Adsorptive removal of Cu(II) from aqueous solution using modified rice husk

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Abstract:

In this study, the modified rice husk was tested to remove Cu(II) from water. Batch experiments were carried out to evaluate the adsorption characteristics of the modified rice husk for Cu(II) removal from aqueous solutions. The adsorption isotherms, thermodynamic parameters, kinetics, pH effect, and desorbability were examined. The results show that the maximum adsorption capacity of the modified rice husk was approximately 43.5 mg Cu(II)/g absorbent at temperature of 25 ℃ and at the initial Cu(II) concentration of 400 mg/L and pH 7.0. And the adsorption isotherm data could be well fitted by both Langmuir equation and Freundlich equation. Thermodynamic studies confirmed that the process was spontaneous and endothermic. The adsorbed amounts of Cu(II) tend to increase with the increase of pH. The adsorption kinetic data can be satisfactorily described by either of the power functions and simple Elovich equations. The desorbability of Cu(II) is about 15-20%, and it is relatively difficult for the adsorbed Cu(II) to be desorbed. The relatively low cost and high capabilities of the rice husk make it potentially attractive adsorbent for the removal of Cu(II) from wastewater.

Key words: Rice husk, Cu(II) removal, Adsorption capacity, Adsorption isotherm

1. Introduction

Duo to the toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention in the recent years. Copper, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. Several industries like mining, printing, painting, dyeing, battery manufacture and other industries discharge effluent containing Cu(II), to surface water. For example, copper smelting and mining are major industrial processes that lead to copper contamination of water and soil. Developing innovative treatment technologies for copper smelting and mining industry wastewater is currently of great urgency and high priority in many countries including Chile, China, and India.

However, there are several methods for the treatment of wastewaters containing Cu(II), including ion exchange, adsorption, precipitation and membrane separation [1-3]. During last decades, the process of adsorption using activated carbon [4-5] has been found to be an efficient technology for the removal of Cu(II) from wastewater. Though the removal of Cu(II) through adsorption is quite effective, its use is restricted sometimes due to the higher cost of activated carbon and difficulties associated with regeneration. Attempts have therefore been made to utilize natural as well as waste materials as alternative adsorbents. However, sawdust of Meranti wood [6], camphora leaves powder [7], tea waste [8], peanut hull [9], agro-based waste materials [10], soil samples [11], shells of lentil [12], shells of wheat [12], sugar beet pulp [13] and modified loquat leaves[14] are some of the alternatives of costly activated carbons. Although many of these adsorbents can effectively remove Cu(II), most of them present some disadvantages such as poor adsorption capacity, low efficiency/cost ratio and ineffectiveness for low metal concentrations.

China produces millions of tons of rice annually. Rice husk is a by-product of the rice milling industry and the amount of rice husk available is far in excess of any local uses, thus frequently causing disposal problems. Therefore, rice husk is very inexpensive, with a cost of 1/50-1/40 of that of active carbon, and thus its use would significantly lower the cost of wastewater treatment. In addition, the use of rice husk would represent effective utilization of waste matter. The modified rice husk has been successfully used to remove Cd(II) from water [15].

The objective of this work was to study the feasibility of using modified rice husk as adsorbents for the removal of Cu(II) from wastewater. Rice husk was chosen due to its granular structure, insolubility in water, chemical stability and local availability. In this work, batch experiments were carried out to evaluate the adsorption characteristics of the modified rice husk for Cu(II) removal from aqueous solutions. The adsorption isotherms, thermodynamic parameters, kinetics, pH effect, and desorbability were examined.

2. Materials and methods

2.1. Materials

The used rice husk was purchased at a local market. It was dried in an oven at 105 ℃ for a period of 24 h, and then ground and sieved to obtain uniform material (<75 μm). The chemical compositions and physical properties of rice husk are given in Table 1. The BET surface area was measured by the N_2 adsorption-desorption technique using a NOVA-1000 (Ver.3.70) analyzer. The bulk density of the adsorbent was determined with a densitometer. Mercury porositometry determined porosity of the adsorbent. Chemical analysis of the rice husk showed the presence of various oxides of Ca, Si, Mn, Mg, and Fe.

