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Utilization of Low-cost Bio-adsorbent (modified sawdust) for Removal of Iron from Aqueous Solution

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Abstract

Sawdust, a locally available waste material, was used to prepare adsorbent through simple modification for the removal of total iron from aqueous solution. A simple modification of mahogany (Swietenia macrophylla) sawdust was carried out by means of formaldehyde treatment. Batch equilibrium experiments were carried out to find effects of pH, adsorbent dose, time, and temperature and thus an overall scenario of iron adsorption on sawdust was comprehended. Moreover, thermodynamic parameter such as activation energy was also studied. An optimum adsorption dose was found to be 10 g/l for adsorption purpose whereas 480 min was found to be favorable for a complete adsorption to occur at room temperature. The sorption capacity of sawdust for removal of iron was found to be 7.85 mg/g while the Langmuir isotherm model was best fitted. The extent of activation energy (21.49 kJ·mol^{-1}) implied that the reaction was of chemisorption type.

Keywords: Adsorption, Sawdust, Kinetics, Sorption capacity, Aqueous solution.

1. Introduction

With increased industrialization, various industries i.e. electrical and electronic industries, mineral processing plants, rerolling mills, chemical industries and electroplating factories are being set up with a great pace. Wastewater effluents from those industries are associated with different types of heavy metals (e.g. iron, nickel, chromium, lead, cadmium, zinc, copper, arsenic and so forth) depending on the nature of the industry. Heavy metals are generally toxic pollutants and are continuously released into the aqueous system and thus polluting both surface water as well as groundwater. A large number of aquatic plants and crops take up these heavy metals and accumulate within them. Therefore, when human consumes food and water with iron concentration exceeding the permissible limits then various kinds of diseases occur. Although iron is an essential nutrient, its excessive intake causes haemochromatosis to human body [1]. Permissible limit of iron intake in Bangladesh is 0.3 – 1.0 mg/l, whereas the standard set by the World Health Organization (WHO) is 0.3 mg/l [2]. So it is really essential to remove iron from aqueous solution for the sake of the mankind.

There are many methods reported for the removal of iron and other metal ions from solution, which include but not limited to coagulation-precipitation, solvent extraction, membrane process, ion exchange and electrochemical techniques [3, 4]. However, almost all of those methods have some drawbacks such as high operating cost or complicated operating procedures. Although coagulation-precipitation has been widely used because of its simplicity, this process produces huge amount of sludge, which creates problem for safe disposal. Anion exchange processes are also commonly used but they have low selectivity in presence of other competing ions [5, 6].

Adsorption process, on the other hand, has shown advantages such as it is quite selective and effective. Moreover, this process is able to remove different levels of soluble heavy metals from solution. Since adsorptive removal with commercial resins is expensive hence low-cost, locally available biowaste materials are needed to address the problem. Considering this, adsorption of heavy metals using biowaste materials has been emerged as a very good alternative. Several bioadsorbents such as rice husk [1], sawdust [7, 8], orange waste [9], waste paper [10], wheat straw and barley straw [11] etc. have been used for uptaking heavy metal ions from aqueous solutions. Although a number of biological materials have been used for several heavy metal adsorptions, only a limited number of studies have been conducted on removal of iron using sawdust [7]. In this study, sawdust was used to adsorb iron from aqueous solution through conducting numerous sets of batch experiments where various parameters were tested.

2. Materials and methods

2.1. Adsorbent preparation

Mahogany (*Swietenia macrophylla*) sawdust was collected from sawmill of Jashore town, Bangladesh. The sawdust was first cleaned with distilled water to eliminate dust and other unwanted particles. It was then dried in a dryer at 70°C until all the moisture had completely evaporated. The sawdust was ground to a fine powder using mortar and pestle. The resulting material was sieved to obtain the smallest particle size. The ground powder was treated with 2% formaldehyde at a ratio of 1:4 (sawdust: formaldehyde, w/v) to immobilize the water-soluble and color substances at room temperature by shaking for three hours. After that, the sawdust was filtered and washed with distilled water to eliminate free formaldehyde, and dried in a dryer (HDG-9030, Korea) at 70°C for 24 hours. Thus the prepared adsorbent was stored in airtight vessel for further use.

