Hevea brasiliensis – A Biosorbent for the Adsorption of Cu(II) from Aqueous Solutions

N. Sivarajasekar♠

School of Biotechnology, K. S. Rangasamy college of Technology, K. S. R. Kalvi Nagar, Thiruchengode-637209, India
♠e-mail: *sivarajasekar@gmail.com*

Abstract

The activated carbon produced from rubber wood sawdust by chemical activation using phosphoric acid have been utilized as an adsorbent for the removal of Cu(II) from aqueous solution in the concentration range 5-40 mg/l. Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of contact time, initial copper ion concentration, carbon dosage, and pH on percentage removal have been studied. Adsorption results obtained for activated carbon from rubber wood sawdust were compared with the results of commercial activated carbon (CAC). The adsorption on activated carbon samples increased with contact time and attained maximum value at 3 h for CAC and 4 h for PAC. The adsorption results show that the copper uptake increased with increasing pH, the optimum efficiency being attained at pH 6. The precipitation of copper hydroxide occurred when pH of the adsorbate solution was greater than 6. The equilibrium data were fitted using Langmuir and Freundlich adsorption isotherm equation. The kinetics of sorption of the copper ion has been analyzed by two kinetic models, namely, the pseudo first order and pseudo second order kinetic model. The adsorption constants and rate constants for the models have been determined. The process follows pseudo second order kinetics and the results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich model. It was concluded that activated carbon produced using phosphoric acid has higher adsorption capacity when compared to CAC.

Keywords : Biosorption, Copper removal, Chemical activation

1. Introduction

Cu(II) ion is present in the waste water of several industries and it is highly toxic. The excessive intake of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous problems followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur [1]. Therefore, considerable research has been carried out in developing cost effective copper removal techniques. Though the maximum permissible concentration by Indian Council of Medical Research (ICMR), WHO, USPHS are 3.0 mg/l, 1.5 mg/l and 1.0 mg/l respectively, the maximum recommended concentration of Cu^{2+} for drinking water by these agencies is 1.0 mg/l [2].

The physical and chemical technique such as precipitation, ion exchange, reverse osmosis, electrochemical treatment and evaporative recovery are generally used for removal of copper from wastewater. The use of precipitation technique has been limited due to the problem associated with the disposal of the precipitated cupric hydroxide [3]. This technique also lacks a sufficiently high affinity and selectivity to reduce residual copper to the levels dictated by government regulations. The other above mentioned techniques such as ion exchange, reverse osmosis, electrochemical treatment and evaporative recovery can effectively reduce metal ions, but they does not appear to be viable from due to the high cost of the material and operational cost in addition to the limited pH range for the ion exchange resin [4]. Consequently there is a growing need for efficient and cost effective alternative methods for the elimination of heavy metals.

In recent years, considerable attention has been devoted to the study of removal of copper from aqueous solution by adsorption phenomenon using some adsorbents under optimum operating conditions. Several adsorbents such as sawdust [5], silica and iron oxide [5], sewage sludge ash [6], anatase type titanium dioxide [7], olive mill residues [8], inorganic colloids [9], blast furnace sludge [10], fictionalized silica [11], red mud and fly ashes [11], peat [12], paper mill sludge [13], activated carbon [14, 15] have been used for the treatment of copper(II) rich effluents at the solid solution interface.

Activated carbon, because of their high porosity, large surface area, a microporous structure, high affinity and selectivity have been considered to be very good adsorbent for the removal of heavy metal ions from wastewater. Activated carbon from cheap and readily available sources such as coal, coke, peat [16], wood charcoal [17], heat treated sulphurised activated carbon [18], sugarcane begasse pith [19], bioresource [20], rice husk [21] may be successively employed for removal of heavy metals.

The objective of this work is to identify the prospects of using low cost materials as starting material for producing adsorbents for removing heavy metals from aqueous solution. Therefore the present study deals with adsorption studies of copper on activated carbon produced from rubber wood sawdust.

