Removal of Iron (II) from Wastewater by Locally Prepared of Activated Carbon

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ABSTRACT
The use of low-cost activated carbon derived from reed, an agricultured waste material, has been investigated for the removed of Fe (II) from wastewater, using batch method. The influences of the weight of adsorbent (0.2-2) g, pH of solution (1-9) and initial Fe(II) concentration (10-80) mg/l have been studied. The suitability of the activated carbon used was tested by fitting the adsorption data with Langmuir and Freundlich isotherms. The study showed that the adsorption data obtained are obey the Freundlich isotherm fitting.

Keywords: Metal Ion, Adsorption, Activated Carbon, Adsorption Isotherm.

INTRODUCTION
Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluents that contain high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable and persistent nature. In addition, mining mineral processing and extractive metallurgical operations also generate toxic liquid wastes [1, 2, 3]. The removal of toxic heavy metal contaminants from aqueous waste streams is currently one of the most important environmental issues being investigated [4, 5, 6]. Adsorption on low cost-adsorbent for removal of toxic metals from wastewater has been investigated extensively. These materials include thioglycolic acid and modified oil-palm [7, 8, 9, 10]. The aim of this research is to
investigate the use of locally prepared of activated carbon in the removal of metal ions from aqueous solutions. Activated carbon is a low cost adsorbent which was derived from an agricultural reed. The study involves the examination of experimental conditions such as pH of the solution and adsorbent weight on the removal of Fe(II) from aqueous solutions. The Freundlich and Langmuir adsorption isotherms were used to investigate the adsorption process.

CHEMICALS
The chemicals used are annular grad FeSO$_4$ supplied by Fluka company. (1000) mg/l Stock solution was prepared by dissolving (2.85)g of FeSO$_4$ in (1000) ml of distilled water. Fe(II) solution of different concentrations (10-80) mg/l was prepared by dilution of the stock solution with distilled water.

These concentration cover a wide range of Fe(II) in waste water $^{[11]}$. pH of solution was adjusted by adding solution of 0.1M NaOH and 0.1M HCl. NaOH and HCl supplied by Fluka company.

EXPERIMENTAL
PREPARATION OF THE ADSORBENT
The activated carbon was prepared as described by M.I. Mohamed et al $^{[12]}$. Raw material (Reed) was crushed to size ranging from (0.3-0.5) mm and dried in oven at 80°C for (24) hr. The raw material was impregnated with ZnCl$_2$ solution for (24) hr and then after dried in oven at 80°C about (20) g of the Reed was placed in a closed container which was then placed in a chamber of muffle furnace. The sample was heated up to 450 °C under inert condition for (30) min. The physical properties of activated carbon prepared by this method are summarized in table (1).

ADSORPTION EXPERIMENTS
The adsorption was carried out in (50) ml flask by mixing together a constant amount of activated carbon with constant volume of aqueous solution of Fe(II). The contents were shaken at (300) rpm for a time period of (1) hr using an electric shaker to attain equilibrium and then the activated carbon was removed by filtration using a filter paper type GM (0.00016). The filtrate solutions were analyzed via metal content by Atomic Absorption Spectrometer (Shimadzu AA6300). The following experiments were done in order to optimize the variable conditions:

EFFECT OF ADSORBENT WEIGHT ON EXPERIMENT
In order to determine the optimum weight of activated carbon used for removal of metal ions, a volume of (20) ml of the metal ion solution of concentration (10) mg/l for Fe(II) was placed in (50) ml tubes containing different amounts of activated carbon (0.2, 0.4, 0.6, 0.8, 1, 1.5 and 2) g. A series of tubes were shacked at a constant speed of (300) rpm at temperature 25°C and agitated continuously for (1) hr. After shaking, the activated carbon was separated by filtration. The filtrate was analyzed for the remaining metal ion
concentration by Atomic Absorption Spectrometer (AAS). The optimum mass of adsorbent was obtained by plotting the weight of adsorbent versus the percentage removal.

EFFECT OF METAL ION CONCENTRATION
The experiments were made by mixing a fixed weight of activated carbon (1.5) g with (20) ml of Fe(II) solutions of concentrations (10-80) mg/l for 1hr. The pH of the solutions was about pH (5.5). The mixture was then filtered, and then the filtrate was analyzed for the determining Fe(II) concentration.

