Adsorption (2010) 16: 75–84
DOI 10.1007/s10450-010-9209-2

PROCEEDINGS OF PBAST5

Chemically activated Ipomoea carnea as an adsorbent for the copper sorption from synthetic solutions

Michael Angelo Miranda · P. Dhandapani ·
M. Helen Kalavathy · Lima Rose Miranda

Received: 24 July 2009 / Accepted: 11 February 2010 / Published online: 2 March 2010

Abstract An indigenously prepared zinc chloride activated Ipomoea carnea (morning glory), a low-cost and abundant adsorbent, was used for removal of Cu(II) ions from aqueous solutions in a batch adsorption system. The chemical activating agent $ZnCl_2$ was dissolved in deionised water and then added to the adsorbent in two different ratios 1:1 and 1:0.5 adsorbent to activating agent ratio by weight. Studies were conducted as a function of contact time, initial metal concentration, dose of adsorbent, and pH. Activated Ipomoea carnea (AIC) were characterised using scanning electron microscopy (SEM), iodine number and methylene blue number. High iodine numbers indicates development of micro pores with zinc chloride activation. Maximum adsorption was noted within pH range 6.0(±0.05). Adsorption process is fast initially and reaches equilibrium after about 4 hours. The kinetic data were analysed using pseudo-first-order and pseudo-second-order models. The pseudo-second-order kinetic model was found to agree well with the experimental data. Adsorption equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The Langmuir model represented the sorption process better than the Freundlich model. Based on the Langmuir isotherm, the monolayer adsorption capacity of Cu(II) ions was 7.855 $\mathrm{mg\,g^{-1}}$ for AIC (1:1) and 6.934 $\mathrm{mg\,g^{-1}}$ for AIC (1:0.5).

Keywords Adsorption of copper · Ipomoea carnea · Zinc chloride activation · Kinetics · Micro- and meso-porous carbon

Abbreviations

RIC	Raw Ipomoea carnea
AIC	Activated Ipomoea carnea
Pred	Predicted
Exp	Experimental

Nomenclature

a	Radius of spherical adsorbent particles (m)
C_0	Concentration of Cu^{2+} before adsorption (mg/l)
C_e	Equilibrium concentration of Cu^{2+} in solution (mg/l)
C_r	Concentration of Cu^{2+} after adsorption (mg/l)
D_{eff}	Effective diffusion coefficient (m^2/s)
D_2	Particle diffusion coefficient (m^2/s)
F	Fractional attainment of equilibrium at time t
K	Freundlich constant representing multilayer adsorption capacity (mg/g)
K_f	Pseudo first-order rate constant (min^{-1})
K_{id}	Initial rate of intraparticle diffusion (mg/(g $min^{0.5}$))
K_L	Langmuir constant representing adsorption intensity (l/mg)
K_s	Pseudo second-order rate constant (g/mg min)
M	Mass of the adsorbent (g)
n	Freundlich constant representing adsorption intensity (g/l)
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Adsorption capacity at any time t (mg/g)
Q_0	Langmuir constant representing maximum monolayer adsorption capacity (mg/g)

This work was originally presented in Pacific Basin Conference on Adsorption Science and Technology (Pbast 5), Singapore, May 25–27.

M.A. Miranda
Department of Chemical Engineering, Sri Venkateswara College of Engineering, Pennalur, Sriperumbudur 602105, India

P. Dhandapani · M.H. Kalavathy · L.R. Miranda (✉)
Department of Chemical Engineering, A. C. College of Technology, Anna University, Chennai 600025, India
e-mail: limamiranda2007@gmail.com

R^2	Regression coefficient
t	Contact time (min)
V	Volume of adsorbate solution (l)

1 Introduction

The large-scale production of a variety of chemical compounds has lead to global deterioration of the environmental quality. Unlike organic pollutants, heavy metals are essentially non-biodegradable and hence accumulate in living organisms. Some metals such as Cd, Hg, Ag and Pb can become extremely toxic to living beings. Others such as Cu, Zn, Mn, Fe, Ni and Co though essential for plants and animal livers, when present in excess concentrations and above certain limits, can be very harmful to living organisms. One of the heavy metals that is toxic to humans and widely studied by many researchers is copper. Copper, is considered a micronutrient but is extremely toxic to living organisms at high concentrations. The main sources of copper pollution are metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry. Copper may also be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. The World Health Organization (WHO) recommends a maximum acceptable concentration of 1.5 mg/l (Dundar et al. 2008) for Cu(II) in drinking water. It has been reported that excessive intake of copper by humans leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation (Ngah and Hanafiah 2008). Copper can be removed by precipitation as copper hydroxide but this method is only efficient at high pH values. Conventional methods include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, application of membrane technology and evaporation recovery. However, these processes have considerable disadvantages including incomplete metal removal, requirement of expensive equipment and monitoring systems, large reagent or energy requirements or generation of toxic sludge or other waste products that require disposal. Adsorption, another process for conventional wastewater treatment, has received considerable attention for the development of an efficient, clean and cheap technology. In recent years, attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials (Kalavathy et al. 2005). Many researchers have investigated low-cost materials as viable adsorbents for heavy metal removal, namely, rice husk (Wong et al. 2003), barks (Reddy et al. 1997), teak leaves powder (King et al. 2006), tree fern (Ho et al. 2002), groundnut shells (Shukla and Pai 2005), macadamia nutshell (Ahmadpour and Do 1997), holly oak (Prasad and Freitas 2000), and paper mill sludge (Nasrin et al. 2000).