2. Experimental procedures

### 2.1. Phosphoric acid activation of rubber wood saw dust

The samples for activation were prepared by mixing the rubber wood sawdust with the required ratio of phosphoric acid based on the dry weight of the sample. The sawdust of average particle size 0.074 mm (PAC) was mixed with the 200% by weight of phosphoric acid and soaked for 24 h so that the reagents are fully adsorbed into the raw material. After impregnation, the mixture was transferred to a pyrex glass plate and placed in the muffle furnace for drying at 110°C for 1.5 h. After drying, the mixture was transferred to a sealed ceramic container and was activated in a muffle furnace the temperature of carbonization being 400°C for a period of 1 h. The carbons thus produced were then repetitively washed with distilled water to recover all the acid from the material until it attains neutral pH. After washing, the activated carbon was dried in an hot air oven at a temperature of 105±5°C. The drying was continued until a constant weight of activated carbon was reached.

2.2. Characterization of activated carbon

Activated carbons prepared from rubber wood sawdust were characterized by finding out its yield, iodine number [22], methylene blue number [23], methyl violet number [23] and surface area [24]. The iodine number is a measure of the porosity of the activated carbon and it is defined as the milligrams of iodine adsorbed per gram of carbon. Methylene blue and methyl violet number indicates the decolorizing power and are defined as milligrams of methylene blue and methyl violet adsorbed per gram of carbon. These numbers are determined as per the standard procedures. The surface area was determined using N_2 adsorption method. The values obtained are compared with commercial activated carbon and are summarized in Table 1 and 2. The SEM photographs of Phosphoric acid activated rubber wood saw dust carbon is shown in Fig. 1.

Table 2. Thermogravimetric analysis values for Activated Carbon from Rubber Wood Sawdust

Composition (%)	Value
Ash (%)	0.85
Carbon (%)	65.62
Moisture (%)	2.08
Volatile (%)	31.45
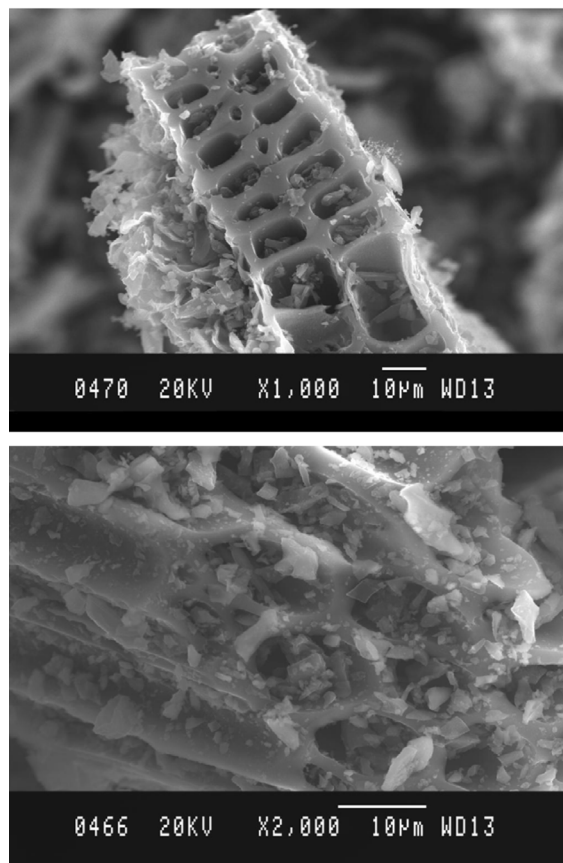
Fig. 1. SEM images of phosphoric acid activated carbon.

2.3. Adsorption studies

The stock solution containing copper ions was prepared by dissolving copper sulphate pentahydrate in double distilled water. All other reagents used for analysis were of analytical grade. Batch adsorption experiments were carried out using commercial activated carbon (CAC) and powder activated

Table 1. Characterization of Commercial Activated Carbon and Activated Carbon from Rubber Wood Sawdust

S. No.	Activated carbon	pH	Iodine number (mg/g)	Methylene Blue number (mg/g)	Methyl violet number (mg/g)	BET Surface area (m²/g)	Avg. pore diameter (Å)	Yield
1.	CAC	6.67	834.02	210	125	1239.27	–	–
2.	PAC	5.88	794.53	255	165	1673.86	22.8	0.628

carbon (PAC) using phosphoric acid activation produced from rubber wood sawdust.

