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Equilibrium adsorption and kinetics study of chitosan-dust kenaf fiber composite

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ABSTRACT

Kenaf-dust filled chitosan biocomposite was prepared for the adsorption of metal ion. The adsorption property of the biocomposite towards Cu^{2+} ion was evaluated. Various factors affecting the uptake behavior such as contact time, pH and initial concentration of the metal ion was investigated. The equilibrium data were analysed using Langmuir and Freundlich isotherm models. The adsorption kinetics followed the mechanism of the pseudo-second order and the intra particle diffusion was studied. The maximum adsorption capacity of the adsorbent for Cu^{2+} was in the range of $232\pm134 \text{ mg} \cdot \text{g}^{-1}$.

Keywords: chitosan, Kenaf, biocomposite, adsorption and kinetics.

INTRODUCTION

Heavy metals are very harmful because of their non-biodegradable nature, long biological halflives and their potentiality to be accumulated in different body parts [1, 2]. It is well known that some heavy metals which are essential component in metabolism are toxic when present in high concentration [3]. Trace metal like iron, copper, zinc, cobalt and manganese are essential metals since they play important role in biological systems [4, 5]. However, some research also confirmed that heavy metals such as Cd, Pb, Cu, Zn and Ni have carcinogenic or toxic effects on human beings and environment [6-8]. Heavy metals enter in the environment through a wide variety of sources, including combustion, wastewater discharges and manufacturing facilities [9, 10]. Mining and processing of metal ore can be a significant source of heavy metal contamination of the environment [11, 12]. One of the major routes of the excessive accumulation of heavy metals in agricultural soil is wastewater irrigation that adulterates the soil and later affects the food quality and safety [13]. Other potential sources of entering the heavy metals to the human body are inhalation and ingestion through the plants produces in

contaminated areas [14, 15]. It is observed that serious systemic health problems can develop as a result of excessive dietary accumulation of heave metals such as Cd and Pb in human body [16].

In recent years, biosorption by biologically originated materials in removing heavy metals has drawn more and more attention, largely due to the unique properties of these biomaterials being environmentally benign, low cost, effective at low metal concentrations and easily reusable. Chitosan attracted particular consideration because of its capability to adsorb various heavy metal ions chemically or physically [17-19]. The nitrogen in the amino group of the chitosan molecule acts as an electron donor and is presumable responsible for selective chelation with metal ions [20, 21]. Chitosan can be produced easily from chitin, poly- β -(1, 4)-N-acetyl-D-glucosamine and it is the most common polysaccharide after cellulose found in the nature extracted from crustacean shell, such as prawns, crabs, insects and shrimps [22-24].

Kenaf, a member of the hibiscus family (Hibiscus cannabinus L), is a 4,000 year old annual crop, native to Africa. Mechanical properties of kenaf fibers are similar to those of jute, but kenaf fibers are stronger, whiter, and more lustrous. Kenaf has been used for thousands of years as cordage, canvas, sacking, and fish net due to its mildew resistance [25]. Kenaf, bast fiber, and reinforcement consist of individual fibers which are composites of predominantly cellulose, lignin and hemicelluloses. Crystalline cellulose is the main reinforcing element, while lignin and the hemicelluloses can be considered as the binding matrix. Additionally, Kenaf, like most other natural fibers, demonstrates lowderity, high specific mechanical properties, and is easily recycled [26].

The main objective of present study was to investigate the feasibility of using chitosan-kenaf fiber reinforced comoposite for the removal of Cu(II) from aqueous solution. The experimental data were fitted to Langmuir and Freundlich adsorption isotherm models. The results were also analysed on the basis of Lagergren pseudo-first order, pseudo-second order kinetics equation and intraparticle dissucion model. Batch adsorption studies were conducted to evaluate the metal adsorption capacity of the chitosan-kenaf fiber reinforced composite.

MATERIALS AND METHODS

Materials

Chitosan (from Crab Shell) was obtained from India Sea foods, Cochin, Kerala. The Kenaf (Hibiscus Cannabinus) fiber in this study was obtained from vibrant nature, Chennai. Analytical grade Copper Sulphate, Hydrochloric acid, Sodium hydroxide, Acetic acid were purchased from S.D. fine chemicals, Chennai. Highly pure water is prepared form in the laboratory by double distillation of deionised water. All chemicals were used as received.