Table 1 : Chemical compositions and physical properties of rice husk

Chemical composition		Physical properties	
Moisture	8.25%	Surface area (m^2/g)	438.05
Volatile matter	42.80%	Bulk density (g/cm^3)	0.3086
Fixed carbon	30.56%	Porosity (fraction)	0.38
Ash (oxides of Ca, Mn, Si, Fe, Mg, etc.)	18.39%		

About 20 g of dried s were treated with 200 mL 3 M sodium hydroxide at 60 ^{0}C for 2 h in a paraffin bath. The sodium hydroxide used was an equivalent amount required to remove all silica present in the husks. The husks were then filtered and washed with distilled water until the filtrate was neutral. The treated husks were dried at 105 ^{0}C in an oven and left overnight. The dried husk was carbonized with 50 mL 30% sodium hydroxide under nitrogen atmosphere at temperatures ranging from 400 to 650 ^{0}C, for 45 min. Then the carbonized husks were washed with distilled water until the filtrate was about pH 6–7. The samples were then dried at 105 ^{0}C in an oven overnight and ball-milled into powder that passed through 75μm mesh.

2.2. Experimental procedure

In the present investigation the batch mode of operation was selected in order to measure the progress of adsorption. It was carried out by shaking 100 mg of modified rice husk with 100 mL aqueous solution of adsorbate ($CuSO_4$) of different concentrations (30, 60, 90, 120, 150, 200, 300, 400 mg/L) at different temperature (15 ℃, 25 ℃, 35 ℃) and different pHs (3.1, 4.5, 6.2, 7.0, 7.6, 8.1) in different glass bottles in a shaking thermostat at a constant speed of 120 rpm. The pH of the adsorbate solution was adjusted by manually adding 0.1 M HCl or

0.1 M NaOH solutions using a pH meter. The progress of adsorption was noted at different time intervals till the attainment of saturation. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by centrifugation at 12000 rpm for 25 minutes in a Sorvall RC-5C centrifuge. And the supernatant liquid was analyzed for Cu(II). Desorption experiments were conducted by shaking 100 mg of adsorbent containing adsorbed Cu(II) with 100 mL of distilled-deionized water at 25 ℃ and pH 7.0.

Blank samples were run under similar conditions of concentration, pH, and temperature without adsorbent in all cases to correct for any adsorption on the internal surface of the bottles. The duplicate experiments demonstrated the high repeatability of this adsorption method and the experimental error could be controlled within 5-10%.

2.3. Analysis of Cu(II)

Cu(II) was estimated through atomic absorption spectrophotometer using a Varian Spectra AA 10 Plus atomic absorption spectrophotometer. The band pass was 1 nm. The adsorbed Cu(II) was calculated from the difference of the Cu(II) in solution and the known initial concentration. Each analysis point was an average of three independent parallel sample solutions. Triplicate tests showed that the standard deviation of the results was ±3%.

3. Results and discussion

3.1. Cu(II)) adsorption isotherm

Experiments were performed at different initial Cu(II) concentrations (30, 60, 90, 120, 150, 200, 300, 400 mg/L) at temperature of 15, 25, 35 ℃, respectively, and pH of 7.0. The results of the Cu(II) adsorption isotherm experiments are shown in Fig. 1. It can be found that the Cu(II) adsorption capacity of the modified rice husk increased with the Cu(II) equilibrium concentration increasing from 0 to 100 mg/L. This capacity was approximately 38.2, 40.6, 47.8 mg Cu(II)/g absorbents respectively at temperature of 15, 25, 35 ℃ and at the Cu(II) equilibrium concentration of 100 mg/L and pH 7.0. With a further increase of the Cu(II) equilibrium concentration, the increase of the adsorption capacity was less significant.

