Removal of copper from industrial wastewaters by activated carbon prepared from periwinkle shells

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Abstract−The present study aims at the removal of copper from industrial wastewater by using a low - cost adsorbent. Activated periwinkle shell carbon (PSC) was prepared and characterized for various physiochemical properties. To determine copper removal capacity, the performance of PSC was compared with commercial activated carbon (CAC) and a mixture of activated periwinkle shell carbon and commercial activated carbon (PSC : CAC) in a ratio 1 : 1. The effect of adsorbent dose, contact time, pH, agitation speed and adsorbent particle size was studied for adsorption of copper from wastewater under batch conditions. The result obtained showed that PSC competes favourably with CAC. The maximum adsorption capacity was observed for PSC : CAC with 88.12% removal at an optimal pH of 8. The PSC and CAC had 84.19% removal and 85.15% removal, respectively. The equilibrium data obtained fitted both the Langmuir and the Freundlich models. Good correlation coefficients were obtained for the pseudo-second-order kinetic model.

Key words: Copper Adsorption, Batch, Industrial Wastewaters, Periwinkle Shell, Kinetic Model

INTRODUCTION

In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. Industrial processes generate wastewater containing heavy metal contaminants. Since most heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before being discharged into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water. A principal source of copper in industrial waste streams is metal cleaning and plating baths, and rinses, as brass, boiler pipe, cooking utensils, fertilizers, and from copper metal working, which requires periodic oxide removal by immersing the metal in strong acid baths.

Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Therefore, the elimination of heavy metals from water and waste water is important to protect public health. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life forms. According to the World Health Organization (WHO), the metals of most immediate concern are chromium, copper, zinc, iron, mercury and lead [1].

For humans, copper is an essential element and the body can regulate its level haemostatically, although large, acute doses can have harmful, even fatal, effects. In particular, copper is highly toxic as it is carcinogenic and mutagenic in nature [2-4].

Some of the conventional techniques for removal of metals from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, and electrolytic techniques, to mention a few [5-13]. Among them, adsorption is found to be the most effective method.

In this study, activated carbon prepared from periwinkle shells (PSC) was used as an adsorbent for the removal of copper (II) from industrial wastewater. The aim was to demonstrate the use of activated carbon prepared from periwinkle shells (*Typanotonus Fuscatus*) as an alternative media over conventional activated carbon, to investigate the optimum conditions of metal uptake and to calculate the adsorption capacity. Also, various parameters affecting adsorption like contact time between the waste water and the adsorbent, adsorbent dose, pH of the sample, agitation speed and size of the adsorbent particles have been investigated and data for adsorption isotherm were obtained.

MATERIALS AND METHODS

Industrial effluent was collected from a stream carrying wastewater from the plant. Materials used for sample collection were pretreated by washing the container with dilute hydrochloric acid and later rinsing with distilled water. The containers were later dried in an oven for 1 hr at 110 ± 5 °C and allowed to cool to ambient temperature. At the collection point, containers were rinsed with samples thrice and then filled with sample, corked tightly and taken to the laboratory for treatment and analysis. The method of analysis was consistent with standard methods [14,15]. The pH of the sample was measured onsite and other parameters were measured in the laboratory. Samples were stored at a temperature below 3 °C to avoid any change in physico-chemical characteristics. An atomic absorption spectrophotometer, model Phillip PU 9100×, was used to determine the concentrations of metal ions absorbed by the adsorbents.

1. Periwinkle Shell

Periwinkle shells were collected from a large dumpsite in Port Harcourt, Nigeria and transported to the laboratory for immediate use.

The periwinkle shells were washed to remove dirt and sorted out

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by removing unwanted ones. The samples were charred by carbonizing them in a furnace at 300 °C for about 2 hr, after which they were ground with 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.

1-1. Periwinkle Carbon Activation

Activation of the charred periwinkle was carried out as follows:

200 g of the charred sample was mixed with 250 ml of 5.5 M HCl and refluxed by boiling for 2 hr. After slight cooling, the slurry was filtered, washed free of acid and dried at 110 °C for 3 hr, ground using a mortar and pestle and sifted using mesh of different sizes to obtain various particle sizes.