2.2. Chemicals

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was used to prepare synthetic solution of iron. A stock solution of iron of 500 mg/l was prepared and diluted as necessary. As-received formaldehyde (H-CHO) was used to prepare 2% of its solution. However, solutions of 0.1M HCl and 0.1M NaOH were prepared for pH adjustments during experiment.

2.3. Batch adsorption tests

Batch adsorption tests were carried out by taking 1000 mg of the sawdust in an Erlenmeyer flask in which 100 ml of iron solution was taken at required concentration. The suspension was then shaken at 150 rpm for about 8 h using a hotplate magnetic stirrer (MS300HS, Korea). The suspension was then filtered and the filtrate was analyzed to know its metal ion concentration by using atomic absorption spectrophotometer (AA-700, Shimadzu, Japan). The pH of the solution was adjusted (as required) by adding 0.1M HCl and 0.1M NaOH. The pH was measured by a portable pH meter (EZODO 6011, Taiwan). All experiments were carried out at room temperature unless and otherwise stated. All the experiments were replicated three times and the mean value was used to determine results.

In order to obtain removal percentage and adsorption capacity, the following equations were used:

$$\%R = \{(C_{in} - C_{eq})/C_{in}\} \times 100 \quad (1)$$

$$q_e = \lfloor (C_{in} - C_{eq}) \times V \rfloor / M \quad (2)$$

Where R is the removal (%), q_e is the amount adsorbed at equilibrium (mg/g), C_{eq} is the equilibrium concentration of metal ions (mg/l), C_{in} is the initial concentration of metal ions (mg/l), M is the amount of the sawdust used (g) and V is the volume of the aqueous phase (l).

3. Results and discussion

3.1. Characterization of Adsorbent

3.1.1. Bulk density, moisture content and pH

The bulk density, moisture content and the pH of the adsorbent was determined to be 0.25 mg/cm^3, 0% and 6.19, respectively. The moisture content of raw sample (raw sawdust) was found to be 17.14 %, which indicated that the moisture has been completely removed from the prepared adsorbent. This is certainly very helpful for understanding the actual adsorption capacity and rate constants of the adsorption reaction.

3.1.2. FT-IR Analysis

The FT-IR spectra of the adsorbent (before and after iron adsorption) are shown in Fig. 1(a) and (b). As shown in Fig. 1(a), the adsorption peaks around 3475.27 cm^{-1} indicates the existence of free hydroxyl groups. The peaks around 2923.63 cm^{-1} corresponds to the presence of C-H stretching of alkane functional group. The peaks around 1631.31 – 1737.74 cm^{-1} corresponds to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups. The C=C stretching vibrations between 1546.80 – 1652.88 cm^{-1} indicates alkenes and aromatic functional groups. The peak around 1380 cm^{-1} is indicative of CH_3. A peak at 1379.01 cm^{-1} may be attributed to the aromatic CH and carboxyl-carbonate structures. The peak around 1238.21 cm^{-1}, corresponds to CHOH stretching. The presence of polar groups on the surface provides considerable cation exchange capacity of the adsorbent [12].

As shown in Fig. 1(b), after adsorption of metal ions through sawdust resulted in a change -OCH_3 (400.71 cm^{-1}), aromatic –CH and carboxyl carbonate (1384.42 cm^{-1}), C-H stretching band alkenes (2923.63 cm^{-1}), strong OH stretching indicating strong alcoholic bonds (3427.53 cm^{-1}). These were replaced by the primary functional groups of C=O (1617.33, 1638.06). Based on these observations, it can be stated that the functional groups (-OCH_3, C-H, -OH, -CO) at these wave numbers have participated in iron adsorption.

