Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell

Orawan Sirichote¹, Wanna Innajitara², Laemthong Chuenchom³, Doungporn Chunchit³ and Kanokrat Naweekan³

Abstract

Sirichote, O.¹, Innajitara, W.², Chuenchom, L.³, Chunchit, D.³ and Naweekan, K.³
Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell

The adsorptions of iron (III) from aqueous solution at room temperature on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell have been studied by atomic absorption spectrophotometry. The activated carbons were prepared by carbonization of these raw materials and followed by activation with ZnCl₂. The adsorption behavior of iron (III) on these activated carbons could be interpreted by Langmuir adsorption isotherm as monolayer coverage. The maximum amounts of iron (III) adsorbed per gram of these activated carbons were 0.66 mmol/g, 0.41 mmol/g and 0.18 mmol/g, respectively. Study of the temperature dependence on these adsorptions has revealed them to be exothermic processes with the heats of adsorption of about -8.9 kJ/mol, -9.7 kJ/mol and -5.7 kJ/mol for bagasse, pericarp of rubber fruit and coconut shell, respectively.

Key words: activated carbons, bagasse, pericarp of rubber fruit, coconut shell, Langmuir adsorption isotherm

¹Ph.D. (Physical Chemistry), Asst. Prof., ²B.Sc. (Chemistry), Asst. Prof., ³B.Sc. (Chemistry), Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112 Thailand.
Corresponding e-mail : sorawan@ratree.psu.ac.th
Received, 13 September 2001 Accepted, 2 March 2002
Adsorption of iron ion on activated carbons

Sirichote, O., et al.

Materials and Methods

Preparation of activated carbons

The production process of activated carbons from bagasse, pericarp of rubber fruit and coconut shell, all consisted of carbonization and chemical activation with ZnCl₂. Each dried raw material was cut into small pieces approximately 1 cm² and placed into stainless steel box with cover. The carbonization was then conducted in a...
muffle furnace at 300 °C, 400 °C and 450 °C for bagasse, pericarp of rubber fruit and coconut shell, respectively. The heating period was 3 hrs for all materials.

After carbonization, the residual char was ground using a laboratory jar mill to pass through a 325 mesh (40-45 µm) sieve. The chemical activation was done in the next step by mixing the ground char with concentrated solution of ZnCl₂ in the crucible. Activation had been carried out by varying sample to ZnCl₂ ratio and activation temperature. Sample to ZnCl₂ ratios were 1:2 and 1:3 by weight. The samples were activated at 600 °C and 800 °C for 3 hrs in a muffle furnace. The obtained activated carbon was washed with 5% HCl solution followed by hot water to remove chloride including zinc compounds and dried at 110 °C for 3 hrs. The obtained activated carbons were kept in a dessicator and were characterized for iodine number, methylene blue number (in accordance with American Standard of Testing Material, 1999) and BET surface area. The iodine number gives an indication of the adsorption capacity of activated carbon in micropores. While the methylene blue number gives an indication of the adsorption of activated carbon for molecules having similar dimensions to methylene blue and the existence of mesopores on surface area of activated carbon (Vitidsant et al., 1999).

### Adsorption experiments

All activated carbons shown in Table 1 were used to study adsorption of iron ion. Adsorption equilibrium study of iron ion was carried out in a 250 mL stoppered conical flask by adding 0.2500 g of activated carbon to 20 mL of FeCl₃ solution. The concentrations of iron (III) in the FeCl₃ solution were varied in the range of 50 to 800 ppm. All experiments were done at room temperature. After gentle shaking for 1 hr in a mechanical shaker, the contents were filtered through filter paper No.1 by neglecting the first 5 mL of the filtrate in order to saturate the filter paper with FeCl₃ solution. Concentrations of iron ion in the

