Utilization of maize husk (Zea mays L.) as low-cost adsorbent in removal of iron from aqueous solution
S. Indah, D. Helard and A. Sasmita

ABSTRACT
Adsorption of iron from aqueous solution by using maize husk (Zea mays L.) as a low-cost adsorbent was studied. Batch experiments were carried out at ambient temperature, 0.075–0.250 mm of particle size and 100 rpm of agitation speed to determine the influence of initial pH, adsorbent dose, initial concentration and contact time on the removal of iron. Langmuir and Freundlich models were applied to describe the adsorption isotherm of iron by maize husk. The results showed that optimum condition of iron removal were 4 of pH solution, 20 g/L of adsorbent dose, 10 mg/L of Fe concentration and 15 min of contact time of adsorption with 0.499 mg Fe/g maize husk of adsorption capacity. Experimental data fitted well to Langmuir’s adsorption equilibrium isotherm within the concentration range studied. This study demonstrated that maize husk, which is an agricultural waste, has potential for iron removal from groundwater or other polluted waters.

Key words | adsorption, groundwater, iron, maize husk

INTRODUCTION
Nowadays, the removal of heavy metal contaminants from aqueous wastewater is one of the most important environmental issues being investigated. Some heavy metals usually form compounds that can be toxic, carcinogenic or mutagenic, even in very low concentrations. Apart from the fact that their existence in aquatic ecosystems may cause harmful effects to organisms living in water, heavy metals are also accumulated throughout the food chain and may affect the health of human beings (Zhang et al. 2014).

Iron is found in rocks and soil. Under proper conditions, iron will leach into the water resources from rock and soil formations; therefore, iron is common in groundwater supplies used by many small water systems. Exceeding the suggested maximum contaminant levels usually results in water staining that adversely affect plumbing fixtures, dishware and clothes and produce a yellow to reddish appearance in water. These levels may also deliver taste and odour of drinking water. This, in turn, results in consumer complaints and a general dissatisfaction with the water utility. The problems caused by iron are not only aesthetic problems, but also indirect health concerns (Ahayla et al. 2006). There are many problems that result from iron toxicity including anorexia, oliguria, diarrhea, hypothermia, diaphasic shock, metabolic acidosis and even death. The US Environmental Protection Agency has established a secondary drinking water regulation of 0.3 mg/L for iron (Machmeier 1990). Therefore, it becomes necessary to remove this heavy metal from water by an appropriate treatment technology before releasing it into the environment (Moreno-Piraján et al. 2011).

Conventional methods for heavy metal removal include chemical precipitation, ion exchange, electrodialysis, adsorption process, membrane separations, reverse osmosis, and solvent extraction. Most of these methods suffer from some disadvantages such as high operational cost and are not suitable for small-scale industries or do not lead to a satisfactory result. Among these methods, adsorption is a most common technique for the metal removal because adsorption is low cost, has a simple design, is easy to perform and is insensitive to toxic substances (Bingöl et al. 2012). Adsorption onto activated carbon has been widely applied for removing metals from water and wastewater. However, adsorbent-grade activated carbon is expensive, and the regeneration of activated carbon for reuse increases the cost (Gong et al. 2009; Anirudhan & Sreekumari 2011). Therefore, more interests have recently arisen in the investigation of low-cost adsorbents with a good sorption capacity to remove heavy metal ions from water and wastewater. For the past few decades, several researchers have reported on...
the potential use of agricultural byproducts as good adsorbents for the removal of metal ions from aqueous solutions and wastewaters, such as pine bark wastes (Acemioğlu 2004), coir fibres (Shukla et al. 2006) and rice husk ash (Zhang et al. 2014). This process attempts to put into use the principle of using waste to treat waste and becomes even more efficient because these agricultural byproducts are readily available and often pose waste disposal problems (Abidin et al. 2011). The use of waste material as an adsorbent would minimize the total amount of waste, which is a step towards a more ‘earth-friendly’ process (Jalil et al. 2012).

