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Kinetic and Equilibrium Studies of Adsorption of Cu(II) Ions on Rice Husk†

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The present work deals with the removal of copper ions from water by treatment with rice husk. The factors affecting adsorption such as pH, metal ion concentration and time of contact have been varied to obtain an optimum set of conditions for maximum adsorption. It has been observed that maximum adsorption (65%) occurs at pH 10 for a time of contact of 2 h in the concentration range 30–300 mg L^{-1}. The removal is strongly hindered by the presence of a complexing agent such as EDTA. The adsorption data follows the Freundlich and Langmuir isotherm. The results obtained point towards the use of rice husk as a potential adsorbent for copper(II) ions. An attempt to study the kinetics shows that the adsorption of copper ions on rice husk follows first order kinetics as calculated by using the rate equation and confirmed by applying the Lagergren first order rate equation. A tentative mechanism has been proposed.

Key Words: Adsorption, Rice husk, Low cost adsorbents, Kinetics, Copper(II) ions, Removal.

INTRODUCTION

The potential threats associated with the accumulation of heavy metals in the environment are well known[1, 2]. The toxic effects on humans have also been extensively studied, but because of their essential role in industry heavy metals often end up being discharged in lakes or streams resulting in accumulation of these metals in the human food chain. The treatment of wastewater has thus drawn tremendous attention during the past few years. Technologies being used today for the removal of heavy metal ions include precipitation, membrane processes, ion-exchange and adsorption. Out of these adsorption on activated carbon is an important method[3–9].

However, taking into consideration the cost factor, low cost adsorbents like fly ash, saw-dust, bagasse, wollastonite (a clay mineral), mango seed powder and rice husk ash have been extensively tried[10–19]. The use of rice husk ash[20] for removal of Cr(VI) and rice husk for Zn(II)[21] and Cd(II)[22] have shown promising results. The extent of metal ion removal from solution depends upon the contact time, metal ion concentration, ion type and the type of adsorbent.

In the present study, an attempt has been made to investigate the adsorption of Cu(II) ions on rice husk at varying pH, metal ion concentration and time of contact in order to evaluate the potential of rice husk as an adsorbent for Cu(II) ions and to obtain an optimum set of conditions for maximum removal.

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The main sources of copper have been found to be from electroplating industries, alloys making industries, paints and pigments making industries, etc. Copper is a micronutrient but excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems[5]. For these reasons WHO has prescribed[23] the maximum concentration of copper for potable water as 1.3 mg L^{-1}.

EXPERIMENTAL

Rice husk was collected from the agricultural land of Kharar, Punjab (India). It was washed several times with distilled water, dried and then sieved through I.S. sieve No. 20 and used as an adsorbent during all the batch experiments.

Proximate analysis of rice husk was carried out in the laboratory: moisture content 5%, ash content 47.3% and silica 12%.

Copper sulphate and copper chloride (Merck, A.R.) were used for the preparation of synthetic effluents. Solutions of copper sulphate and copper chloride having the desired metal ion concentration 30–300 mg L^{-1} were prepared in distilled water. A known weight of rice husk 2.5 g was placed in contact with metal ion solutions (100 mL) of different concentrations. The suspension was subjected to continuous shaking at a fixed temperature. The effects of pH, time of contact and initial metal ion concentration have been studied for the pH range 2–11.5 metal ion concentration ranging from 30–300 mg L^{-1} and contact time from 0.5–2.5 h. The pH of the solution was adjusted by the addition of HCl, H_2SO_4 or NH_4Cl/NH_4OH (as the case may be). The effect of the complexing agent has been studied by the addition of 5 mL of 0.01 M EDTA solution, to the solution of the metal ion before the addition of the adsorbent. Estimation of the metal has been carried out iodometrically in accordance with the standard analytical procedure[24]. The amount of metal ions adsorbed was calculated from the difference of the metal ion concentration in aqueous solution before and after adsorption. Each set of experiments was carried out in duplicate in order to check the reproducibility of the results.

RESULTS AND DISCUSSION

In order to optimize the conditions for maximum removal the effects of pH, time of contact and initial adsorbate concentration on the metal ion removal were studied.

