

REMOVAL OF IRON FROM AQUEOUS SOLUTION BY RICE HUSK: ISOTHERM AND KINETIC STUDY

Studi Isothermal Dan Kinetika:

Penyisihan Logam Besi Dalam Larutan Menggunakan Sekam Padi

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ABSTRACT

This work was focused on iron adsorption by rice husk. The use of rice husk for the removal of iron from aqueous solution at different contact time, pH, adsorbent doses and initial iron concentration was investigated. This study was also aimed to recognize the mechanisms that govern iron removal, and to find an appropriate isotherm and kinetic model in batch process. The equilibrium adsorption isotherms have been analyzed by Freundlich and Langmuir model. The pseudo-first, and pseudo-second order kinetic models have been used to investigate the mechanism of adsorption and potential rate controlling steps. The equilibrium data fitted well to Freundlich model and mechanism of adsorption described well to pseudo first order kinetic. The iron adsorption process was highly dependent on pH, dosage and initial concentration dependent. Iron was reduced higher with decrease in iron concentration and increase in rice husk dosage. The suitable contact time for iron removal was found to be 180 minutes.

Keyword: adsorption, iron, rice husk, isotherm, kinetic

ABSTRAK

Fokus penelitian ini adalah adsorpsi besi dengan menggunakan adsorban sekam padi. Eksperimen dilakukan dengan memvariasikan waktu kontak, nilai pH, dosis adsorban dan konsentrasi awal besi. Penelitian bertujuan untuk mengamati mekanisme yang mempengaruhi penyisihan besi dan menemukan model isothermal dan kinetika yang tepat untuk proses adsorpsi besi. Kesetimbangan model isothermal dianalisis dengan model Freundlich dan Langmuir. Model kinetika order pertama dan kedua digunakan untuk mengamati mekanisme adsorpsi dan tahap kontrol kecepatan potensial. Hasil penelitian menunjukkan bahwa model adsorpsi yang tepat untuk penyisihan besi adalah model Freundlich dan mekanisme adsorpsi yang sesuai adalah kinetika orde pertama. Proses adsorpsi besi sangat dipengaruhi oleh pH, dosis adsorban dan konsentrasi awal besi. Persentase penyisihan besi meningkat jika konsentrasi awal besi menurun dan dosis adsorban meningkat. Hasil penelitian menunjukkan bahwa adsorpsi besi terjadi dengan baik pada waktu kontak sekurang-kurangnya 180 menit.

Kata kunci: adsorpsi, besi, sekam padi, isothermal, kinetika

INTRODUCTION

Heavy metal contained in wastewater is a cause of toxic metal contamination of surface, sea and groundwater resources. Iron, is one of heavy metal discharged from industries, tends to accumulate in living organisms, thus becoming a permanent source of hazard to their health and life, and degradation of the environment. Iron has undesirable effects, even if they are present in trace quantities (Alloway & Ayres, 1993; Klimmek et al., 2001 *cit.* Feng et al., 2004). Various treatment to reduce heavy metal including chemical precipitation as metal hydroxide (Berbenni et al., 2000), electrocoagulation (Bazrafshan, et al., 2006), reverse osmosis, ion exchange, membrane separation and adsorption have been applied (Kurniawan et al., 2006). However, Adsorption is by far most adaptable and effective method to reduce any contaminants like heavy metal, especially, if adhered with suitable regeneration steps.

Adsorption is a process in which a single or a group of ions/compounds get accumulated on the surface of another solid or liquid. Its process involves a mass transfer operation through which constituents in the liquid phase are transferred to the solid phase (Metcalf & Eddy, 2003; Kumar et.al, 2004). The substance on which the adsorption occurs is known as adsorbent and the substance which gets adsorbed or accumulated is called adsorbate. Many adsorbents have been tested for the adsorption of iron. Previous research has reviewed the potential use of adsorbents for the removal of iron from aqueous solutions such as clinoptilolite (Oztaz et al., 2008), eggshell (Yeddou et al., 2007) and activated carbon (Okoniewska et al., 2007). However, some researchers have been reported that rice husk showed good result for reducing heavy metal (Mahvi et al., 2005; Ajmal et al., 2003; Vadivelan et al., 2005; Akhtar et al., 2006; Kumar et al., 2006)

Rice husk contains various organic compounds (lignin, cellulose, and hemicelluloses) that might be useful for binding heavy metal ions (IRRI, 2010). Furthermore, it is also considered plentiful

product in Southeast Asia, reasonable cost, and reusable byproduct of rice grinding.

