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Adsorption of Pb(II) onto Modified Rice Bran

Hengpeng Ye*, Zhijuan Yu

School of Chemistry and Material Science, South Central University for Nationalties, Wuhan, China.
Email: *yehengpeng@126.com

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ABSTRACT

In this study, the modified rice bran was tested to remove Pb(II) from water. Batch experiments were carried out to evaluate the adsorption characteristics of the modified rice bran for Pb(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 bran was approximately 70.8 *mg Pb(II)/g absorbent at temperature of* 25℃ *and at the initial Pb(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 Pb(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 Pb(II) is about* 15-20%*, and it is relatively difficult for the adsorbed Pb(II) to be desorbed. The relatively low cost and high capabilities of the rice bran make it potentially attractive adsorbent for the removal of Pb(II) from wastewater.*

Keywords: *Rice Bran, Pb(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. Lead, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. All lead compounds are cumulative poisons. Several industries like mining, printing, painting, dyeing, battery manufacture and other industries discharge effluent containing lead, to surface water. Lead has toxic effects on neurobehavioral development and on the brain cell function [1]. The accumulation of lead in river beds [2] has been detected and gives cause for concern. This underlines the need for developing methods for effective removal of lead from water at least below the regulatory level.

However, there are several methods for the treatment of wastewaters containing Pb(II), including ion exchange, adsorption, precipitation and membrane separation [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 Pb(II) from wastewater. Though the removal of Pb(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, preparation of carbons from low-cost materials [6-7], use of clay minerals [8-9], waste materials [10-12], and wheat bran [13-14] are some of the alternatives of costly activated carbons. Although many of these adsorbents can effectively remove Pb(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 bran is a by-product of the rice milling industry and the amount of rice bran available is far in excess of any local uses, thus frequently causing disposal problems. Therefore, rice bran 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 bran would represent effective utilization of waste matter. The modified rice bran 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 bran as adsorbents for the removal of Pb(II) from wastewater. Rice bran 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 bran for Pb(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 bran 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 bran 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 bran showed the presence of various oxides of Ca, Si, Mn, Mg, and Fe.

About 20 g of dried rice husks were treated with 200 mL 3 M sodium hydroxide at 60℃ 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℃ 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℃, 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℃ in an oven overnight and ball-milled into powder that passed through 75 μm 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 bran with 100 mL aqueous solution of adsorbate ($Pb(NO_3)_2$) 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 HNO_3 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 Pb(II). Desorption experiments were conducted by shaking 100 mg of adsorbent containing adsorbed Pb(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%.

Table 1. Chemical compositions and physical properties of rice bran.

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%		

2.3. Analysis of Pb(II)

Pb(II) was estimated through atomic absorption spectrophotometer using a Varian Spectra AA 10 Plus atomic absorption spectrophotometer, at wavelength of 217 nm. The band pass was 1 nm. The adsorbed Pb(II) was calculated from the difference of the Pb(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. Pb(II) Adsorption Isotherm

Experiments were performed at different initial Pb(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 Pb(II) adsorption isotherm experiments are shown in **Figure 1**. It can be found that the Pb(II) adsorption capacity of the modified rice bran increased with the Pb(II) equilibrium concentration increasing from 0 to 100 mg/L. This capacity was approximately 59.5, 68.0, 75.8 mg Pb(II)/g absorbents respectively at temperature of 15, 25, 35℃ and at the Pb(II) equilibrium concentration of 100 mg/L and pH 7.0. With a further increase of the Pb(II) equilibrium concentration, the increase of the adsorption capacity was less signifycant.

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

Freundlich equation:

$$q_e = KC_e^{1/n} \tag{1}$$

Langmuir equation:

$$q_e = q_m bC_e / (1 + bC_e) \quad (2)$$

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 **Figure 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 **Figure 1**. It is shown that the experimental data of Pb(II) adsorption on modified rice bran could be well fitted by the two isotherms. Clearly, Langmuir equation provided better fitting in terms of R^2 and SE values.

The Pb(II) adsorption on different materials has been widely studied during recent years, such as, on granulated blast-furnace slag [10], bentonite [8], bagasse fly ash [12], zeolite [9], sepiolite [9], etc. At respective optimal pH value and approximately the same Pb(II) equilibrium concentration, their reported Pb(II) adsorption capacities (mg/g) are given in **Table 3**. For comparison, the Pb(II) adsorption capacity of the modified rice bran obtained in this study is also listed in **Table 3**. In comparison with granulated blast-furnace slag [10], bentonite [8], bagasse fly ash [12], zeolite [9], sepiolite [9], and wheat bran [13-14], the relatively low cost and high capabilities of rice bran make it potentially attracttive adsorbent for the removal of Pb(II) from wastewater.

