RESEARCH ARTICLE

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Chemical Sciences Journal, Vol. 2012: CSJ-17

Study of Biosorption of Cu (II) from Aqueous Solutions by Coconut Shell Powder

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Accepted: November 4, 2011; Published: April 23, 2012

Abstract

The metal taking capacity of several types of biomass, agro products and by-products has gained attention during recent years. Coconut shell powder was chosen as the biosorbent for the removal of Cu (II) from aqueous solutions. The adsorption capacity of this sorbent was investigated by batch experiments. High adsorption (>90 %) is achieved in the present study. The influence of pH and particle size was studied and adsorption isotherm models were fitted. An appropriate kinetic model was also attempted.

Keywords: *Biosorption; copper; coconut shell powder; adsorption isotherms.*

1. Introduction

In recent years contamination of aquatic bodies by various pollutants has intensified the deterioration of several ecosystems. Among these, heavy metals cause severe damage to the living systems at various levels. Exposure of the aquatic systems to heavy metal pollutants from various industrial operations like metal ore refining, electroplating, pigments, mining, battery and accumulator manufacturing has been a serious threat to the environment. Acute ingestion of excess copper in drinking water can cause gastrointestinal (GI) tract disturbances and chronic ingestion can lead to liver toxicity in sensitive populations.

The uptake of both metal and non-metal species by biomass is termed as biosorption. Work on the metal binding capacity of some type of biomass and agroproducts [1-3] has gained momentum recently. A number of agricultural waste and by-products like coffee beans, rice husk, cellulose extracted from rice husk (RH-cellulose), cellulose and lignin extracted from coirpith, tea waste, *Aspergillus niger*, spent-grain, litter of natural trembling poplar (*Populus tremula*) forest, nutshells of walnut, hazelnut, pistachio, almond, apricot stone and *Aspergillus fumigatus, Bacillus sphaericus, Anoxybacillus gonensis* immobilized on Diaion [4-13] are studied in literature for their removal capacity Cu (II) ions and other heavy metals from aqueous solutions.

Coconut (*Cocos nucifera*) shell is an attractive and inexpensive option (0.05-0.1% of activated carbon powder) for the biosorption removal of dissolved metals. Various metal binding mechanisms are thought to be involved in the biosorption process including ion exchange, surface adsorption, chemisorption, complexation, and adsorption complexation [14-16]. Coconut shell powder is composed of several constituents, among them lignin acid, around 35-45% and cellulose around 23-43%, bear various polar functional groups including carboxylic and phenolic acid groups which are involved in metal binding [14, 17]. Cellulose and lignin are biopolymers and are considered appropriate for the removal of heavy metals.

In the current work, coconut shell powder as biosorbent for Cu (II) ions and influence of parameters like pH and particle size is presented. Characterising of coconut shell powder was done. Adsorption equilibrium isotherms and kinetic models were studied.

2. Methods

2.1. Biosorbent material

The coconut shell powder used in the present work was prepared in our laboratory using mechanical unit operations equipment like jaw crusher, hammer mill, rotap sieve shaker and standard sieves using the method described by Coconut Board of India.

2.2. Biosorption experiments

Biosorption experiments were performed batch wise at 27^{o} C in Erlenmeyer flasks, stirred in reciprocal shaker for 4 h. In all sets of experiments, accurately weighed coconut shell powder was thoroughly mixed into 250 ml of aqueous metal solution. At regular intervals of time (15 min), a sample of the mixture is filtered to remove the fine particulates and the filtrate was analyzed by atomic adsorption spectrometer (AAS) for the concentration of metal species. The solution of metal species was prepared dissolving $CuSO_4.5H_2O$ (analytical grade supplied by Merck, Mumbai, India) in deionised water and pH adjustments were made using HCl and NaOH solution.

2.3. Apparatus

Perkin-Elmer Analyst 200 atomic absorption spectrometer was used in the studies. All measurements were carried out in an air/acetylene flame and hollow cathode lamps were used. The pre reading calibration is done with four samples prepared from standard 1000ppm solution from Merck (Mumbai, India). The initial metal concentrations indicated by AAS are used for further investigation.

