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Kinetics Study of Nickel (II) Ions Sorption by Thermally Treated Rice Husk

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ABSTRACT

The utilization of agricultural wastes, in the original or modified form, as heavy metal ion sorbents has been widely investigated. In this paper, we report the results of our study on kinetics of Ni(II) ion sorption by thermally treated rice husk. The sorbent was prepared by heating the rice husk at 650°C for two hours. For the kinetic study, the solute sorbent contact periods were varied between 30 to 180 minutes, whereas, the other parameters (pH, initial concentration, temperature and adsorbent dosage) were kept constant. The results revealed that the sorption capacity increased with the increase of contact period. The sorption data were evaluated using pseudo-first order, pseudo-second order and intraparticle diffusion models. The rate constants of sorption and diffusion were also determined. The data were best fitted with pseudo-second order kinetics model sorption which indicates that the sorption of Ni(II) ion by this thermally treated rice husk is via chemisorption process.

INTRODUCTION

Heavy metals are vital for plants, animals and human beings, but excessive amounts of them in the environment are harmful. Nickel is one of the heavy metals, which is commonly found in wastewaters (Ngah & Hanafiah 2008) and a toxic and hazardous element (Raju & Naidu 2013). Consumption of drinking water with high concentration of nickel damages our lungs and kidneys, and causes gastrointestinal distress (Garg et al. 2008). Frequent exposure to coins and jewellries that contain nickel may create skin problems (Bansal et al. 2009). In addition, high concentrations of nickel in the environment damages living organisms in the system (Patil et al. 2012). World Health Organization (WHO) and United States Environmental Protection Agency (EPA) recommends that the concentration of nickel in drinking water should not exceed 0.1 mg/L (Patil & Shrivastava 2010, Malkoc & Nuhoglu 2005).

Rice husk, either in the original or modified form, has been studied for heavy metal removal from aqueous solutions. It can be modified by phosphoric acid (Dada et al. 2013) or various bases (Mas Haris et al. 2011), and normally the modified rice husks show higher heavy metal adsorption performance than that of the unmodified ones (Chuah et al. 2005).

In this paper, we describe the results of our study on kinetics of nickel ion sorption by thermally treated rice husk. Kinetic analysis gives information about the sorbent capacity, rate of solute uptake and sorption mechanism which are important for designing the nickel ion removal technique by this sorbent. Adsorption kinetic studies of Ni(II) ion by protonated rice bran (Zafar et al. 2007), boiled rice husk (Bansal et al. 2009), and cashew nut shell (Kumar et al. 2011) have been studied. These studies showed that the adsorption of Ni(II) ion by these sorbents is pseudo-second order adsorption. Our literature search also apparently indicates that this is the first report on a kinetic study of nickel ion sorption by thermally treated rice husk.

MATERIALS AND METHODS

The obtained rice husk was ground and washed with ultra pure water several times until constant pH was obtained. The washed rice husk was then dried in an oven at 105°C for

24 h. The dried rice husk was sieved to obtain particle size between 300 and 600 μm and labelled as raw rice husk (RRH). RRH was heated in a furnace (WiseTherm Programmable Digital PID Control) at 650°C for two hours, and then cooled in a desiccator before been stored in polyethylene bottles. The thermally treated rice husk was labelled as RH-650.

A 120 mg/L of nickel nitrate solution was prepared by diluting 1000 mg/L of nickel nitrate standard solution using ultra pure water. The pH of nickel solution was adjusted to pH 6 (pH meter Eutech Instruments) using 1.0 M NaOH and/or 0.1 M HCl. Adsorption studies were carried out by mixing 100 mL of 120 mg/L of nickel solution with 2 g of RH-650. The mixture was agitated in a conical flask at 150 rpm for 30 minutes at 30°C. The mixture was filtered using a 0.45 μm cellulose nitrate membrane filter and the solution was then analysed using an inductively coupled plasma optical emission spectrometry (ICP-OES)(Perkin Elmer, OPTIMA 5300 DV). The experiments were also performed at contact periods of 60, 90, 120, 150 and 180 minutes. All experiments in this study were duplicated. The amount of adsorbed Ni(II) ions per unit mass was calculated using Equation 1 to determine the adsorption capacity of the adsorbent.

$$q_t(mg/g) = \frac{C_o - C_e}{m} \times V \qquad ...(1)$$

Where, q_t is the amount of Ni(II) ions adsorbed on the adsorbent (mg/g), *Co* and *Ce* are initial and equilibrium concentrations of Ni(II) ion solutions, respectively, *V* is the volume of solution (L), and *m* is the mass of adsorbent (g) used.

