Estimation of Adsorption Isotherm for Iron Ion on Three Different Active Carbon Types

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Abstract

The purpose of this experimental study is to estimate a suitable isotherm for the adsorption of iron ions from an aqueous solution onto three different types of active carbon. Three types of active carbons were selected, they include granular activated carbon prepared from date stone (GACD), granular active carbon prepared from charcoal (GACCH), and granular active carbon bought from the market (GACM) used for home desalination unit. The experiments were performed in a batch system at a constant temperature 20 °C and pH 7. Iron solutions of different concentrations were prepared from ferrous chloride. At equilibrium, linear forms of Langmuir isotherm, Freundlich isotherm, Timken isotherm, Dubinin–Radushkevich isotherm, and Elovich isotherm were tested with adsorption data to find the best-fit model. Freundlich and Langmuir was found to be good model for GACM, Freundlich isotherm was good model for GACCH and Langmuir isotherm best fits experimental data for GACD.

Keywords: Activated carbon, Adsorption, Charcoal, Date stone, Iron ions, Market.

ملخص

غرض من هذه الدراسة التجريبية هو تقدير متساوي الحرارة المناسب لامتصاز أيون الحديد من محلول مائي على ثلاثة أنواع مختلفة من الكربون النشط. تم اختيار ثلاثة أنواع من الكربون النشط، وهي الكربون النشط الحبيبي المحضر من نواة التمر (GACD) والكربون النشط الخبيبي المحضر من الفحم (GACCH) والكربون النشط الخبيبي النشاط الذي تم شراؤه من السوق (GACM) ومستخدم لوحدة تحلية المياه المنزلية. تم إجراء التجارب في نظام شبه مكشوف عند درجة حرارة ثابتة 20 °C وpH 7. تم تحضير محلول الحديد من كلوريد الحديدوز. في حالة التوازن، تم اختبار الأشكال الخطية من متساوي الحرارة لانجموير، متساوي فروندليش، متساوي الحرارة تيمكين، متساوي الحرارة دوبين–رادوشكيفيتش، وielovich باستخدام بيانات الامتصاص للعثور على أفضل تفويض متساويات. تم العثور على متساويات من متساوي الحرارة لانجموير، متساوي فروندليش كنموذج جيد للGACD، وكتابه متساويات من متساوي الحرارة لانجموير بناءً على البيانات التجريبية لـ GACM.

الكلمات الدالة: الكربون النشط، الامتصاز، الفحم، نواة التمر، أيونات الحديد، السوق.
1. Introduction

The problems of the ecosystem are increasing with developing technology. The industrial activity is the major source to the environmental pollution. Heavy metal pollution especially in industrial wastewaters is one of the main problems (Parmer and Thakur, 2013). Toxic metal compounds coming from industry can contaminate both the earth’s waters (seas, lakes, ponds and reservoirs), and also underground water. Therefore, the earth’s waters may contain various toxic metals. And because the Drinking water is obtained from earth’s waters (seas, lakes, ponds and reservoirs), the treatment of the different pollutants including heavy metal containing wastewater is necessary prior to its discharge.

Many different treatment techniques such as adsorption, ion exchange, biodegradation, solvent extraction, and oxidation, have been used for removal of the different pollutants including heavy metal ions from industrial wastewaters. However, adsorption is considered as one of the most effective pollutant removal process, especially with pollutants removal at low concentrations from wastewater. Many researchers showed the ability of the carbon to remove pollutant like phenol, halogenated compounds, pesticides, caprolactam, chlorine (John Thomas and Crittenden, 1998), Copper ion (Alshuiref et al., 2017), and H₂S (Lau et al., 2016). The adsorption process has many Advantages like low cost, ease in handling, low consumption of reagents.

The aim of this paper is to prepare active carbon and use it as adsorbent to remove iron by adsorption technique and to estimate best isotherm (which is important in the design stage) for iron adsorption on each carbon type.