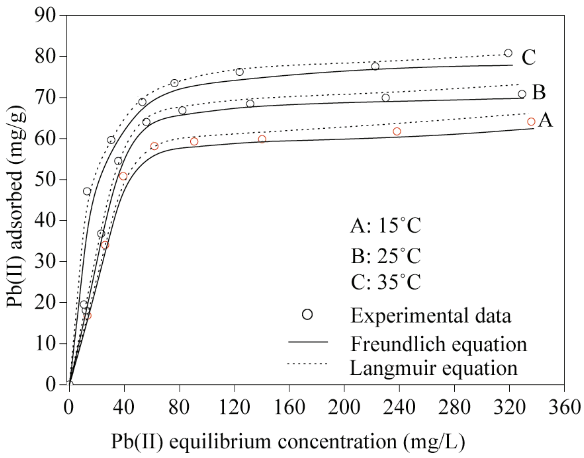

Figure 1. Pb(II) adsorption isotherm.

Table 2. Estimated isotherm parameters for Pb(II) adsorption.

Temperature	*Freundlich equation* ($q_e = KC_e^{1/n}$)				*Langmuir equation* ($q_e = q_m bC_e/(1+bC_e)$)			
	K	$1/n$	R^2	SE	q_m (mg/g)	b (L/mg)	R^2	SE
15℃	29.9	0.162	0.925	1.33	60.1	1.22	0.975	0.625
25℃	32.6	0.248	0.910	1.62	73.9	0.708	0.936	0.772
35℃	34.2	0.303	0.898	1.92	78.9	0.552	0.922	0.836

Table 3. Pb(II) adsorption capacities of different low cost and easily available materials (at 20-25℃).

Material	Capacity (mg/g)	Source
granulated blast-furnace slag	34.0	[10]
bentonite	21.5	[8]
bagasse fly ash	4.1	[12]
zeolite	30.5	[9]
sepiolite	38.2	[9]
wheat bran	68.79	[13-14]
rice bran	73.9	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 Equations (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:

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

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 Pb(II) concentration of 30 mg/L were calculated using Equations (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 energeticcally favorable sorption. (ΔH^0) and (ΔS^0) were obtained from the slope and intercept of a plot of ln K_d against $1/T$ (**Figure 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.

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 Pb(II) concentration of 150 mg/L at 25℃. The results of the effect of pH on adsorption of Pb(II) are presented in **Figure 3**. It was found that the total amount of adsorption of Pb(II) onto modified rice bran increases with an increase of pH from 3.1 to 8.1. Similar trends were also observed for Pb(II) adsorption on granulated blast-furnace slag [10], and on red mud [11]. The pH of the aqueous solution is an important variable that influences the adsorption of Pb(II) at the solid-liquid interfaces. However, the modified rice bran 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 bran surface). Furthermore, a lower pH value causes the rice bran surface to carry more positive charges and thus would more significantly repulse the positively charged species (Pb(II)) in solution.

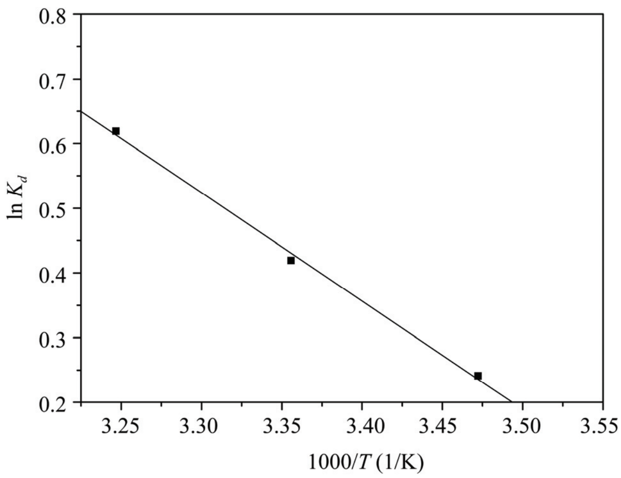

Figure 2. A plot of ln K_d against 1/T for Pb(II) adsorption by rice bran.

Table 4. Thermodynamic parameters for adsorption of Pb(II) on rice bran.