All adsorption experiments were carried out by agitating the carbon with 100 ml of copper sulphate solution of desired concentration at particular and at a temperature of 30°C in a mechanical shaker at a fixed agitation speed of 180 rpm. The experiments were carried out for various carbon loading, different initial Cu(II) concentration, for different retention times, temperature and pH.
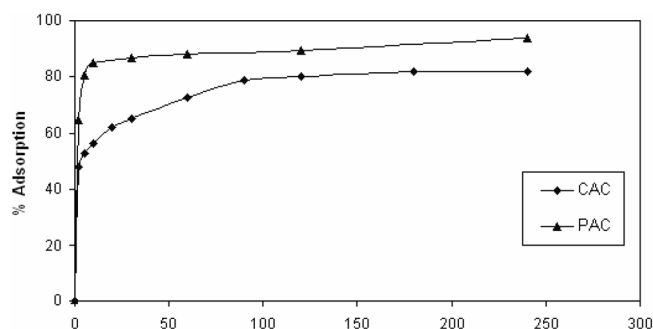
At the end of predetermined time interval, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual copper concentration. The concentration of copper was determined spectrophotometrically at a wavelength of 435 nm by forming complex with sodium diethyl dithio carbamate, using standard analytical procedure [25].

3. Results and Discussion

3.1. Effect of contact time on percentage adsorption

The dependence of adsorption of copper ions on CAC and PAC with contact time is shown in Fig. 2. The adsorption was carried out in a solution containing 20 mg/l of copper sulphate solution with constant carbon loading of 0.5 g/100 ml of solution at a temperature of 30°C and at pH 6. The adsorption on activated carbon samples increased with contact time and attained maximum value at 3 h for CAC and 4 h for PAC. Further increase in the contact time did not show a significant change in percentage adsorption. The equilibrium time was hence taken as 3 h and 4 h respectively. Therefore, for further studies, the time for attaining equilibrium was set at 3 h for CAC and 4 h for PAC.

Fig. 2 indicates that the rate of Cu(II) removal by activated carbon in the aqueous solution follow nearly similar trends. The initial rate of adsorption being very high during the first few minutes and then gradually dropping to zero as the equilibrium time is reached. As an approximation, the removal of copper ions can be said to take place in two distinct steps: a relatively fast one followed by a slower one. This behaviour is due to a larger surface area of the activated carbon being available for the adsorption of copper ions. Once the external surface area of the activated carbon are occupied by the Cu(II) ions, then with time, the Cu(II) uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent. It was observed from the Fig. 2, that the percentage removal of Cu(II) from aqueous solution was higher for PAC (93.82%) when compared to CAC (82.01%).

It can be observed from Table 1, that the surface area of PAC > CAC, indicating more surface available for the adsorption of Cu^{2+} ions, justifying the percentage removal of Cu(II) from aqueous solution has been maximum for PAC than CAC. It can also be observed that the initial rate of adsorption is higher in the case of PAC when compared to CAC.

3.2. Effect of pH on percentage of adsorption

The effect of pH on adsorption of Cu(II) on CAC and PAC were studied at a temperature of 30°C by varying the initial pH of 20 mg/l of Cu(II) solution from 2 to 12 for a constant carbon dosage of 0.5 g/100 ml of solution and this is presented in Fig. 3. The adsorption experiments were conducted for equilibration time previously determined. The pH of the aqueous solution is an important controlling parameter in the adsorption process [26]. The percentage removal of Cu(II) was found to increase with increasing pH, showing maximum adsorption at pH 8. The optimum initial pH was however chosen to be 6 because precipitation of copper hydroxide was observed at pH greater than 6 [6]. At pH 2, there was only little adsorption. The decrease in the copper uptake at low pH is due to the fact that the H^+ ions compete with copper cation for the exchange of sites in the system, thereby partially releasing the latter [27]. Further, at low pH, the carbon surface gets positively charged and copper is also present only as Cu^{2+} and hence adsorption is poor. Under these conditions, adsorption is mainly due to chemical interaction and must posses enough energy to overcome the

