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Isotherm Study of Nickel(II) Adsorption from Aqueous Solution Using Thermally Treated Rice Husk

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The adsorption of heavy metals using low cost adsorbents is being widely investigated. Various modifications and treatments of adsorbents either chemically or physically have been applied to enhance the adsorption capacity. Thermal treatment is one of the approach of improving the porosity of the adsorbent. In the present study, the adsorption of nickel(II) ions using thermally treated rice husk is reported. The adsorption data were evaluated with Langmuir and Freundlich adsorption models. It was found that the equilibrium data fitted well with Langmuir isotherm as indicated with high coefficient of determination (R^2 = 0.9947). The adsorption capacity of the thermally treated rice husk was found to be 1.68 mg/g. It can be seen that nickel(II) ions are considerably adsorbed on thermally treated rice husk and the method used in this study could be an economic approach for removal of nickel(II) ions from aqueous solutions.

Keywords: Nickel(II) ions, Adsorption isotherm, Thermally treated rice husk.

INTRODUCTION

Wastewater which contains highly toxic and hazardous heavy metal ions that exceed the permissible limit could harmful to humans and the environment. Consequently proper treatment of wastewater contaminated by heavy metals should be carried out before discharge into receiving waters to avoid accumulation of heavy metals in the food chain and persistence in the ecosystem [1]. Cadmium, chromium, copper, nickel, mercury, lead and zinc are among the heavy metals, which are frequently released from industrial activities and should become a major concern to the environment [2].

Nickel is usually released from industrial processes such as electroplating, plastics manufacturing, metal finishing, nickel-cadmium batteries [3] and its maximum permissible concentration of nickel in drinking water recommended by U.S. Environmental Protection Agency (EPA), Agency for Toxic Substances and Disease Registry (ATSDR) and World Health Organization (WHO) is 0.02 mg/L [4]. In fact, nickel is vital to humans but it could cause a few health problems such as skin irritation, dermatitis and gastrointestinal distress if consumed excessively [5].

Various technologies have been developed to reduce heavy metals including chemical precipitation, ion exchange, chemical coagulation, extraction and membrane separation [6]. However, some drawbacks were reported, for instance formation of secondary pollution, high cost, high energy input, large quantities of chemical reagents and poor treatment efficiency at low metal concentration [7]. To overcome these problems, adsorption by various low cost adsorbents derived from industrial by-product, natural material, modified biopolymers and agricultural waste were developed [8]. According to Mohammed *et al.* [9], the application of agricultural wastes such as palm oil fuel ash, coconut shell, mangosteen peel, rice husk, durian peel and corncob is environmental friendly and able to compete with activated carbon in terms of adsorption capacity, effectiveness and economic value.

Hence, a simple thermal treatment on rice husk was conducted in this study in order to develop a low cost and environmental friendly adsorbent for removal of nickel(II) ions from the aqueous solution. The main objective of this study is to determine the adsorption isotherm of nickel(II) ions onto the thermally treated rice husk by evaluating the experimental data using well-known isotherm models namely Langmuir and

Freundlich isotherm to determine the interaction mechanism of adsorbate ions on the surface of the adsorbent.

EXPERIMENTAL

Preparation of adsorbent: Samples of *Oryza sativa* L. rice husk were obtained from a nearby local rice mill. Then it was ground and washed with ultrapure water to remove apparent excess material and colour. The process of washing were conducted several times until constant pH. The cleaned and wet rice husk was dried in an oven at 105 °C for 24 h to remove moisture. The dried rice husk was sieved through the sieves (Endecotts Ltd, England) between 150 and 300 µm and labelled as raw rice husk (RRH). The RRH was heated in a furnace at 650 °C for 2 h. This treated rice husk was labelled as RH-650 and stored in airtight polyethylene bottles for further use.

Preparation of Ni(II) solution: Various concentrations (30 to 180 mg/L) of Ni(II) working solutions were prepared by diluting correct amounts of 1000 mg/L of $Ni(NO_3)_2$ stock solution using ultrapure water. Then the solutions were adjusted to pH 6 using 1.0 M NaOH and/or 0.1 M HCl solutions without any further adjustment during the adsorption process.

Adsorption study: A mixture consists of 100 mL of 30 mg/L Ni(II) solution and 2 g of RH-650 in a 250 mL Erlenmeyer flask. The flask was agitated at a constant agitation speed of 150 rpm at 30 °C for 180 min in a temperature controlled incubator shaker. The mixture was filtered using a cellulose nitrate membrane filter with a pore size of 0.45 µm. The supernatant liquid was analyzed for residual concentration of Ni(II) ions using an inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer, OPTIMA 5300 DV). Similar experiments were conducted using 60, 90, 120, 150 and 180 mg/L of Ni(II) mg/L working of solutions. All the experiments were performed in duplicates. In order to evaluate the performance of the adsorption, the amount of adsorbed Ni(II) ions per unit mass was calculated using eqn. 1:

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

where q_e is the amount of Ni(II) ions adsorbed on the adsorbent (mg/g), C_o and C_e are initial and equilibrium concentrations of Ni(II) ions solutions, respectively. V is the volume of heavy metal solution and m is the mass of adsorbent (g) used.

RESULTS AND DISCUSSION

Adsorption isotherm studies: Adsorption isotherm models are applied to determine the interaction between adsorbent and sorbate. There are several isotherms used to explain the adsorption equilibrium data, but Langmuir and Freundlich isotherm models were widely applied to determine the best isotherm model in experiments [10]. Thus, Langmuir and Freundlich isotherm models were used to evaluate the adsorption equilibrium data of this study. The coefficients of determination (R^2) of the models were compared and used to determine the best fitted isotherm model.