Two typical isotherms, as described below in Eqs. (1) - (2), were used for fitting the experimental data:

Freundlich equation: $q_e = K C_e^{1/n}$, (1)

Langmuir equation: $q_e = q_m b C_e / (1 + b C_e)$, (2)

Where q_e is the amount adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In this study, the isotherm data from Fig. 1 were fitted to the above two models by non-linear regression using the method of least squares. The estimated model parameters with the correlation coefficient (R^2) and the standard error of estimate (SE) are shown in Table 2. The fitting curves from the two isotherms are also illustrated in Fig. 1. It is shown that the experimental data of Cu(II) adsorption on modified rice husk could be well fitted by the two isotherms. Clearly, Langmuir equation provided better fitting in terms of R^2 and SE values.

Table 2 : Estimated isotherm parameters for Cu(II) adsorption

	Freundlich equation ($q_e=KC_e^{1/n}$)				*Langmuir equation* ($q_e=q_m bC_e/(1+bC_e)$)			
Temperature	K	$1/n$	R^2	SE	q_m(mg/g)	b(L/mg)	R^2	SE
15 ℃	20.1	0.163	0.928	0.93	42.1	1.25	0.977	0.626
25 ℃	22.8	0.247	0.912	1.13	45.5	0.706	0.935	0.782
35 ℃	23.9	0.305	0.895	1.34	55.2	0.542	0.928	0.856

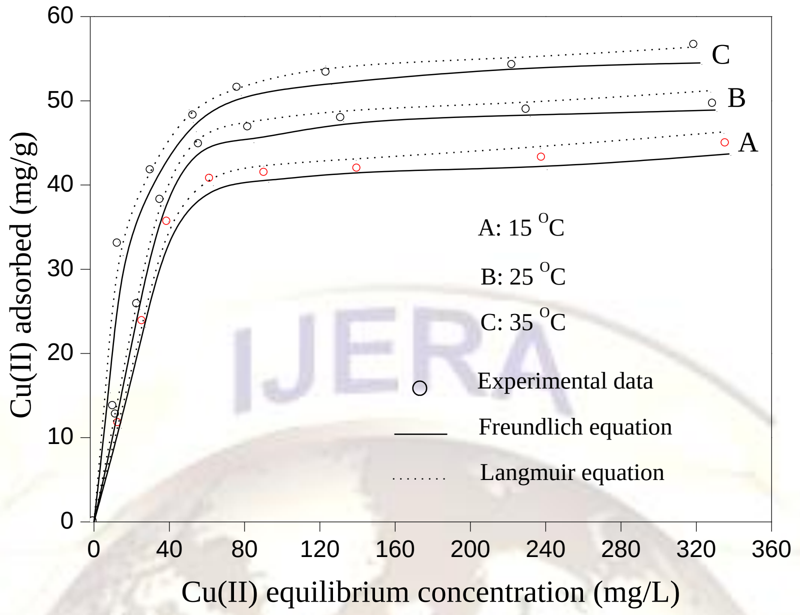

Figure 1. Cu(II) adsorption isotherm.

The Cu(II) adsorption on different materials has been widely studied during recent years, such as, on shells of lentil [12], shells of wheat [12], sugar beet pulp [13] and modified loquat leaves[14], etc. At respective optimal pH value and approximately the same Cu(II) equilibrium concentration, their reported Cu(II) adsorption capacities (mg/g) are given in Table 3. For comparison, the Cu(II) adsorption capacity of the modified rice husk obtained in this study is also listed in Table 3. In comparison with shells of lentil [12], shells of wheat [12], sugar beet pulp [13] and modified loquat leaves[14], the relatively low cost and high capabilities of rice husk make it potentially attractive adsorbent for the removal of Cu(II) from wastewater.

Table 3 : Cu(II) adsorption capacities of different low cost and easily available materials (at 20-25 ^{0}C)

Material	Capacity (mg/g)	Source
shells of lentil	8.98	[12]
shells of wheat	9.51	[12]
sugar beet pulp	28.5	[13]
modified loquat leaves	33.3	[14]
rice husk	45.5	This study

3.2. Thermodynamic parameters

Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) change of adsorption can be evaluated from eqs. (3):

$$K_d = q_e / C_e, \quad (3)$$

Where K_d is the sorption distribution coefficient. The K_d values are used to determine the ΔG^0, ΔH^0, and ΔS^0,

$$\Delta G^0 = -RT \ln K_d, \quad (4)$$

where ΔG^0 (cal mol^{-1}) is the free energy of adsorption, T (Kelvin) is the absolute temperature, and R is the universal gas constant.