Three active carbon types were used in this study and each is tested with Langmuir isotherm, Freundlich isotherm, Timken isotherm, Dubinin-Radushkevich isotherm and Elovich isotherm (all are two parameter models) to estimate the best model for each carbon type (Hamdaouia and Naffrechoux, 2007; and Rania & Yousef, 2015).

These carbon types include Granular active carbon prepared from date stone, granular active carbon prepared from charcoal, and commercial active carbon brought from market.

2. Materials and Methods

2.1. Chemicals

Iron solution of six different concentrations prepared from ferrous chloride AR grade as in Table (1) and confirmed using laboratory equipment DR 900 COLORIMETER.

Phosphoric acid and hydrochloric acid used for activation are AR grade from BDH chemicals.

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of iron solution in (mg/L).</td>
<td>4.5, 15.6, 33, 58, 73, 98</td>
</tr>
<tr>
<td>Weight of Ferrous Chloride (mg) dissolved in one L of distilled water</td>
<td>16.1, 55.815, 118.071, 207.519, 261.188, 350.636</td>
</tr>
</tbody>
</table>
2.2. Preparation of Activated Carbon

2.2.1. GACD (Granular active carbon from date stone) preparation

2.2.1.1. Cleaning and drying

Stones were collected and washed many times with water then left for enough time to dry.

2.2.1.2. Carbonation

The cleaned dry stones were put into oven at 100 °C for one hour in absence of oxygen. The carbonized stones were left to cool then crushed with mortar and pestle into granular form (Yahia, 2006).

2.2.1.3. Activation and sieving

Sieves are used to get granules of size 2000 μm. After that, the hydrochloric acid with concentration of 5 N as chemical activator. HCl 5N is added to granules and left 24 hours to ensure complete activation. After that, it was washed thoroughly well with distilled water to remove acidity with using PH paper as acidity indicator and filter paper for filtration.

2.2.1.4. Drying and pyrolysis

The activated carbon was left in drying oven for 24 hrs, then put in a furnace at 450 – 500 °C for two hours.

2.2.2. GACH (Granular active carbon from charcoal) preparation

2.2.2.1. Crushing, grinding and sieving

Local ordinary charcoal of olive type from market was used. This charcoal was crushed and grinded using mortar and pestle. After that we used sieving equipment and selected size of 850 - 2000 μm as granular type.

2.2.2.2. Activation

Phosphoric acid was used to do activation. Granular carbons were immersed in a solution of 60% phosphoric acid and left for 24 hrs. This work has been done in glass beakers 250 mL.

2.2.2.3. Drying

The chemically activated carbon were washed well with distilled water to remove acid, finally we get pH 7 using PH paper and that mean all residual acid has been removed. After that, carbon has been dried using drying oven. The drying process was done at temperature of 100 °C for 24 hrs.

2.2.2.4. Pyrolysis

After drying 50 mg of carbon were placed in steel containers and placed in a furnace for purpose of pyrolysis. Temperature of furnace selected was 450 -500 °C for two hours.

2.3. Batch Adsorption Experiments

Experiments were performed by batch adsorption technique at constant temperature 20 °C and pH 7. Equal weights (6 No.) of 1.5 g have been taken from each of the three carbons, and have been placed in 18 flasks of 50 mL. 30 mL from solutions of different concentration (C₀) have been added to each flask including 4.5, 15.6, 33, 58, 73, 98 mg/L. These concentrations were prepared from ferrous chloride and then read by DR 900 COLORIMETER. Flasks left for enough time to reach equilibrium, and then concentration at equilibrium (Cₑ) have been taken using dilution then reading by DR900.
Amount of iron adsorbed in mg per gram of active carbon were calculated from mass balance equation (Eqn. (1));

\[ q_e = \frac{V}{m} (C_0 - C_e) \]  

Where;  
- \( q_e \): Amount of iron adsorbed per gram of adsorbent, (mg/g).  
- \( C_0 \): Initial concentration in (mg/L).  
- \( C_e \): Concentration at equilibrium in (mg/L).  
- \( V \): Volume, which is 30 mL (0.03 L).  
- \( m \): Mass of adsorbent (1.5 g).