2.4. Equilibrium modelling

This set of experiments are conducted at different initial concentrations of Cu (II) (20–90 ppm) and different adsorbent loading (1g/l to 7 g/l). Adsorption isotherms are basic requirements for the design of adsorption systems. Classical adsorption models like Langmuir and Freundlich were studied to describe the equilibrium between adsorbed metal ions over coconut shell powder (q_{eq}) and metal ions in the solution (C_{eq}) at a constant temperature. The Langmuir equation is valid for mono layer sorption on to a surface with finite number of identical sites and is given by Eq. (1)

$$q_{eq} = \frac{q_{\max} b C_{eq}}{1 + b C_{eq}} \qquad (1)$$

Where q_{max} (mg/g) is the maximum amount of metal ion per unit weight of coconut shell powder and b (1/mg) is a constant related to the affinity of the binding sites. The q_{max} represents practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiment. The q_{max} and b can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} [14, 18-20]. The empirical Freundlich equation based on sorption on a heterogeneous surface is given by Eq. (2).

$$q_{eq} = K_f C_{eq}^{1/n} \qquad (2)$$

where K_f and n are the Freundlich constants, characteristic of the system. K_f and n are indicators of adsorption capacity and adsorption intensity respectively. The linearized Eq. (2) in logarithmic form is used to determine Freundlich constants [14, 19-21].

2.5. Kinetic modelling

A pseudo-second order model [22] can be used to explain the adsorption kinetics. This model is based on the assumption that adsorption follows second order chemisorption.

The pseudo-second order model can be expressed as:

$$\frac{dq}{dt} = k_{ad}(q_{eq} - q)^2 \qquad (3)$$

where k_{ad} is the rate constant of second-order biosorption (g mg^{-1}min^{-1}). For the boundary conditions t=0 to t=t and q=0 to q=q_{eq}, the integrated form of Eq. (3) becomes

$$\frac{1}{q_{eq} - q} = \frac{1}{q_{eq}} + k_{ad} t \qquad (4)$$

This integrated rate law for a second-order reaction can be rearranged to a linear form:

$$\frac{t}{q} = \frac{1}{k_{ad} q_{eq}^2} + \frac{1}{q_{eq}} t \qquad (5)$$

The plot of t/q against t of Eq. (5) should give a linear relationship, from which q_{eq} and k_{ad} can be determined from the slope and intercept of the plot.

3. Results and Discussion

3.1. Effect of pH

pH is an important parameter in determining biosorption levels. The effect of pH (in the range 5-9) on the uptake levels of powder of coconut shell from an aqueous solution is evaluated. The effect of initial pH is presented in Figure 1. The Cu (II) removal increased from 42 % at pH 5 to 96% at pH 9. There is no significant increase from pH 7 onwards. Both the surface functional groups present on the coconut shell powder and metal chemistry in solution relate to the dependence of metal uptake on pH. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of repulsive force [23]. Further, the pH dependence on the metal ion uptake by coconut shell powder can be justified by association-dissociation of certain functional groups like carboxylic and hydroxyl group present on biomass. At low pH, most of carboxylic group are not dissociated and cannot bind the metal ions, though they take part in complexation reactions whereas at high pH carboxylic groups are dissociated and can further bind more metal ions to increase the percentage adsorption. With these observations, further experiments are performed at pH 7 only.