RESULTS AND DISCUSSION

The relationship between sorption rate and sorption time is investigated through sorption kinetic studies (Zafar et al. 2007). The experimental data were evaluated with kinetic models, namely, pseudo-first order, pseudo-second order and intraparticle diffusion models in order to investigate the adsorption kinetics of Ni(II) onto thermally treated rice husk. The conformity between experimental data and the model predicted values was evaluated by the correlation coefficient (r^2). The best fitted model is indicated by the highest r^2 value.

Pseudo-first order model: Lagergren's first order kinetic model is based on the assumption that the sorption process is controlled by diffusion step and the sorption rate is proportional to the difference between equilibrium sorption capacity and adsorbed quantity at time *t* (Ding et al. 2012). Pseudo-first order model is presented in Equation 2, where the rate expression is based on solid capacity:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad ...(2)$$

Where, q_e and q_t are amount adsorbed per gram of adsorbent at equilibrium and time *t* (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first order adsorption (min^{-1}). The values of k_1 and q_e can be determined from the plot log (q_e-q_t) versus *t*. Fig. 1 shows pseudo-first order plot for adsorption of Ni(II). The values of k_1, q_e calculated, q_e experimental and r^2 are presented in Table 1.

Pseudo-second order model: Pseudo-second order kinetic model is also based on the assumption that the sorption rate is controlled by a chemical sorption mechanism involving electron sharing or electron transfer between adsorbent and adsorbate (Ho & McKay 1999). Pseudo-second order model equation is defined as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad ...(3)$$

Where, q_e and q_t are amount adsorbed per g of adsorbent at equilibrium and time *t* (mg g^{-1}), respectively, and k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}). The values of k_2 and q_e can be determined from the plot t/q_t versus *t*. The plot of pseudo-second order model for adsorption of Ni(II) is shown in Fig. 2 and the values of k_2, q_e calculated, q_e experimental and the values of r^2 are presented in Table 1.

Intraparticle diffusion model: Apart from pseudo-first order and pseudo-second order models, some diffusion processes controlled by multiple diffusion mechanism can be presented by intraparticle diffusion model which describes the dynamic diffusion process in particles (Ding et al. 2012) and it is expressed as follows:

$$q_t = k_{id} t^{1/2} + C \qquad ...(4)$$

Where, q_t is the amount adsorbed per g of adsorbent at time

Table 1: Kinetic constant and coefficients of determination for adsorption of Ni(II).

Kinetic model	Parameters
Pseudo-first order model	$q_{e\ exp}$ = 1.5215 mg g^{-1} k_1 = 0.02303 min^{-1} $q_{e\ cal}$ = 1.1981 mg/g r^2 = 0.9622
Pseudo-second order model	$q_{e\ exp}$ = 1.5215 mg g^{-1} k_2 = 0.0209 g mg^{-1} min^{-1} $q_{e\ cal}$ = 1.7762 mg/g r^2 = 0.9977
Intraparticle diffusion model	k_{id} = 0.0718 mg g^{-1} $min^{-0.5}$ C = 0.6299 r^2 = 0.9753

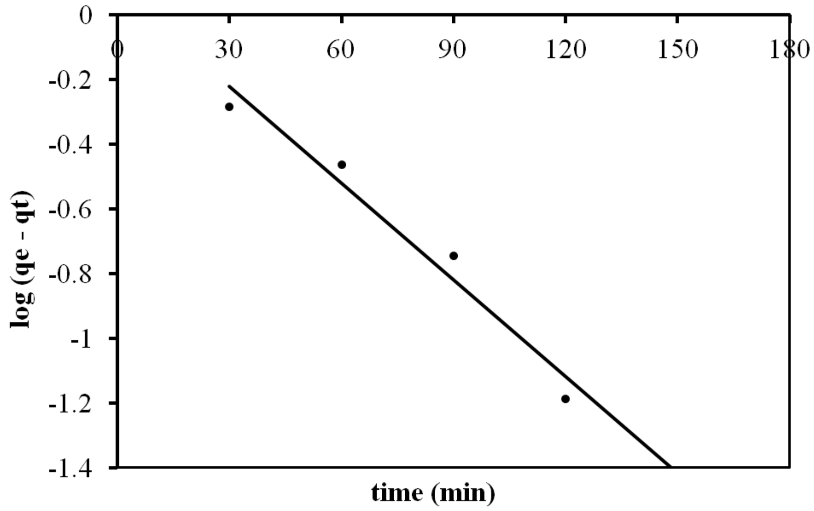

Fig. 1: Pseudo-first order model for Ni(II) adsorption [initial concentration of Ni(II) = 120 mg/L; adsorbent dosage = 2 g; initial pH = 6, time = 30-180 mins].