Fig. 2. Effect of contact time on percentage adsorption using CAC and PAC.
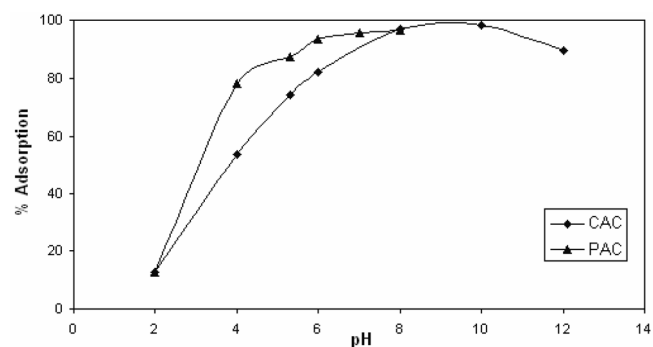
Fig. 3. Effect of pH on percentage adsorption using CAC and PAC.
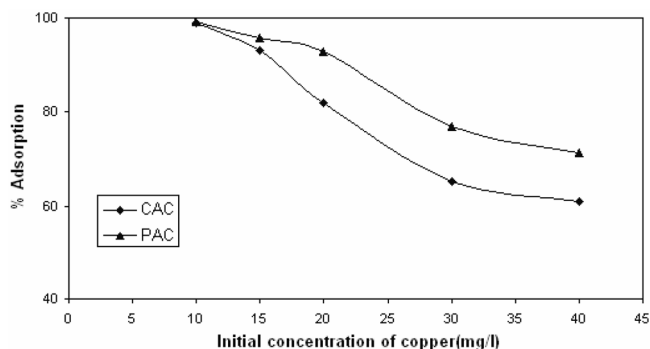
Fig. 4. Effect of initial concentration on percentage adsorption using CAC and PAC.

repulsive forces between the positively charged carbon surface and copper cation, Cu^{2+}. An increase in pH shows increase in Cu(II) adsorption, in which the surface of the activated carbon finds less H^+ ions competing for the adsorption site with Cu^{2+} ions. In this case adsorption occurs by electrostatic force of attraction between Cu^{2+} and surface of the adsorbent. At still higher pH (i.e.) above pH 8, a decrease in adsorption of Cu(II) was observed due to the formation of soluble hydroxyl complexes. Henceforth, all experiments were carried out at a pH of 6.

3.3. Effect of initial concentration of Cu(II) ions on percentage adsorption

The results for CAC and PAC are presented in Fig. 4. The plot represents the percentage removal of copper with change in initial Cu(II) concentration at pH 6 maintained at the temperature of 30°C for a period of 3 h, with a constant carbon loading of 0.5 g/100 ml of solution containing different concentration of Cu(II). As the initial concentration of copper was increased, the percentage removal decreases. The decrease in the percentage removal of Cu(II) was greater at lower initial Cu(II) concentration and smaller for higher initial Cu(II) concentration. As the concentration of the adsorbate increases the number of sites for adsorption remaining the same, the availability of free sites for adsorption decreases. Further, increase in concentration does not show an appreciable change in the percentage adsorption.

It was observed that PAC produced using phosphoric acid activation had the best capacity for removal of copper ions from aqueous solution when compared to CAC. At lower concentration below 15 mg/l, the performance of the PAC was the same as CAC. However, at concentration above 20 mg/l, the extent of deviation increased to larger than 20%.

The effect of initial concentration of copper ions on adsorption capacity for CAC and PAC are presented in Fig. 5. From the above mentioned figure, it was found that the adsorption capacity increases with increase in initial concentration of copper ions. It was also observed that till the
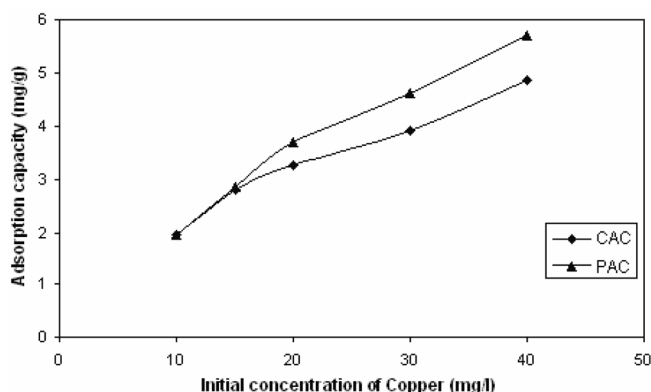

Fig. 5. Effect of initial concentration of copper ions on adsorption capacity using CAC and PAC.

concentration of 15 mg/l, the adsorption capacity of both the carbon samples did not vary and variation increases with increase in the copper concentration.