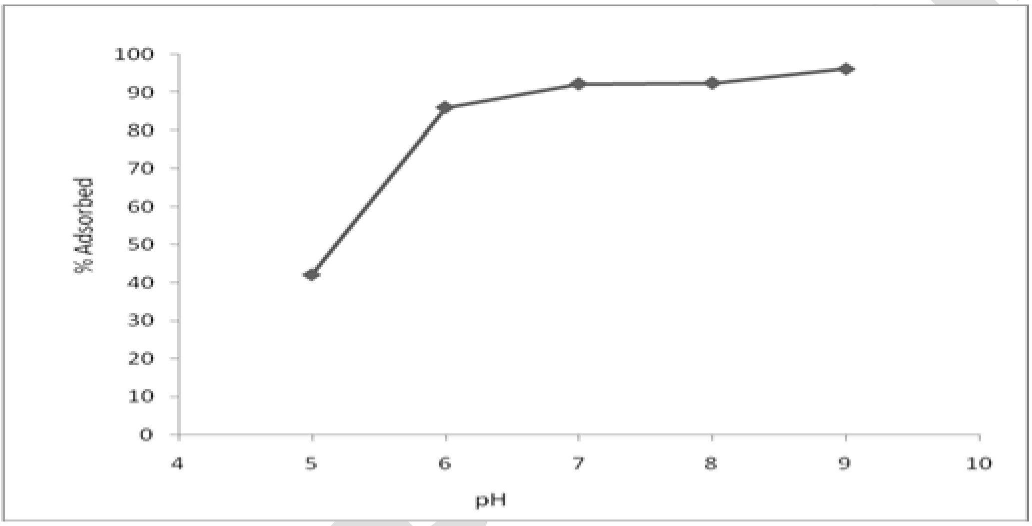

Figure 1: Percentage adsorption of Cu (II) by coconut shell for different pH values. Initial concentration of metal: 30 ppm. Coconut shell concentration: 5g/l. Particle size: 0.105-0.063 mm. Temperature: 27 ^oC. Contact time: 4 h.

3.2. Effect of particle size

Influence of the particle size of coconut shell powder used for uptake of Cu (II) was studied using different particles sizes which are segregated using standard sieves. The results presented in Fig. 2 show a gradual decrease and then increase in removal of Cu (II) with decrease in particle size. It is important to note that larger particles with spherical surfaces, present higher external mass transfer. In this case, higher metal adsorption from these particles is attributed to mass transport inside the sorbent particles [15]. At the same time as the particle size decreases the surface area for adsorption increases which in turn contribute to high adsorption at fine particle size. Optimum particle size can be obtained if precise contributions of mass transport and surface diffusion are ascertained. This has been not formed part of this work.

3.3. SEM Analyses

Scanning Electron Microscope (SEM) was used to evaluate the characteristics of coconut shell powder. The micrographs of coconut shell powder before metal uptake and respective Energy Dispersive Spectroscopy (EDS) analyses are shown in Figure 3 and 4 respectively. Figure 5 and 6 show the same for coconut shell after Cu (II) uptake. Figure 3 shows that the material is irregular and porous. This surface characteristic would substantiate high adsorption through mass transport inside the sorbent. Figure 4 presented EDS analysis, and it shows the presence of C, O, Al, Cl, K as natural species. The presence of these elements could have an effect on adsorption mechanism through ion exchange interactions. Figure 5 does not show any significant difference between the surface before and after metal uptake, same was observed by Pino *et al.* [16], and reason attributed was low per cent of voids are been occupied by the adsorbed species. Fig. 6 shows the particle loaded with Cu (II), the presence of Cu bands and absence of Cl, K bands. The possible reason for the absence of these bands is the ion exchange mechanism between Cu (II) and these elements on the surface of the particle.