The adsorption isotherm was conducted to know the adsorption behavior along with its adsorption characteristics, while the kinetic study was performed to determine the contact time necessary to reach equilibrium concentration of iron in aqueous solution. The study of adsorption kinetics in wastewater treatment is also important as it provides deep understanding of the reaction pathways and the mechanism of adsorption reactions (Ho & McKay, 1999; Lagergren, 1898 *cit.* Sag (2002)).

The objective of the present study is to investigate the removal of iron using rice husk from aqueous solution. Batch experiments are carried out for kinetic studies on the removal of iron from aqueous solutions. The influence of various contributing parameters such as pH, adsorbent concentration, contact time, and initial iron concentration is investigated. Three adsorption isotherm models (Langmuir, Freundlich, and Temkin equation) are used to study the fit of the experimental equilibrium data obtained in the study, and two kinetic models are used to evaluate the mechanism of adsorption.

RESEARCH METHODS

Adsorbent Preparation

Rice husk was collected from a nearby rice mill in Kuala Selangor, Malaysia. To remove all the dirt particles and impurities, rice husk was washed several times with tap water followed by distilled water. The washed rice husk was then dried at 100°C in an oven until constant weight. Then, it was ground to particle size $\leq 600 \mu\text{m}$. The prepared rice husk adsorbent was kept in air tight container at room temperature. It was called rice husk (RH).

Batch Adsorption Studies

Amount of 4.964 g ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was dissolved in 1000 mL of distilled water, to prepare stock solution of iron. Certain concentrations of the iron were obtained by further dilutions. The pH

of each last solution was adjusted to the required value with diluted and concentrated H₂SO₄ and NaOH solution. All the chemicals used were analytical reagent grade.

Experiment was carried out in batch process and room temperature. An adjusted pH of 100 mL of iron aqueous solution in Erlenmeyer flasks was filled with certain raw rice husk. The flasks were agitated in an orbital shaker at 160 rpm. Samples were collected at the designed contact time, filtered and analyzed by the Inductively Coupled Plasma Optima Emission Spectrometer (ICP-OES). Adsorption isotherm studies were done using five initial iron concentrations (20, 30, 40, 50 and 60 mg/L), with 2 g/100mL adsorbent dosage at pH 7 and room temperature. The sample was collected after 4 hours agitation and filtered. To get kinetic model, those three initial concentrations of iron were 20, 40 and 60 mg/L and with 2 g/100 mL adsorbent at pH 7 was applied, sample was taken every 30 minutes for 4 hours operation. All the experiments were conducted in duplicates and their mean values of iron removal percentage (eq. (1)) are reported here.

$$Y = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

Here, Y = iron removal percentage, C_i = initial concentration (mg/l), C_f = final concentration (mg/l).

RESULTS AND DISCUSSIONS

Effect of pH

Five pH values for separate experiments of 40 mg/L iron concentration to 1 g adsorbent dosage and 150 minutes contact time were performed to examine the effect of pH and to ensure the most suitable pH value. The pH parameter has been identified as one of the most important parameter that is effective on metal adsorption (Mahvi et al., 2005; Ajmal et al., 2003; Akhtar et al., 2006; Kasman & Ibrahim, 2010). It is directly related with competition ability of hydrogen ions with iron ions to active sites on adsorbent

surface. The effect of pH on the adsorption of iron onto RH showed in Figure 1 which notices that the removal of iron on RH became higher as the pH value increased. The removal became constant at pH value between 7 and 9 or in neutral or alkali solution.

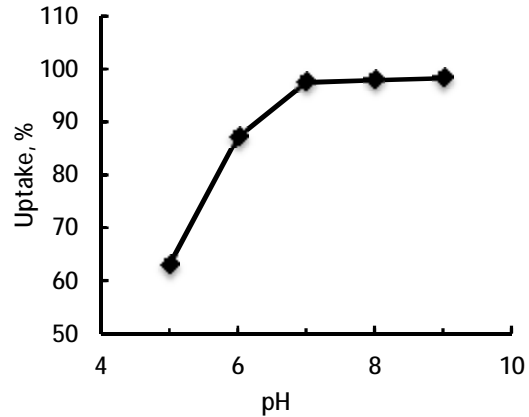


Figure 1: Effect of pH on removal of iron

Effect of adsorbent dosage

Five adsorbent dosages were varied in this experiment combined with pH value of 7, contact time of 150 minute, certain iron initial concentration.