Although activated carbon has been extensively used as an adsorbent in a variety of industrial and environmental applications, its adsorption capabilities are shown to be largely controlled by its surface characteristics. The type of precursor and the method employed for activation are the key factors that determine the quality of the carbon produced. The combination of the chemical and physical activation processes leads to the production of activated carbon with specific surface properties. Chemical activation involves impregnation of the raw material with chemicals such as phosphoric acid, potassium hydroxide, and zinc chloride (Sabio et al. (1995, 2004); Nadeema et al. 2006). The common feature of these impregnants is their ability for carbonization and therefore, for development of a desired pore structure. The degradation of cellulose material and the aromatization of the carbon skeleton upon $ZnCl_2$ treatment results in the creation of a porous structure. Zinc chloride acts as a dehydrating agent that promotes the decomposition of carbonaceous material during the carbonization process, restricts the formation of tar, and increases the carbon yield. Essentially, vacant interstices in the carbon matrix are formed upon extensive post pyrolysis washing of the pores. The extent of chemical activation can significantly alter the characteristics of the produced carbons.

The need for a cost-effective process and a safe method for removing heavy metals from discharging effluents have resulted in the search for other unconventional materials such as organic or inorganic sorbents. A number of works have been carried out using activated carbon from hazelnut husk (Imamoglu and Tekir 2008), rice hulls (Teker et al. 1999), apricot stones, coconut shells (Budinova et al. 1994) and peanut hulls (Periasamy and Namasivayam 1994) for heavy metals removal. However, no attempt has been made to produce activated carbon using Ipomoea carnea plants for the removal of Cu(II) ions. The reasons for using Ipomoea carnea plants are, it is not region specific and available in plenty. It has low calorific value and hence cannot be used as fuel. It is toxic to cattle. Therefore its disposal has always been a problem. So Ipomoea carnea is employed for the preparation of activated carbon. The main objective of this study is to ascertain whether Ipomoea carnea is a suitable raw material for the production of activated carbon, the quality of the carbon produced and its effectiveness in the removal of copper from aqueous solutions.

2 Experimental

2.1 Materials and method

Copper sulphate pentahydrate, chloroform, citric acid, ethylenediamine tetra acetic acid (E.D.T.A) disodium salt, and sodium diethyldithiocarbomate used in this study were obtained from RANKEM (Mumbai). Zinc chloride the chemical activating agent used in this study was obtained from Ranbaxy Fine Chemical Ltd (Mumbai).

The experiments were conducted in two parts

- Preparation of activated carbon
- Adsorption studies (batch studies)

2.1.1 *Preparation of adsorbent*

In this study, the Ipomoea carnea (morning glory), a low-cost and abundantly available plant, was used for removal of Cu(II) ions from aqueous solutions. Ipomoea carnea stems were collected in and around Chennai, India. The stem of Ipomoea carnea was dried at room temperature for a few days and then oven dried at 110 °C overnight. Dried material was ground to an average particle size of 1 mm. The material was washed thoroughly with deionised water to remove all impurities.

2.1.2 *Activation with $ZnCl_2$*

The process of chemical activation involves two steps. The first involves the chemical impregnation of the activating agent into the Ipomoea carnea, followed by thermal activation. In this work the reagent (zinc chloride) was dissolved in water (10% solution), mixed with the precursor and the mixture kept at 85 °C for 14 hours without evaporation. $ZnCl_2$ was added in two different ratios 1:1 and 1:0.5, adsorbent to activating agent ratio by weight. After impregnation, the material was carbonized under closed conditions. The temperature was raised at 4 °C/min to 500 °C, which was maintained for 3 h. The samples were cooled and then washed to remove excess reagent, the washed water was analysed for zinc using zincon in a UV spectrophotometer. Washing was repeated till the zinc content was found to be negligible and then dried at 110 °C until a constant weight was obtained.

2.2 Batch adsorption experiments

Experiments were carried out by varying the initial adsorbate concentration, adsorbent loading and the initial pH of the Cu(II) solution. A known weight of the adsorbent was added to 100 ml of the Cu(II) solution in a 250 ml conical flask. The mixture was agitated at 180 rpm in an orbital shaker for a pre-determined time interval. Cu(II) samples were analyzed in a UV spectrophotometer by forming complex with sodium diethyldithiocarbomate at a $\lambda_{\max}$ of 435 nm (Jeffery et al. 1989). The amount of copper adsorbed, q_e (mg/g) was computed by the following equation:

$$q_e = \left(\frac{(C_0 - C_r)}{M} \times V\right) \tag{1}$$

The percent removal of copper is calculated by the following equation:

$$\text{Removal}(\%) = \left(\frac{(C_0 - C_r)}{C_0} \times 100\right). \tag{2}$$

Where C_0 and C_r copper concentrations (mg/l) before and after adsorption, V is the volume of adsorbate (l) and M is the weight of the adsorbent (g).

3 Results and discussion

3.1 Characterisation of the adsorbents

3.1.1 *SEM photomicrograph*

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the adsorbent. SEM images were recorded using JOE-JSM840 field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during FESEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere. The coated samples were then transferred to the SEM specimen chamber to get the images. SEM photomicrographs of raw adsorbent and activated carbon at 8000× magnification reveal the nature of the surface of Ipomoea carnea. Figure 1A shows very few pores and highly irregular surface, thus makes possible the adsorption of Cu(II) ions on different parts of the adsorbent. This is because of the heterogeneous structure of raw adsorbent. The degradation of cellulose material and the aromatization of the carbon skeleton upon $ZnCl_2$ treatment result in the creation of the porous structure. Ahmadpour and Do (1997) described pore evolution with respect to the activating agents and showed that micropore formation is predominant when the $ZnCl_2$ to precursor mass ratio is less than one. They also observed that creation and widening of the micropores take place simultaneously, when the impregnation ratio is greater than 1. It is quite obvious from the obtained SEM images Figs. 1B and C that chemical modification of the carbon adsorbents significantly alters the physico-chemical properties and porosity of the materials. The SEM photographs clearly shows that after activation with zinc chloride a lot of micro pores were produced (Fig. 1B). It is also observed that, as impregnation ratio increases, widening of pores occurs leading to the formation of macropores (Fig. 1C).

