respectively;

q_o and k are obtained from the intercept and slope of the plot of C_e/q_e and C_e.

Figures 6 shows the adsorption isotherms of lead, while Figure 7 shows Langmuir isotherms of lead on the different adsorbents used.

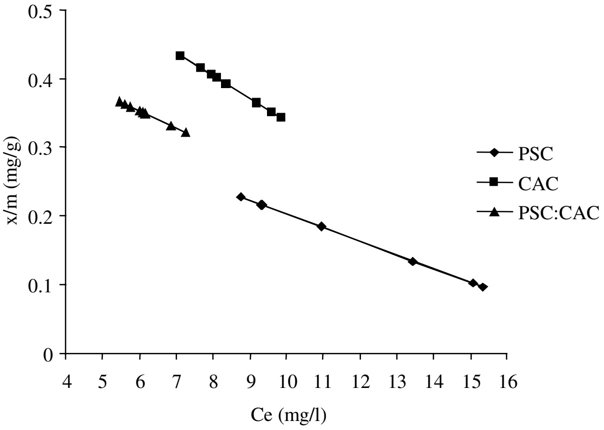

Figure 6. Adsorption isotherm of lead on activated periwinkle shell carbon (PSC).

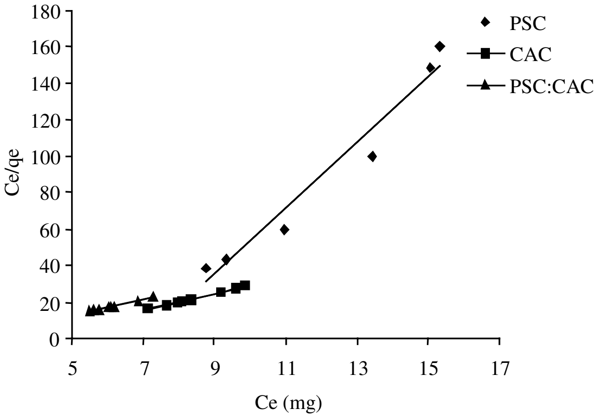

Figure 7. Comparison of Langmuir isotherms of activated periwinkle shell carbon (PSC), commercial activated carbon (CAC), and mixture of PSC and CAC (1:1).

The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface. The general form of the isotherm is given as

$$q_e = k C_e^{\frac{1}{n}} \tag{5}$$

A linear form of this expression is given as

$$\log\left[\frac{x}{m}\right] = \log k + \frac{1}{n} \log C_e \tag{6}$$

k and n are the Freundlich constants and represent the significance of adsorption capacity and intensity of adsorption, respectively. Values of k and n were calculated from the intercept and slope of the plot log q_e and log C_e (Figure 8).

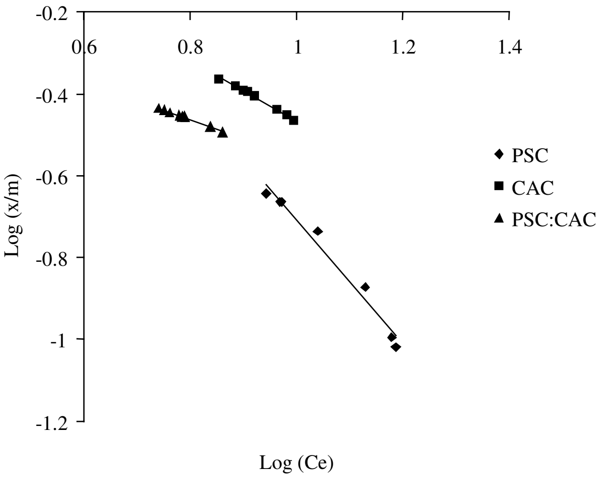

Figure 8. Comparison of Freundlich isotherms of activated periwinkle carbon (PSC), commercial activated carbon (CAC), and mixture of PSC and CAC (1:1).

This Freundlich type behaviour is indicative of the surface heterogeneity of the adsorbents, i.e. the adsorptive sites (surface of activated carbon) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption site takes place, leading to increased adsorption probably through the surface exchange mechanism.

A comparison of isotherm parameters for all 3 adsorbents was done to determine the effectiveness of the adsorbents. The coefficients of determination (r^2) and the isotherm constants are given in Table 3. The high values of r^2 (>95%) for both isotherms show that the adsorption of Pb(II) could be well described by both the Langmuir and Freundlich isotherms.

Adsorption kinetics: Several steps can be used to illustrate the adsorption mechanism. To investigate the mechanism of lead adsorption and the potential rate controlling steps, such as diffusion mass transport and chemical reaction processes, it is necessary to characterise the main adsorption mechanisms. The diffusion process can be controlled by film/external boundary layer diffusion, diffusion in the liquid filled-pores of adsorbents, or surface diffusion of adsorbed-soluble molecules that migrate along the surface of the adsorbent. The rate controlling mechanism may be one diffusion mass transfer resistance or a combination of 2 or 3 of these processes.