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Activation temperature (°C)</th>
<th>Sample to ZnCl₂ ratio</th>
<th>IA (mg/g)</th>
<th>MB (mg/g)</th>
<th>S_BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>600</td>
<td>1:2</td>
<td>934</td>
<td>281</td>
<td>1150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>935</td>
<td>280</td>
<td>1239</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1:2</td>
<td>1212</td>
<td>283</td>
<td>1396</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>1192</td>
<td>279</td>
<td>1553</td>
</tr>
<tr>
<td>Pericarp of rubber fruit</td>
<td>600</td>
<td>1:2</td>
<td>1063</td>
<td>276</td>
<td>1508</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>1027</td>
<td>280</td>
<td>1549</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1:2</td>
<td>1260</td>
<td>281</td>
<td>1472</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>1281</td>
<td>281</td>
<td>1737</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>600</td>
<td>1:2</td>
<td>1055</td>
<td>164</td>
<td>1097</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>1281</td>
<td>164</td>
<td>1140</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1:2</td>
<td>1002</td>
<td>162</td>
<td>970</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:3</td>
<td>907</td>
<td>164</td>
<td>899</td>
</tr>
</tbody>
</table>

IA = iodine number, MB = methylene blue number, and S_BET = BET surface area

The BET surface areas were analysed by Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University.
filtrate were then determined by Perkin-Elmer AAnalyst 300 model atomic absorption spectrophotometer. The amount of iron ion adsorbed was calculated based on the difference between the iron ion concentration in aqueous solution before and after adsorption.

For adsorption at higher temperatures iron solutions and activated carbons in the stoppered conical flasks were shaken in a thermostat shaker bath maintained at 32 °C, 42 °C, 51 °C, and 70 °C for 1 hr. Only one concentration of iron ion solution that exhibited maximum adsorption on each type of activated carbon was used to run these experiments.

Results and Discussion

Table 1 shows some characteristics of three activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell. When comparing each raw material at different activation conditions, it is found that bagasse and pericarp of rubber fruit activated at 800 °C with sample to ZnCl₂ ratio of 1:3 and coconut shell activated at 600 °C with sample to ZnCl₂ ratio of 1:3 give the greatest values of iodine number (IA) of 1200. Their BET surface areas also give the same trend as their iodine numbers. The methylene blue numbers (MB) of activated carbons obtained from bagasse and pericarp of rubber fruit activated at various conditions are the same. Their values of 280 are greater than those for activated carbons obtained from coconut shell with values of 160.

The experimental equilibrium isotherms at room temperature and different feed concentrations of iron (III), C_{initial} are shown in Figure 1. In this figure all types of activated carbons were prepared by activation with a sample to ZnCl₂ ratio of 1:3 at 600 °C. On each isotherm the amount adsorbed increased with feed concentration and became level off at higher feed concentrations. The maximum adsorption capacities were read when they became independent of the feed concentrations. The amount of iron ion adsorbed on all types of activated carbons increased in the increasing order from coconut shell to pericarp of rubber fruit and highest for bagasse.

The Langmuir equation is expressed as follows (Wan Ngah and Liang, 1999):

\[
\frac{C}{X} = \frac{C_{\text{max}}}{X_{\text{max}}} + \frac{1}{X_{\text{max}}b}
\]

where C is the equilibrium or final concentration of iron ion in mmol/L, X is the amount of iron ion adsorbed per unit weight of activated carbon at equilibrium concentration (mmol/g), X_{max} is the maximum adsorption at monolayer coverage.

Figure 1. Adsorption isotherms of iron ion on three types of activated carbons at room temperature.
(mmol/g), and b is the adsorption equilibrium constant (L/mmol).

From equation (1) the plot of C/X versus C should give a straight line of slope 1/\(X_{\text{max}}\) and an intercept of 1/\(X_{\text{max}}\) b on the C/X axis. This linear plot shows that the adsorption obeys the Langmuir isotherm model. The Langmuir adsorption isotherm is based on the characteristic assumption that only monolayer adsorption takes place (Shaw, 1980).

Figures 2 to 4 show the Langmuir plots that have the greatest values of iron adsorption on three types of activated carbons with a sample to ZnCl, ratio, 1:3 and activation temperature at 600 °C. The values of \(X_{\text{max}}\) calculated from slopes of the Langmuir plots for all activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell at room temperature are in the range 0.25 - 0.66 mmol/g, 0.11 - 0.41 mmol/g and 0.12 - 0.19 mmol/g, respectively.