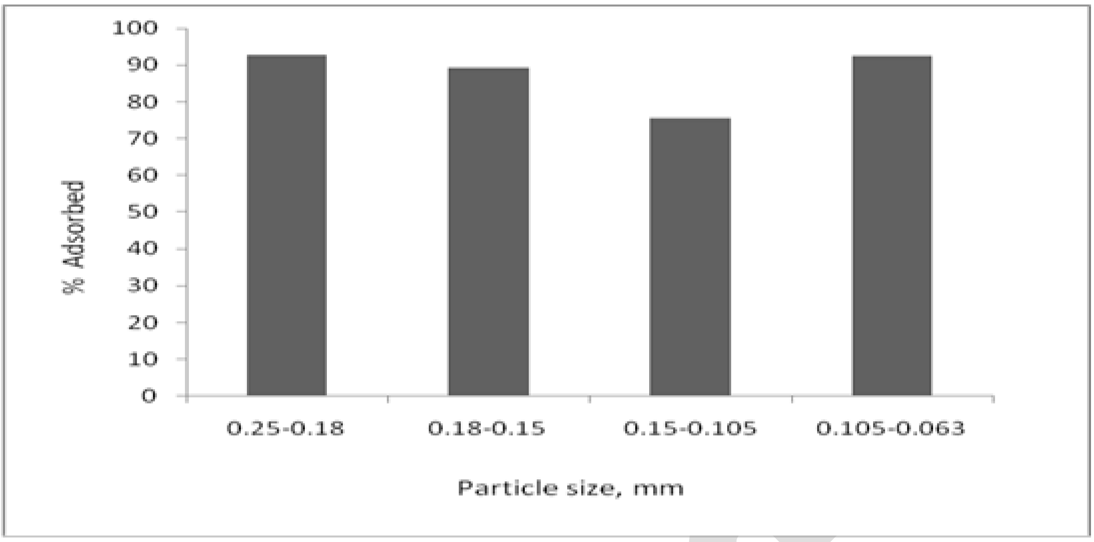

Figure 2: Percentage adsorption of Cu (II) by coconut shell for different ranges of particle size. Initial concentration of metal: 30 ppm. Coconut shell concentration: 5 g/l. pH value: 7. Temperature: 27 ^{o}C. Contact time: 4 h.

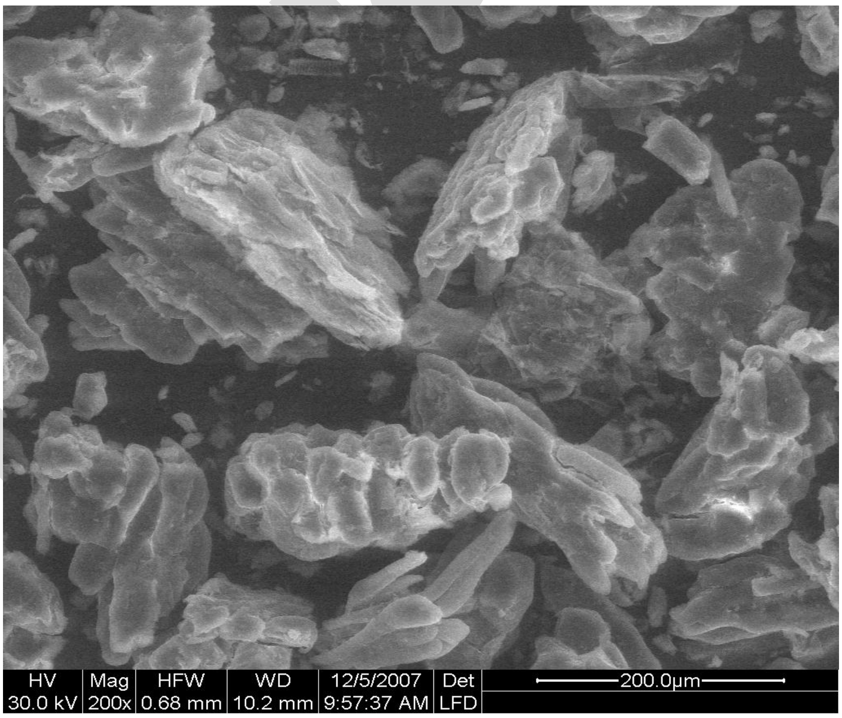

Figure 3: Scanning electron micrograph of coconut shell powder before Cu (II) adsorption.

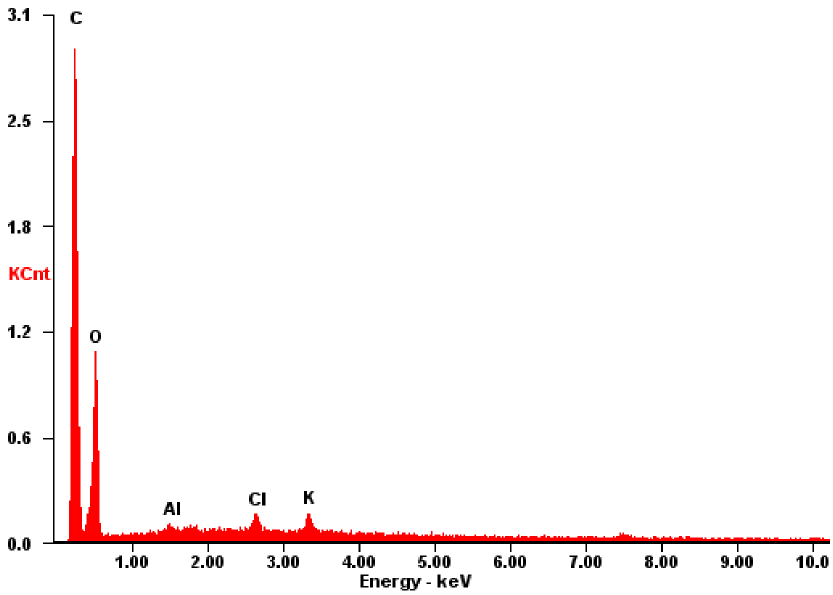

Figure 4: EDS diffractogram of micrographs of coconut shell powder before Cu (II) adsorption.