The aim of this research is to develop inexpensive, highly available, effective metal ion adsorbents from agricultural wastes as an alternative to existing commercial adsorbents. The ability of maize husk, a byproduct of agricultural activities, that is available in great abundance in Padang, West Sumatera, Indonesia, for removal of iron in aqueous solution was investigated. Maize husk is known as a lignocellulosic-rich material with the major constituents being 38.2% cellulose, 44.5% hemicellulose, 6.6% lignin, 1.9% protein, 2.8% ash, and the rest being undetermined materials (Barl et al. 1991). Batch experiment and isotherm studies were carried out in a laboratory scale to evaluate the adsorption capacity of maize husk. The parameters affecting the adsorption process such as pH, dose of adsorbent, initial concentration and contact time on iron removal were studied.

MATERIALS AND METHODS

Preparation of adsorbent

The maize husk used as the adsorbent was obtained from the waste of agricultural activities in Padang, West Sumatera, Indonesia. It was washed with distilled water, dried, ground, sieved (range from 0.075 to 0.250 mm) and used as adsorbent in present study.

Preparation of iron solution

Iron solutions with known concentrations were prepared by dissolving Fe(NH4)2(SO4)2.6H2O in deionized water.

Biosorption experiments

Batch biosorption experiment was carried out at room temperature (20–25 °C) by varying pH of solution, adsorbent dose and contact time. In each experiment, 100 mL of iron solutions of known initial concentration was treated with a specified known concentration of maize husk (20–60 g/L) and known pH (3–5) for a specified period of time (15–60 min) in a set of Erlenmeyer flasks. The Erlenmeyers were shaken with a shaker machine at a speed of 100 rpm. After a period of time, the adsorbent was separated from the metal solution by using Whatman’s filter paper no. 42 and the concentration of iron in the filtrate was determined by atomic absorption spectrometry (Rayleigh WFX 320, China). The amount of metal ion adsorbed by the maize husk was gotten as the difference between the initial and final ion concentrations of the solutions. All experiments were repeated three times and results presented are, consequently, the averaged values of replicate tests.

At any time, t, the adsorption capacity of iron adsorbed (qt, mg/g) or the Fe uptake on maize husk was calculated by the following mass-balance equation:

\[ qt = \frac{C_0 - C_t}{W} \times V \]  

where \( C_0 \) is the initial concentration of iron (mg/L), \( C_t \) is the equilibrium concentration of iron (mg/L), \( V \) is the volume of the solution (L), and \( W \) is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

Effect of pH

The initial solution pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the solubility of metal and the competition of metallic ions. Differences in initial pH directly affect the competitive ability of hydrogen ions with metal ions for the active sites on the adsorbent surface (Ahayla et al. 2005). The effect of pH on the adsorption of iron onto maize husk was studied at pH 3–5 and the results are presented in Figure 1. For this, the initial concentration of iron was chosen at 10 mg/L and the maize husk dosage was taken as 60 g/L. It was observed that in the period of time from 15 to 60 min, as pH increased from 3 to 4, the Fe uptake also increased from 0.127–0.139 mg/g to 0.137–0.148 mg/g. However, at pH 5, the Fe uptake decreased to 0.122–0.124 mg/g. Thus, the optimum pH for adsorption of iron onto maize husk was observed at pH 4. Similar findings on pH trend has been reported in iron studies by other researchers (Abdulrasaq & Basiru 2010; Lugo-Lugo et al. 2012). At low pH, the binding sites of adsorbent are being protonated.

## References


and charge repulsion occurred between the binding sites and the cations. In addition, the cations compete with the H\(^+\) ions in the solution for the binding sites and, thus, reduce the adsorption process. Conversely, at high pH, the binding sites of adsorbent are deprotonated and causes negative charges on the binding sites to appear and, thus, attract the cations (Amarasinghe & Williams 2010). At very high pH values, the metal hydroxide complexes forms and results precipitation and, therefore, the separation may not be due to adsorption. All the following experiments were carried out with pH values of 4.