Five important known isotherms have been tested and compared with result data and checked which type of isotherm should these data follow by using Microsoft excel program, these isotherms are Langmuir isotherm, Freundlich isotherm (Richardson et al., 2002), Timken isotherm (Tempkin and Pyzhev1940), Dubinin-Radushkevich isotherm (Dubinin 1960), and Elovich isotherm (Elovich and Larinov, 1962).

Linear form of each isotherm was used by plotting \( x \)-axis against \( y \)-axis of each isotherm, using Microsoft excel, the regression line and correlation for each data set was collected. Table (2) contain linear form and constants that can be calculated from slops and intercepts.

<table>
<thead>
<tr>
<th>Isotherm Name</th>
<th>Linear form of isotherm</th>
<th>( x )-axis</th>
<th>( y )-axis</th>
<th>Constants and parameters calculated from slop and intercept</th>
</tr>
</thead>
</table>
| Langmuir                       | \( \frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \) | \( \frac{1}{C_e} \) | \( \frac{1}{q_e} \) | \( q_m \) maximum amount adsorbed, calculated from intercept \( \frac{1}{q_m} \).  
  \( K_L \) langmuir equilibrium constant  
  Measured from slop \( \frac{1}{q_m} \).  
| Freundlich                     | \( lnq_e = lnK_F + \frac{1}{n} lnC_e \)          |             | \( lnC_e \) | \( lnq_e \) \( K_F \) freundlich constant, measured from Intercept (\( lnK_F \)).  
  \( n \) constant, measured from slop \( (\frac{1}{n}) \).  
| Timkin                         | \( q_e = BlnA_T + BlnC_e \)                       | \( lnC_e \) | \( q_e \) | \( b_T \) temkin isotherm constant, measured from slop \( RT/b_T \).  
  \( A_T \) constant measured from intercept \( BlnA_T \).  
| Dubinin–Radushkevich          | \( lnq_e = lnq_m - \beta \varepsilon^2 \)        | \( \varepsilon^2 \) | \( lnq_e \) | \( \beta \) D-R constant, measured from slop \( \beta \).  
  \( q_m \) maximum amount adsorbed, calculated from intercept \( lnq_m \).  
| Elovich                       | \( lnq_e C_e = lnK_E q_m - \frac{q_e}{q_m} \)       | \( q_e \) | \( lnq_e C_e \) | \( q_m \) maximum amount adsorbed, calculated from slop \( \frac{1}{q_m} \).  
  \( K_E \) Elovich equilibrium constant, calculated from intercept \( lnK_E q_m \).  

3. Results and Discussion

Initial concentration $C_o$, concentration of iron at equilibrium $C_e$, and calculated values of $q_e$ for the three types of active carbon are shown in Table (3).

<table>
<thead>
<tr>
<th>No.</th>
<th>$C_o$ (ppm)</th>
<th>$C_e$ (ppm)</th>
<th>$q_e$ (mg/g)</th>
<th>$C_e$ (ppm)</th>
<th>$q_e$ (mg/g)</th>
<th>$C_e$ (ppm)</th>
<th>$q_e$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>0.3</td>
<td>0.084</td>
<td>4.5</td>
<td>0</td>
<td>0.15</td>
<td>0.087</td>
</tr>
<tr>
<td>2</td>
<td>15.6</td>
<td>3.29</td>
<td>0.2462</td>
<td>15.54</td>
<td>0.003</td>
<td>4.55</td>
<td>0.221</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>9.6</td>
<td>0.468</td>
<td>30</td>
<td>0.06</td>
<td>13.9</td>
<td>0.382</td>
</tr>
<tr>
<td>4</td>
<td>58</td>
<td>26.6</td>
<td>0.628</td>
<td>47</td>
<td>0.22</td>
<td>35.8</td>
<td>0.444</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>40.8</td>
<td>0.644</td>
<td>50.4</td>
<td>0.452</td>
<td>60</td>
<td>0.26</td>
</tr>
<tr>
<td>6</td>
<td>98</td>
<td>49</td>
<td>0.98</td>
<td>57</td>
<td>0.82</td>
<td>68</td>
<td>0.6</td>
</tr>
</tbody>
</table>

3.1. Estimation of isotherms for iron adsorption on GACM

The linear forms of Langmuir, Freundlich, Tiirken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACM are illustrated in Table (4).