Preparation of chitosan – dust kenaf fiber composite: Preparation of adsorbent:

Chitosan-dust kenaf fiber composite:

Chitosan (from Crab shell) was obtained from India sea foods, Cochin, Kerala. Chitosan obtained was 92% deacetylated from chitin of Crab shell. 10g of chitosan was dissolved in

100ml of acetic acid (8%) and stirred for 30 minutes in vertical mechanical stirrer and homogeneous viscous gel of chitosan-acetic acid formed.

The kenaf bast fibers (*Hibiscus Cannabinus*) were immersed in the 10% sodium hydroxide solution at room temperature for one hour with mild agitation for mercerization and then washed with water several times for the removal of sodium hydroxide. Then the fibers were dried in hot air oven for three hours and cut into dust fiber. To the chitosan gel, dust kenaf fibers were reinforced.

Standard solution

The stock solutions of Cu (II) were prepared by dissolving 0.786 mg of copper sulphate in 1000 mL of double distilled water. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1} . The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

Instrumentation

Batch adsorption method was used in this study. Synthetic solution of Cu(II) ion taken in stoppered bottles and agitated with composite films at 30° C in orbit shaker at fixed speed, 160rpm. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time of shaking and changing pH of the solution.

After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer (Vatian AAA 220FS).

Effect of pH

Sample solutions of copper were taken in the measuring flasks. CS/KF binary composite (1g) was added to each. pH of each sample solution was adjusted from 4 to 8. Flasks were agitated on orbital shaker (top loaded) at 150 rpm for 30 min. The solutions were filtered and the filtrates were subjected to atomic absorption. The same procedure is repeated for copper with adsorbent dose of 1g. From graph, the concentrations were measured for copper.

Effect of contact time

Sample solutions of copper were taken in 6measuring flasks. 1g CS/KF binary composite was added to each flask. pH of each sample solution was adjusted to 5.5. Flasks were agitated on orbital shaker (top loaded) at 150 rpm for the time ranging from 60 to 360 min with the difference of 60 min. The solutions were filtered and the filtrates were subjected to atomic absorption to record the absorbance of copper. The concentrations were measured.

FTIR spectral studies

RESULTS AND DISCUSSION

FTIR spectroscopy is one of the most powerful techniques for investigation of multi component systems, because it provides information in the blend composition as well as on the polymer-

polymer interaction [27]. Figure - 1 shows the FT-IR spectra of Chitosan/kenaf dust fiber composite. The peak at 3450.43cm⁻¹ corresponding to –OH stretching, -NH stretching, Intermolecular hydrogen bonding and the strong polymerization of chitosan/dust fiber. Peak at 2923.64 cm⁻¹ corresponds to aliphatic C-H stretching. The peaks at 1626.27cm⁻¹, 320.36 cm⁻¹, 1221.30 cm⁻¹, 1093.19 cm⁻¹, 988.40 cm⁻¹ and 670.50 cm⁻¹ are due to amide I band [28], C-O stretching, C-O-C linkage, C-N stretching, N-H wagging and O-H out of plane bending respectively.



Figure 1. FT-IR spectra of Chitosan/kenaf dust fiber composite



Figure 2. Effect of pH on the uptake of Cu²⁺ ion by the chitosan/dust kenaf fiber composite.



Figure 3. Effect of contact time on the uptake of Cu²⁺ ion by the chitosan/dust kenaf fiber composite.

Effect of pH on Cu biosorption

The experiments was carried out at different pH shows that there was a change in the percentage removal of copper over the range of 4 to 8 shown in the figure - 2, pH is one of the important parameter which affects the adsorption process. In general very little or no Cu uptake was observed at pH less than 2.0. Little copper uptake at low pH values is an indication of competition of excess of protons for the same binding sites on composite film [29]. The copper uptake increased with increasing pH, to the maximum near pH 5.5(Figure - 2), then decreased with higher pH value. From the figure - 2 it is observed that pH significantly affects the adsorption process for copper. The best result was obtained at pH 5 for copper around 92%.