3.1.2 *Iodine number and methylene blue number*

Activated carbons prepared from Ipomoea carnea were characterized by their iodine number, methylene blue number and methyl violet number. From Table 1 it is observed that the iodine value, which is an indication of micro pores

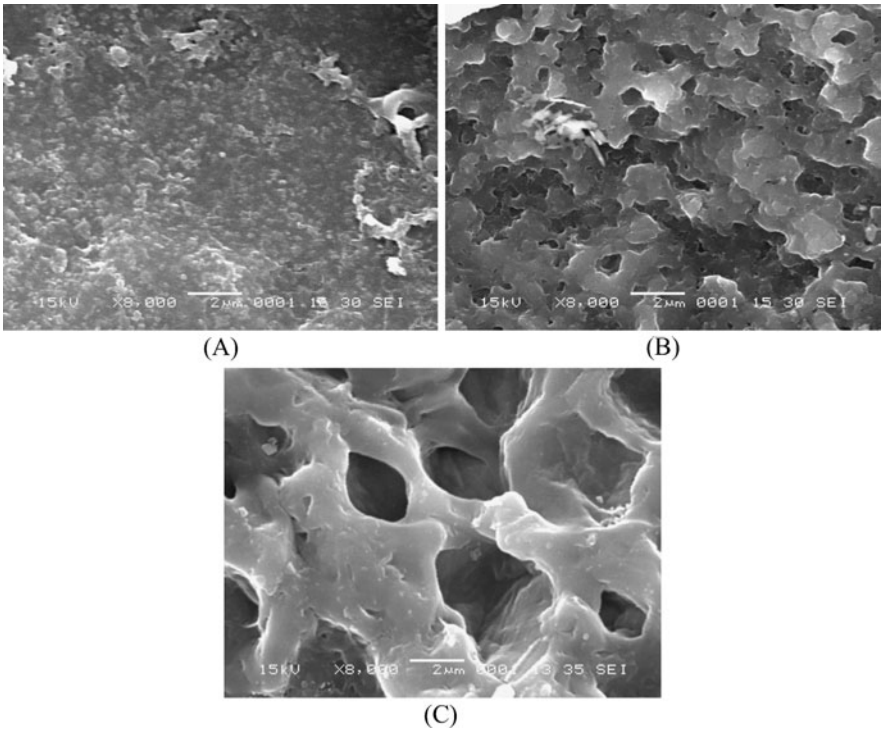

Fig. 1 (**A**) SEM micrograph of raw Ipomoea carnea (RIC). (**B**) & (**C**) SEM micrograph of activated Ipomoea carnea (AIC) activated with $ZnCl_2$ in the ratio of 1:0.5 and 1:1 adsorbent to $ZnCl_2$ weight

present, is higher for AIC (1:0.5) as observed in the SEM photographs. Also the increased values of methylene blue and methyl violet, which represent mesopore development, are higher for AIC (1:1) and conformed by the SEM photographs.

3.2 Effect of concentration

Different initial concentrations of copper solution varying from 10 to 40 mg/l with 0.5 g of adsorbent are used to optimize the required contact time under prescribed conditions for maximum uptake. Experiments were done separately with raw Ipomoea carnea (RIC) and activated Ipomoea carnea (AIC). With increase in concentration, the adsorption capacity increases (Fig. 2). The amount of Cu(II) adsorbed increased with increase in initial concentration and remained nearly constant after equilibrium. Equilibrium was attained within 120 min for RIC and 240 min for both AIC (1:0.5) and (1:1), and the equilibrium times are found to be the same for all concentrations studied.

3.3 Effect of dosage

Different amounts of raw adsorbent varying from 0.25 g to 1 g/100 ml of solution with 20 mg/l concentration of copper were used to optimize the amount of adsorbent required for maximum uptake. In Fig. 3 it was found that adsorption capacity increases with increase in dosage of the adsorbent. This is due to the fact that, the more carbon there is, greater will be the active sites to adsorb copper, but the adsorbate concentration remains the same. Hence, adsorbate available for adsorption per gram of adsorbent will be less when the amount of adsorbent is increased. The difference in adsorption capacity q (mg/g) at the same initial metal ion concentration and contact time may also be attributed to the difference in their chemical affinities and ion exchange capacity, with respect to the chemical functional group on the surface of the adsorbent.

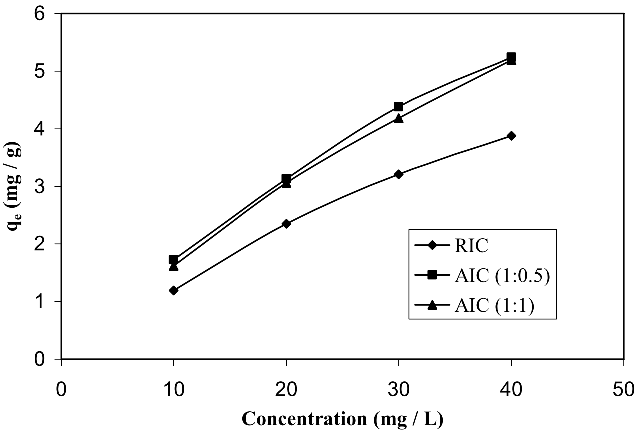

Fig. 2 Effect of concentration on adsorption capacity. Conditions: adsorbent dosage 0.5 g/100 ml, pH 6.0 and at equilibrium time

3.4 Effect of pH

The solution pH affects the surface charge of the adsorbent and the degree of ionization of the adsorbate. The influence

Table 1 Characterization of activated carbon

Adsorbent	Surface area (m^2/g)	Iodine number (mg/g)	Methylene blue number (mg/g)	Methyl violet number (mg/g)
RIC	482.61	756	90	50
AIC 1:0.5 ratio	858	1263	112	89
AIC 1:1 ratio	794	1239	184	138

