

Heavy Metals (Cr (VI), Cd (II) and Pb (II)) Ions Removal by Modified Jute: Characterization and Modeling

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ABSTRACT

Jute modified has been used for adsorption of Cr (VI), Cd (II) and Pb (II) ions over a range of initial metal ion concentration. Adsorption process is done in batch mode. Adsorption isotherms of the heavy metals on adsorbents prepared were determined and correlated with common isotherm equations. It was found that the Freundlich isotherm is better than Langmuir for explaining the behavior of adsorption. The effect of some parameters such as adsorbent quantity, pH value and temperature were investigated. The enlargement of pH value until 5 and adsorbent quantity increase the adsorption quantity. Whereas exceed of the temperature has the reverse effect.

Keywords: Heavy metals; Jute; Kinetic adsorption; Freundlich isotherm; Langmuir isotherm

INTRODUCTION

Nowadays heavy metals are among the most important pollutants in surface and groundwater. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions [1]. Levels of heavy metals in the environment have increased due to pollution caused by industries [2 - 6]. Therefore, the elimination of heavy metals from water is important to protect public health. Treatment process for metals contaminated water includes chemical precipitation, membrane filtration, ion exchange and adsorption [7]. Many unconventional methods have been thought of for this purpose, which include bio- sorption [8 - 9], activated carbon adsorption [10 - 15] etc. Over the last few years, adsorption has been shown to be an economically feasible alternative method for removing metal ions in

water [16 - 22]. All of these technologies also have their inherent advantages and limitations.

In this work, jute was modified by diethanolamine. Then batch adsorption experiments have been carried out to characterize and to understand adsorption mechanism by modeling the adsorption kinetic. The aim of the present paper is to study the possibility of the removal of metal ions by modified jute as well as the effects of adsorbent quantity, pH value and temperature. A kinetic study according to two different models has been applied.

EXPERIMENTAL

A. Materials and Methods

Modified jute preparation

Jute (2g) was added to 100 ml water. pH was increased by addition of 5 ml of 10% sodium hydroxide solution. The mixture was left one

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hour, then 2% w/w diethanolamine was added and finally refluxed at 40-50 °C for 3 hours. The flask was cooled and the sample was washed with 50 ml water 3 times [23 - 24].

Metal ion Solutions

All Cr (VI), Cd (II) and Pb(II) solutions were prepared using $K_2Cr_2O_7$, $CdCl_2$ and $PbCl_2$. The metal ions concentrations were 1000 ppm. pH of all solutions were controlled by sulfuric acid 1N and sodium hydroxide 1N.

Adsorption Experiments

Spectrophotometric a measurement method for adsorption assays of different metal ions. The absorption spectra is 540 nm for Cr (VI) and atomic absorption is 228 nm for Cd(II) and Pb(II).

B. Characterization of Modified Jute

All of the experiments were done on modified jute in 500 cm³ Erlenmeyer flasks. About 100ml of metal solutions were added to the flask already containing modified jute. The solutions were shaken for 3 minutes by means of a magnetic agitation at 600 rpm.

C. Consideration of Effective Parameters on Adsorption

Adsorbent quantity

2 and 4g (with size 0.5 mm) modified jute samples were placed in contact with 100 ml solutions of different concentrations of heavy metal for the adsorption of Cr(VI), Cd(II) and Pb(II) ions. The results are given in Figures 1, 2 and 3.

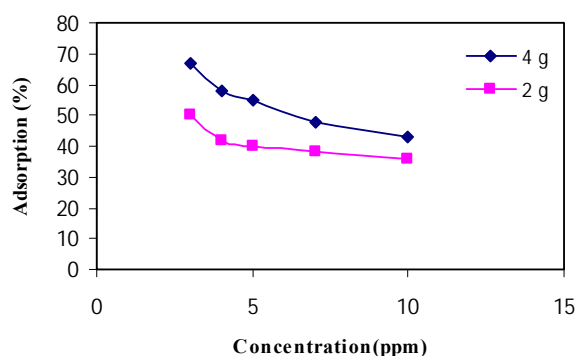


Fig.1. Adsorption of Cr(VI): Evolution of adsorbed quantity in relation to concentration.

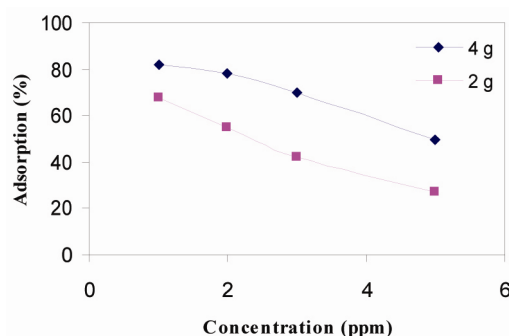


Fig.2. Adsorption of Cd(II): Evolution of adsorbed quantity in relation to concentration.

