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Biosorption of Zinc from Aqueous Solutions by Rice Bran: Kinetics and Equilibrium Studies

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Abstract: Rice bran, an agricultural by-product, was used for the removal of zinc ions from aqueous solution. The work considered the determination of zinc-biomass equilibrium data in batch system. These studies were carried out in order to determine some operational parameters of zinc sorption such as the time required for the Zinc-biosorbent equilibrium, the effects of biomass particle size, pH, and temperature. The results showed that pH has an importance effect on zinc biosorption capacity. The biosorbent size also affects the zinc biosorption capacity. The sorption process follows pseudo-second-order kinetics. The intraparticle diffusion may be the rate-controlling step involved in the adsorption zinc ions onto the rice bran up to 30 min. The equilibrium data could be best fitted by the Langmuir sorption isotherm equation over the entire concentration range (40–160 mg/dm^3). Thermodynamic parameters, such as ΔG°, ΔH°, ΔS°, have been calculated. The thermodynamics of zinc ion/rice bran system indicate spontaneous and endothermic nature of the process.

Keywords: Biosorption, zinc (II), rice bran, adsorption kinetic, Langmuir isotherm, thermodynamic property

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INTRODUCTION

Heavy metal pollution is an environmental problem of worldwide concern due to its non-biodegradability and toxic characteristics. The heavy metal, zinc, is one of the most common pollutants found in industrial effluents. Although zinc is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. In some respects the intake of essential elements is more critical than for toxic elements (1). The EPA requires zinc in drinking water not to exceed $5\,mg/dm^3$. Conventional treatment methods such as precipitation, ion exchange, and adsorption have been employed to remove zinc from aqueous solutions. However, these methods have disadvantages, which include incomplete zinc removal and toxic sludge generation. On the other hand, the use of artificially prepared ion-exchange resins is effective, but too expensive to be applied on a large scale. As an alternative, extensive research on biosorption has been carried out with the aim of identifying low-cost biosorbents. Many types of biosorbents have been studied for their heavy metal uptake capacities and suitability, which include bacteria, fungi, yeast, freshwater, and marine algae. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat (2), rice bran (3), banana pith (4), soybean hulls (5), cottonseed hulls (5), sawdust (6), apple wastes (7), and tree fern (1, 8). Most of these works have shown that natural products can be good sorbents for heavy metals.

Rice bran is abundant and commercially available in China. This work's goal was to study the possibility of the utilization of rice bran for the sorption of zinc ions from the aqueous solutions. This study examined the effects of the contact time, particle size, and initial pH on zinc adsorption with rice bran. The adsorption capacity of rice bran for zinc ions has been investigated by determining the equilibrium isotherm. In addition, kinetic analysis was performed to correlate the experimental data, based on the pseudo-second-order equation.

MATERIALS AND METHODS

The major interest of this study was to investigate sorption performance of zinc ions from aqueous solution by using rice bran. The raw rice bran was dried in an oven at 100°C for a period of 24 h, and then ground and sieved to get geometrical size ($<125\,\mu m$). This process took place to produce a uniform material for the complete set of sorption tests which was stored in an air-tight plastic container for all investigations.

The stock solutions of Zn^{2+} ($2000\,mg/dm^3$) were prepared in de-ionized water using zinc sulfate ($ZnSO_4 \cdot 6H_2O$) (analytical grade reagent). All working solutions were prepared by diluting the stock solution with de-ionized water.