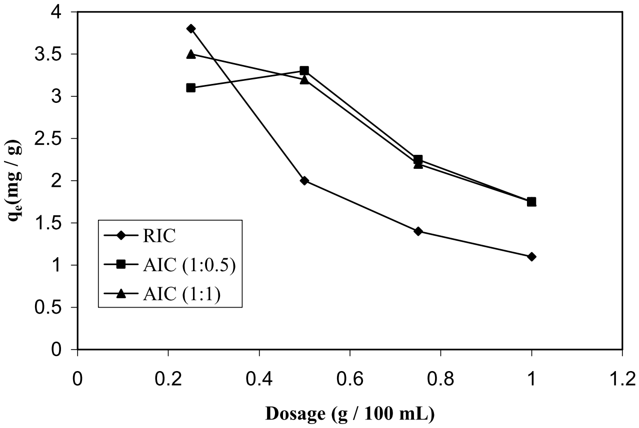

Fig. 3 Effect of adsorbent dosage on adsorption capacity. Conditions: initial concentration 20 mg/l, pH 6.0 and at equilibrium adsorption time

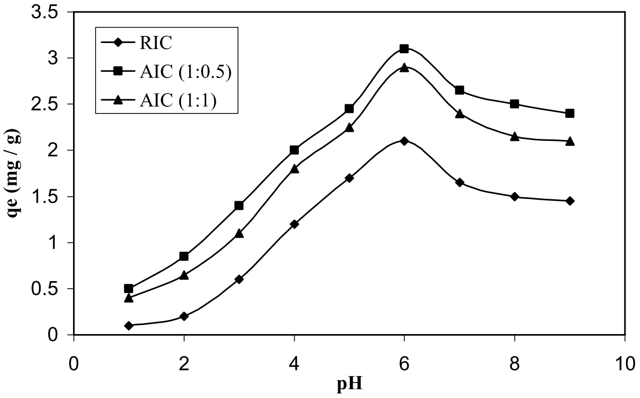

Fig. 4 Effect of pH on copper removal. Conditions: initial concentration 20 mg/l, adsorbent dosage 0.5 g/100 ml and at equilibrium adsorption time

of pH on the adsorption of copper(II) is presented in Fig. 4. These results indicate that an increase in pH has a positive effect on metal uptake up to pH 6, since the competition between protons and metal cations for the active sites of the biomass decreases. The maximum adsorption of copper(II) ions on the adsorbent was observed at pH 6. Above pH 6, Cu(II) adsorption significantly decreased. Beyond pH 6.0 the Cu(II) ions was found to precipitate as its hydroxide complexes (Ho et al. 2002). At very low pH values, copper adsorption was found to be very low due to competition between H^+ and Cu(II) ions for the adsorption sites. As pH was increased, more adsorbent surface was exposed and carried negative charges, which results in less repulsion of Cu(II) ions. These results seem to suggest that the adsorption of Cu(II) to biomass is mainly due to ionic attraction.

3.5 Adsorption kinetics

The prediction of kinetics is necessary for the design of sorption systems. Chemical kinetics explain how fast the rate of chemical reaction occurs and also the factors affecting the reaction rate. In batch adsorption processes the adsorbate molecules diffuse into the interior of the porous adsorbent. Investigations showed that the adsorption of copper ions from aqueous solution is linear during the initial 2 hours for RIC and 4 hours for AIC of 1:1 and 1:0.5 ratios. In order to observe the sorption process of copper ions on unmodified and chemically modified adsorbents, two kinetic models pseudo-first and second-order model were implemented.

3.5.1 Pseudo-first-order model

The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3}$$

where q_t (mg/g) is the amount of adsorbate absorbed at time t, q_e (mg/g) the adsorption capacity in equilibrium, k_f (min^{-1}) the rate constant for pseudo-first-order model and t (min) is the time (Dundar et al. 2008; Ngah and Hanafiah 2008; Kalavathy et al. 2005; Nadeema et al. 2006). The linear form of Eq. 3 is

$$\ln(q_e - q_t) = \ln q_e - k_f t \tag{4}$$

Adsorption rate constants (k_f) and adsorption capacity (q_e) for the adsorption of copper ions by raw and chemically activated adsorbents were calculated from the slope and intercept of the plots of ln $(q_e - q_t)$ against t and are tabulated in Table 2.

3.5.2 Pseudo-second-order model

The pseudo-second-order model can be presented in the following form

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{5}$$

Table 2 Pseudo first order parameter for RIC and AIC

Concentration	RIC				AIC (1:0.5)				AIC (1:1)			
(mg/l)	q_e (mg/g)		K_f	R^2	q_e (mg/g)		K_f	R^2	q_e (mg/g)		K_f	R^2
	Pred	Exp	(min^{-1})		Pred	Exp	(min^{-1})		Pred	Exp	(min^{-1})	
10	0.920	1.18	0.0370	0.9878	1.635	1.73	0.0154	0.9967	1.296	1.16	0.0168	0.9781
20	1.352	2.13	0.0324	0.97	2.797	3.13	0.0138	0.9981	2.451	3.06	0.0172	0.9821
30	1.535	3.07	0.0264	0.9108	3.435	4.38	0.0123	0.9849	2.966	4.18	0.0159	0.9728
40	1.289	3.69	0.0297	0.9030	3.520	5.24	0.0115	0.9828	3.281	5.19	0.0119	0.9766

Table 3 Pseudo second order parameter for RIC and AIC

Concentration	RIC				AIC (1:0.5)				AIC (1:1)			
(mg/l)	q_e (mg/g)		K_s	R^2	q_e (mg/g)		K_s	R^2	q_e (mg/g)		K_s	R^2
	Pred	Exp	(g/mg min)		Pred	Exp	(g/mg min)		Pred	Exp	(g/mg min)	
10	1.22	1.18	0.075	0.9995	2.08	1.73	0.0083	0.9956	1.77	1.16	0.0204	0.9989
20	2.31	2.13	0.047	0.9994	3.59	3.13	0.0068	0.9958	3.32	3.06	0.0128	0.9993
30	3.28	3.07	0.042	0.9990	4.92	4.38	0.0067	0.9896	4.46	4.18	0.0123	0.9971
40	3.90	3.69	0.057	0.9993	5.80	5.24	0.0072	0.9884	5.47	5.19	0.0102	0.9942

where k_s is the rate constant of pseudo-second-order model (g/mg min).