Effect of pH, initial metal ion concentration and contact time

Adsorption isotherms have been plotted in the concentration range 30–300 mg L^{-1} (Figs. 1 and 2). The amount adsorbed shows an increase with the increase in initial concentration of the metal ions. At equilibrium the amount adsorbed increases from 0.817 to 7.2 mg g^{-1} for an increase in concentration from 30 to 300 mg L^{-1}. However, the equilibrium percentage adsorption shows a decrease from 68.7 to 56.6% with an increase in the concentration. The decrease in percentage removal is explained on the basis of the availability of large number of surface sites of the adsorbent for a relatively smaller number of adsorbing species at higher dilutions[25].

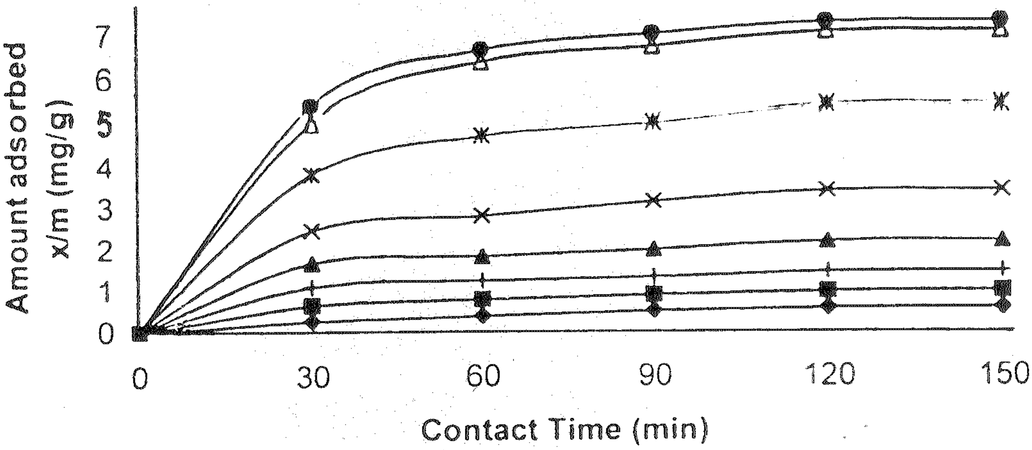

Fig. 1. Plot of amount adsorbed *vs.* contact time showing time dependence of adsorption of Cu^{2+} on rice husk at different pH (initial concentration = 300 mg L^{-1}) [pH 2 (◆), pH 4(■), pH 5(▲), pH 7 (×), pH 9 (✳), pH 10 (●), pH 10 + EDTA (+), pH 11.5 (Δ)]

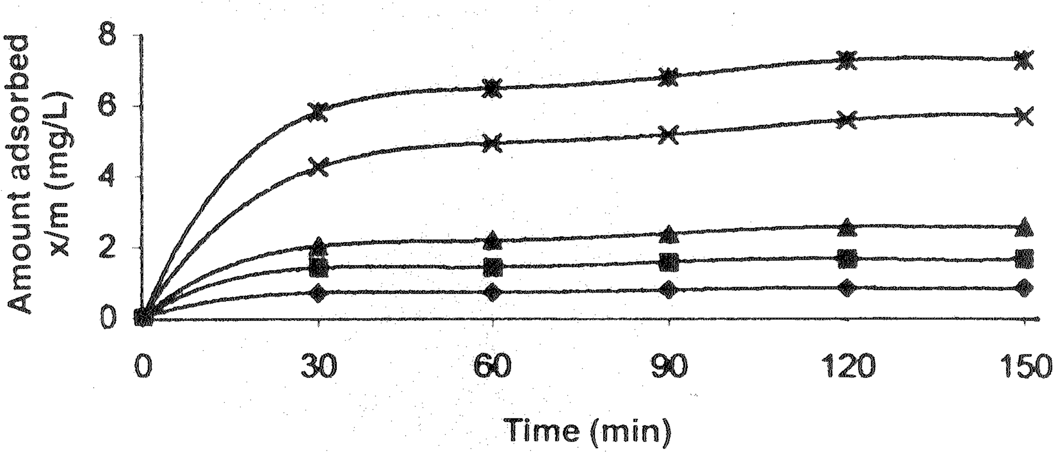

Fig. 2. Amount of Cu^{2+} adsorbed at pH 10 at different contact times for various concentrations of adsorptive solution [30 (◆), 60 (■), 120 (▲), 225 (×), 300 (✳)]

There is no effective change in the amount of metal ion adsorbed by varying the anion (Cl^-, SO_4^{2-}). However, the amount adsorbed decreases substantially in the presence of EDTA (Fig. 1). The curves for amount adsorbed *vs.* time are continuous and smooth (Fig. 2) suggesting the formation of a monolayer on the surface of adsorbent[26, 27] and equilibrium time is independent of initial concentration of metal ion. The figure clearly shows a relatively fast uptake of Cu(II) ions during the initial stages, but the time required for attaining equilibrium adsorption is 2 h for all concentrations studied. An equilibrium time of 1 h has been observed by Khan and Khattak[28] for adsorption of Cu(II) ions on activated carbon.