EFFECT OF PH
The experiment was conducted to obtain the optimum pH of solution required for optimum adsorption. In this case five samples of metal ion solution with different pH (1, 3, 5, 7, and 9) were prepared. (2) g of activated carbon was mixed carefully with each sample. The experiment was carried out at room temperature for (1) hr (mixing time); so as to ensure a good homogeneity between activated carbon and the ion solution and also to give a chance for the adsorbent to remove all of Fe(II) ions from the solution. Then the activated carbon was separated from the solution by filtration and the filtrate was analyzed by Atomic Adsorption Spectrometry. pH values was plotted versus Fe(II) ion concentration remaining in the solution to obtain the optimum pH in which activated carbon removed the maximum amount of Fe(II) ion.

ADSORPTION MODEL
The adsorption models used in this experiment are Freundlich and Langmuir model. The Freundlich models:

\[ q_e = k_f C_e^{1/n} \]  \hspace{1cm} (1)

The linear form of eq (1) is:

\[ \log(q_e) = \log(k_f) + \frac{1}{n} \log(C_e) \]  \hspace{1cm} (2)

The constants \( k_f \) and \( n \) are determined by plotting \( \log(q_e) \) versus \( \log(C_e) \).

The Langmuir model:

\[ q_e = \frac{abC_e}{1 + bC_e} \]  \hspace{1cm} (3)

The linear form of equation (3) is:

\[ \frac{C_e}{q_e} = \frac{1}{ab} + \frac{1}{a} C_e \]  \hspace{1cm} (4)
The constants a and b are obtained by plotting \((C_e/q_e)\) versus \(C_e\).

where

- \(a\) = Langmuir constants relating to adsorption capacity, (mg/g).
- \(b\) = Langmuir constants related to energy of adsorption, (l/mg).
- \(C_e\) = Equilibrium liquid – phase concentration, (mg/l).
- \(C_0\) = Initial liquid - phase concentration, (mg/l).
- \(K_f\) = Freundlich constant relating to adsorption capacity, (g/l)\(^{-1/n}\).
- \(n\) = Freundlich constant relating to adsorption intensity.
- \(q_e\) = Adsorption capacity at Equilibrium, (mg/g).

RESULTS AND DISCUSSION

Effects of Adsorbent Weight Experiment

Figure (1) shows the effect of activated carbon weight increasing on the removal of Fe(II). This figure shows that percentage removal of Fe(II) from water increases with increasing the weight of activated carbon. The maximum weight of activated carbon required to remove all of Fe(II) was found to be (2) g in which the removal of Fe(II) reached maximum value. These results agree well with the result obtained by Oyedeji O. et al [14]. The increasing in weight provided more surface area which are responsible for Fe(II) removal.

Effect of Initial Fe(II) Concentration Experiment

The amount of Fe(II) adsorbed per unit mass of adsorbent at different concentration \((C_0)\) is shown in Figure (2). The amount increases almost linearly with an increase in Fe(II) concentration. This can explain by the fact that at low metal ion concentration the ratio of number of moles of metal ion to the available adsorption sites is low, and therefore, the amount adsorbed per unit mass of adsorbent increases [15].

Effect of Ph on The Adsorption Process

The removal of metal ions Fe(II) by using activated carbon, as a function of pH is presented in Figure (3). The pH of the aqueous solution is an important variable which controls the adsorption and plays an important role in the precipitation and adsorption mechanisms. The experiments were performed by varying pH level of the samples ranging from 1 to 8 before adding adsorbent. The maximum mass of adsorbents used was (2) g. Figure (3) shows that the adsorption of metal ions Fe(II) on the activated carbon increases with the increase in pH. The adsorption of these metal ions at low pH increases more rapidly with increasing pH up to a certain value of pH equal to (5) then the removal of Fe(II) decreases and then becomes more constant. At low pH values, where there is high concentration of \(H^+\) (proton) in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites. At high pH values the removal takes place by adsorption as well as precipitation, due to formation of metal hydroxide. This can be explained by the fact that, as the pH of the solution increases the \(OH^-\) ions in the solution increase and form some complexes with metal ions and precipitate as metal hydroxide [12]. Based on the present work.
the optimum initial pH amount chosen for Fe(II) was (5.5) for adsorption of this metal in single component system.