**Effect of adsorbent dose**

The study on the effect of adsorbent dose is necessary and very useful in order to find out the optimum amount of maize husk required for the removal of iron. Figure 2 shows the effect of the maize husk dose (20–60 g/L) on the adsorption of iron from aqueous solution. The initial concentration of iron was fixed as 10 mg/L. It was revealed that the Fe uptake decreased as the adsorbent dose increased. The uptake capacity of Fe decreases from 0.381–0.402 mg/g to 0.125–0.128 mg/g by increasing the adsorbent dose from 20 to 60 g/L in the period of time from 15 to 60 min. The highest Fe uptake was obtained at the lowest dose of maize husk studied (20 g/L). This may be due to the agglomeration of adsorbent particles at high adsorbent dose, reducing the available external surface area, as well as to the strong limitations of Fe species mobility in the adsorption medium, leaving some binding sites unsaturated (Amarasinghe & Williams 2007; Aryal et al. 2010; Nieto et al. 2010). Since the highest sorption was found on 20 g/L of adsorbent dose on the removal of iron, all the following experiments were carried out with 20 g/L of adsorbent dose.

**Effect of initial concentration**

The effect of initial concentration of iron in the range of 1–10 mg/L on adsorption was also investigated. Figure 3 shows the variation of iron adsorption over time for three experiments with different initial iron concentrations. The results showed that as the initial iron concentration increased, the adsorption capacity or Fe uptake increased and it remained nearly constant until the end of contact time. The Fe uptakes were found in the range of...
Effect of contact time

The contact time is one of the important factors that influence the adsorption process of metals in a medium. Selection of proper adsorption time of heavy metals in wastewater treatment has certain economic benefits (Zhang et al. 2014). The effect of contact time on iron adsorption onto maize husk is shown in Figures 1–3. For all of the experiments, the adsorption of iron is most rapid in the initial stages and the equilibrium was achieved within 15 min (Figures 1–3). After that, the uptake capacity of Fe increases slowly until 45 min and a further increase in contact time has a negligible effect on adsorption capacity. This result may be due to the availability of vacant adsorption sites on the adsorbent surface during the initial stage of sorption. After a lapse in time, the remaining vacant surface sites were occupied due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase, resulting in the relative inaccessibility of the remaining binding sites (Aryal et al. 2010). However, the contact time of 1 h could be considered for adsorption of iron onto maize husk for entire batch studies.

Adsorption isotherm models

Adsorption isotherms describe the adsorption process and how adsorbates interact with a biosorbent. It is important to establish the most acceptable correlations for the batch equilibrium data for analysis and design of adsorption systems. The most frequently used models to describe the equilibrium data of adsorption are Langmuir and Freundlich isotherm models. Those models were applied in the present work to study the adsorption isotherms of iron onto maize husk. The Langmuir model assumes that the uptake of metal ions is monolayer sorption on a homogenous surface and without any interaction between adsorbed ions (Langmuir 1918). This model is represented by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}}
\]

(2)

where \(C_e\) is the equilibrium concentration of iron in solutions (mg/L), \(q_e\) is the equilibrium concentration of iron on the adsorbent (mg/g), \(q_{max}\) is the maximum adsorption capacity of the adsorbent (mg/g), and \(K_L\) is the Langmuir adsorption constant (L/mg).

The favourability of the adsorption could also be demonstrated by the value of essential characteristics of the Langmuir isotherm (\(R_L\)), which is a dimensionless constant that is the separation factor. The \(R_L\) can yield an isotherm shape that is unfavourable \((R_L > 1)\), linear \((R_L = 1)\), favourable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\). Using the following equation:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(3)

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy (Freundlich 1906). Freundlich model is represented by the following equation:

\[
q_e = K_F C_e^{1/n}
\]

(4)