The physico-chemical characterization of the sample was carried out by standard procedures. In addition, physical properties such as density and surface area were also determined. The major components of the sample are alumina, silica, iron oxide, and calcium oxide.

2. Commercial Activated Carbon

The commercial activated carbon used as standard was obtained from the Biotechnology Division of the Federal Institute of Industrial Research, Oshodi, Lagos, Nigeria.

3. Chemicals

All the chemicals used were of good analytical grade and they were obtained from chemical suppliers in Benin-City, Nigeria and the Biotechnology Division of the Federal Institute of Industrial Research, Oshodi, Lagos, Nigeria.

4. Experimental Conditions

4-1. Adsorbent Dose

The studies were conducted by varying the amount of adsorbent. 100 ml of wastewater sample was treated with different doses of prepared periwinkle carbon, 20-70 g/l. The samples were agitated for 60 min, filtered and then analyzed.

4-2. Contact Time

These studies were conducted by agitating 100 ml sample with best adsorbent dose in and agitating it for different time period, 30-300 min. After the predetermined time intervals, the samples were withdrawn, filtered and analyzed.

4-3. pH

pH effect was performed by keeping constant the adsorbent dose and contact time, and varying the pH values from 2-12 using dilute NaOH/HCl solutions. The samples were agitated for specific time, filtered and then analyzed.

4-4. Agitation Time

Studies for agitation time were performed by varying agitation speed from 100 rpm to 700 rpm and keeping all conditions constant after which the samples were withdrawn and analyzed.

4-5. Adsorbent Particle Size

Similarly, studies for adsorbent particle size were performed by keeping all conditions constant and varying the particle size from 0.5 to 3.0 mm. The samples were analyzed after each run. The removal of parameters was quoted as (%) relative to the values measured for the untreated effluent.

For comparative studies, similar kinds of experiments were performed using commercial activated carbon (CAC) and a ratio 1 : 1 mixture of activated periwinkle shell carbon and commercial activated carbon (PSC : CAC).

5. 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 an average speed 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 by using dilute NaOH/HCl solutions. Each flask was filled with a known volume of sample having desired pH commencing the stirring. The flask containing the sample was withdrawn from the shaker at a predetermined time interval, filtered through Whatman No. 44 filter paper with 3 μm pore diameter. The experiments were carried out under different experimental conditions.

RESULTS AND DISCUSSION

Table 1 shows the physico-chemical analysis of the wastewater

Table 1. Characterization of the effluent wastewater

Parameter	Value
pH	8.7
TSS (mg/l)	42
Copper (mg/l)	14.0278
Temperature (°C)	31
Turbidity (NTU)	22.5

Table 2. Characterization of activated carbon prepared from periwinkle shell

Chemical characteristics (%)		Proximate analysis (%)		General characteristics	
Silicon dioxide (SiO$_2$)	60.2	Ash	4.6	Surface area	840 m^2/g
Aluminum oxide (Al$_2$O$_3$)	20.5	Loss on ignition	20.8	Bulk density, kg/m^3	0.147
Iron oxide (Fe$_2$O$_3$)	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$_2$O$_5$)		1.82			
Titanium oxide (TiO$_2$)		2.10			
Alkali oxide (Na$_2$O/K$_2$O)	2.3				
Sulfur trioxide (SO$_3$)		1.37			

sample, depicting the level of copper in the wastewater.

The composition of typical Niger Delta, Nigeria periwinkle shell carbon is shown in Table 2. The analysis shows that the periwinkle shell carbon is predominantly siliceous followed by the insoluble oxides of aluminum, iron, calcium, magnesium, titanium, alkali oxides and a negligible amount of phosphorus pentoxide and sulfur 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.

1. Calculation of Cu²⁺ 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 adsorbent [16]. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium.

The amount of metal adsorbed was obtained from the differences between metal quantity adsorbed by the adsorbent and the metal content of the wastewater sample by using the following equation:

$$q = \frac{v}{m}(C_o - C_f) \tag{1}$$

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 in (g).