Effect of contact time

Uptake of the Chromium ion with the effect of contact time by the chitosan/dust kenaf fiber composite was studied and the results are shown in Figure - 3. The efficiency increases with increase in time of contact, due to the availability of more time for metal ions to make an attractive complex with the composite. Initial removal occurs immediately as soon as the metal and composite came into contact and after some extent further increase in contact time did not increase the uptake due to decrease of the easily available active sites for the binding of metal ions, the equilibrium is reached. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

Adsorption isotherm

The use of biological materials, in particular of chitin and its derivatives, is an enormous complicating factor, i.e the uptake process is a complex one. The sorption data can be interpreted using several relationships which describe the distribution of metal ion between the biomaterial and the liquid phase. The utilization of a model rests solely on the adequacy between the experimentally observed tendencies and the shape of the mathematical laws associated with these models. Such an approach, however, is of limited utility, because the isotherm equations obtained from data fitting cannot be used to predict the effect of the various solution variables

such as pH, ionic strength, and type of electrolyte as well as the effect of electrostatics on the extent of adsorption [30]. Such predictive models have value in comparing different biomaterials under different operating conditions. Furthermore, these models can be used to design and optimize an operating procedure [31]. Among these, the Langmuir [32] and Freundlich [33] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. These models were tested in the present work. This modelling permits us to determine the maximal capacity of removal. 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 unity is deemed to provide the best fit.

Removal of Cu (II) by chitosan as a function of time at pH 5, at various initial Cu (II) concentrations, is shown in Figure - 4. The results indicate that as the concentration of the Cu (II) is increased, so does the time taken before equilibrium is reached. It also appears that at lower concentrations less Cu (II) adsorbs onto the chitosan than at higher concentrations.

The results of the Cu (II) concentration dependence study were subjected to analyses by means of both Langmuir and Freundlich adsorption isotherms. The Langmuir equation (Eq. (1)), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as:

$$C_{ads} = (K_L C_{eq})/(1 + bC_{eq})$$
(1)

In this study the following linearised form of the Langmuir isotherm was used.

$$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$$
(2)
and
$$C_{max} = K_L/b$$
(3)

where:

 C_{ads} = amount of Cu (II) adsorbed (mg·g⁻¹) C_{eq} = equilibrium concentration of Cu (II) in solution (mg·dm⁻³) K_L = Langmuir constant (dm³·g⁻¹) b = Langmuir constant (dm³·mg) C_{max} = maximum Cu (II) to adsorb onto 1 g chitosan (mg·g⁻¹)

The constant *b* in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant K_L can be used to determine the enthalpy of adsorption. A plot of C_{eq}/C_{ads} vs. C_{eq} yielded a straight line (see Figure - 4), confirming the applicability of the Langmuir adsorption isotherm. The values of K_L and *b* were obtained by a least square fit and were calculated to be $K_L = 0.6751 \pm 0.8885 \text{ dm}^3 \cdot \text{g}^{-1}$, $b = 0.0029 \pm 0.0066 \text{ dm}^3 \cdot \text{mg}$ and $C_{\text{max}} = 232 \pm 134 \text{ mg} \cdot \text{g}^{-1}$.

The values of K_L and b, were found to be $K_L = 0.7818 \text{ dm}^3 \cdot \text{g}^{-1}$, $b = 0.004764 \text{ dm}^3 \cdot \text{mg}$ and $C_{\text{max}} = 164 \text{ mg} \cdot \text{g}^{-1}$. However, a Freundlich equation plot of log C_{ads} vs. log C_{eq} yielded a straighter line as shown in Figure - 5 ($R^2 = 0.95$). The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study. The Freundlich equation (Eq. 4) which is used to describe heterogeneous surface energies is expressed as:

 $C_{ads} = PC_{eq}^{1/n}$



Figure - 4. Langmuir isotherm for copper

In this study the following linearised form of the Freundlich equation was used.