Batch adsorption experiments were carried out by shaking 0.25 g of rice bran with 50 mL aqueous solution of the desired concentration in a temperature-controlled water-batch shaker. The pH of the solutions was adjusted to constant values. Continuous mixing was provided during the experiments with a constant agitation speed of 200 rpm. Kinetic studies were carried out at constant pH with fixed initial concentration (100 mg/dm^3) and adsorbent dose from 2 to 4 g/dm^3. After shaking, the samples were withdrawn at suitable time intervals, filtered through a 0.45 μm membrane filter and then analyzed for Zn^{2+} concentrations with atomic absorption spectrophotometer (AAS). For the isotherm studies, 0.25 g of rice bran was put into 50 mL solutions of various concentrations of Zn^{2+} (40 to 160 mg/dm^3). The flasks were shaken for 5 h to reach equilibrium. A known volume of the solution was removed and filtered for Zn^{2+} analysis. Effect of pH on the adsorption of Zn^{2+} was studied by varying the pH from 3.0 to 5.0. The effect of temperature on adsorption equilibrium was studied by varying temperatures from 30 to 50°C. In the experiment to investigate the effect of particle size, batch sorption tests were done at two different tests with particle sizes ranged <74 μm and 125–250 μm, respectively. Each used a range of initial Zn^{2+} concentrations from 40–160 mg/dm^3.

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DATA EVALUATION

Biosorption of the metal ions (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - Ce)}{W} \tag{1}$$

where V is the solution volume, W is the amount of biomass, and C_i and C_e are the initial and final (equilibrium) metal concentrations, respectively.

The Langmuir isotherm was used to fit the experimental data. The Langmuir isotherm can by expressed as (9):

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_m and b are Langmuir constants, which reflect the maximum sorption capacity and the affinity between the ion and biosorbent.

RESULTS AND DISCUSSION

Equilibrium Studies

The isotherm experimental results are shown in Fig. 1 at various temperatures. In all cases favorable isotherms are observed, and the data could be well modeled according to the Langmuir sorption isotherm equation. Results

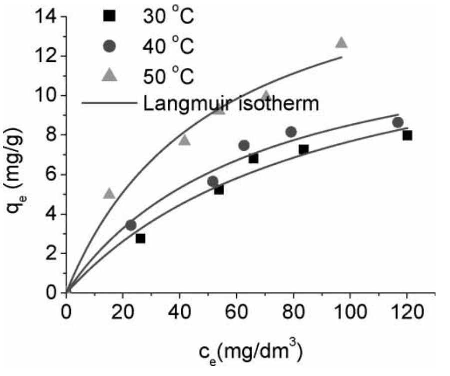

Figure 1. Langmuir isotherms for the sorption of zinc ions on rice bran.

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indicate that the capacity of rice bran for sorption of zinc (II) increases with temperature which is typical for the biosorption of most metal ions from their solutions (8).

The Langmuir isotherm is applicable to homogeneous sorption where each zinc ion/rice bran sorption process has equal sorption activation energy. The maximum adsorption capacity (q_m) and the affinity constant (b) have been determined with Eq. (2) and are shown in Table 1. The equilibrium sorption capacity was found to increase from 14.17 to 18.31 mg/g for an increase in the solution temperatures from 30 to 50°C. It is clear that the sorption of zinc ions onto rice bran is an endothermic process. On the other hand, the initial gradient of the adsorption isotherm is an important factor in evaluating sorbent performance, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant (b). A high value of the affinity constants is thus desirable (10). Table 1 also shows the affinity constant (b) increases from 0.011 to 0.019 dm^3/mg with increasing temperature, which suggests that the sorption of zinc ions onto rice bran is favorable with increasing temperature.

Table 1. Langmuir constants and thermodynamic parameters for the adsorption of Zn (II) onto rice bran

Temperature (°C)	Langmuir constants		Determination coefficients R^2	Thermodynamic parameters ΔG (kJ/mol)
	q_m (mg/g)	b (dm^3/mg)		
30	14.17	0.011	0.981	−16.49
40	14.84	0.015	0.981	−17.92
50	18.31	0.019	0.981	−19.16

The change in apparent enthalpy (ΔH°), free energy (ΔG°), and entropy (ΔS°) of adsorption were calculated from the variation of the Langmuir constant, b (dm^3/mol), with change in temperature using the following equations:

$$\Delta G^\circ = -RT \ln b \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where R is universal gas constant, 8.314 J/mol K and T is absolute temperature, K.