3.4. Effect of carbon dosage on percentage adsorption

To determine the necessary activated carbon quantity required for the maximum removal of Cu(II) ions, the effect of activated carbon dosage on % removal was studied. This is shown in Fig. 6. The adsorption studies were carried out at pH 6, temperature 30°C for equilibration time, taking 100 ml of 20 mg/l of $CuSO_4$ solution for various activated carbon dosage. It can be easily inferred that the percent removal of copper ions increases with increasing weight of the activated carbon. This is due to the fact that more the activated carbon, greater will be the availability of the exchangeable sites or surface offered to the adsorption of Cu(II) ions. As already mentioned, it has been observed that the carbon prepared from rubber wood sawdust activated using H_3PO_4 shows better performance over CAC. The carbon dosage required for 100% removal of copper from aqueous solution was found to be 0.7 g in the case of PAC and 0.9 g in the case of CAC. From the Table 1, it has been observed that the surface
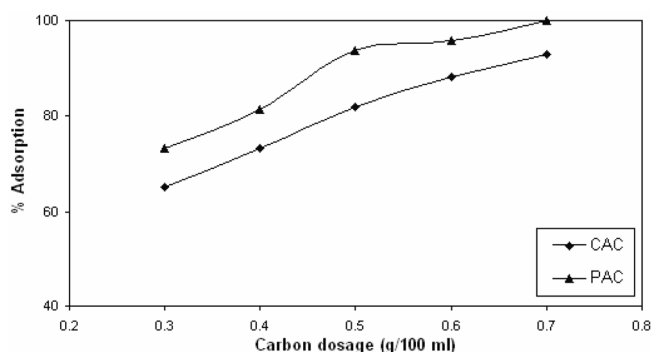
Fig. 6. Effect of carbon dosage on percentage adsorption using CAC and PAC.

area obtained for PAC is more than CAC. Also, the methylene blue number and methyl violet number for PAC is greater than CAC. Methylene blue number and methyl violet number is an indication of the mesopore development in an activated carbon. This clearly shows that the increase in adsorption is due to the mesoporosity of the carbon. The iodine number is nearly same for both the carbons. The adsorption of Cu^{2+} ions can be assumed to take place in both micropores and the mesopores.

3.5. Kinetics of Cu(II) ion adsorption

To evaluate the differences in the adsorption kinetic rates, the kinetics of copper uptake by CAC and PAC were described with pseudo first order and pseudo second order rate equation.

The pseudo first order plot can be obtained from equation

$$dq_t/dt = K_1 (q_e - q_t) \qquad (1)$$

Where q_t is amount of copper uptake capacity at time t, q_e equilibrium uptake capacity, K_1 is first order rate constant.

On integration, equation (1) becomes,

$$\ln (q_e - q_t) = \ln q_e - K_1 t \qquad (2)$$

The values of q_e and K_1 are obtained by plotting a graph of $\ln (q_e - q_t)$ vs t,

Similarly, pseudo second order rate equation is given as

$$dq_t/dt = K_2 (q_e - q_t)^2 \qquad (3)$$

Where q_t is amount of copper uptake capacity at time t, q_e equilibrium uptake capacity, K_2 is second order rate constant.

On integration, equation (3) can be rearranged to obtain

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \qquad (4)$$

The values of K_2 and q_e can be determined experimentally by plotting a graph of t/q_t vs. t.

The kinetic plot obtained by fitting pseudo first order and pseudo second order rate equation for the adsorption of copper ions onto CAC and PAC are shown in Fig. 7 and Fig. 8. The corresponding rate constants and uptake capacities for CAC and PAC are summarized in Table 3. The adsorption of copper follows pseudo second-order reaction and this is evident from the correlation coefficients. The validity of the two models can also be checked by studying the kinetics under different initial metal ion concentration, because it is well understood that, in the case of a first order kinetic
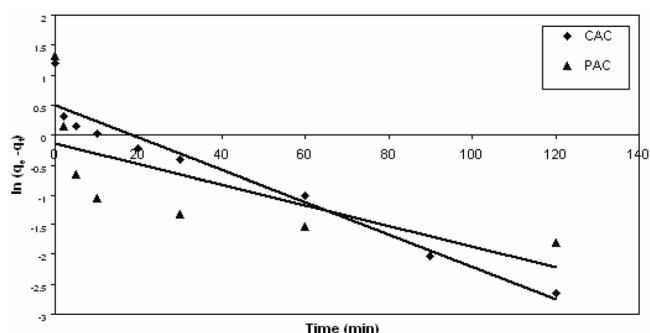
Fig. 7. Pseudo- first order plots for adsorption of copper ions using CAC and PAC.
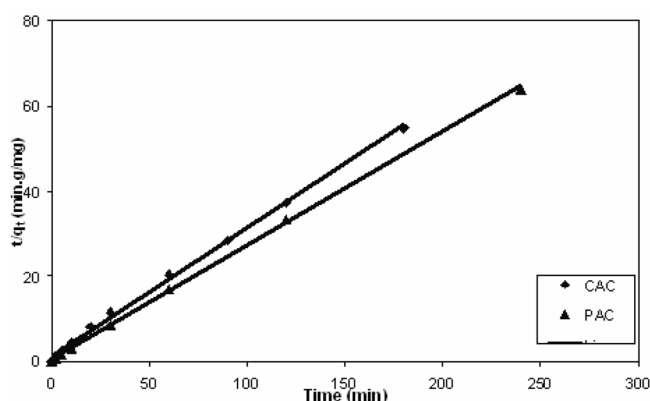
Fig. 8. Pseudo- second order plots for adsorption of copper ions using CAC and PAC.