Definite integration of the above equation for boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$, the following form of equation can be obtained (Dundar et al. 2008; Ngah and Hanafiah 2008; Kalavathy et al. 2005; Nadeema et al. 2006):

$$\frac{t}{q_t} = \frac{1}{(k_s q_e^2)} + \left(\frac{1}{q_e}\right)t \tag{6}$$

The equilibrium adsorption capacity (q_e) and the pseudo-order rate constants k_s were obtained from the slope and intercept of the plots of t/q_t against t for various adsorbents and are shown in Fig. 5. They are also reported in Table 3. The calculated correlation coefficients are consistent and closer to unity for pseudo-second-order kinetic model than the pseudo first order kinetic model, and also the q_e predicted was found to be nearly the same as that of the q_e experimental for pseudo second order. Therefore, the adsorption kinetics could well be explained and approximated more favourably by pseudo second-order kinetic model for raw and activated carbon adsorbents, respectively.

3.6 Adsorption isotherms

The Langmuir and Freundlich isotherms are the equations most frequently used isotherms that are discussed here to represent the data on adsorption from solution (Dundar et al. 2008; Ngah and Hanafiah 2008; Kalavathy et al. 2005; Nadeema et al. 2006).

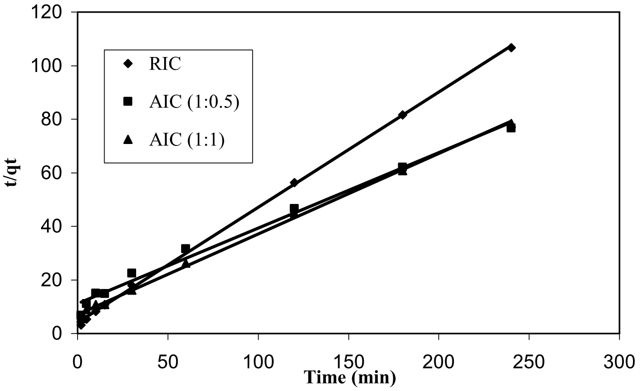

Fig. 5 Pseudo second order plot for the adsorption of copper. Conditions: pH 6.0, adsorbent dosage 0.5 g/100 ml

3.6.1 Langmuir isotherm

The equilibrium adsorption behaviour can be described by the Langmuir adsorption equation. The linear form is given below

$$\frac{C_e}{q_e} = \frac{1}{(K_L Q_0)} + \frac{C_e}{Q_0} \tag{7}$$

where Q_0 and K_L are the Langmuir constants representing maximum monolayer adsorption capacity (mg/g) and adsorption intensity of the system, respectively. Langmuir isotherms are plots of C_e/q_e versus C_e. Straight lines were obtained from which Q_0 and K_L are calculated. The values are shown in Table 4.

Table 4 Langmuir and Freundlich parameters

Adsorbents	Langmuir parameters			Freundlich parameters		
	Q_0 (mg/g)	K_L (l/mg)	R^2	n	K (mg/g)	R^2
RIC	7.651	0.0438	0.9815	1.428	0.447	0.995
AIC (1:0.5)	6.934	0.2146	0.9915	2.037	1.502	0.9948
AIC (1:1)	7.855	0.1337	0.9957	1.72	1.157	0.9892

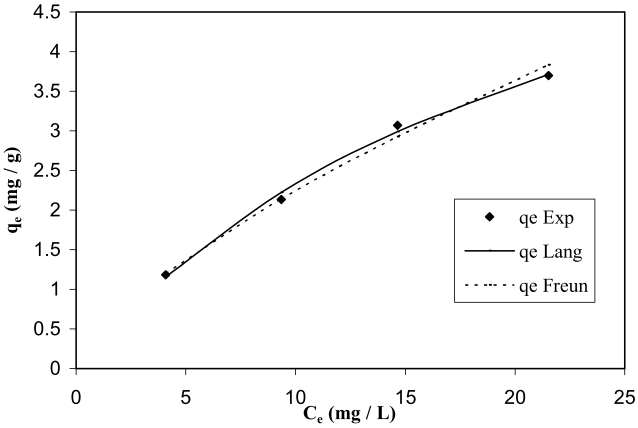

Fig. 6 Isotherm plot for adsorption of copper using RIC

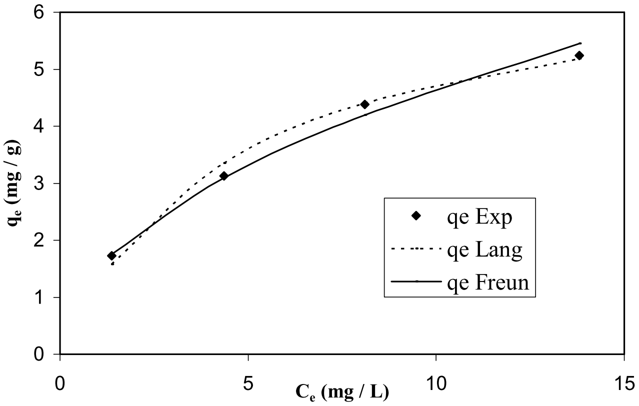

Fig. 7 Isotherm plot for adsorption of copper using AIC (1:0.5)

3.6.2 *Freundlich isotherm*

Freundlich isotherms are represented by the following equation

$$\log q_e = \log K + \left(\frac{1}{n}\right) \log C_e \tag{8}$$

where q_e is the amount of copper adsorbed by unit mass of adsorbent, K the sorption capacity, n the adsorption intensity and C_e is the equilibrium concentration. A plot of log q_e versus $\log C_e$ gives values for n and K, shown in Table 4. The results illustrate that AIC (1:0.5) has good adsorption of copper.