The K_d may be expressed in terms of the ΔH^0 (kcal mol^{-1}) and ΔS^0 (cal mol^{-1} K^{-1}) as a function of temperature:

$$\ln K_d = \Delta H^0/(RT) + \Delta S^0/R, \qquad (5)$$

The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of a plot of ln K_d vs $1/T$.Thermodynamic parameters such as free energy of adsorption (ΔG^0), the heat of adsorption (ΔH^0), and stand entropy changes (ΔS^0) during the adsorption process at the initial Cu(II) concentration of 30 mg/L were calculated using Eqs. (3), (4), and (5). The temperature range used was from 15 to 35 ℃. The Gibbs free energy indicates the degree of spontaneity of the sorption process and the higher negative value reflects more energetically favorable sorption. (ΔH^0) and (ΔS^0) were obtained from the slope and intercept of a plot of ln K_d against $1/T$ (Fig. 2). The values of the parameters thus calculated are recorded in Table 4. Negative values of ΔG^0 indicate the spontaneous nature of the adsorption process. The value of ΔG^0 becomes more negative with increasing temperature. This shows that an increase in temperature favors the adsorption process. The positive values of ΔH^0 indicate that the adsorption process was endothermic in nature and the negative values of ΔS^0 suggest the probability of favorable adsorption.

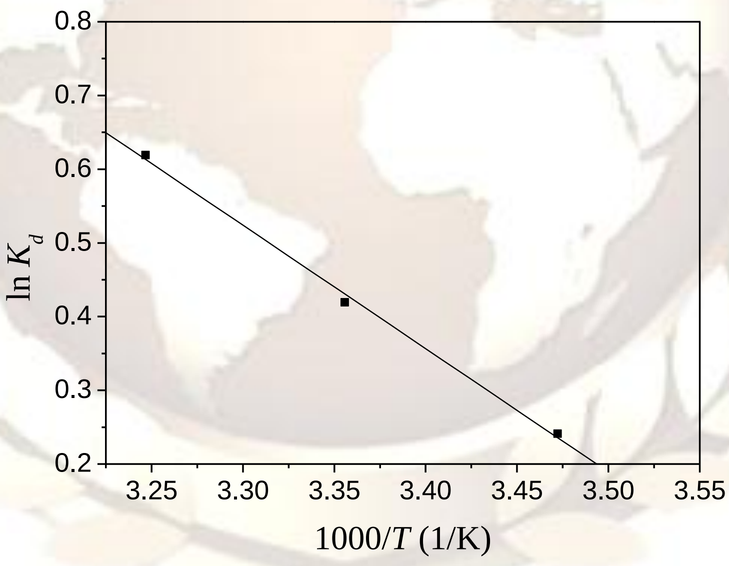

Figure 2. A plot of ln K_d against $1/T$ for Cu(II) adsorption by rice husk.

Table 4 : Thermodynamic parameters for adsorption of Cu(II) on rice husk

$-\Delta G^0$ (cal mol^{-1})			ΔH^0	$-\Delta S^0$
15 ℃	25 ℃	35 ℃	(kcal mol^{-1})	(cal mol^{-1} K^{-1})
478.0	940	1495	13.88	50.35

3.3. Effect of pH

Experiments were performed at different pH (3.1, 4.5, 6.2, 7.0, 7.6, 8.1) and the initial Cu(II) concentration of 150 mg/L at 25 ℃. The results of the effect of pH on adsorption of Cu(II) are presented in Fig. 3. It was found that the total amount of adsorption of Cu(II) onto modified rice husk increases with an increase of pH from 3.1 to 8.1. The pH of the aqueous solution is an important variable that influences the adsorption of Cu(II) at the solid-liquid interfaces. However, the modified rice husk possesses a negative surface charge in solution. As pH changes, surface charge also changes, and the sorption of charged species is affected (attract ion between the positively charged metal ion and the negatively charged rice husk surface). Furthermore, a lower pH value causes the rice husk surface to carry more positive charges and thus would more significantly repulse the positively charged species (Cu(II)) in solution.