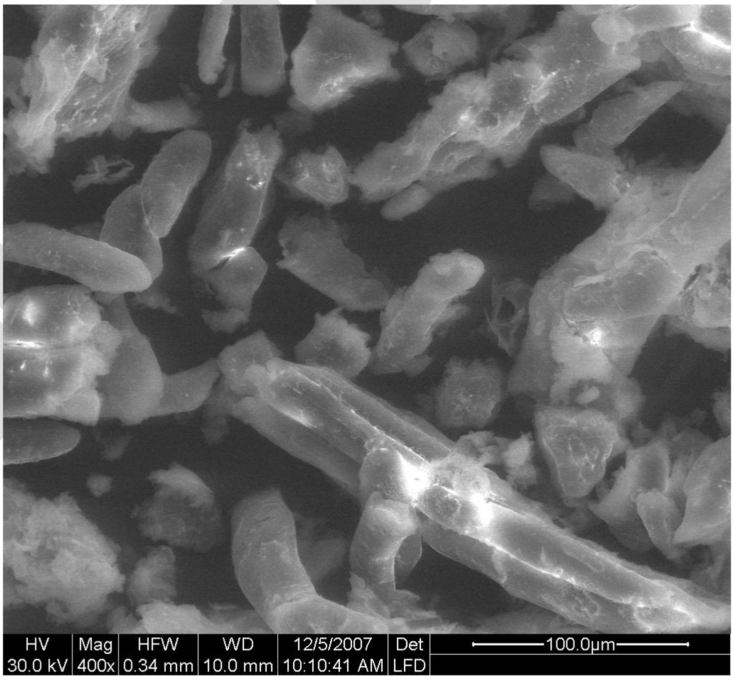

Figure 5: Scanning electron micrograph of coconut shell powder after Cu (II) adsorption.

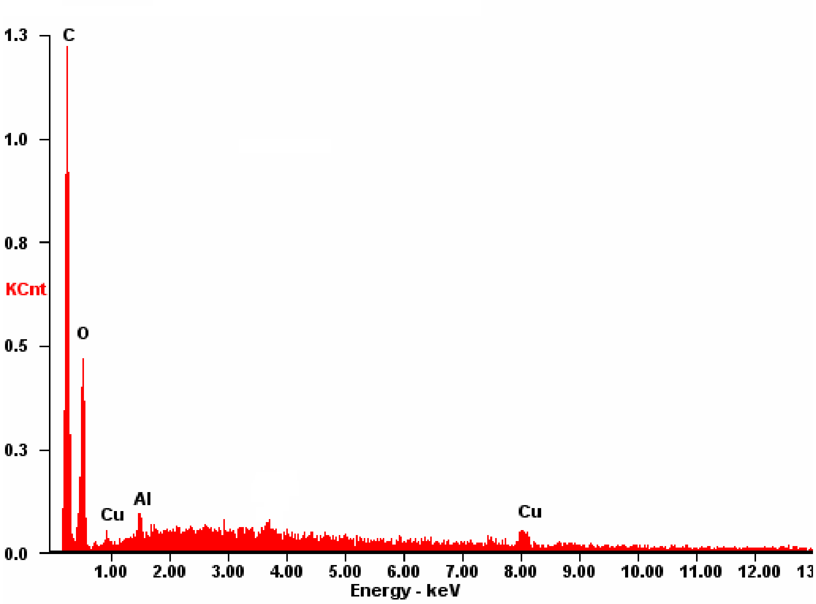

Figure 6: EDS diffractogram of micrographs of coconut shell powder after Cu (II) adsorption.