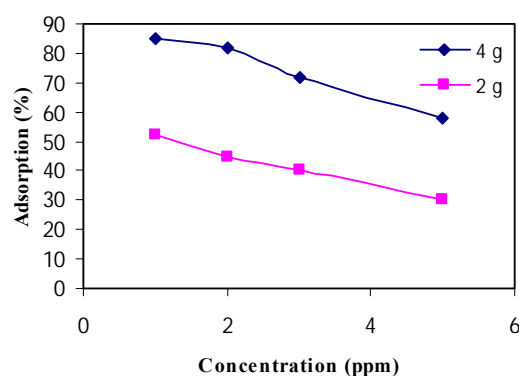


Fig.3. Adsorption of Pb(II): Evolution of adsorbed quantity in relation to concentration.

pH value

pH effect was determined on adsorption. The pH was measured in a suspension of 4g of modified jute in 5 and 2.5, other parameters were similar. The results for Cr(VI), Cd(II) and Pb(II) ions are shown in Figures. 4, 5 and 6.

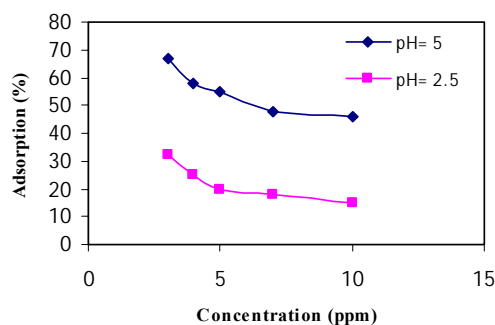


Fig.4. Adsorption of Cr(VI): Evolution of adsorbed quantity in relation to concentration.

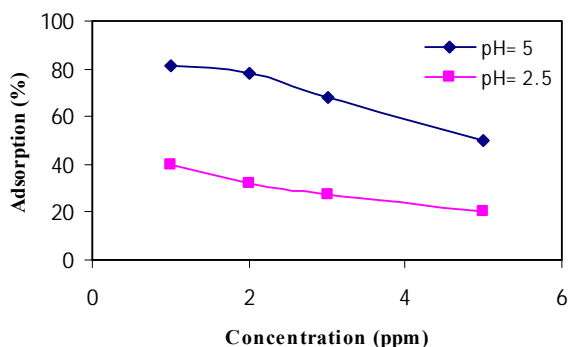


Fig.5. Adsorption of Cd(II): Evolution of adsorbed quantity in relation to concentration.

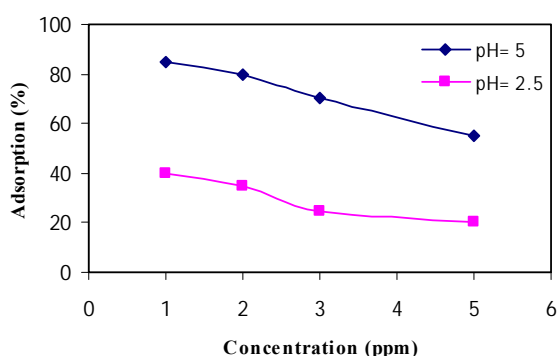


Fig.6. Adsorption of Pb(II): Evolution of adsorbed quantity in relation to concentration.

Temperature

In order to know the optimum temperature for adsorption, 4g of modified jute was performed by 25 and 50 C. Other parameters were similar. The results for Cr(VI), Cd(II) and Pb(II) ions are compared in figures 7, 8 and 9.

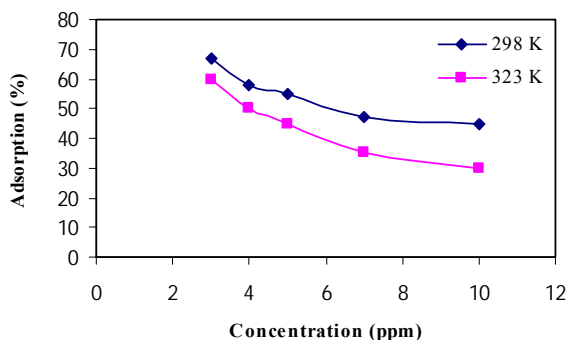


Fig.7. Adsorption of Cr(VI): Evolution of adsorbed quantity in relation to concentration.