A plot of Gibbs free energy change, ΔG°, versus temperature, T, was found to be linear (Fig. 2). The values of ΔH° and ΔS° were determined from the intercept and slope of the plot. The values of ΔG° are shown in Table 1. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of sorption with a high preference of Zn^{2+} on rice bran. The enthalpy change (ΔH°) and entropy change (ΔS°) for sorption processes are calculated to be 23.93 and 0.134 KJ/mol K, respectively. The value of ΔH° is positive, indicating that the sorption reaction is endothermic. The positive value of ΔS° reflects the affinity of the rice bran for Zn^{2+} and suggests some structural changes in zinc and rice bran (8). In addition, the positive value of ΔS° also shows the increasing randomness at the solid/liquid interface during the sorption of zinc ions onto rice bran. These results are in agreement with the result obtained in the study of copper ion biosorption onto tree fern (8).

The specific surface area occupied by Zn (II) was calculated by the following equation (1):

$$S = \frac{q_m N A}{M} \quad (5)$$

where S is the specific surface area, m^2/g rice bran; q_m is monolayer sorption capacity, gram zinc per gram rice bran; N is Avogadro number, 6.02×10^{23};

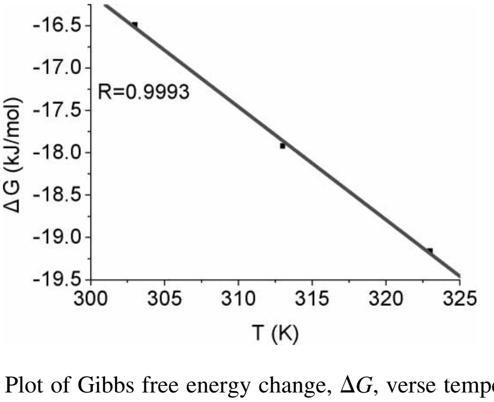

Figure 2. Plot of Gibbs free energy change, ΔG, verse temperature, T.

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A is the cross−sectional area of zinc ions, m^2; M is molecular weight of zinc. For Zn^{2+}, the molecular weight is 65.4 and the cross sectional area has been determined to be 1.72 $\mathring{A}^2$ in a close packed monolayer. Therefore the specific surface areas calculated for Zn^{2+} at different temperatures are 2.24, 2.35, 2.89 m^2/g, respectively. These values are comparable to the result obtained in the study of zinc ion biosorption onto the tree fern (1). It is clear that the specific surface area of the rice bran increases with increasing temperature. This result also shows that increasing the temperature may produce a selling effect within the internal structure of rice bran enabling Zn ions to penetrate further (1).

Kinetic Studies

Kinetic experiments were carried out to determine the equilibrium time required for the uptake of zinc ions by rice bran. The results are presented in Fig. 3. In general, a two-stage kinetic behavior is observed: very rapid initial biosorption in a contact time of 30 minutes, followed by a second stage with a much lower sorption rate. In process application, this rapid biosorption phenomenon is advantageous.

Three kinetic models, i.e. the pseudo-first-order equation [equation (6)], (11) the pseudo-second-order equation [equation 7], (8) and an intraparticle diffusion equation [equation (8)], (12) were considered for interpreting the experimental data:

$$\frac{1}{q_t} = \left(\frac{k_1}{q_{\max}}\right)\left(\frac{1}{t}\right) + \frac{1}{q_{\max}} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\max}^2} + \frac{1}{q_{\max}} t \quad (7)$$

$$q_t = k_p t^{0.5} \quad (8)$$

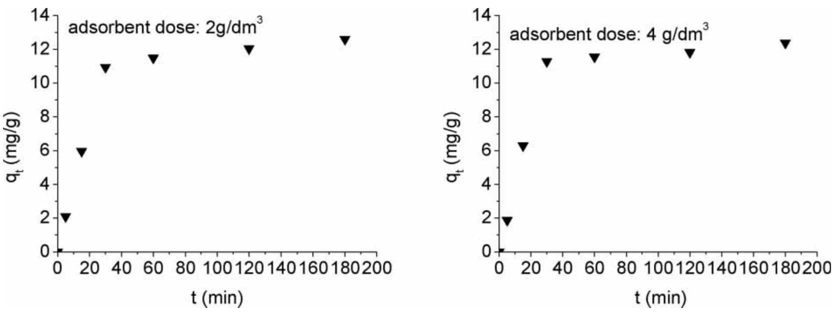

Figure 3. Kinetic experimental studies of zinc uptake at various adsorbent doses.