Figures 6, 7, and 8 show the comparison between the experimental, Langmuir and Freundlich isotherms. Our results show that for RIC, Freundlich isotherm fits better than Langmuir isotherm. This may be due to the fact that before treatment the raw Ipomoea carnea had irregular surface (heterogeneity) which was homogenized after treatment with zinc chloride, and the monolayer adsorption capacity found may not be accurate because of the poor regression coefficient. The Langmuir adsorption equation fitted better with equilibrium data from experiments of batch adsorption for AIC (1:0.5) and AIC (1:1). From the experimental values (Figs. 1, 2 and 3) it was found that both AIC (1:0.5) and (1:1) have close values, but the Langmuir plot AIC (1:1) shows the better adsorption capacity 7.855 mg/g than AIC (1:0.5).

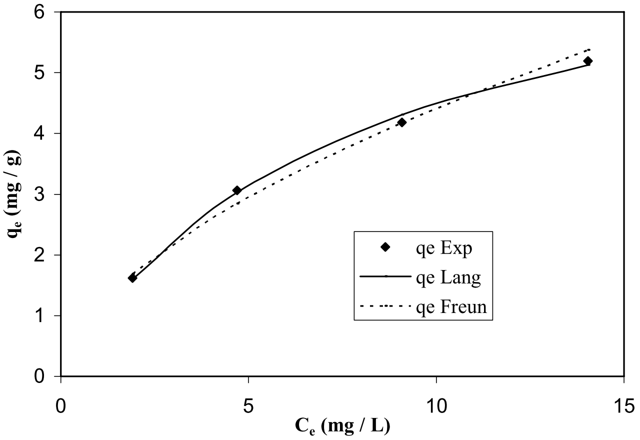

Fig. 8 Isotherm plot for adsorption of copper using AIC (1:1)

3.7 Comparison of AIC with other adsorbents

The adsorption capacity of Cu(II) onto Ipomoea carnea was compared with other adsorbents reported in literature and is shown in Table 5. It can be observed that a pH of 6.0 was found to be an optimum in nearly all cases whatever the method of activation is. Further, it can also be seen that the activated carbon produced from Ipomoea carnea compares well with the activated carbons from most of the raw materials listed in Table 5. Few raw materials exhibit very high adsorption capacity; this could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw mater-

Table 5 Comparison of adsorption capacity of Ipomoea carnea with other adsorbents

Adsorbent	Adsorption capacity (mg/g)	pH	C_0 (mg/l)	Reference
RSAC	5.729	6.0	40	Kalavathy et al. (2005)
Wheat shell	10.84	5.0	250	Basci et al. (2004)
Herbaceous peat	4.84	5.5	38.4	Gündogan et al. (2004)
Cork biomass	3.00	5	10	Chubar et al. (2004)
Bagasse fly ash	2.26	4	50	Gupta and Ali (2000)
Turkish coals	1.62	4	30	Karabulut et al. (2000)
Areca—a food waste	2.84	5.6	12	Zheng et al. (2008)
Tea industry waste	8.64	5.5	100	Cay et al. (2004)
Peanut hulls	10.17	–	113.55	Brown et al. (2000)
Hazelnut husk A.C	6.645	5.7	200	Imamoglu and Tekir (2008)
Tobacco dust	36	4–5	15	Qi and Aldrich (2008)
Modified Rice husk	29	5–6	100	Wong et al. (2003)
Raw Pomegranate peel	1.3185	5.8	2.5	El-Ashtoukhy et al. (2008)
Pomegranate peel A.C	18.050	5.8	2.5	El-Ashtoukhy et al. (2008)
LNTPF	30–200	4.5	19.531	Dundar et al. (2008)
Potato peel charcoal	150–400	6	0.3877	Aman et al. (2008)
RHBL	3–10	5	9.92	Ngah and Hanafiah (2008)
CA-BWSS	1271	5	28.6	Zhu et al. (2008)
RIC	7.651	6.0	40	Present work
AIC (1:0.5)	6.934	6.0	40	Present work
AIC (1:1)	7.885	6.0	40	Present work

ial. Hence, Ipomoea carnea can be considered to be a viable adsorbent for the removal of Cu(II) from dilute solutions.

3.8 Adsorption mechanism

The prediction of rate limiting step is an important factor to be considered in the adsorption process (Sarkar et al. 2003). For a solid-liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion) or intra particle diffusion, or both. The three steps of the mechanisms of adsorption are film diffusion, particle diffusion, and adsorption of the adsorbate on the exterior surface of the adsorbent.

Generally, the last step is the equilibrium reaction and it is very rapid; the resistance is hence assumed to be negligible (Kalavathy et al. 2005). The slowest step determines rate controlling parameter in the adsorption process. However, the rate controlling parameter might be distributed between intra particle and film diffusion mechanisms. The adsorption of copper onto carbon activated with zinc chloride may be controlled, due to film diffusion at earlier stages and later by the particle diffusion. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting an intra particle diffusion plot and McKay plot.