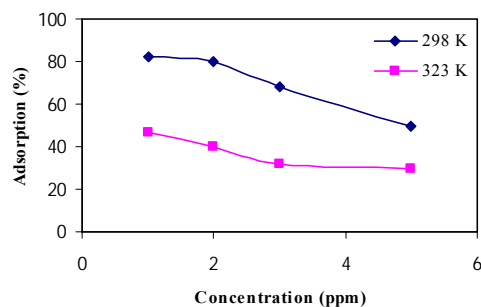


Fig.8. Adsorption of Cd(II): Evolution of adsorbed quantity in relation to concentration.

D. Isotherm modeling

In order to optimize the design of an adsorption system to remove the heavy metal, it is important to establish the most appropriate correlation for the equilibrium data for each system. The amount of heavy metal adsorbed, x/m , was determined as follows [25]:

$$x/m = (C_0 - C_e)V/W \quad (1)$$

Where C_0 and C_e are the initial and equilibrium liquid phase concentrations of heavy metal solution (mgdm^{-3}), respectively, V is the volume of heavy metal solution (dm^3), and W is the mass of dry modified jute sample used (g).

For the analysis of kinetics, equilibrium sorption of Cr(VI), Cd(II) and Pb(II) ions was carried out at fixed temperature using various initial concentrations. The experimental data was considered by Langmuir and Freundlich equations. The applicability of the isotherm equations is compared by judging the correlation coefficients, R^2 [26].

Langmuir model

The Langmuir equation is the most widely used by two parameter equation, commonly expressed as [26]:

$$C_e/x/m = 1/KV_m + C_e/V_m \quad (2)$$

C_e : equilibrium concentration (ppm)

X : Cr(VI), Cd(II) and Pb(II) adsorbed (mg)

m : amount of adsorbent (g)

K : Langmuir isotherm constant

V_m : capacitance adsorbed (mg/g)

The results for Cr(VI), Cd(II) and Pb(II) are shown in Tables 1, 2 and 3.

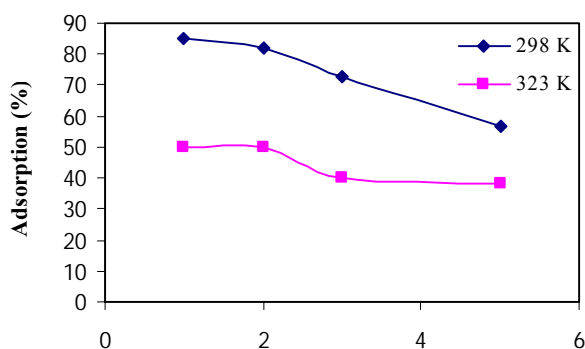


Fig.9. Adsorption of Pb(II): Evolution of adsorbed quantity in relation to concentration.

Table 1. Comparison of experimental adsorption with Langmuir model Cr(VI), $R^2=0.98$

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
3	0.7	0.345	0.0862	8.12
4	1.18	0.423	0.1057	11.16
5	2	0.45	0.1125	17.77
7	3.26	0.561	0.1402	23.25
10	5.27	0.708	0.177	29.77

Table 2. Comparison of experimental adsorptive with Langmuir model Cd(II), $R^2 = 0.98$

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
1	0.08	0.345	0.0861	8.12
2	0.18	0.423	0.1057	11.16
3	0.27	0.45	0.1125	17.77
5	0.46	0.561	0.1402	23.25

Table 3. Comparison of experimental adsorptive with Langmuir model Pb(II), $R^2 = 0.98$

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
1	0.06	0.092	0.023	2.60
2	0.15	0.18	0.045	3.33
3	0.22	0.27	0.068	23.3
5	0.38	0.452	0.113	2.81

Freundlich model

The Freundlich isotherm is an empirical equation and shown to be satisfactory for low concentrations. The equation is commonly given by [27]:

$$x/m = K_F \cdot C_e^{1/n} \quad (3)$$

x/m: Cr(VI), Cd(II) and Pb(II) adsorbed on adsorbent (mg/g)

K_F : Freundlich isotherm constant

n : Freundlich isotherm constant

The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [25]. Value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [28]. A plot of $\ln x/m$ vs. C_e enables the empirical constants K_F and $1/n$ to be determined from the intercept and slope of the linear regression. For predicting the favorability of an adsorption system, the Langmuir equation, like the Freundlich equation, can also be expressed in terms of a dimensionless separation factor, R, defined as [29]:

$$R = 1 / (1 + KC_0) \quad (4)$$

C_0 and K: as defined in eqs. (1) and (2), respectively

$R=1$ and 0 : the adsorptions are linear and irreversible, respectively.

