Adsorption isotherm study of copper removal from aqueous solutions onto agricultural by-product.

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Abstract
Pollution by heavy metals is a serious global problem, both for the environment and for any form of life. There is a growing interest to find low cost agricultural by-products with high adsorption capacity for the removal of heavy metals. In the present study the adsorptive capacity of chemically modified rice husk was evaluated for the removal of copper ions from aqueous solutions. Equilibrium isothermal experiments were conducted and five mathematical models were used to investigate the adsorption isotherm. The three parameters models Sips and Redlich-Peterson fitted better the experimental data. The maximum adsorption capacity of modified rice husk for copper ions was 34.38 mg/g and the maximum adsorption removal was 92.76%. Modified rice husk could be one of the low costs and effective adsorbent for copper removal from aqueous solutions.
Keywords: *Adsorption isotherm, copper, rice husk*

1. Introduction

Metals can pose a risk to the human and environmental health through bioaccumulation along the food chain. Human activities are largely responsible for the pollution of water resources by heavy metals. A wide variety of agricultural waste and byproducts has been explored for sequestering heavy metals due to their strong affinity and high selectivity toward heavy metals and their low cost (Kumar, 2006). The purpose of this work was to investigate the adsorption ability of modified rice husk to remove copper from aqueous solutions. Equilibrium isotherm data were obtained and the applicability of different adsorption isotherm models were studied. Adsorption models can provide information on the adsorption mechanism and the parameters involved in the absorbate interaction with the absorbent materials.

2. Materials and Methods

2.1. Preparation of adsorbent and aqueous solutions

Rice husk obtained from a local mill was screened and washed with deionized water to remove impurities, dried at 60°C for 24 hours and then it was ground and sieved to obtain different particle sizes 0-0.125 mm, 0.125-0.2 mm, 0.2-0.5 mm. The sieved rice husk was treated with 0.1M $Ca(OH)_2$ for 24h, with a stirring speed of 150 rpm at ambient temperature. The mixture was filtered and the adsorbent was washed several times with distilled water and dried in an oven at 60^0C for 24 hours. All the chemicals used were of analytical grade. Stock solutions (1000 mg/l) were prepared with distilled water using $Cu(NO_3)_2$ and $Zn(NO_3)_2$.

2.2. Adsorption studies

Adsorption studies were carried out in the batch mode. The experiment conditions such as pH, particle sizes, doses, contact time were investigated. Equilibrium adsorption experiments were conducted in 25 ml samples, with initial copper concentrations from 25 to 700 mg/l, adsorbent dose of 5 g/l in the presence of 0.01M KNO_3 as background electrolyte. The pH of the samples was adjusted to 5 and samples were agitated with a stirring speed of 150 rpm for 24 hours at 25°C temperature. The concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (Varian model AA-20). The procedure was repeated three times for each condition and the mean concentration was determined. Five isotherm models were tested to describe the biosorption data of the modified rice husk.

3. Results and Discussion

Chemically modified rice husk was found to have a significant higher adsorption capacity comparing to the untreated rice husk. The copper removal obtained for modified and untreated rice husk, at copper concentration of 100 mg/l, was 76.50% and 33.07% respectively. The removal of copper from water samples is affected by the pH being low at pH 2 and increasing until pH 6. At low pH H^+ ion competes with Cu^{2+} resulting in low removal. Above pH 6 copper starts precipitating as $Cu(OH)^{2+}$. Adsorption of copper was very fast at the beginning of process, 70% was absorbed at the first 15 minutes and reached equilibrium at 180 minutes.

The obtained equilibrium data for copper were fitted with the two parameters (Langmuir, Freundlich, Temkin) and the three parameters (Redlich–Peterson, Sips) models, by nonlinear regression analysis (Foo and Hameed, 2010; Shahbeig et al, 2013**)**. Nonlinear regression is a more proper technique for getting the parameters (Ho and al., 2002). The obtained model parameters and the error functions used to quantify the models (the coefficient of determination, R^2, the sum of squared errors, SSE, the hybrid fractional error function, HYBRID and Marquardt's percent standard deviation, MPSD) are presented in Table 1. The fitting of the isotherm models to the experimental data is presented in Figure 1.