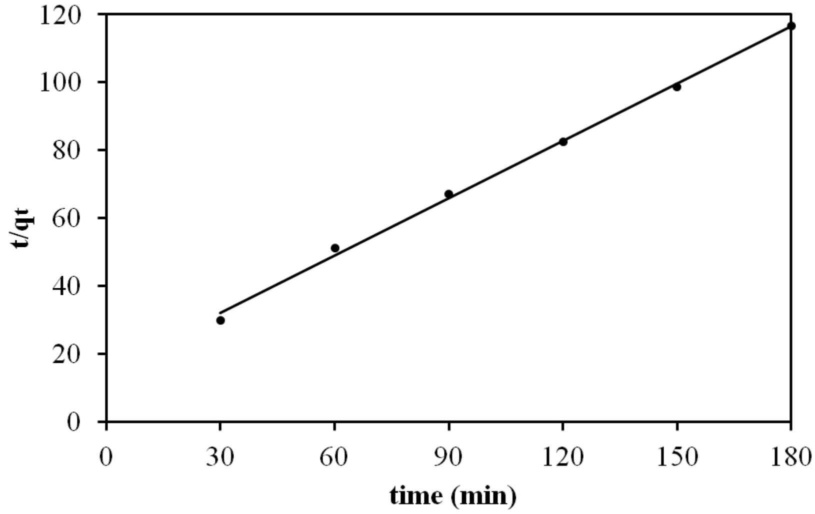

Fig. 2: Pseudo-second order model for Ni(II) adsorption [initial concentration of Ni(II) = 120 mg/L; adsorbent dosage = 2 g; initial pH = 6, time = 30-180 mins].

t (mg g^{-1}), k_{id} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and C is the intercept. The value of rate constant k_{id} can be directly evaluated from the slope of q_t versus $t^{1/2}$ plot. The plot of q_t versus $t^{1/2}$ is shown in Fig. 3, while all the constants are presented in Table 1.

Table 1 presents the kinetic constants and correlation coefficients for adsorption of Ni(II) ions. From the table, it is clearly indicated that the highest correlation coefficient (r^2) was recorded for pseudo-second order model with the value of 0.9977, followed by intraparticle diffusion model with r^2 of 0.9753 and pseudo-first order model with r^2 of 0.9622. Hence, pseudo-second order model was found to be the best fitted model, as the application of pseudo-second-order model provides best correlation of the experimental data. In addition, the value of q_e calculated for pseudo-second order model was 1.7762 mg/g which was close to 1.5215 mg/g, the value of q_e experimental. Therefore, the results revealed that the adsorption of Ni(II) ions onto thermally treated rice husk was best described by pseudo-second order model which was based on the assumption that the rate limiting step may be chemisorption through sharing or exchange of electron between sorbent and sorbate. Similar finding was reported by Bansal et al. (2009) where the removal of nickel ions from aqueous solution was using boiled rice husk.

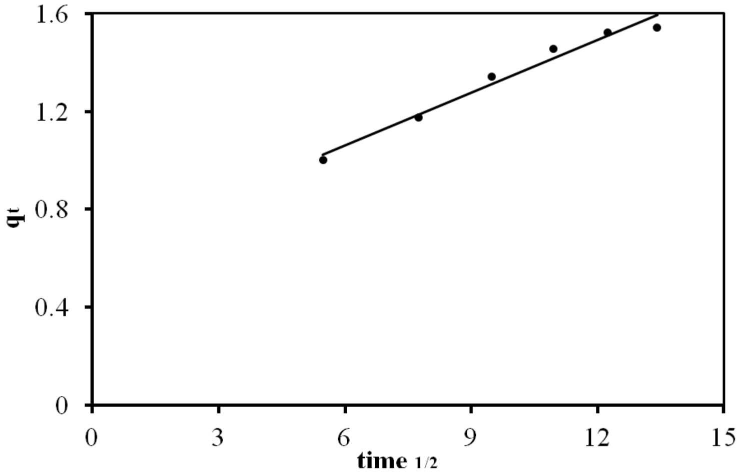

Fig. 3: Intraparticle diffusion model for Ni(II) adsorption [initial concentration of Ni(II) = 120 mg/L; adsorbent dosage = 2 g; initial pH = 6, time = 30-180 mins].

CONCLUSION

Thermally treated rice husk can be used as a sorbent for Ni(II) ions from aqueous solution. The sorption is best described by pseudo-second order kinetics model (where $r^2 = 0.9977$) indicating the sorption occurs via chemisorption.

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