3.4. Adsorption isotherms

Linearized Langmuir and Freundlich adsorption isotherms of Cu (II) at 27 °C are given in Figure 7 and 8. Adsorption constants evaluated from both isotherms are presented in Table 1. It is observed that very high regression correlation coefficient (0.98) is obtained for Langmuir model, but Freundlich model gave low regression correlation coefficient (0.014). An adsorption isotherm is characterized by certain constants, the values of which indicate the surface properties, biosorptive capacity of biomass. Values of q_{max} and b have been calculated from Langmuir plot. The maximum capacity q_{max} determined from Langmuir isotherm defines the total capacity of biosorbent for Cu (II) (7.463 mg/g) and value of b is -0.68. Freundlich constants K_f and n values are found as 10.592 and -20.408 respectively.

Table 1: Adsorption isotherm coefficients of Langmuir and Freundlich models.

Metal	Langmuir			Freundlich		
	q_{max}(mg/g)	b	R^2	K_f	n	R^2
Cu (II)	7.463	-0.68	0.98	10.592	-20.408	0.014

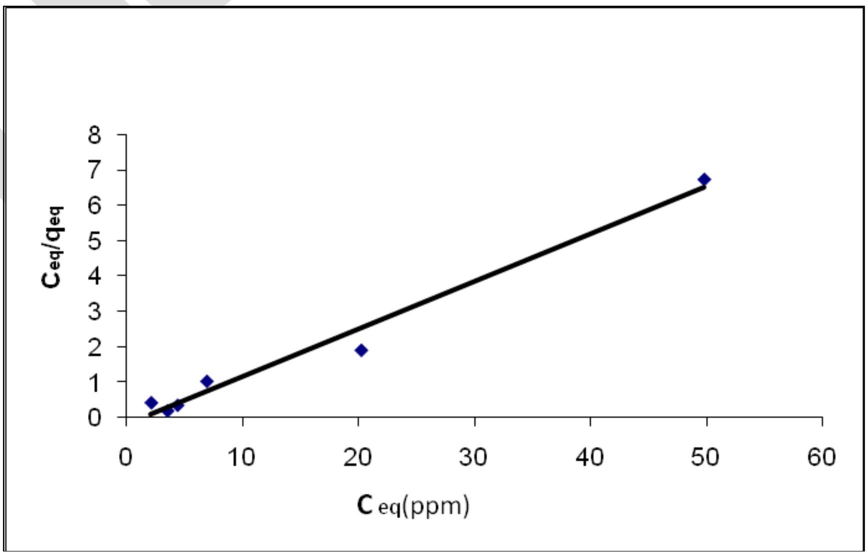

Figure 7: The linearized Langmuir adsorption isotherms of Cu (II) by coconut shell powder. Particle size: 0.105-0.063 mm. pH value: 7. Temperature: 27 °C. Contact time: 4 h.

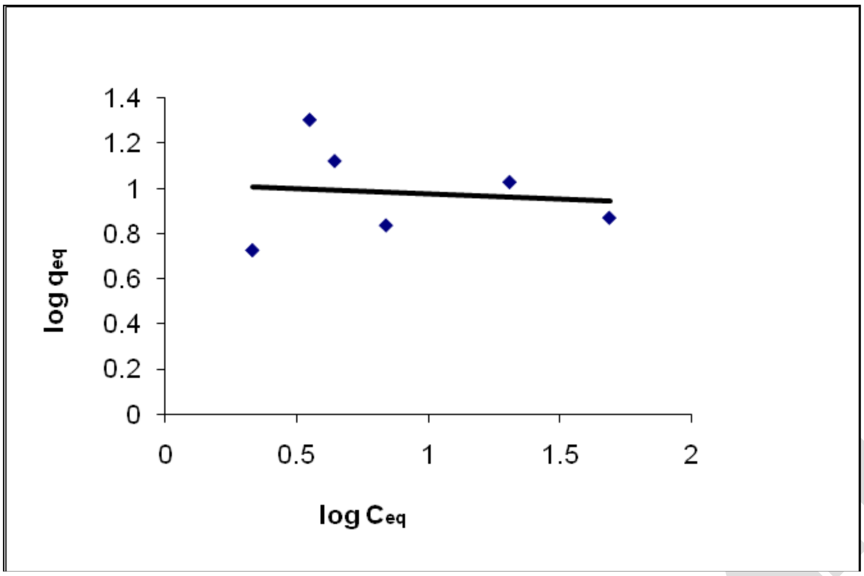

Figure 8: The linearized Freundlich adsorption isotherms of Cu (II) by coconut shell powder. Particle size: 0.105-0.063 mm. pH value: 7. Temperature: 27 ^{o}C. Contact time: 4 h.