reaction, the half life time is constant whatever the initial adsorbate concentration [28]. But the half life time was found to vary with the initial metal ion concentration, thus validating the assumption of a pseudo second - order adsorption mechanism rather than a first order one. Many literature reviews have pointed out that the majority of adsorption studies can be represented as a pseudo first - order mechanism. However, it was clearly found that the pseudo second - order rate equation, which agrees with chemisorption as the rate controlling mechanism, was able to better describe the adsorption of Cu^{2+} on activated carbon. As observed from the Fig. 8, good agreement between the predicted and experimental results was found for pseudo second-order rate equation over the range of metal initial concentration. Hence, the applied pseudo second-order rate model succeeded in representing properly the experimental kinetic data for the

Table 3. The Kinetic Parameters for the Adsorption of Cu(II) on CAC

S. No.	Activated carbon	Pseudo first - order constants			Pseudo second - order constants		
		q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g·mg^{-1}min^{-1})	R^2
1.	CAC	1.6435	0.027	0.9433	3.318	0.0698	0.9978
2.	PAC	0.8744	0.0173	0.4869	3.7355	0.1649	0.9995

adsorption of Cu(II) on adsorbent samples.

3.6. Adsorption behaviour of activated carbon (Isotherm studies)

The distribution of copper between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can be generally expressed by two of the most popular isotherm theories. Viz., the Langmuir and the Freundlich adsorption isotherms. The Langmuir [29] adsorption isotherm equation is given as

$$q_e = X_m b C_e / (1 + b C_e) \qquad (5)$$

Where X_m is uptake quantity for monolayer adsorption, C_e is equilibrium concentration, b is Langmuir constant.

The linear representation of Langmuir isotherm is expressed as,

$$C_e/q_e = 1/X_m b + C_e/X_m \qquad (6)$$

Hence a plot of C_e/q_e vs. C_e yields a straight line with slope $1/X_m$ and intercept as

$$1/X_m b$$

According to Freundlich [30] adsorption isotherm, the following equation is used.

$$q_e = K_f C_e^{1/n} \qquad (7)$$

Where K_f and n are Freundlich constants.

The linear representation of Freundlich adsorption isotherm equation is,

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (8)$$

Thus a plot of $\ln q_e$ vs $\ln C_e$ yields a straight line with slope $1/n$ and intercept $\ln K$.

The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent, while the Langmuir type isotherm hints towards surface homogeneity of the adsorbent.

The Freundlich and Langmuir adsorption isotherm equations were fitted with the experimental equilibrium adsorption data for different copper ion concentration at pH 6. The isotherm plots are shown in Fig. 9 and Fig. 10. The related parameter values are summarized in Table 4. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression, i.e., the isotherm giving an R^2 value closest to
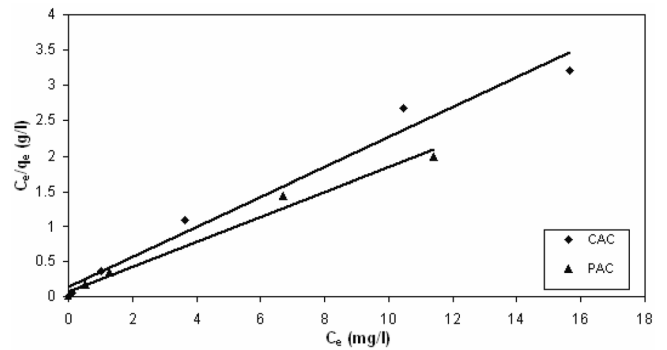
Fig. 9. Langmuir plots for adsorption of copper ions using CAC and PAC.
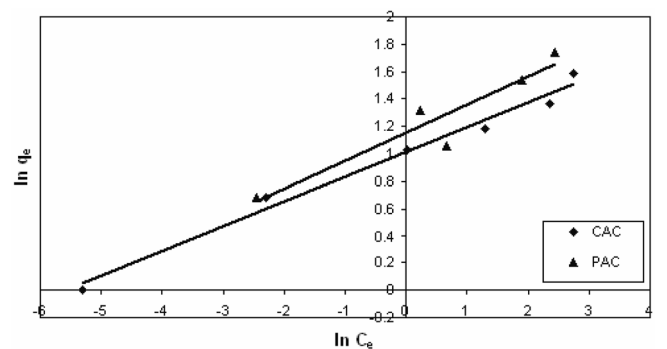
Fig. 10. Freundlich plots for adsorption of copper ions using CAC and PAC.