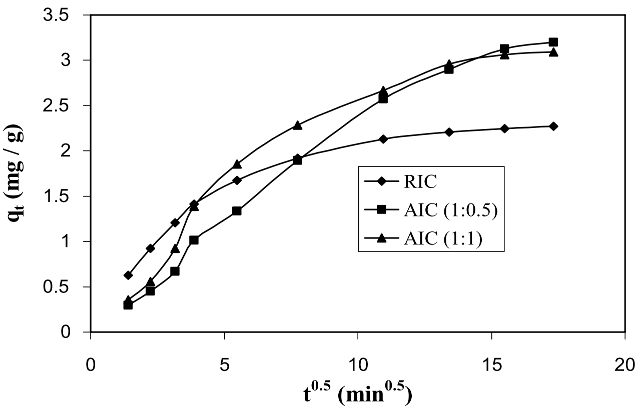

Fig. 9 Intra particle diffusion for adsorption of copper

According to Weber and Morris, an intra-particle diffusion coefficient K_{id} is given by the equation

$$q_t = K_{id} t^{0.5} \tag{9}$$

The plot of q_t vs $t^{0.5}$ as shown in Fig. 9 represents different stages of adsorption for RIC, AIC (1:0.5) and AIC (1:1), respectively. The initial curved portion relates to the film diffusion and the latter linear portion represents the intraparticle diffusion (Sun and Yang 2003). The slope of the second linear portion of the plot has been defined to yield

Table 6 Intra-particle rate parameter and diffusion co-efficient at different concentrations

Concentration (mg/l)	RIC		AIC (1:0.5)		AIC (1:1)	
	K_{id} (mg/g min$^{0.5}$)	$D_{eff} \times 10^{-6}$ (cm^2/s)	K_{id} (mg/g min$^{0.5}$)	$D_{eff} \times 10^{-6}$ (cm^2/s)	K_{id} (mg/g min$^{0.5}$)	$D_{eff} \times 10^{-6}$ (cm^2/s)
10	0.0022	4.782	0.0707	1.700	0.0729	1.849
20	0.0560	3.572	0.1420	1.520	0.0669	1.899
30	0.0749	2.863	0.1921	1.340	0.0572	1.748
40	0.0606	3.268	0.2214	1.270	0.0480	1.317

the intraparticle diffusion parameter K_{id} (mg g^{-1} min$^{-0.5}$). On the other hand, the intercept of the plot reflects boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient K_{id} values are listed in Table 6.

Adsorption kinetic data were further analysed by the procedure given by Reichenberg (1953) and Helfferich (1962) in order to determine the rate controlling step of copper onto activated carbon made from Ipomoea carnea. Assuming the adsorbent particle to be a sphere of radius ‘a’ (cm) and the diffusion follows Fick’s law, the relation between weight uptake and time is given by

$$F = 6\left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}\left[\pi^{\frac{-1}{2}} + 2\sum_{n=1}^{\infty} ierfc\left(\frac{na}{\sqrt{Dt}}\right)\right] - 3\left(\frac{Dt}{a^2}\right) \tag{10}$$

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp[-n^2 Bt] \tag{11}$$

$$F = \frac{q_t}{q_e} \tag{12}$$

where F is the fractional attainment of equilibrium at time t,

$$B = \frac{\pi^2 D_{eff}}{a^2} \tag{13}$$

where D_{eff} (cm^2/s) is the effective diffusion coefficient.

To further verify the above observations, McKay plots of $\log(1 - q_t/q_e)$ vs t at different initial concentrations are shown in Fig. 10 for activated carbons and raw adsorbent made from Ipomoea carnea. These plots are based on the assumption that adsorption follows Fick’s law. At longer times of adsorption, Eq. 10 reduces to the form

$$\log\left(1 - \frac{q_t}{q_e}\right) = \log\frac{6}{\pi^2} + \left(-D_2\frac{\pi^2}{a^2}\right)t \tag{14}$$

where D_2 is the particle diffusion coefficient.

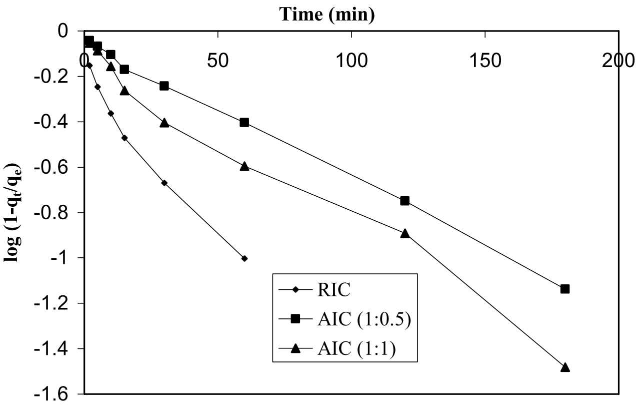

Fig. 10 McKay plot for the adsorption of copper

The rate controlling mechanism was analyzed for adsorbents RIC and AIC using this plot. The plot was more scattered, which supports the assumption that particle diffusion becomes the rate-controlling step at this concentration. From the Weber and Morris plot (Weber and Morris 1963) and McKay plot, it was found that particle diffusion is the rate controlling step.

4 Conclusion

The present investigation evaluates that the activated carbon made from Ipomoea carnea can be used as an effective adsorbent for the removal of copper from synthetic waste water. The adsorption isotherms fit both Langmuir and Freundlich isotherms but Langmuir isotherm is found to be more favourable than Freundlich isotherm. It was concluded that the activated carbon produced from morning glory by zinc chloride activation has better adsorbing capacity for copper than the raw adsorbent. SEM photographs clearly show that after activation with zinc chloride a lot of micro pores were produced. With the increase in micro pores the adsorption percentage of copper was increased. The adsorption of copper was found to be maximum at pH 6. The adsorption of copper by raw adsorbent and activated carbon both follow pseudo second order rate kinetics.