(4)

 $\log C_{ads} = \log P + 1/n \log C_{eq}$ (5)

where:

 $C_{ads} = amount of Cu (II) adsorbed (mg \cdot g^{-1})$ $C_{eq} = equilibrium concentration in solution (mg \cdot dm^{-3})$ $1/n = Freundlich constant (mg \cdot g^{-1})$ $P = Freundlich constant (g \cdot dm^{-3})$



Figure - 5. Freundlich isotherm for copper

From Figure - 5 it is evident that the values of 1/n and *P*, which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit and were found to be 0.64+0.08 mg·g⁻¹ and 0.98+0.16 g·dm⁻³ respectively.

From the Freundlich plot the values for 1/n and *P* can be calculated. The values for 1/n and *P* for chitosan/dust kenaf composite are $0.98\pm0.08 \text{ mg}\cdot\text{g}^{-1}$ and $0.12\pm0.10 \text{ mg}\cdot\text{dm}^{-3}$ respectively. The 1/n value suggests that the adsorption forces of Cu (II) acting on the surface of the chitosan/dust kenaf composite are stronger.

Tab	le - 1. Adsorption isotherm constant, \mathbf{C}_{max} and corr	elation coefficients
	T • 4 4	

Motoliona	Langmuir constants				Freundlich constants		
Metal Ions	$K_L (dm^3/g)$	b (dm ³ /mg)	C _{max} (mg/g)	\mathbf{R}^2	K	n	\mathbf{R}^2
Cu(II)	0.7818	0.004764	164.11	0.9561	1.7159	1.1907	0.9982

Kinetic studies

The transient behavior of the batch biosorption process was analysed using the pseudo-firstorder, the pseudo-second-order and the intraparticle diffusion kinetic models. The linearized form of first order Lagergren equation is given as Eq. (6).

$$log (q_e-q_t) = log q_e - k_1 t - \frac{k_1 t}{2.303}$$
(6)

The pseudo-second-order rate equation is given as Eq. (7) [34] t 1 t (7)

 $\begin{array}{c} \hline q_t & k_2 q_e^2 & q_e \end{array} \tag{7}$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the adsorption rate constant of pseudo-first-order, pseudo-second-order adsorption rate, respectively.

The linear plots of log $(q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

The pseudo-second-order equations show a good correlation of the experimental results with the linearized form (R^2 is 1.0000). The results elucidate that the kinetic behavior of Cu sorption by chitosan/dust kenaf fiber composite has been satisfactorily explain with the pseudo-second-order sorption equation. Compared with the former, the pseudo-first-order equation shows a poor correlation relationship with the experimental data (R^2 ranged from 0.7609 to 0.9971). Thus, only the pseudo-second- order equation can be useful for the kinetic study.



Figure - 6. Pseudo-first-order kinetics for copper



Figure - 7. Pseudo-second-order kinetics for copper

The kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism,

$$q_t = k_{id} t^{1/2} + C$$
 (8)

where *C* is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g min 0.5), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Figure - 8). If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole ratelimiting step [35]. For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the. Final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [36]. As seen from Figure - 8, the

plots were not linear over the whole time range, implying that more than one process affected the adsorption.



Figure - 8. Intraparticle diffusion for copper

CONCLUSION

The prepared composite was characterized by means of FTIR. The adsorption properties towards copper ion were evaluated. Various factors affecting the uptake behavior such as adsorbent dose, contact time, pH and initial concentration of the metal ions were investigated. The equilibrium data were analyzed using the Langmuir and Freundlich models. The equilibrium data were well fitted with a Freundlich isotherm equation according to the nonlinear curve fitting regressive analysis. The kinetic parameters were evaluated utilizing the pseudo-first-order and pseudo-second-order followed by intraparticle diffusion. The kinetic study of copper adsorption revealed that the pseudo-second order model yields a much better fit than the pseudo-first order model. Intraparticle diffusion analysis demonstrates that copper diffuses quickly among the particles at the beginning of the adsorption process, and then the diffusion slows down and stabilizes. It can be recommended that chitosan/dust kenaf composite is an effective and low cost adsorbent for the removal of copper ions from waste water.

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