The linearized logarithmic form of the equation is:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(5)

where \(K_F\) is the Freundlich constant of the relative adsorption capacity of the adsorbent and the empirical parameter \(1/n\) indicates the adsorption intensity. Smaller value of \(1/n\) implies stronger interaction between the adsorbent and heavy metal, while \(1/n\) values exist between 0 and 1, indicating the identical adsorption process and adsorption energies for all sites.
In order to determine the adsorption isotherm of iron adsorption onto maize husk, the initial iron concentration was varied in the interval ranging from 1 to 10 mg/L with 4 of pH and 20 g/L of adsorbent dose. Figure 4(a) shows the linearized form of the Freundlich isotherm model which was obtained by plotting log $q_e$ against log $C_e$ values. From this plot, the values of the $R^2$ was found to be 0.951 for iron adsorption. Moreover, the Langmuir isotherm was obtained by plotting $C_e/q_e$ against $C_e$ values, and the correlation coefficient ($R^2$) was 1 (Figure 4(b)). These results indicate that the Freundlich model was not adequate to describe the relationship between the amount of adsorbed iron and its equilibrium concentration in the solution. Therefore, the result showed that the Langmuir isotherm model fitted well with the equilibrium data as it presents higher $R^2$ value. These results revealed that on the adsorption of iron onto maize husk, the surface of maize husk as adsorbent is homogeneous and all active sites are energetically symmetrical resulting in monolayer adsorption. It means that the adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites (Vijayaraghavan et al. 2006). In addition, ion exchange was predicted as the predominant mechanism of the adsorption of iron onto maize husk, since the maize husk is a lignocellulosic-rich material. Ion exchange has been reported as the predominant mechanism involved in many adsorption processes by lignocellulosic wastes (Ngah & Hanafiah 2008).

The parameters of iron adsorption isotherms for maize husk are shown in Table 1. For favourable adsorption the value of $R_L$ should range in between 0 and 1. The $R_L$ values for the adsorption process were estimated at initial concentration from 1 to 10 mg/L of iron. The $R_L$ were found to be 0.175–0.021 for the initial iron concentration of 1–10 mg/L, indicating that the adsorption of iron by maize husk was favourable.

**Comparison study**

A comparison of the maximum capacities of different adsorbents, including this study, for the removal of iron from aqueous solutions is presented in Table 2. It is evident that maximum adsorptive capacities for iron were different for different materials used. This will depend on the physical nature and chemical composition of the materials used. The comparison showed that the adsorption capacity of maize husk for iron removal was relatively low compared to other adsorbents reported in the literature. However, as the adsorption of iron by maize husk was favourable, some modifications or pre-treatment steps can be taken to improve the adsorption capacity of maize husk. Further investigation is needed to develop effective metal ion adsorbent from agricultural waste as an alternative to existing commercial adsorbents.

| Table 1 | Parameters of the Freundlich and Langmuir models for adsorption of iron onto maize husk at pH 4, 20 g/L of adsorbent dose and 60 min of contact time

<table>
<thead>
<tr>
<th>Freundlich isotherm model</th>
<th>Langmuir isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_F$ (L/g)</td>
<td>$1/n$</td>
</tr>
<tr>
<td>0.427</td>
<td>0.536</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this study, the potential of using an agricultural waste, maize husk, has been assessed for the adsorption of iron. In batch mode studies, adsorption was dependent on pH, adsorbent dose, initial iron concentration and contact time. The maximum adsorption capacity (q_{max}) of maize husk was found to be 0.499 mg/g for iron at 10 mg/L of the initial concentration, 4 of pH, 20 g/L of adsorbent dose and 60 min of contact time. The equilibrium adsorption experiments fitted better with Langmuir than Freundlich isotherm models and contact time. The equilibrium adsorption experiments fitted better with Langmuir than Freundlich isotherm models and showed a correlation coefficient R^2 equals 1 and 0.951, respectively. The R_L were found to be 0.175 to 0.021 for the initial iron concentration of 1–10 mg/L, indicating that the adsorption of iron by maize husk was favourable. It can be concluded that the maize husk, an agricultural waste, is a potential alternative material for the removal of iron from groundwater or other polluted waters.

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