The definition of removal efficiency is as follows

$$\text{Removal efficiency } (\%) = \left(\frac{C_o - C_f}{C_o}\right) \times 100 \tag{2}$$

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

2. Comparison of Different Adsorbents for Cu(II) Removal

Equilibrium studies were performed for analyzing the performance of all the adsorbents. The data was generated by varying the adsorbent doses (20 to 70 g/l) at room temperature with activated periwinkle shell carbon (PSC), commercial activated carbon (CAC)
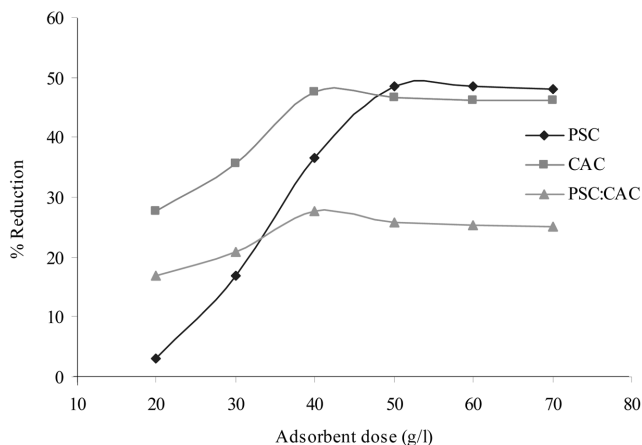
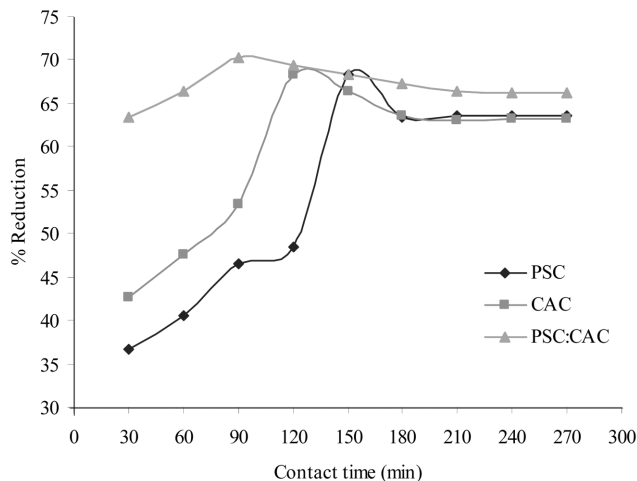Fig. 1. Effect of adsorbent dose on quality of effluent obtained.

Fig. 2. Effect of contact time on quality of effluent obtained.

and a ratio 1 : 1 of PSC and CAC (PSC : CAC), which is shown in Fig. 1. About 40% of Cu(II) can be removed with PSC and CAC, and about 50% can be removed with PSC : CAC.

The distribution of copper 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.

2-1. Effect of Reaction Time

The removal of Cu(II) from water sample using different adsorbents as a function of time is shown in Fig. 2. The result shows that for PSC and CAC, the removal rate was rapid within the first 120 minutes, sharply increased for 30 minutes, slowed down between 150-180 minutes and then gradually approached equilibrium after 180 minutes, whilst for PSC : CAC the adsorption process was rapid, being complete in 150 minutes.

These changes and differences in metal ion uptake rate could be attributed to two different adsorption processes, namely, a fast ion exchange followed by chemisorption [17].

2-2. Effect of pH

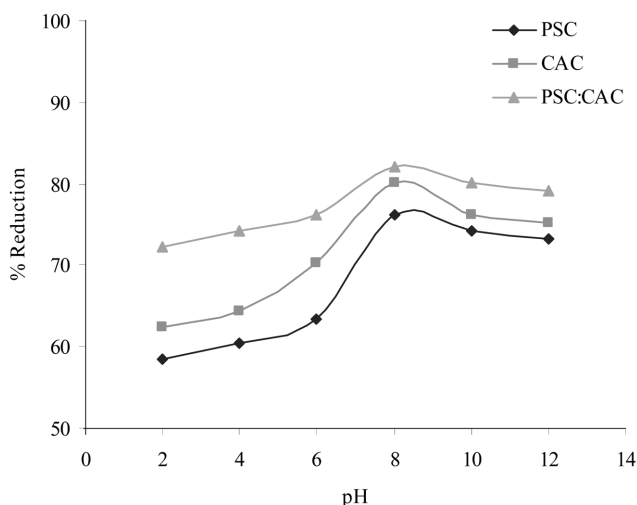Effect of pH on the adsorption of Cu(II) is presented in Fig. 3.