Table 1. Isotherm constants and error functions for the sorption of Cu (II) ions

Equation	Parameters		R^2 /SSE	HYBRID /MPSD
Langmuir	q_m	34.384	0.952 60.31	111.87 37.29
	k_L	0.035		
Freundlich	k_F	6.115	0.977 18.944	37.68 25.73
	$1/n$	0.285		
Temkin	A_T	1.204	0.976 19.380	22.08 12.60
	b_T	472.67		
Redlich-Peterson	k_{RP}	6.692	0.987 10.683	16.37 12.75
	a_{RP}	0.765		
	n_{RP}	0.775		
Sips	k_S	4.897	0.988 10.147	19.73 15.72
	a_S	0.083		
	n_S	0.459		

From the analysis of the isotherm models and the error functions the three parameter models (Sips and Redlich-Peterson), having higher correlation coefficients, R^2 and smaller SSE, HYDRID and MPSD values, seemed to be the best-fitting models for the experiment results. Redlich-Peterson model is a hybrid model describing both homogenous and heterogenous adsoption by combining the Langmuir and Freundlich equations with the values of n_{PR} summarizing the behavior. The Sips isotherm model also is an extremely flexible equation reducing to Freundlich, Langmuir and to Henry's law according to n_S and concentration values (Foo and Hameed, 2010). The error values of the two models are very similar. The best fit of adsorption isotherm models was in the order of: Sips> Redlich-Peterson> Freundlich> Temkin> Langmuir. The error values for Freundlich and Temkin models are similar and show a good correlation of the models with the experimental results. The applicability of Freundlich model indicates multilayer adsorption to heterogeneous surfaces. The n value of 3.05 suggests relatively strong adsorption of copper ions onto the surface of rice husk. The b_T value of 0.4727 Kj/mole of Temkin model corresponds to physical adsorption. The Langmuir isotherm model, that describes monolayer adsorption into homogeneous surfaces, gives a maximun adsorption capacity value of 34.384 mg/g and values of separation factors R_L below 1, indicating favorable adsorption of Cu(II) ions into rice husk. Although the Langmuir isotherm model is usually used to describe the adsorption of metals into different biosorbents, the error values indicate that it is the least satisfactory model to fit the experimental data.

Isotherm parameter values obtained by linear regression analysis, using the linear forms of the isotherm models, differ significantly with those of nonlinear regression. The corresponding values of linear regression are k_F=4.885 mg/g and 1/n=0.033 for Freundlich model and q_m=36.006 mg/g, k_L=0.033 l/mg for Langmuir model (type 1 linear equation). Temkin model gives the same parameter values for linear and non linear regression. Error values indicate that the non linear regression analysis is preferable.

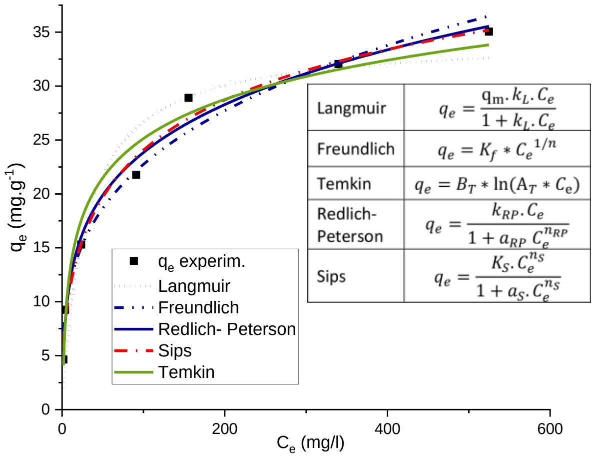

Figure 1. Representation of isotherm models for Cu(II) ions adsorption onto rice husk

4. Conclusions

Modified rice husk has a significant adsorption capacity toward the Cu(II) ions and could remove about 92.76% of ions from the aqueous solution. The Sips and Redlich-Peterson are the best fitted models, under the experimental conditions, followed by Freundlich and Temkin models. Modified rice husk could be a cost effective and efficient absorbent.

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