As a clear from Fig. 1, an increase in adsorption is observed with increasing pH value, maxima being observed at pH 10, thereafter there is a decrease. These results are consistent with earlier studies[5, 29] where pH dependence has been reported with maximum adsorption occurring in the alkaline range.

Adsorption Kinetics

The rate constants and order for the removal of Cu(II) by adsorption on rice husk, at pH 10, have been determined by following the rate expression $R = kC^n$ were R is the rate of adsorption (mg g^{-1} min^{-1}); k is rate constant, min^{-1}; C is dye concentration, mg L^{-1} and n is the order of reaction.

A plot of log R *vs.* log C at different contact times has been found to be a straight line (Fig. 3) which gives the values of k and n in each case. The values of k and n are given in Table-1. These observations point towards first order kinetics for the adsorption process. This is further substantiated by applying the Lagergren model[26], $\log (q_e - q) = \log q_e - [k_{ad/2.303} \times t]$ where q_e is the amount of metal adsorbed at equilibrium, q is the metal adsorbed at any time t and k_{ad} is the rate constant for adsorption of metal ion. A plot of $\log (q_e - q)$ *vs.* t is a straight line which suggests the validity of the equation to the experimental observation; the value of k_{ad}, as found from the slope of this plot, has been found to be 0.0779 min^{-1}.

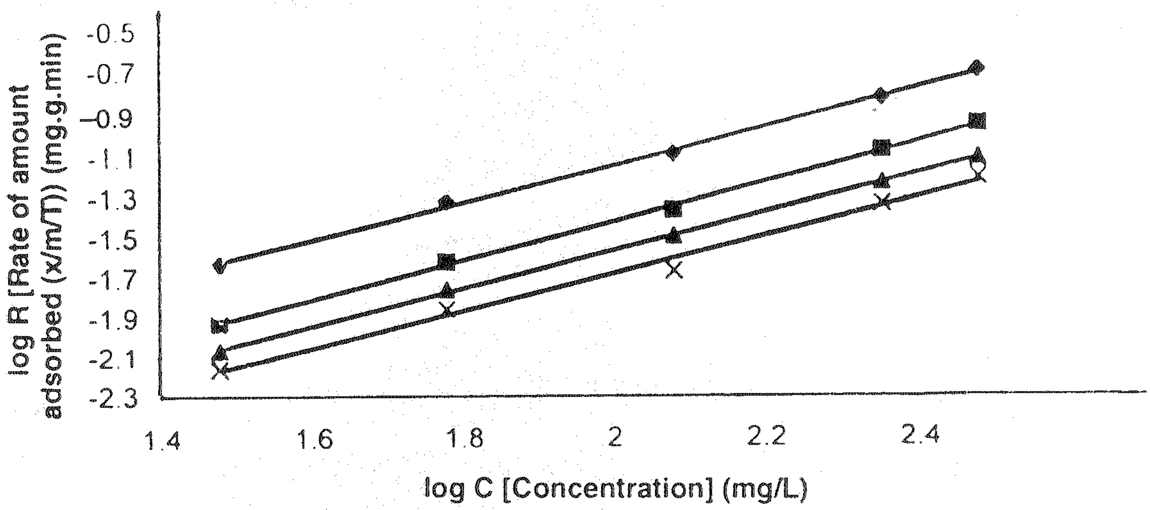

Fig. 3. Plot of log R *vs.* log C for Cu^{2+} for different contact times, [30 min. (◆), 60 min. (■), 90 min. (▲), 120 min. (×)]

TABLE-1
VALUES OF RATE CONSTANT (k) AND ORDER OF ADSORPTION KINETICS (n) ALONG WITH THEIR CORRELATION COEFFICIENTS (r) FOR DIFFERENT CONTACT TIMES FOR Cu(II) IONS ON RICE HUSK