References

Ahmadpour, A., Do, D.D.: The preparation of activated carbon from macadamia nutshell by chemical activation. Carbon **35**, 1723–1732 (1997)

Aman, T., Kazi, A.A., Sabri, M.U., Bano, Q.: Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. Colloids Surf. B, Biointerfaces **63**, 116–121 (2008)

Basci, N., Kocadagistan, E., Kocadagistan, B.: Biosorption of copper (II) from aqueous solutions by wheat shell. Desalination **164**, 135–140 (2004)

Brown, P., Jefcoat, I.A., Parrish, D., Gill, S., Graham, E.: Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution. Adv. Environ. Res. **4**, 19–29 (2000)

Budinova, T.K., Gergova, K.M., Petrov, N.V., Minkova, V.N.: Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials. J. Chem. Technol. Biotechnol. **60**, 177–182 (1994)

Cay, S., Uyanik, A., Ozasik, A.: Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste. Sep. Purif. Technol. **38**, 273–280 (2004)

Chubar, N., Carvalho, J.R., Correia, M.J.N.: Cork biomass as biosorbent for Cu(II), Zn(II) and Ni(II). Colloids Surf. A, Physicochem. Eng. Aspects **230**, 57–65 (2004)

Dundar, M., Nuhoglu, C., Nuhoglu, Y.: Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest. J. Hazard. Mater. **151**, 86–95 (2008)

El-Ashtoukhy, E.S.Z., Amin, N.K., Abdelwahab, O.: Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination **223**, 162–173 (2008)

Gündogan, R., Acemioglu, B., Alma, M.H.: Copper (II) adsorption from aqueous solution by herbaceous peat. J. Colloid Interface Sci. **269**, 303–309 (2004)

Gupta, V.K., Ali, I.: Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. Sep. Purif. Technol. **18**, 131–140 (2000)

Helfferich, F.: Ion Exchange. McGraw-Hill, New York (1962)

Ho, Y.S., Huang, C.T., Huang, H.W.: Equilibrium sorption isotherm for metal ions on tree fern. Process Biochem. **37**, 1421–1430 (2002)

Imamoglu, M., Tekir, O.: Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. Desalination **228**, 108–113 (2008)

Jeffery, G.H., Bassett, J., Mendham, J., Denney, R.C.: Vogel's Textbook of Quantitative Chemical Analysis, 5th edn. Wiley, New York (1989)

Kalavathy, M.H., Karthikeyan, T., Rajgopal, S., Miranda, L.R.: Kinetic and isotherm studies of Cu(II) adsorption onto H3PO4-activated rubber wood sawdust. J. Colloid Interface Sci. **292**, 354–362 (2005)

Karabulut, S., Karabakan, A., Denizli, A., Yürüm, Y.: Batch removal of copper(II) and zinc(II) from aqueous solutions with low-rank Turkish coals. Sep. Purif. Technol. **18**, 177–184 (2000)

King, P., Srivinas, P., Kumar, Y.P., Prasad, V.S.R.K.: Sorption of copper(II) ion from aqueous solution by Tectona grandis l.f. (teak leaves powder). J. Hazard. Mater. B **136**, 560–566 (2006)

Nadeema, M., Mahmooda, A., Shahid, S.A., Shah, S.S., Khalid, A.M., McKay, G.: Sorption of lead from aqueous solution by chemically modified carbon adsorbents. J. Hazard. Mater. B **138**, 604–613 (2006)

Nasrin, R.K., Campbell, M., Sandi, G., Golas, J.: Production of micro- and mesoporous activated carbon from paper mill sludge effect of zinc chloride activation. Carbon **38**, 1905–1915 (2000)

Ngah, W.S.W., Hanafiah, M.A.K.M.: Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies. Biochem. Eng. J. **39**, 521–530 (2008)

Periasamy, K., Namasivayam, C.: Process development for removal and recovery of cadmium from wastewater by a low-cost adsorbent: adsorption rates and equilibrium studies. Ind. Eng. Chem. Res. **33**, 317–320 (1994)

Prasad, M.N.V., Freitas, H.: Removal of toxic metals from solution by leaf, stem and root phytomass of Quercus ilex L. (holly oak). Environ. Pollut. **110**, 277–283 (2000)

Qi, B.C., Aldrich, C.: Biosorption of heavy metals from aqueous solution with tobacco dust. Bioresour. Technol. **99**, 5595–5601 (2008)

Reddy, B.R., Mirghaffari, N., Gaballah, I.: Removal and recycling of copper from aqueous solutions using treated Indian barks. Resources, Conserv. Recyc. **21**, 227–245 (1997)

Reichenberg, D.: Properties of ion-exchange resins in relation to their structure, III: kinetics of exchange. J. Am. Chem. Soc. **75**, 589–597 (1953)

Sabio, M.M., Reinoso, F.R., Caturla, F., Selles, M.J.: Porosity in granular carbons activated with phosphoric acid. Carbon **33**, 1105–1113 (1995)

Sabio, M.M., Reinoso, F.R.: Role of chemical activation in the development of carbon porosity. Colloids Surf. A, Physicochem. Eng. Aspects **241**, 15–25 (2004)

Sarkar, M., Acharya, P.K., Battacharya, B.: Modelling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. J. Colloid Interface Sci. **266**, 28–32 (2003)

Shukla, S.R., Pai, R.S.: Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. Sep. Purif. Technol. **43**, 1–8 (2005)

Sun, Q., Yang, L.: The adsorption of basic dyes from aqueous solution on modified peat-resin particle. Water Res. **37**, 1535–1544 (2003)

Teker, M., Imamoglu, M., Saltabas, O.: Adsorption of copper and cadmium ions by activated carbon from rice hulls. Turkish J. Chem. **23**, 185–191 (1999)

Weber, W.J., Morris, J.C.: Kinetics of adsorption on carbon solution. J. Sanit. Eng. Div. ASCE **89**, 31–59 (1963)

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J.: Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. Chemosphere **50**, 23–28 (2003)

Zheng, W., Li, X.M., Wang, F., Yang, Q., Deng, P., Zeng, G.M.: Adsorption removal of cadmium and copper from aqueous solution by areca—a food waste. J. Hazard. Mater. **157**, 490–495 (2008)

Zhu, B., Fan, T., Zhang, D.: Adsorption of copper ions from aqueous solution by citric acid modified soybean straw. J. Hazard. Mater. **153**, 300–308 (2008)