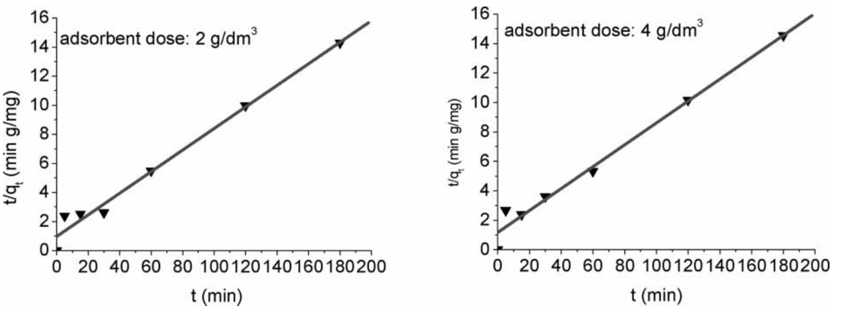

Figure 4. Pseudo-second-order kinetic plots for the adsorption of zinc ion onto rice bran at various adsorbent doses.

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where q_t is the amount of zinc ion adsorbed (mg/g) at various times t, q_{max} is the maximum adsorption capacity (mg/g), k_1 (min^{-1}) is the rate constant of the pseudo-first-order model for the adsorption process, k_2 [g/(mg min)] is the rate constant of the pseudo-second-order model for the adsorption process and k_p is the intraparticle diffusion rate constant. All three models adequately described the adsorption kinetics.

Figure 4 demonstrates the application of the pseudo-second-order model to the adsorption data for two different adsorbent doses. Both plots were employed to obtain the relevant rate parameters. The values of k_1, k_2 and the correlation coefficients r_1 and r_2 calculated for the adsorption of zinc ions under different conditions are listed in Table 2. The correlation coefficient (r_1) for the pseudo-first-order kinetic model was 0.98. This shows that adsorption of zinc ions onto rice bran approximates to a pseudo-first-order reaction. In contract, the correlation coefficient (r_2) for the pseudo-second-order kinetic model was 0.998. This indicates the adsorption system was best described by this model.

Intraparticle diffusion may be the rate-controlling step. If this does occur, then the plot of q_t versus $t^{0.5}$ should be linear and if it passes through the origin then intraparticle diffusion will be the sole rate-limiting process (11). In the present study, it was found that the plots of q_t versus $t^{0.5}$ exhibited an initial linear portion followed by a plateau which occurred after 30 min (Fig. 5). The initial linear portion of the plots seems to be due to intraparticle diffusion with the plateau corresponding to equilibrium.

Table 2. Kinetic parameters for the adsorption of zinc ions onto rice bran (adsorbent dose: 2 g/dm^3)

Adsorbent	k_1 (min^{-1})	r_1	k_2 ($\times 10^{3}$) [g/(mg min)]	r_2	k_p [mg/(g $min^{0.5}$)]	r_p
Rice bran	45.4	0.98	3.83	0.998	2.89	0.994

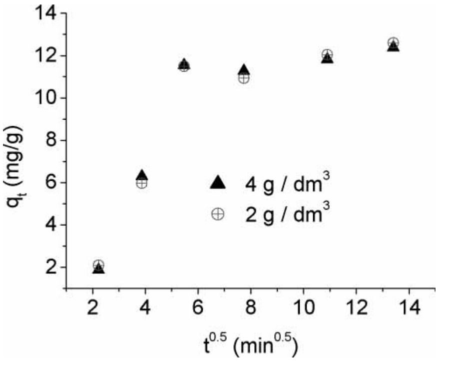

Figure 5. Intraparticle diffusion plots for the adsorption of zinc ion onto rice bran at two adsorbent doses.