unity is deemed to provide the best fit. Although Langmuir and Freundlich approximations of the observed adsorption data in the linearized forms gave satisfactory correlation coefficient for most of the covered concentration range, the Langmuir model had more practical utility for representing the limiting adsorption capacities of the adsorbents than the exponentially increasing Freundlich isotherm.

The linear plots C_e/q_e Vs C_e in Fig. 9, shows that the Langmuir adsorption isotherm model describes satisfactorily the adsorption of copper on activated carbon samples. The agreement of Langmuir plot with experimental data suggests that the copper ion adsorbed form a monolayer coverage on the outer surface of the adsorbent surface. The main assumption of the Langmuir method is that adsorption occurs uniformly on the active part of the surface, and when a molecule is adsorbed on a site, the latter does not have any effect upon other incident molecules. It was also found that,

Table 4. The Related Parameters for the Adsorption of Cu(II) on CAC

S. No.	Activated carbon	Langmuir constants			Freundlich constants		
		X_m (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n (g/l)	R^2
1.	CAC	4.7125	1.4746	0.9760	2.8477	6.4683	0.9881
2.	PAC	5.6275	2.4111	0.9857	2.1775	4.8705	0.8915

during the adsorption process, desorption is negligible and that the process is irreversible. Therefore, the kinetic analysis suggested by Langmuir for gas adsorption may be applied for this case. So the application of the Langmuir isotherm seemed to be more appropriate than the Freundlich isotherm. Therefore the Langmuir model is assumed to give the best fit to the experimental results over the range of concentration with good coefficients of correlation.

For the comparison of the performance of adsorbents, the X_m values of the CAC were compared with the metal adsorption capacity reported for PAC shown in Table 4. More generally, the metal adsorption capacity of PAC was higher than that of CAC. Therefore, the activated carbon prepared from rubber wood sawdust using phosphoric acid as activating agent has better metal removing capacity than CAC.

4. Conclusion

The activated carbon prepared from rubber wood sawdust using phosphoric acid as impregnating agent has been used as an adsorbent for the removal of Cu(II) from synthetic waste water. The data obtained was compared with CAC. Various experimental parameters such as effect of contact time, initial concentration of copper ions, adsorbent dosage, and pH on the removal of Cu(II) have been studied. It was found that the adsorption process reached equilibrium at 3 h for CAC and 4 h for PAC. The adsorption of copper was found to increase with increasing pH, the optimum efficiency being attained at pH 6. The kinetics of the copper ion adsorption were described by pseudo first - order and pseudo second - order equation and the adsorption of copper follows pseudo second - order rate kinetics. The theories of Freundlich and Langmuir adsorption isotherms were used to describe the adsorption process of Cu(II) and the Langmuir model is assumed to give the best fit to the experimental results than Freundlich model. It was concluded that the activated carbon produced from rubber wood sawdust by H_3PO_4 activation has better adsorbing capacity of copper ions than CAC.

Nomenclatures

t	: time (min)
q_t	: uptake capacity at time t (mg/g)
q_e	: equilibrium uptake capacity (mg/g)
K_1	: first order rate constant (min^{-1})
K_2	: second order rate constant (g mg^{-1} min^{-1})
X_m	: uptake quantity by monolayer formation (mg/g)
C_e	: equilibrium concentration (mg/l)
b	: Langmuir isotherm constant (l/mg)
K_f	: Freundlich isotherm constant (mg/g)
n	: Freundlich isotherm constant (g/l)

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