Fig. 3. Effect of pH on quality of effluent obtained.

The pH of the aqueous solution is an important controlling parameter in the adsorption process [18] and thus the role of H_2 ion concentration was examined from samples at different pH converting a range of 2-10. As Fig. 3 shows, adsorption of Cu(II) increased at a steady rate as pH increased up to 8 attaining a maximum value of around 76.24%, 80.20% and 82.18% for PSC, CAC and PSC : CAC, respectively. But after pH 8, there was a decrease in the adsorption, which may be due to the formation of soluble hydroxyl complexes. As the solution pH increased, the onset of the metal hydrolysis and the precipitation began at pH>8. As solution pH is increased, the onset of adsorption therefore occurs before the beginning of hydrolysis [18].

The hydrolysis of cations occurs by the replacement of metal ligands in the inner co - ordination sphere with the hydroxyl groups [19]. This replacement occurs after the removal of the outer hydration sphere of metal cations. 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 Cu(II) from wastewater sample by adsorbents involves a complex mechanism which is partly controlled by adsorption and partly by chemical precipitation at the solid wastewater sample interface [20] and also by pore filling mechanism.

2-3. Effect of Agitation Speed

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

About 10-20% increase in adsorption was observed in agitated samples during 300 minutes of adsorption. This 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.

2-4. Effect of Adsorbents Particle Size

The effect of altering adsorbent particle size on % removal showed that, between 0.5 and 2 μm, there was a more rapid removal of Cu(II) by small particles (Fig. 5). This was most probably due to the increase in the total surface area which provided more adsorption sites for the metal ion.

3. Adsorption Model

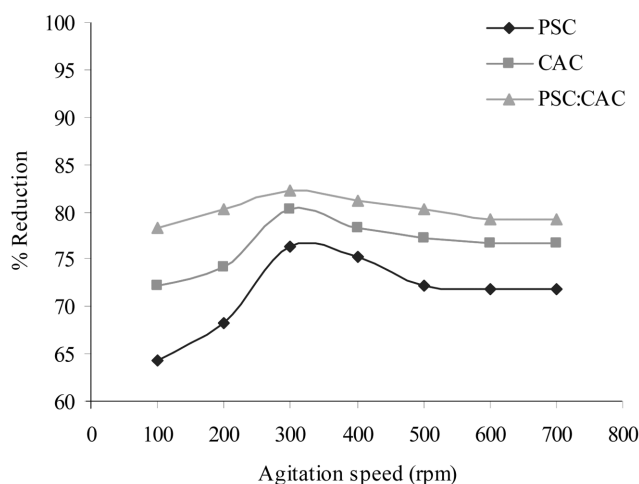Adsorption isotherm was used to characterize the equilibrium

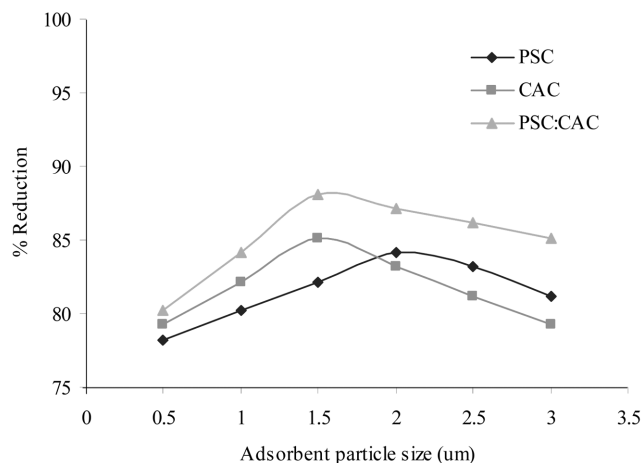Fig. 4. Effect of agitation speed on quality of effluent obtained.

Fig. 5. Effect of adsorbent particle size on quality of effluent obtained.

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 two common isotherms used to describe equilibria [21-23]. 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).

Eq. (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 linearized 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.

Figs. 6 shows the adsorption isotherms of copper, while Fig. 7 shows Langmuir isotherms of copper on different adsorbents used, respectively.