When the water sample is shaken, the adsorbate species, i.e. lead, are transported to the solid phase by the intraparticle transport phenomenon. The intraparticle transport is supposed to be the rate controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. The amount of adsorbed species, lead, varies proportionately with a function of retention time. The equation can be expressed as

$$X = K.t^n \tag{7}$$

where X is the % reduction, t is the contact time in minutes, n is the slope of the linear plot (Figure 9), and Kt is the constant coefficient. The deviation of the line from the origin shows that intraparticle transport is not the only rate limiting step (Badmus et al., 2007). Probably, the transport of the water sample through the particle-sample interface into the pores of the particles, as well as the adsorption on the available surface of the adsorbents, is responsible for adsorption.

The study of the adsorption kinetics is the main factor for designing an appropriate adsorption system and quantifying the changes in adsorption with time requires that an appropriate kinetic model is used.

Table 3. Adsorption isotherm constants and coefficient of determination for different adsorbents.

Adsorbent	**Langmuir isotherm constants**			**Freundlich isotherm constants**		
	q_o (mg/g)	k (l/mg)	r^2	k (mg/g)	n	r^2
PSC	0.0558	- 0.1430	0.972	6.5509	- 0.6554	0.981
CAC	0.2191	0.2751	0.996	1.8621	- 1.3587	0.998
PSC:CAC	0.2344	0.4983	0.999	0.8043	- 2.1744	0.996

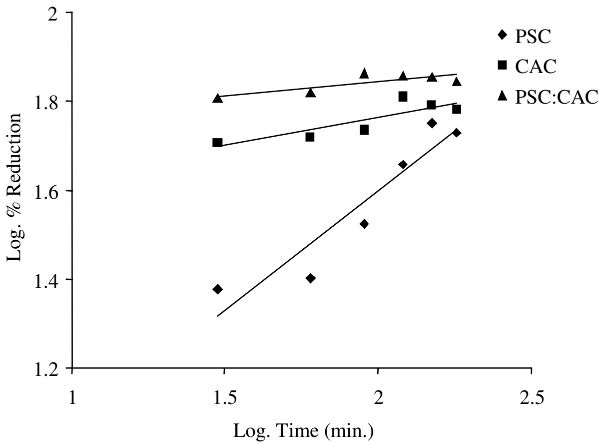

Figure 9. Log % reduction vs. log time.

The Elovich equation was developed to describe the kinetics of chemisorption of a gas onto solids (Low, 1960), and its differential form is represented in Eq. (8). The parameter α represents the rate of chemisorption at zero coverage and the parameter β is related to the extent of surface coverage and the activation energy of chemisorption. The application of the Elovich equation is rapidly gaining popularity (Aharomi and Ungarish, 1976; Sparks, 1986). Taylor et al. (1995) successfully used the Elovich equation for the sorption of zinc ions onto solids. Ho and McKay (2004) studied the sorption of copper from aqueous solution by peat, and Juang and Chen (1997) studied the sorption kinetics of metal ions from sulphate solutions onto solvent impregnated resins. Other applications include work on radioisotopes (Mishra and Singh, 1995; Mishra et al., 1996; Raouf and Daifullah, 1997).

The Elovich equation is generally expressed as

$$\frac{dq_t}{dt} = \alpha \exp\,(-\beta q_t) \tag{8}$$

where q_t is the amount adsorbed at time t, and α and β are constants during any one experiment. The constant α can be regarded as the initial rate since $\frac{dq_t}{dt} \to \alpha$ as $q_t \to 0$. Integration of Eq. (8) assuming the initial boundary conditions $q_t = 0$ at $t = 0$ yields

$$q_t = \left(\frac{1}{\beta}\right) In\,(1 + \alpha\beta t) \tag{9}$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t >> 1$ and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (9) becomes (Sparks, 1986)

$$q_t = \left(\frac{1}{\beta}\right) In\,(\alpha\beta) + \left(\frac{1}{\beta}\right) In\,(t) \tag{10}$$

Hence, the constants can be obtained from the slope and intercept of the linearised plots of q_t against In(t). Equation (10) will be used to test the applicability of the Elovich equation to the kinetics of lead adsorption.

For the rate constant of the pseudo-second-order chemical adsorption process,

$$\frac{dq_t}{dt} = k\,(q_e - q_t)^2 \tag{11}$$

The concentrations are expressed in terms of lead adsorbed on adsorbent, q, and for a second-order process the rate of lead adsorption is expressed to the power of the adsorbed lead loading difference to the power of 2.