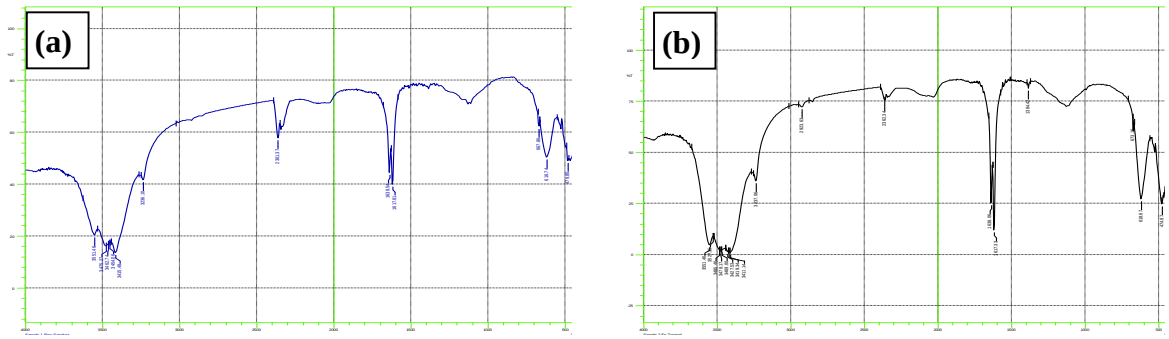

Fig. 1. FT-IR spectrum of adsorbent (a) before and (b) after iron adsorption.

3.2. Effect of pH

The pH is an important parameter for adsorption studies. The effect of pH on the removal of iron from aqueous solution was studied from pH 3 to 7.5. The test result is depicted in Fig. 2. It indicates that iron adsorption is strongly dependent on pH. It is also evident that removal of iron gradually increased from 64% (at pH 3) to 84% (at pH 6.5) and then started to decrease. Relatively less removal percentage of iron at low pH is due to the fact that, there are considerably large numbers of hydrogen ion, which compete with iron ion [13]. On the other hand, at higher pH, precipitation might occur which results lower removal of iron.

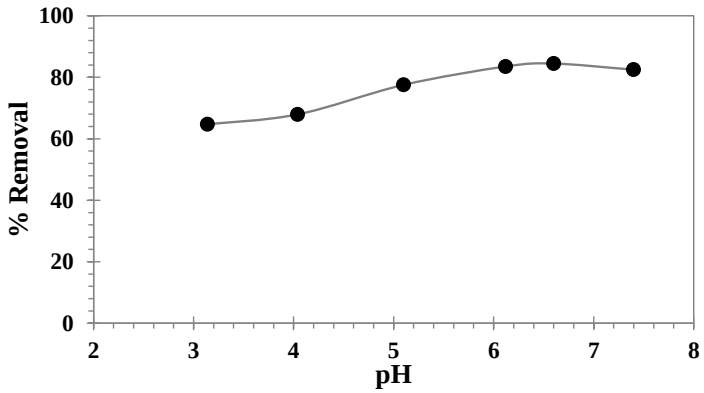

Fig. 2. Effect of pH on the removal of iron by modified sawdust.
(Condition: C_{in} = 10 mg/l, T = 298 K, t = 8 h, dosage 10 g/l)

3.3. Effect of adsorbent dosage

For the sake of determining the optimum amount of adsorbent to be used at the stated conditions, it is necessary to carry out experiments with varying adsorbent dosages. Effect of adsorbent dosages (from 2.5 to 15 g/l) for the adsorption of iron on chemically modified sawdust was studied and presented in Fig. 3. It is found that percent removal of iron gradually increases with the increase in adsorbent dose. At a dose of 10 g/l, the percent removal reaches the maximum. With further increase in dose, the percent removal remains the same. Therefore, a dose of 10 g/l was selected for further adsorption tests. The increase in the percentage of the iron removal with the increase in adsorbent dose is due to the available active sites of the adsorbent with increasing amount of adsorbent (sawdust).