The temperature dependence of the adsorption of iron ion on these activated carbons is shown in Figure 5. The experimental result shows that the amount of iron ion adsorbed on activated carbons decreased with increasing adsorption temperature. This suggested that the adsorption mechanism was physical adsorption, in contrast to chemical adsorption in which the amount of adsorbate adsorbed on an adsorbent increases with increasing adsorption temperature (Uchida et al., 2000).

The heat of adsorption was calculated by applying the Clausius-Clapeyron equation to the adsorption isotherm as follows (Alberty and Silbey, 1992; Tanada et al., 2000):

\[
\frac{dP}{dT} \frac{P\Delta H_{\text{m}}}{RT^2} = \frac{P\Delta H_{\text{m}}}{RT^2}
\]  

(2)
where \( P \) is the equilibrium pressure of gas, \( T \) is the absolute temperature, \( \Delta H_{\text{vap}} \) is the heat of vaporization, and \( R \) is the gas constant. On rearrangement equation (2) becomes

\[
\frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{RT^2} dT \tag{3}
\]

\[
d\ln \frac{P}{P^o} = \frac{\Delta H_{\text{vap}}}{RT^2} dT \tag{4}
\]

where \( P^o \) is the standard pressure used.

Replacement of \( P \) by \( CRT \) and \( P^o \) by \( C^oRT \) from ideal gas law where \( C \) is the molar concentration and \( C^o \) is the standard value of the molar concentration (1 mol/L) equation (4) becomes

\[
d\ln \frac{C}{C^o} = \frac{\Delta H_{\text{vap}}}{RT^2} dT \tag{5}
\]

For adsorption in solution the \( \Delta H_{\text{vap}} \) is replaced by \( \Delta H_{\text{ads}} \) which is the heat of adsorption.

Integrating on the assumption that the \( \Delta H_{\text{ads}} \) is independent of temperature and concentration and since the term \( \ln C^o \) is equal to zero, equation (5) yields

\[
\int d\ln C = \frac{\Delta H_{\text{ads}}}{R} \int T^{-2} dT = -\frac{\Delta H_{\text{ads}}}{R} \ln T + c \tag{6}
\]

where \( C \) is the molar concentration of adsorbate and \( c \) is the integration constant. Plot of \( \ln C \) versus \( 1/T \) should give a straight line of slope \(-\Delta H_{\text{ads}}/R\).

The plots of applied Clausius-Clapeyron equation to adsorption isotherm in equation (7) as \( \ln C \) versus \( 1/T \) are shown in Figures 6 to 8.
Adsorption of iron ion on activated carbons

Sirichote, O., et al.

by the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry. The authors would like to thank Department of Mining and Material Engineering and Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, for kindly giving permission to use a 325 mesh sieve and a thermostat shaker bath.

References


Figure 8. Clausius-Clapeyron plot at various temperatures for adsorption of iron ion on activated carbon obtained from coconut shell.

Table 2. The maximum adsorption of iron ion at monolayer coverage \( (X_{\text{max}}) \) and the heats of adsorption \( (\Delta H_{\text{ads}}) \) for iron ion on three types of activated carbons with a sample to ZnCl\(_2\) ratio, 1:3 and activation temperature at 600 °C.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>( X_{\text{max}} ) (mmol iron/g)</th>
<th>( \Delta H_{\text{ads}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>0.66</td>
<td>-8.9</td>
</tr>
<tr>
<td>Pericarp of rubber</td>
<td>0.41</td>
<td>-9.7</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>0.19</td>
<td>-5.7</td>
</tr>
</tbody>
</table>

The heat of adsorption was calculated from the slope of those straight lines. The numerical value of Langmuir isotherm constant for the maximum adsorption at monolayer coverage \( (X_{\text{max}}) \) and the heats of adsorption \( (\Delta H_{\text{ads}}) \) of iron ion on three types of activated carbons with a sample to ZnCl\(_2\) ratio, 1:3 at 600 °C was summarized in Table 2.

Acknowledgments

This research was supported by Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, and partially supported...