Similar behavior has been reported for adsorption of Cu(II), iron (III) and lead (II) ions by using Coconut Husk [14], for adsorption of Cu(II) and Cd(II) by activated carbon from rice Hulls [16]. All those investigators show that the removal of metal ions increases with an increase in the pH of the solution.

**Adsorption Isotherm**

Equilibrium adsorption isotherm is important in the design of adsorption systems. Equilibrium studies on adsorption give the capacity of the adsorbent $q_e$. It is described by adsorption isotherms which are usually the ratio between the quantities at fixed temperature at equilibrium. In order to investigate the adsorption isotherm, two equilibrium models were analyzed. These models are the Freundlich isotherm and Langmuir isotherm. The linear regression equation for the Freundlich adsorption isotherm is shown in Figure (5). The value of $K_f$ and $n$ were calculated from the intercepts and slopes of the Freundlich plots respectively and are shown in table (2). Equilibrium isotherm studies also are used to obtain the equilibrium isotherm curves, the equilibrium isotherm curve is obtained by plotting $q_e$ (the weight of the adsorbate per unit mass of adsorbent) versus the equilibrium concentration $C_e$ as shown in Figure (6). The experimental value of $q_e$ is calculated using the following equation.

$$ q_e = \frac{V}{W}(C_0 - C_e) $$

where

$V$= Volume of solution, ($m^3$).

$W$=Weight of adsorbent in batch experiments, (Kg).

Table (2) also shows the comparison of the coefficient of regression $R^2$ for the two isotherms. For the Freundlich isotherms we have $R^2$ equal to (0.96), For the Langmuir $R^2$ is equal to (0.86). These results indicate that Freundlich isotherm gives the best fit with the experimental data better than the Langmuir isotherm.

**CONCLUSIONS**

This study, adsorption of Fe(II) onto activated carbon derived from an agricultured waste material of reed has been investigated. The data obtained from this work shows that the low cost activated carbon is an effective adsorbent for the removal of iron from aqueous solution. The adsorption of Fe(II) ions depends on the amount of activated carbon, concentration of metal ion and pH of the metal solution. Maximum removal of Fe(II) is at pH (5.5). The equilibrium data are correlated by Langmuir and Freundlich isotherm and give best fit with Freundlich isotherm.

**REFERENCES**

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Table (1) The Physical Properties of Actived Carbon Used[^12].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.48</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>500</td>
</tr>
<tr>
<td>Pore volume (ml/g)</td>
<td>0.12</td>
</tr>
<tr>
<td>Total Ash, by weight (%)</td>
<td>~10</td>
</tr>
<tr>
<td>Moisture, w %</td>
<td>~ 4</td>
</tr>
</tbody>
</table>

Table (2) The Effect Linear Regression Equation and Constant of Langmuir and Freundlich Isotherm for Adsorption of Fe(II) on to Activated Carbon.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>R²</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Y=0.7723X+25.052</td>
<td>0.86</td>
<td>a = 1.38 mg/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b = 0.028 /mg</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Y=0.7797X-1.3237</td>
<td>0.96</td>
<td>Kf = 0.047</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>n = 1.276</td>
</tr>
</tbody>
</table>

Figure (1) The Effect of Weight of Activated Carbon on the Removal of Fe(II) (C₀ = 10 mg/l, pH= 5.5, Temp= 25 °C)
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Figure (2) The Effect of Initial Concentration of Fe(II) on The Removal of Fe(II)(AC = 1.5 gm, Temp = 25°C)

Figure (3) The Effect of pH of The Solution on The Removal of Fe(II) by Activated Carbon (C₀ = 50mg/L, AC = 2 gm, Temp = 25°C)
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Figure (4) Langmuir Isotherm Curve for Adsorption of Fe(II) onto Activated Carbon

\[ y = 0.772x + 0.05 \]
\[ R^2 = 0.855 \]

Figure (5) Freundlich Isotherm Curve for Adsorption of Fe(II) onto Activated Carbon

\[ y = 0.779x - 1.323 \]
\[ R^2 = 0.958 \]
Figure (6) the Adsorption Isotherm Curve of the Experimental Data for Adsorption of Fe (II) onto Activated Carbon