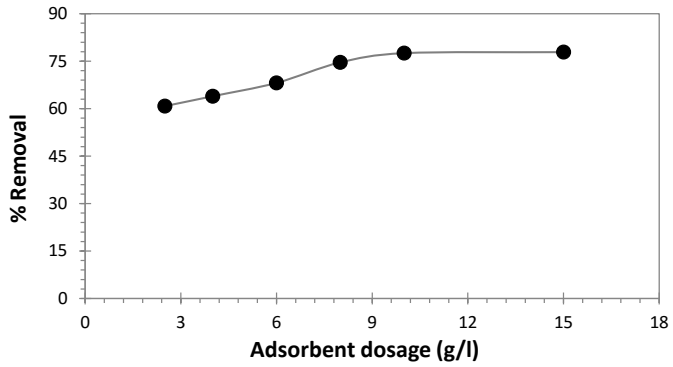

Fig. 3. Effect of the adsorbent dosage on the metal removal efficiencies of modified sawdust.
(Condition: C_{in} = 10 mg/l, pH = 6.5, T = 298 K, t = 8 h)

3.4. Effect of contact time

Adsorption of iron (at a concentration of 10 mg/l) with varying time was conducted keeping all other parameters fixed. As can be seen from Fig. 4, adsorption increases with increasing contact time upto a certain period and then the adsorption remains constant. The adsorption was found to be faster at the initial stage where almost 70% removal was attained in only 30 min. This result is the indicative of adsorption of metal ions at the surface of the adsorbent. Similar result was found and reported by Lim et al., who studied lead ion adsorption onto sawdust [4]. However, after the initial rapid stage, the rate of adsorption became slow. This has happened due to the fact that the free active sites of the adsorbent were filled in or occupied with time and no more adsorbate (iron ion) can attach to the active sites. This phenomenon can be explained by diffusion of metal ions into the pores of sawdust.

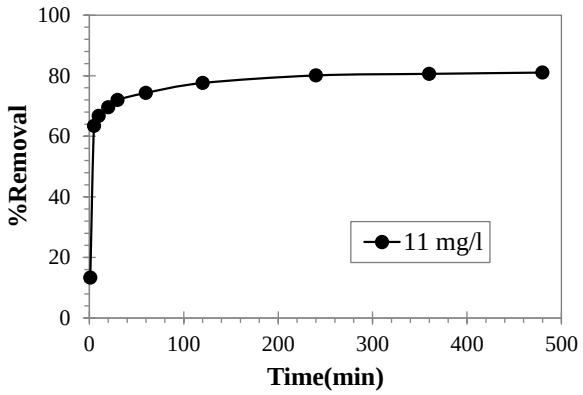

Fig. 4. Effect of contact time on the removal of iron by modified sawdust.
(Condition: C_{in} = 11 mg/l, pH = 6.5, T = 298 K, dosage = 10 g/l)

3.4. Adsorption isotherm

Figure 5 shows the adsorption isotherm from which it is evident that adsorption increases with increasing metal concentration and tends to approach a plateau from where the sorption capacity can be determined. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were tested among which Langmuir was found to the better fitted and is plotted in Fig. 5 (open keys and dotted line). However, the maximum sorption capacity and the binding constant were calculated to be 7.85 mg/g and 19.09 l/g, respectively, at the stated conditions. Since Langmuir model was the best suited model, it is anticipated that a monolayer adsorption was occurred during the sorption.

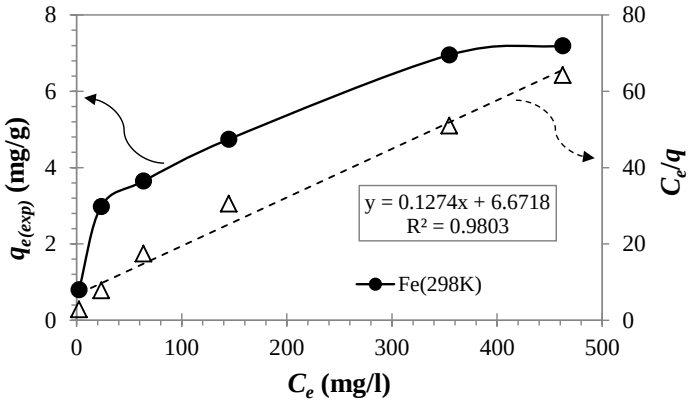

Fig. 5. Adsorption isotherm for iron onto sawdust. (Condition: pH = 6.5, T = 298 K, t = 8 h, dosage = 10 mg/l)