In Eq. (11), q_e is the amount of lead adsorbed at equilibrium, (mg/g); q_t is the amount of lead adsorbed at time t, (mg/g) and k is the equilibrium rate constant of pseudo-second-order adsorption, (g/mg min). Assuming that $q_t = 0$ at $t = 0$, the integrated form of Eq. (11) becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{12}$$

Equation (12) can be rearranged to give

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{13}$$

h can be regarded as the initial adsorption rate since $t \to 0$, hence,

$$h = kq_e^2 \tag{14}$$

hence, Eq. (13) becomes

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \tag{15}$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{16}$$

Thus, a plot of $\frac{t}{q_t}$ *against* $t$would yield a linear relationship with the slope of $\frac{1}{q_e}$ and intercept of $\frac{1}{h}$ *or* $\frac{1}{kq_e^2}$.

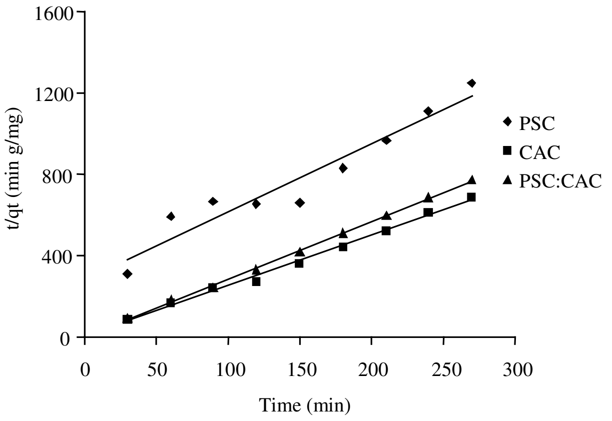

Figure 10. Pseudo-second-order adsorption kinetics of lead on activated periwinkle shell carbon (PSC).

Figure 10 shows the linearised form of the pseudo-second-order model for the adsorption of lead on PSC. The correlation coefficients, r^2, and the pseudo-second-order rate parameters are shown in Table 4.

Table 4. Pseudo-second-order parameters and coefficient of determination for different adsorbents.

Adsorbent	**Pseudo-second-order equation**			
	q_e	H	k	r^2
PSC	0.2962	0.0036	0.0412	0.927
CAC	0.4054	0.1178	0.7168	0.994
PSC:CAC	0.3513	- 1.3184	- 10.6829	0.999

The data show a good compliance with the pseudo-second-order equation, and the regression coefficients for the linear plots were 0.927, 0.994, and 0.999 for PSC, CAC, and PSC:CAC, respectively. The results are also shown in Figure 11 as a plot of q_t against In(t) for adsorption of lead for the Elovich equation. The correlation coefficients, r^2, and the Elovich equation parameters, α and β, are shown in Table 5. Comparison of the 2 models reveals that the r^2 for both pseudo-second-order and the Elovich equations show that the results can be well represented by the pseudo-second-order model. Hence, on the basis of the excellent fit of the pseudo-second-order and the correlation of the experimental results with the pseudo-second-order model, the main adsorption mechanism is probably a chemisorption reaction.

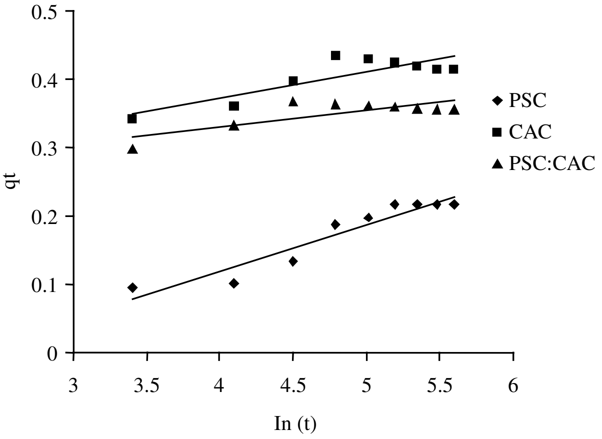

Figure 11. Plot of Elovich equation of lead on activated periwinkle shell carbon (PSC).

Table 5. Elovich equation parameters and coefficient of determination for different adsorbents.

Adsorbent	**Elovich equation**		
	β	α	r^2
PSC	14.7493	0.0073	0.903
CAC	26.2467	12.4595	0.726
PSC:CAC	41.4938	392.1138	0.630

Conclusion

PSC has been successfully used to produce high quality activated carbon because of its inherent high densities and carbon content.

Experiments conducted on the adsorption of Pb^{2+} by PSC, CAC, and PSC:CAC showed similarity in quantity of lead adsorbed. The result showed that PSC can compete favourably with CAC. Equilibrium data were well plotted by both Freundlich and Langmuir models. For the kinetic adsorption studies, adsorption data indicate the applicability of the pseudo-second-order kinetics and the Elovich model. Due to the high correlation coefficients obtained by using the pseudo-second-order kinetic model, the results can be represented well by the pseudo-second-order model. Consequently, the main adsorption mechanism is probably a chemisorption reaction. Hence this model should be used in design applications.

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