Time (min.)	$k \times 10^{-3}$ (min^{-1})	n	r
30	1.1789	0.9247	0.9910
60	0.4727	0.9305	0.9995
90	0.3711	0.9488	0.9988
120	0.2928	0.9861	0.9982

Since the batch experiments are conducted by agitating the adsorbate with the adsorbent, there is a possibility of diffusion of adsorbate into the pores of adsorbent[30]. The rate constant of intra-particle diffusion (k_p) can be determined by the Morris Weber model[18], $q = k_p t^{1/2}$ by plotting Cu^{2+} adsorbed against square root of time of contact. The plots are linear but do not pass through the origin (Fig. 4). This shows that intra-particle diffusion is not the only rate controlling step[18].

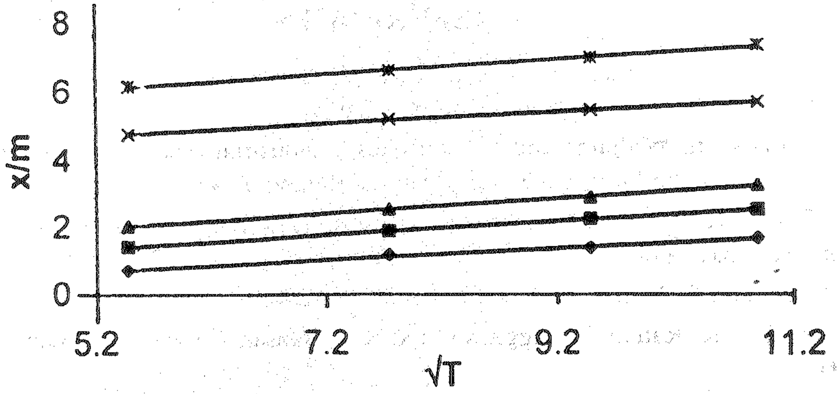

Fig. 4. Plot of amount of Cu^{2+} adsorbed against square root of time at different concentrations [30 mg/L (◆), 60 mg/L (■), 120 mg/L (▲), 225 mg/L (×), 300 mg/L (✻)]

Adsorption isotherm studies

A study of adsorption isotherms is helpful in the determination of adsorption capacity of rice husk. The most popular isotherm models, *viz*., Freundlich and Langmuir isotherms, have been applied and it has been found that the data fits well to both these models.

The Freundlich isotherm is given by the equation $q_e = kC_e^{1/n}$, where q_e is the amount of metal ion adsorbed at equilibrium, C_e is the equilibrium concentration of the adsorbate solution, $1/n$ and k are the Freundlich constants corresponding to adsorption intensity and adsorption capacity[21] respectively. The Freundlich constants have been evaluated at pH 10 from a plot of $\log q_e$ *vs*. $\log C_e$. The values of n and k have been found to be 2.3 and 0.5597 mg g^{-1} respectively. The value of $n > 1$ shows positive adsorption of the metal ions on rice husk[22].

The Langmuir isotherm model is represented by $C_e/q_e = 1/Q_0b + C_e/q_e$. A linear plot of C_e/q_e *vs*. C_e suggests the applicability of the Langmuir isotherm. Q_0 which is a measure of the maximum adsorption capacity of the adsorbent has been found to be 2.147 mg g^{-1}.

Proposed mechanism

Rice husk contains various proteins/amino acids having active functional groups (NH_2, —SH, —COOH, —OH), metal oxides and fibres[22] which are proposed to take part in the adsorption process.

In acidic medium a positive charge develops on the surface of rice husk due to the uptake of H^+ ions from solution as shown below:

$$\text{S—OH} + H^+ \longrightarrow SOH_2^+$$

Hence the surface restricts the uptake of Cu^{2+} ions; however, at higher pH the copper ions exist as $[Cu(NH_3)_4]^{2+}$ which are favourable for adsorption.

$$\text{S—OH} + [Cu(NH_3)_4]^{2+} \longrightarrow \text{S—O—}Cu^{2+} + NH_4^+$$

Thus, the rice husk shows a good affinity for Cu(II) ions in alkaline medium. The ion exchange properties of rice husk are responsible for the adsorption process. This phenomenon has been reported earlier[21] for Zn(II) ion.

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