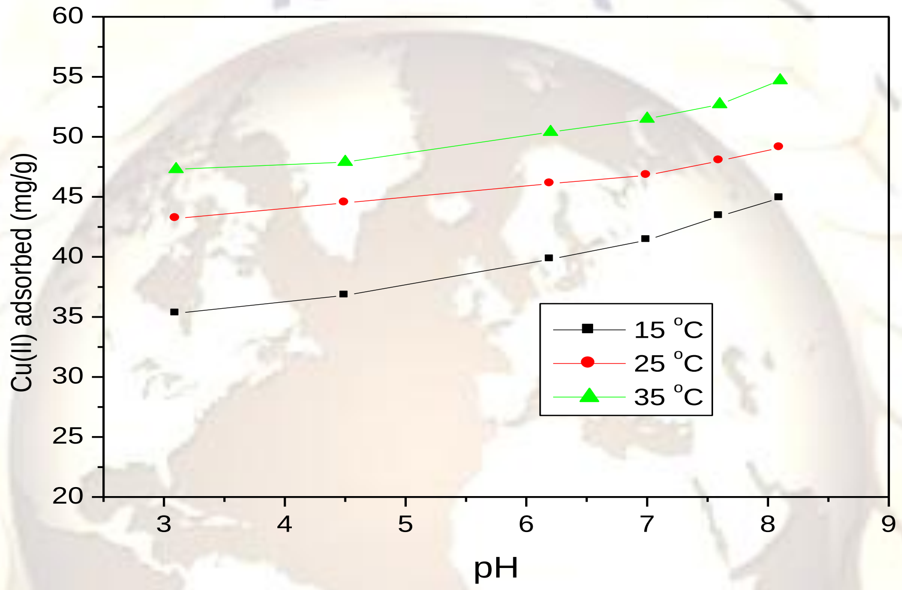

Figure 3. Effect of pH on adsorption of Cu(II).

3.4. Cu(II) adsorption kinetic

Experiments were performed at the initial Cu(II) concentration of 150 mg/L and at temperature of 15, 25, 35 ℃, respectively. The results of Pb(II) adsorption kinetic experiments are shown in Fig. 4. It can be seen that the majority of Cu(II) adsorption on the modified rice husk were completed in 5-15 minutes. For example, after 15 minutes of adsorption, the Cu(II) adsorbed on the rice husk at 15, 25, 35 ℃ was, respectively, 89.2%, 91.1%, 92.6% of that at 180 minutes.

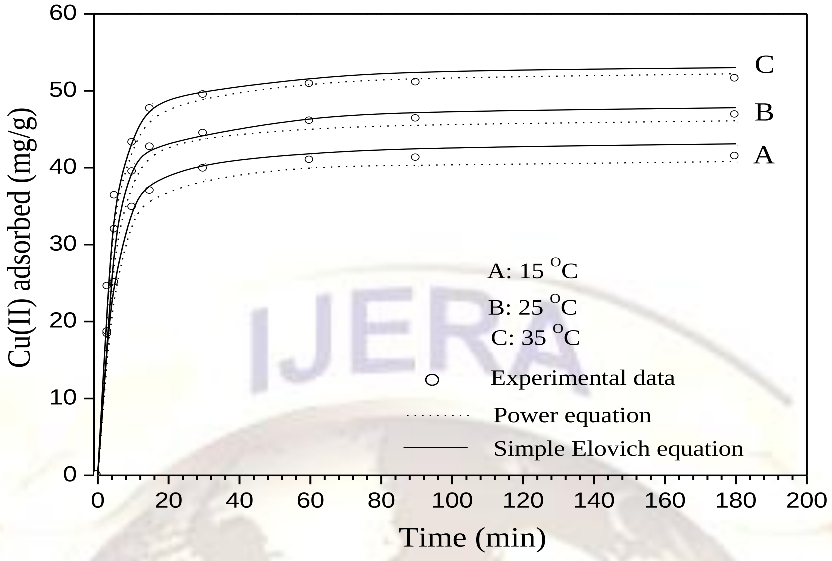

Figure 4. Cu(II) adsorption kinetics.