3.5. Kinetic studies

Kinetic parameter (e.g. rate of adsorption) gives important information for designing the adsorption process. In order to determine the adsorption kinetics, percent adsorption of metal ions was performed with varying time. The data were analyzed in two different kinetic models i.e. pseudo-first-order and pseudo-second-order. From the value of R^2, it was found that pseudo-second-order model was best suited to explain the kinetic data. The pseudo-second-order model for adsorption can be expressed as follows [14]:

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

where q_t and q_e are the amounts of adsorbate (mg/g) at time t (min) and at equilibrium, respectively, k (g·mg^{-1}·min^{-1}) is the pseudo-second-order rate constant. The rate constant can be determined from the plot of t/q_t vs t. However, the kinetic parameters of pseudo-second-order were depicted in Table 1.

Table 1. Calculation of Kinetics parameters for the adsorption of Fe and Ni(II)

Metal	$q_{e(exp)}$	pseudo-second-order		
		$q_{e(cal)}$	k_2 (g.mg^{-1}.min^{-1})	R^2
Fe (C_0 = 11 mg/l)	0.94	0.9427	0.2823	0.999
Fe (C_0 = 23 mg/l)	1.89	1.9179	0.1108	0.999

3.6. Activation Energy

Activation energy is the minimum amount of energy required for a chemical reaction to be initiated in a given system. In this research, the adsorption of iron on sawdust adsorbents was carried out at different temperatures (e.g. 298K and 313K) and the rate constants (k_{298} and k_{313}) were calculated by using pseudo-second-order kinetic models. The plot is shown in Fig. 6 from where the rates were determined. The rate was found to be 0.268 and 0.406 g·mg^{-1}·min^{-1} for 298K and 313K, respectively. According to the Arrhenius equation (Eq. 4), a relationship between natural logarithm of rate constant (k) and inverse of temperature (1/T) was plotted in Fig. 7.

$$k = A \cdot e^{-E_a/RT} \qquad (4)$$

From the above equation the activation energy (E_a) was calculated to be 21.47 kJ/mol. It is to be noted that T is the temperature (K) and A and R be the pre-exponential factor and universal gas constant (kJ·mol^{-1}), respectively.

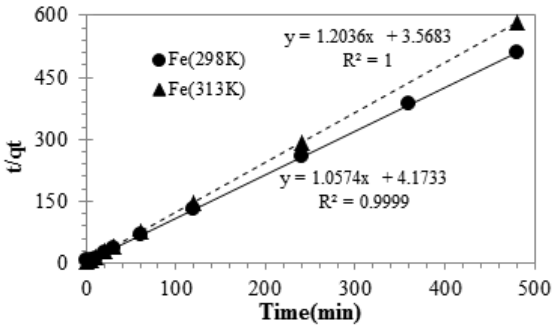

Fig. 6. Pseudo-second-order kinetic model at different temperatures for iron adsorption.

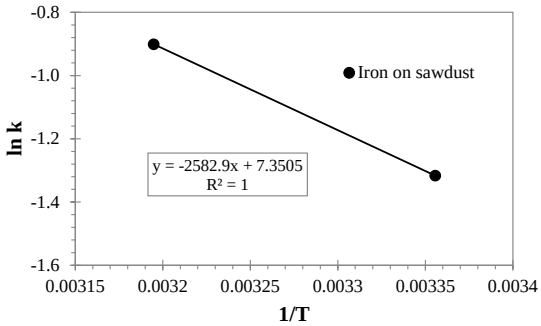

Fig. 7. Determination of activation energy for adsorption reaction of iron onto sawdust.

4. Conclusion

Adsorptive removal of iron was successfully accomplished with the sawdust adsorbent. The sorption capacity of sawdust adsorbent for iron was found to be 7.85 mg/g. At the stated condition optimum dose was 10 g/l, percent removal was 84%. Analysis of data showed that Langmuir isotherm was best fitted for adsorption while pseudo-second-order was found to be appropriate to express kinetics. The study indicated that the sawdust was effective in iron removal from aqueous solution.

5. References

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