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:
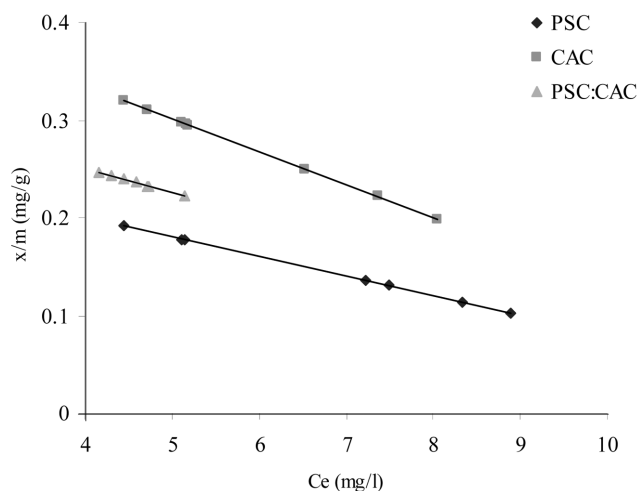
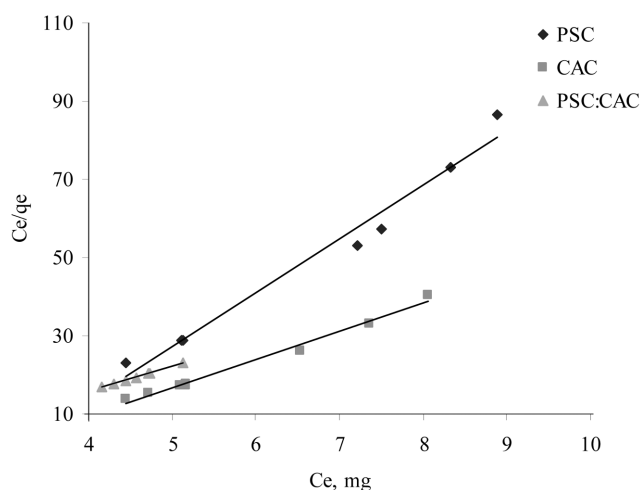Fig. 6. Adsorption isotherm of copper on activated periwinkle shell carbon (PSC).

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

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

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 $\log C_e$ (Fig. 8). This Freundlich type behaviour is indicative of surface heterogeneity of the adsorbents, i.e., the adsorptive sites (surface of activated carbon) are made up of small heterogeneous adsorption patches that are homogenous in themselves. The activation of adsorption site takes place leading to increased adsorption probably through surface exchange mechanism.

A comparison of isotherm parameters for all three adsorbents was done to determine the effectiveness of the adsorbents. The coefficients of determination (R^2) and the isotherm constants are given
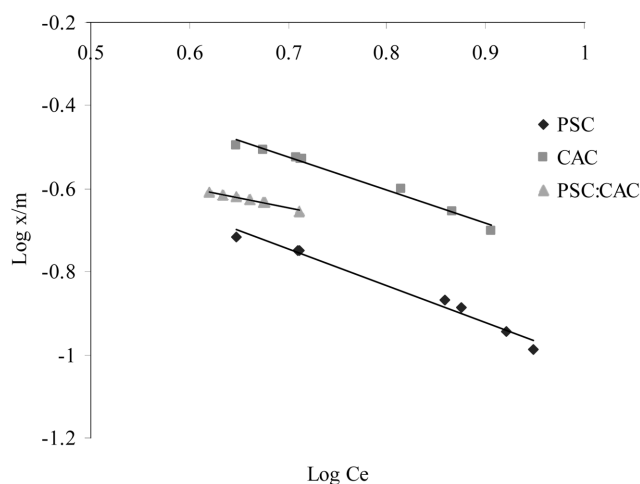
Fig. 8. Comparison of Freundlich isotherms of activated periwinkle carbon (PSC), commercial activated carbon (CAC) and mixture of PSC and CAC (1 : 1).

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	0.0728	−0.331	0.980	0.7506	−1.1297	0.981
CAC	0.1379	−0.370	0.988	1.0720	−1.2636	0.985
PSC : CAC	0.1570	−0.654	0.999	0.4980	−2.0367	0.997

in Table 3. The high values of R-squared (>95%) for both isotherms represent that the adsorption of Cu(II) could be well described by both the Langmuir and Freundlich isotherms.