Langmuir isotherm model: Langmuir adsorption isotherm is widely used to describe the adsorption of organic and inorganic pollutants, such as dyes and heavy metals from aqueous solutions. Langmuir isotherm model suggests that the adsorption onto the adsorbent surface is homogeneous, which means the adsorption of solute from aqueous solution onto the adsorbent surface occur as monolayer adsorption on the homogeneous number of exchanging sites [11]. Langmuir adsorption isotherm was expressed by Langmuir [12]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the amount of metals adsorbed on the adsorbent (mg/g) at equilibrium, C_e is the concentration of metal solution at equilibrium, q_{max} is the maximum adsorption capacity describing a complete monolayer adsorption (mg/g) and b is adsorption equilibrium constant (L/mg) that is related to the free energy of adsorption. q_{max} and b were determined from the linear plot of C_e/q_e *versus* C_e. Fig. 1 shows the Langmuir plot for adsorption of Ni(II). The values of q_{max}, b and R^2 are shown in Table-1. Equilibrium parameter, R_L is a dimensionless constant separation factor to express the essential features and characteristics of Langmuir isotherm [13,14]. R_L can be defined as:

$$R_L = \frac{1}{1 + bC_o} \tag{3}$$

where b is sorption equilibrium constant (L/mg) that is related to the free energy of sorption and C_o is initial concentration of Ni(II) ions (mg/L). The value of R_L shows the sorption either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$, or irreversible if $R_L = 0$. The R_L values for the sorption of Ni(II) ions onto thermally treated rice husk using the lowest initial concentration (30 mg/L) and the highest initial concentration (180 mg/L) were 0.087 and 0.016, respectively. Thus, the adsorption of Ni(II) ions using thermally treated rice husk is a favourable process.

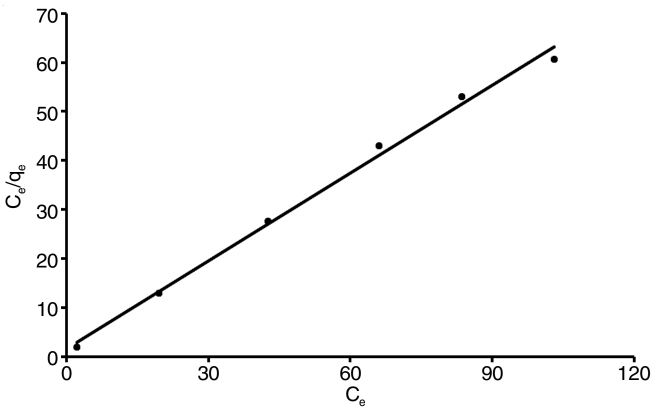

Fig. 1. Langmuir plot for adsorption of Ni(II) ions

TABLE-1
LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM CONSTANTS FOR Ni(II) IONS

Langmuir constants		Freundlich constants	
q_{max} (mg/g)	1.68	K_f ((mg/g)/(mg/L)$^{1/n}$)	0.271
b (L/mg)	0.349	n	2.188
R^2	0.9947	R^2	0.9657

Freundlich isotherm model: Freundlich isotherm model assumed that the adsorption process occur from the interaction of the pollutant molecules on the heterogeneous surfaces. When the occupied binding sites increased, the energy of adsorption declined logarithmically [11]. Freundlich isotherm model was used to evaluate the experimental data and is expressed by the following equation [15]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

where K_f is the Freundlich isotherm constant (mg/g) related to the bonding energy. The constants K_f and n were calculated using Freundlich plot as shown in Fig. 2. The values of K_f, n and R^2 are presented in Table-1. The value of n between 1 and 10 (1/n less than 1) indicates favourable adsorption [14]. From Table-1, the value of n for adsorption of Ni(II) is 2.188, indicating that the adsorption of Ni(II) is favourable.

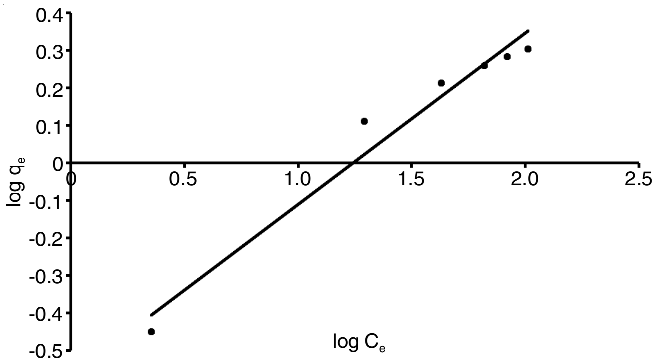

Fig. 2. Freundlich plot for adsorption of Ni(II) ions

From Table-1, the experimental data showed that the adsorption of Ni(II) on thermally treated rice husk was better fitted to Langmuir isotherm model (R^2 = 0.9947) compared to Freundlich isotherm model (R^2 = 0.9657). Zafar *et al.* [16] found that the adsorption behaviour of Ni(II) onto rice bran was well described by Langmuir isotherm model.

Conclusion

Thermally treated rice husk was found to be a suitable adsorbent for the removal of nickel(II) ions from aqueous solutions. The sorption data were evaluated with Langmuir and Freundlich adsorption models. The adsorption processes could be described well by Langmuir isotherm model as indicated with high coefficient of determination (R^2 = 0.9947). The adsorption capacity of the thermally treated rice husk was found to be 1.68 mg/g. It can be concluded that nickel(II) ions are considerably adsorbed on thermally treated rice husk and could be used a low cost adsorbent for removal of nickel(II) ions from aqueous solutions.

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