3.5. Biosorption kinetics

Biosorption kinetics of Cu (II) ions is analysed by applying pseudo first order and pseudo second order kinetic models. The first order rate constant (k_{ad}) and q_{eq} values are determined and the correlation coefficient obtained shows a reasonable value (0.854) but the theoretical q_{eq} value (1.135 mg/g) gave a lower value than experimental q_{eq} value (5.312 mg/g). Hence, using Eq. (5) t/q was plotted against t at 27 ^{o}C and second order biosorption rate constant (k_{ad}) and q_{eq} values were determined from slope and intercept of the plots (Figure 9). The correlation coefficient for the second–order kinetic model obtained was 0.999. The theoretical q_{eq} value (5.405 mg/g) is close to the experimental q_{eq} value (5.312 mg/g) and k_{ad} is 0.048 (g/mg min) in the case of pseudo-second order kinetics. The results suggest that biosorption follows second order model, based on the assumption that the rate limiting step may be biosorption, provides the best correlation of the data.

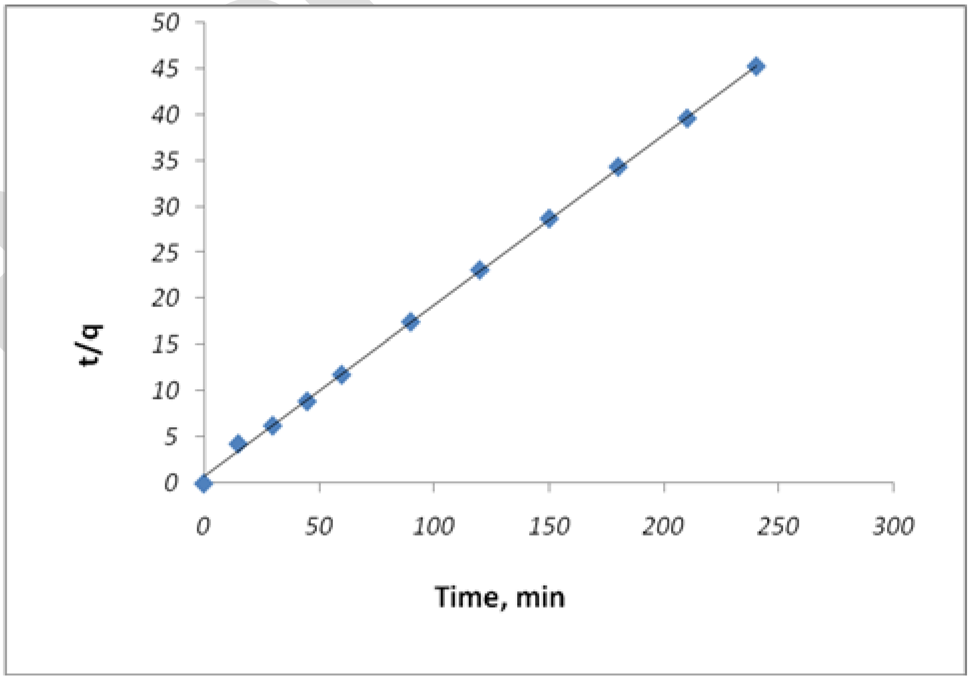

Figure 9: Pseudo second order kinetics of Cu (II) by coconut shell powder. Initial concentration of metal: 30 ppm. Coconut shell concentration: 5g/l. Particle size: 0.105-0.063 mm. pH value: 7. Temperature: 27 ^{o}C.

4. Conclusion

Coconut shell powder was confirmed as a potential biosorbent in the removal of copper from aqueous solutions. Investigations showed that pH and particle size influence the uptake of Cu (II). The micrographs obtained by SEM analyses before and after the uptake by coconut shell powder do not show any significant difference, the Cu bands and absence of Cl, K bands in EDS after metal uptake indicates a possible ion exchange mechanism. The equilibrium study shows that the data fitted Langmuir model with excellent correlation coefficient and a biosorption capacity of 7.463 mg/g was obtained. The pseudo-second order kinetic model provided best correlation coefficient and the theoretical q_{eq} values match with the experimental q_{eq} value.

Competing Interests

Authors have no conflicting interests with the publication of this article.

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