3-1. Kinetics of Adsorption Process

Several steps can be used to illustrate adsorption mechanism. To investigate the mechanism of copper adsorption and the potential rate controlling steps, such as diffusion mass transport and chemical reaction processes, it is necessary to characterize the main adsorption mechanisms. Diffusion 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 two or three of these processes.

When the water sample is shaken, the adsorbate species, i.e., copper, are transported to the solid phase by 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, copper, varies proportionately with a function of retention time. The equation can be expressed as

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

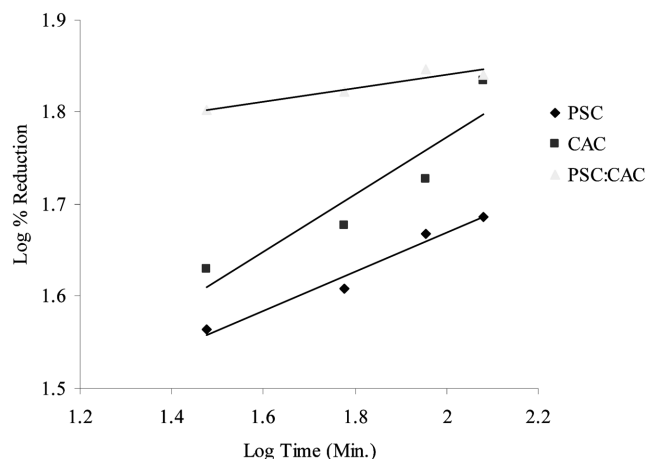where X is the % reduction, t is the contact time in minutes, n is

Fig. 9. Log % reduction vs log time.

Fig. 10. Pseudo-second order adsorption kinetics plot of copper onto PSC, CAC and PSC : CAC.

the slope of the linear plot (Fig. 9) and Kt is the constant coefficient. The deviation of the line from origin shows that intraparticle transport is not the only rate-limiting step [24]. 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 are both 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. In order to consider the kinetics effects, the following Lagergren pseudo-first order equation can be used to determine the rate constants [25]:

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ad}}{2.303}(t) \qquad (8)$$

where q_e is the amount of copper adsorbed at equilibrium (mg/g); q_t is the amount of copper adsorbed at time t (mg/g); $K_{1,ad}$ is the pseudo-first order rate constant (min^{-1}); and t is the time (min).

In many cases, the Eq. (8) cannot be used to describe the kinetics of the adsorption process. In such cases, a pseudo-second order expression may be used and this is more appropriate for describing this type of adsorption. Hence, this model reduces to:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}q_e^2} + \frac{1}{q_e}(t) \qquad (9)$$

where $K_{2,ad}$ is the pseudo-second order rate constant (gmg^{-1}min^{-1}).

In this study, a second order kinetics model was considered for the adsorption process of copper.

Fig. 9 shows the linearized form of the pseudo-second order model

for the adsorption of copper onto PSC, CAC and PSC: CAC. The correlation coefficients, R^2, and the pseudo-second order rate parameters are shown in Table 4.

The data obtained for the adsorbents show a good compliance with the pseudo-second order equation and the regression coefficients for the linear plots were 0.9671, 0.9883, and 0.999 for PSC, CAC and PSC : CAC, respectively.

CONCLUSIONS

The following conclusions were drawn from the present study. The materials used showed different adsorption capacity in all experimental parameters investigated. This may be due to the difference in the composition of the adsorbents, difference in surface area and the extent of surface area modification. The surface areas were determined to be 840 m^2/g and 850 m^2/g for PSC and CAC, respectively. Activated periwinkle shell carbon competed favourably with commercial activated carbon. The results obtained showed that PSC can be used in the removal or recovery of heavy metal ions, especially copper ions from industrial wastewaters. The adsorption data followed both Langmuir and Freundlich isotherms. In addition, a pseudo-second order kinetics appear to model the rate of adsorption.

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

Adsorbent	Parameters		
	q_e (mg/g)	K_{2ad}	R^2
PSC	0.1753	0.1559	0.9671
CAC	0.3209	0.05903	0.9883
PSC : CAC	0.2312	−0.3946	0.999

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