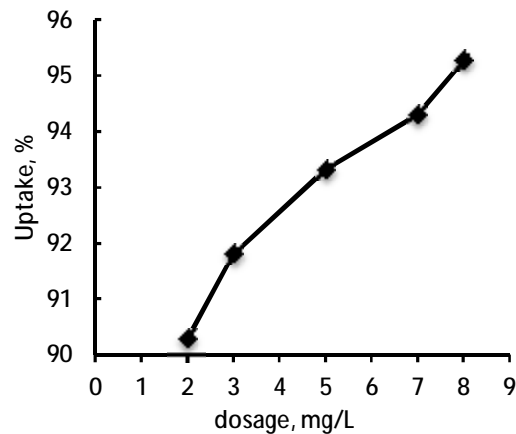


Figure 2: Effect of adsorbent dosage on removal of iron

The removal of iron using RH increased as the adsorbent dosage increased. Similar result was also reported by Ajmal et al (2003), Mahvi et al (2005),

Akhtar et al (2006), and Kasman & Ibrahim (2010). However, value of suitable dosage was still not found in this study. As shown by trend of curve in Figure 2 which it becomes higher as dosage bigger. To achieve better results, continues research is recommended.

Effect of initial concentration

Three initial iron concentrations were 20, 40 and 60 mg/L treated with 7,5 g of adsorbent dosage, and 150 minutes of contact time for iron adsorption. Figure 3 reveals that adsorption process for iron was better in lower initial concentration. Yeddou (2007) found that the increase of initial iron concentration, adsorption capacity increased directly.

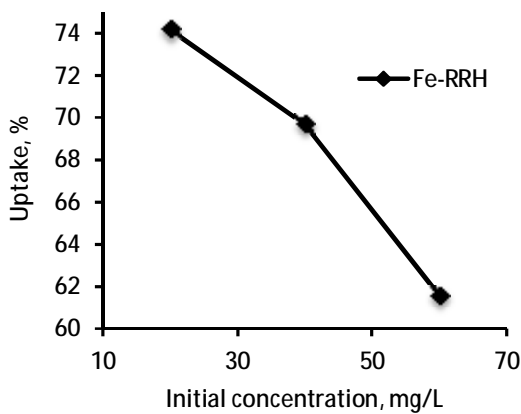


Figure 3: Effect of initial concentration on removal of iron

Effect of contact time

The rate of adsorption is important to design batch experiment. Thus, the effect of contact time on iron adsorption was investigated. The experiment was done for 240 minutes (4 hours) and sample was collected after 60 minutes, 120 minutes, 150 minutes, 180 minutes and 240 minutes processes. The removal of iron was decreased the contact time increased but become constant after 180 minutes. For further experiment, 60 minutes is considerably suitable for iron adsorption process as reported previous report for

similar result in reducing heavy metal using different kind of adsorbents (Ajmal et al., 2003).

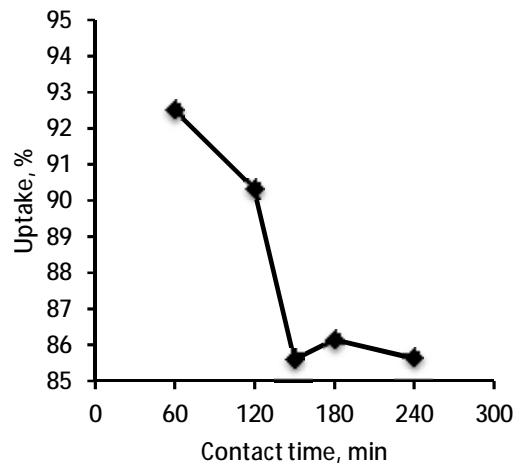


Figure 4: Effect of contact time on removal of iron

Isotherm and kinetics study for iron adsorption

Isotherm of adsorption provides description of adsorbent capacity used, is RH. It expresses the surface properties and affinity of RH. In this study, the adsorption isotherms were investigated using two equilibrium models, which are namely the Langmuir and Freundlich models. Freundlich and Langmuir isotherm expression is given by the following equations (Freundlich et al., 1906; Langmuir et al., 1916 quoted by Yeddou et al., 2007):

Freundlich:

$$q_e = K_f \cdot C_e^{1/n} \tag{2}$$

Where K_f and n are the Freundlich constants characteristic of the system. Equation (2) can be linearized in a logarithmic form and the Freundlich constants can be determined.