The Cu(II) adsorption kinetic data (Fig. 4) were fitted with several kinetic models (first order, second, power function, and simple Elovich [16]) by none-liner regression. The first- and second-order kinetic models were ruled out because their correlation coefficients (R^2) for the present experimental data were too small (< 0.6). Power function and simple Elovich kinetic equations and estimated parameters with R^2 and SE are shown in Table 5. Based on R^2 and SE, the kinetics of Cu(II) adsorption on the rice husk can be satisfactorily described by either of the power functions and simple Elovich equations. Therefore, the fitting curves resulting from both equations are plotted in Fig. 4 as well. The high applicability of the simple Elovich equation for the present kinetic data is generally in agreement with other researchers' results that the Elovich equation was able to describe properly the kinetics of Cu(II) adsorption on lignite [17] and cashew nut shell [18].

Table 5 : Estimated kinetic model parameters for Cu(II) adsorption

	Power function equation ($q=at^b$)				*Simple Elovich equation* ($q=a+b\ln t$)			
Temperature	a	b	R^2	SE	a	b	R^2	SE
15 °C	11.4	0.452	0.967	0.387	7.56	12.2	0.982	0.351
25 °C	13.2	0.491	0.929	0.776	9.52	14.1	0.961	0.425
35 °C	20.5	0.355	0.955	0.513	17.2	13.0	0.979	0.402

3.5. Cu(II) desorption studies

The tests of Cu(II) desorption were conducted with four initial Cu(II) concentrations (60, 120, 200, 400 mg/L) as shown in Table 6. The Cu(II) desorbability can be defined as the ratio of the desorbed Cu(II) over the total adsorbed Cu(II) by the adsorbent. Therefore, the desorbability of Cu(II) can be used to indicate the degree of Cu(II) desorption from the adsorptive materials. The data in Table 6 show that the desorbability of Cu(II) is about 15-20%. And the amount of the desorbed Cu(II) is slightly increased with the increase of the adsorbed Cu(II). These results indicate that the Cu(II) adsorption on the modified rice husk is not completely reversible and the bonding between the rice husk and adsorbed Cu(II) is likely strong. And it is relatively difficult for the adsorbed Cu(II) to be desorbed from the modified rice husk.

Table 6 : Desorbability of the adsorbed Cu(II) on rice husk

Initial Concentration (mg/L)	Adsorbed Cu(II) (mg/g)	Desorbed Cu(II) (mg/g)	Desorbability (%)
60	22.6	3.41	15.1
120	39.3	7.19	18.3
200	42.0	7.77	18.5
400	43.5	8.31	19.1

4. Conclusions

The modified rice husk has been found to be a very effective adsorbent for the efficient removal of Cu(II) from water. The maximum adsorption capacity of the modified rice husk was approximately 43.5 mg Cu(II)/g absorbent at temperature of 25 ℃ and at the initial Cu(II) concentration of 400 mg/L and pH 7.0. And the adsorption isotherm data could be well fitted by both Langmuir equation and Freundlich equation. Thermodynamic studies confirmed that the process was spontaneous and endothermic. The adsorbed amounts of Cu(II) tend to increase with the increase of pH. The adsorption kinetic data can be satisfactorily described by either of the power functions and simple Elovich equations. The desorbability of Cu(II) is about 15-20%, and it is relatively difficult for the adsorbed Cu(II) to be desorbed. The relatively low cost and high capabilities of the rice husk make it potentially attractive adsorbent for the removal of Cu(II) from wastewater.

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