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However, neither plots passed through the origin. This indicates that intraparticle diffusion may be the rate-controlling step involved in the adsorption process. Values of the intraparticle diffusion constant, k_p, was obtained from the slope of the linear portion of the plots (Fig. 5) and is listed in Table 2. The correlation coefficient for the intraparticle diffusion model (r_p) obtained also from the linear portion of the plots was 0.994. This value indicates that the adsorption of the zinc ions onto rice bran may mainly be intraparticle diffusion up to 30 min.

Effect of Solution pH

Figure 6 shows the effect of pH on the biosorption capacity of the rice bran at same temperature. As shown, pH is an important parameter for the sorption process. This pH dependence suggests a competition of zinc ions and

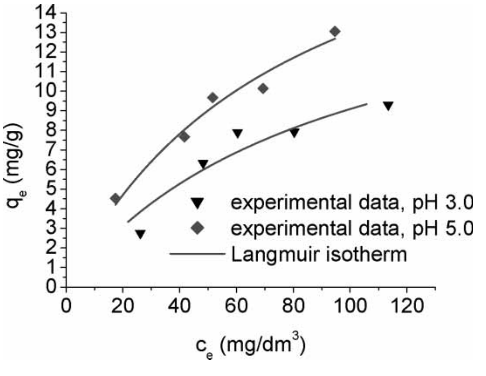

Figure 6. Effect of solution pH on the zinc (II) biosorption by rice bran.

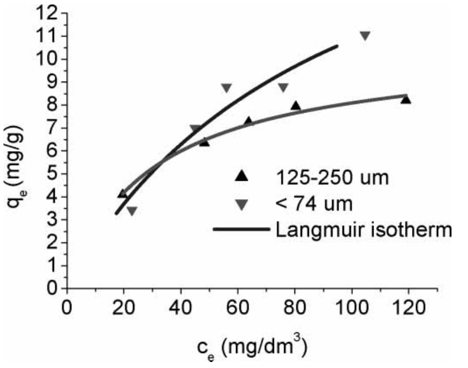

Figure 7. Effect of particle sizes on the zinc (II) biosorption by rice bran (20°C).

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protons by the same binding sites, since in this pH range Zn^{2+} is the dominant species in the solutions. The effect of pH on metal biosorption has been studied by many researchers and the results demonstrated the increasing cation uptake with increasing pH values (13).

Effect of Particle Sizes

Sorption isotherms of zinc ions at two different particle sizes of rice bran are shown in Fig. 7. The amount of zinc ion sorbed by rice bran increased under the condition that the particle size of the rice bran decreased. Langmuir parameters q_m and b for each of the two isotherms and the specific surface area (S) have been calculated and are listed in Table 3. It is clear that the sorption capacity (q_m) increased from 10.56 to 21.07 mg/g with decreasing particle size from 125-250 to <74 µm. This may be attributed to the larger external surface available with small particles at a constant total mass of rice bran in the system.

CONCLUSIONS

Rice bran is able to sorb zinc ions from aqueous solutions. It was noted that an increase in the temperature resulted in a higher zinc loading per unit weight of

Table 3. Langmuir sorption isotherm parameters and specific surface area at different particle sizes

Particle sizes (µm)	R^2	q_m (mg/g)	b (dm^3/mg)	S (m^2/g rice bran)
<74	0.986	10.56	0.033	1.67
125–250	0.946	21.07	0.011	3.29

the sorbent. Decrease in the particle size of rice bran resulted in an increase in the zinc uptake per unit weight of the sorbent. The adsorption of zinc ions onto rice bran was also found to be pH dependent. The sorption of zinc ions onto rice bran is of its spontaneous and endothermic nature. Adsorption data indicate the applicability of pseudo-second-order kinetics. The results show that rice bran can be used for the sorption of the Zn^{2+}.

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