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{3}$$

Langmuir:

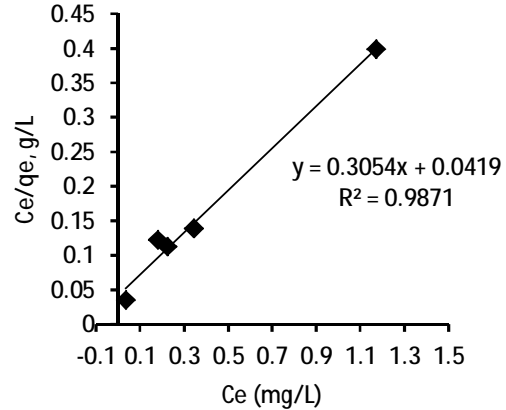
$$q_e = q_o \frac{b C_e}{1+b C_e} \tag{4}$$

Where q_e is the equilibrium iron concentration on the adsorbent (mg/g), C_e is the equilibrium iron concentration in the solution (mg/L), q_o is the monolayer sorption capacity of the sorbent (mg/g), and K_L is the Langmuir sorption constant (L/mg) related with the free energy of sorption.

Table 1. Freundlich and Langmuir constants

Freundlich		
Adsorption capacity, K_f	mg/g	2.999
Typical adsorption, $1/n$		0.325
Intensity of adsorption, n		3.077
Correlation, R^2		0.923
Langmuir		
Adsorption capacity, q_o	mg/g	1.25
Equilibrium adsorption constant, b		0.432
Langmuir constant, R_L		2.315
Correlation, R^2		0.83

These two models have been successfully applied to the iron adsorption processes. The results are showed in Table 1 along with their figures in Figure 5. The values of Langmuir constants R_L and b were obtained from the intercept and slope of the plot between (C_e/q_e) vs. $(1/C_e)$ presented in Figure 5(b).



(b)

Figure 5: Freundlich (a) and Langmuir (b) isotherm model

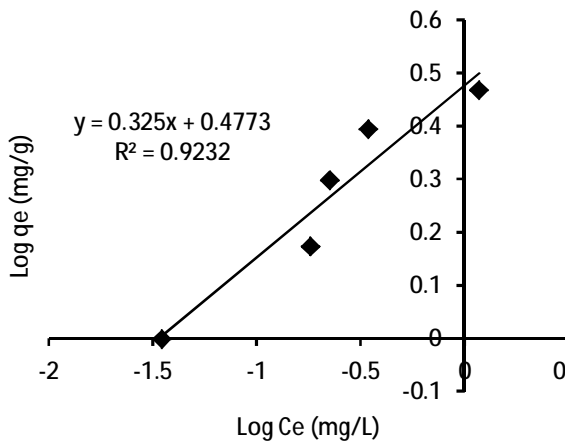
The obtained value of $1/n$ in Freundlich model for RH in iron adsorption are less than 1, while Langmuir model are $0 < R_L < 1$. It indicates that the adsorption process is favorable. The kinetic adsorption results showed in this discussion is only the pseudo second order kinetic since this order is stronger than the pseudo first order kinetic. The values of kinetic parameters are presented in Table 2.