The result for Cr(VI), Cd(II) and Pb(II) are represented in Tables 4, 5 and 6.

Table 4. Comparison of experimental adsorptive with Freundlich model Cr (VI)

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
3	0.7	0.0862	-0.06	-0.155
4	1.18	0.1057	-0.97	0.72
5	2	0.1125	-0.95	0.301
7	3.26	0.1402	-0.85	0.513

R = 0.99

Table 5. Comparison of experimental adsorptive with Freundlich model Cd(II)

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
1	0.08	0.027	-1.568	-1.096
2	0.18	0.054	-1.267	-0.744
3	0.27	0.082	-1.086	-0.568
5	0.46	0.135	0.869	-0.337

R = 0.99

Table 6. Comparison of experimental adsorptive with Freundlich model Pb(II)

Concentration (ppm)	C_e (ppm)	x (mg)	x/m	$C_e/(x/m)$
1	0.06	0.027	-1.568	-1.222
2	0.15	0.054	-1.267	-0.824
3	0.22	0.082	-0.086	0.657
5	0.38	0.135	0.869	-0.420

R = 0.99**E. Comparing the amount of adsorption on modified jute and unmodified jute**

The potential of a lignocelluloses fiber, jute, was assessed for adsorption of heavy metal ions from their aqueous solutions. Therefore, all experiments were carried out on unmodified jute. It can be seen that the amount of adsorbed heavy metal is about 40 to 80% less than the modified jute.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the rate of Cr (VI), Cd(II) and Pb(II) ions, from initial solution of different concentrations for 2 and 4 g modified jute sample. It can be seen that for all elements, the adsorption rate increases with amount of adsorbent.

From the data reported in Figures. 4, 5 and 6, increasing pH from 2.5 to 5 causes the adsorption exceed. As can be observed, in low pH, adsorption is insufficient, because the metal complexes are instable. Also, there is a possibility of the existence of some positively charged sites, where negatively charged Cr (VI), Cd(II) and Pb(II) ions, can be adsorbed. Thus a change in pH of the solution, as a result of the change in conductivity of solution. The adsorption is approximately constant at $pH > 5$, because the conductivity is weak in agreement with the value of pH, which is close to neutrality.

Figures 7, 8 and 9, present the results of the temperature to the adsorption capacity. Comparing the values of adsorption at 25 and 50 °C, show that the adsorptions at 25 °C are higher than those at 50 °C. It implies that at high temperatures, kinetic energy increases and therefore the ions don't have enough time for adsorption.

Tables 1, 2 and 3 present the results of the Langmuir isotherm fits of Cr (VI), Cd(II) and Pb(II) ions to the measured adsorption capacity data for modified jute. The Langmuir isotherm appears to fit the data reasonably well, as reflected with correlation coefficients (R) in the range of 0.98 – 1.00. Also, tables indicate the monolayer adsorption capacity (V_m) and Langmuir constant (K) increase with increasing concentration as expected. This tendency is reasonable since the adsorption affinity and monolayer adsorption capacity will be enhanced with increasing concentration.

Tables 4, 5 and 6 present the effect of concentration on the Freundlich parameters, indicating the satisfactorily good correlation between the model predictions and the experimental data. The Freundlich isotherm appears to fit the data reasonably well, as reflected with correlation coefficients (R) in the range of 0.99- 1.00. Also, tables indicate the monolayer adsorption capacity (V_m) and Langmuir constant (K) increase with increasing concentration as expected. This tendency is reasonable since the adsorption affinity and monolayer adsorption capacity will be enhanced with increasing concentration.

CONCLUSION

The sorption mechanism of jute modified examined under the range of conditions. Sorption mechanism can be set up at different conditions. The adsorption is dependent on adsorbent quantity. On the other hand, the more active sites there are, the more adsorbent is caused. Increase of pH from 2.5 to 5, due to increase the adsorption, but in the higher pH the adsorption approximately is constant. The exceed of the temperature causes a decrease in adsorption. This can be well understood that at high temperature, kinetic energy increases and therefore the ions don't have enough time for adsorption. Also, the amount of adsorbed heavy metal by modified jute is more than the unmodified jute.

The Freundlich model according to the reaction rate equation was found to be more conformity with this system than Langmuir model.

In general, jute modified is an effective absorbent for the removal of Cr (VI), Cd (II) and

Pb (II) ions from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals. This has led to use of parts of the agricultural products that have no food value, for heavy metal by adsorption.

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