$-\Delta G^0$ (cal mol^{-1})			ΔH^0	$-\Delta S^0$
15℃	25℃	35℃	(kcal mol^{-1})	(cal mol^{-1} K^{-1})
577.0	1039	1585	13.92	50.29

3.4. Pb(II) Adsorption Kinetic

Experiments were performed at the initial Pb(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 **Figure 4**. It can be seen that the majority of Pb(II) adsorption on the modified rice bran were completed in 5-15 minutes. For example, after 15 minutes of adsorption, the Pb(II) adsorbed on the rice bran at 15, 25, 35℃ was, respectively, 89.1%, 91.3%, 92.4% of that at 180 minutes.

The Pb(II) adsorption kinetic data (**Figure 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

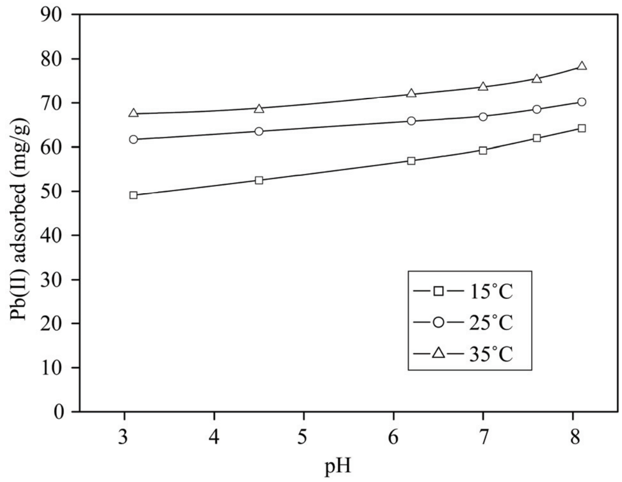

Figure 3. Effect of pH on adsorption of Pb(II).

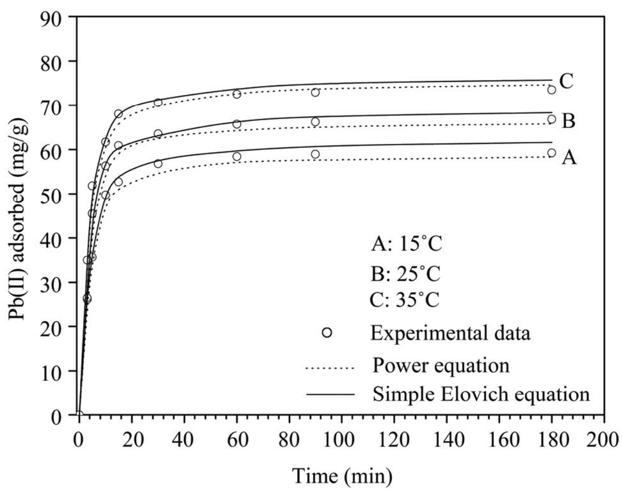

Figure 4. Pb(II) adsorption kinetics.

estimated parameters with R^2 and SE are shown in **Table 5**. Based on R^2 and SE, the kinetics of Pb(II) adsorption on the rice bran 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 **Figure 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 Pb(II) adsorption on lignite [17] and diatomite [18].

3.5. Pb(II) Desorption Studies

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

Table 5. Estimated kinetic model parameters for Pb(II) adsorption.

	Freundlich equation ($q = at^b$)				*Langmuir equation* ($q = a + b\ln t$)			
Temperature	a	b	R^2	SE	a	b	R^2	SE
15℃	16.3	0.455	0.966	0.386	10.8	17.5	0.985	0.352
25℃	18.9	0.493	0.928	0.779	13.6	20.2	0.963	0.422
35℃	29.3	0.354	0.958	0.512	24.6	18.6	0.978	0.403

Table 6. Desorbability of the adsorbed Pb(II) on rice bran.

Initial Concentration (mg/L)	Adsorbed Pb(II) (mg/g)	Desorbed Pb(II) (mg/g)	Desorbability (%)
60	36.8	5.6	15.3
120	64.0	11.6	18.1
200	68.4	12.8	18.8
400	70.8	13.6	19.2

4. Conclusions

The modified rice bran has been found to be a very effective adsorbent for the efficient removal of Pb(II) from water. The maximum adsorption capacity of the modified rice bran was approximately 70.8 mg Pb(II)/g absorbent at temperature of 25℃ and at the initial Pb(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 Pb(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 Pb(II) is about 15-20%, and it is relatively difficult for the adsorbed Pb(II) to be desorbed. The relatively low cost and high capabilities of the rice bran make it potentially attractive adsorbent for the removal of Pb(II) from wastewater.

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