In order to analyze the adsorption kinetic of iron, the pseudo first order and pseudo second order were applied to data. Pseudo first order equation is expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption (min^{-1}). After integration and applying boundary conditions from $t = 0$ to $t = t$ and $q_e = 0$ to $q_t = q_t$, the integrated form of equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$



(a)

The pseudo-second order equation of the adsorption rate is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_o - q_e)^2 \quad (7)$$

Here q_e and q_t are the sorption capacity at equilibrium and at time t , respectively and k_2 is the rate constant of pseudo-second order sorption (min^{-1}). After integrating and applying boundary conditions from $t = 0$ to $t = t$ and $q_o = 0$ to $q_e = q_e$, the integrated form of equation becomes:

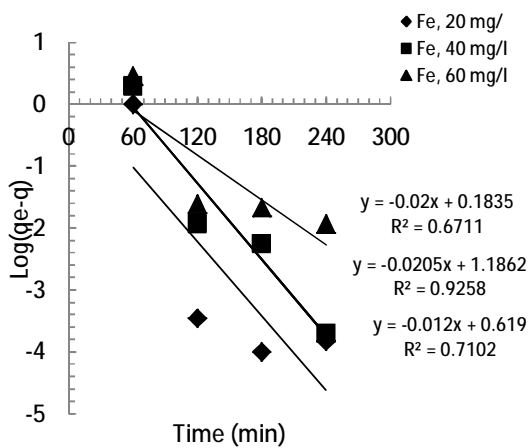
$$\frac{t}{q_e} = \frac{1}{k_2 q_o^2} + \frac{1}{q_o} t \quad (8)$$

For kinetic, Figure 6 (a dan b) depicts the plot of adsorption capacity at equilibrium time versus contact time for iron desorption using RH. Moreover, values of the pseudo-first order and pseudo second order rate constant (K) and the adsorption capacity (q_e) computed from the slope and intercept as well as the correlation values from iron are presented in Table 2. It was observed that the correlation values of iron was close to 1 which confirms that the adsorption process follows a pseudo-second-order mechanism.

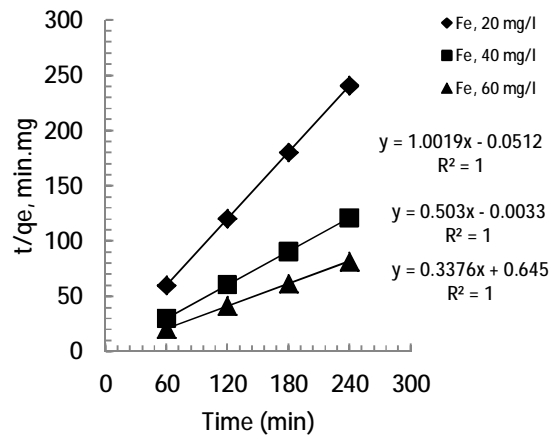
Overall, it can be seen that the values of K and q_e increased with increase in initial concentration as similar reported by Vadivelan & Kumar (2005).

Table 2: Kinetic parameters for the iron adsorption using RH

Initial Fe(II) mg/L	Pseudo 1st order			Pseudo 2nd order		
	K_1 g/min.mg	q_e mg/g	R^2	K g/min.mg	q_e mg/g	R^2
20	0.0184	1.112	0.643	19.336	0.993	1
40	0.0230	1.884	0.576	1317.5	1.988	1
60	0.0392	2.655	0.566	13.652	2.967	1



(a)



(b)

Figure 6: Pseudo first order (a) and pseudo second order (b) kinetic for iron adsorption by RH

CONCLUSIONS

Adsorption studies of iron removal by rice husk from aqueous solution have been carried out varying pH, adsorbent dosage, initial concentration and contact time. The study noticed that rice husk can reduce iron in range of obtained results may be summarized as follows:

- (1) The pH variation studies figured out that the iron adsorption process is highly pH dependent. The optimum pH range for the removal was recommended to be neutral (7–9).
- (2) Increase in adsorbent dosage leads to increase in iron adsorption due to increased number of adsorption sites. Maximum uptake of iron was obtained at adsorbent dosage of 8 mg/L. But, further experiment is needed to attain adsorption equilibrium process.
- (3) The amount of iron was removed lower with increase in initial iron concentration. Similar condition was found in effect of contact time to iron adsorption. Iron was adsorbed lower as the increase of contact time but become constant after 180 minutes which indicates equilibrium phase achieved.
- (4) Equilibrium data fitted very well in a Freundlich isotherm equation, confirming adsorption capacity of iron onto rice husk with adsorption capacity of 2.999 mg/g.
- (5) The rate kinetics for adsorption of iron was best described by pseudo second order model.

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