<table>
<thead>
<tr>
<th>$C_e$ (ppm)</th>
<th>$q_e$ (mg/g)</th>
<th>$1/C_e$</th>
<th>$1/q_e$</th>
<th>ln ($C_e$)</th>
<th>ln ($q_e$)</th>
<th>$\xi^2$</th>
<th>ln($q_e/C_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.084</td>
<td>3.333</td>
<td>11.9</td>
<td>-1.20397</td>
<td>-2.47693</td>
<td>12.759,184</td>
<td>-1.2729</td>
</tr>
<tr>
<td>3.29</td>
<td>0.2462</td>
<td>0.30395</td>
<td>4.06</td>
<td>1.1909</td>
<td>-1.4016</td>
<td>386,995.9</td>
<td>-2.5925</td>
</tr>
<tr>
<td>9.6</td>
<td>0.468</td>
<td>0.1042</td>
<td>2.137</td>
<td>2.2617</td>
<td>-0.7592</td>
<td>58,267</td>
<td>-3.0210</td>
</tr>
<tr>
<td>26.6</td>
<td>0.628</td>
<td>0.03759</td>
<td>1.5923</td>
<td>3.2809</td>
<td>-0.4652</td>
<td>8,081.9</td>
<td>-3.7461</td>
</tr>
<tr>
<td>40.8</td>
<td>0.644</td>
<td>0.0245</td>
<td>1.552</td>
<td>3.7086</td>
<td>-0.441</td>
<td>3,479</td>
<td>-4.1487</td>
</tr>
<tr>
<td>49</td>
<td>0.98</td>
<td>0.020408</td>
<td>1.02</td>
<td>3.8918</td>
<td>-0.02020</td>
<td>409,163</td>
<td>-3.912</td>
</tr>
</tbody>
</table>

3.1.1. Langmuir isotherm plot

From Figure (1), the correlation coefficient ($R^2$) is 0.9688, which is an indication of good correlation.
3.1.2. **Freundlich isotherm plot**
From Figure (2), the correlation coefficient (R²) is 0.9798, which is an indication of better fit than Langmuir.

3.1.3. **Temkin isotherm plot**
From Figure (3), the correlation coefficient (R²) is 0.8425, which is an indication of less suitable fit than Langmuir.
Figure 3. Temkin isotherm plot for iron adsorption on GACM

3.1.4. Dubinin-Radushkevich isotherm plot
From Figure (4), the correlation coefficient (R²) is 0.7564, which is indication of bad fit.

Figure 4. Dubinin-Radushkevich isotherm plot for iron adsorption on GACM

3.1.5. Elovich isotherm plot
From Figure (5), the correlation coefficient (R²) is 0.7849, which is an induction of a bad fit.

Figure 5. Elovich isotherm plot for iron adsorption on GACM
Therefore, by comparison, the order of the isotherm best fits experimental data for GACM is Freundlich > Langmuir > Temkin > Elovich > Dubinin-Radushkevich. When apply Freundlich linear equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm}  y=0.4511x-1.9144

Slope was 0.4511, and \( n = 2.2168 \), while Intercept was –1.9144, and \( K_F = 0.14743 \).

### 3.2. Estimation of isotherms for iron adsorption on GACCH

The linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACCH are illustrated in Table (5).

#### Table 5. Adsorption isotherms calculations for GACCH

<table>
<thead>
<tr>
<th>( C_e )</th>
<th>( q_e )</th>
<th>( 1/C_e )</th>
<th>( 1/q_e )</th>
<th>( \ln (C_e) )</th>
<th>( \ln (q_e) )</th>
<th>( \xi^2 )</th>
<th>( \ln(q_e/C_e) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.54</td>
<td>0.003</td>
<td>0.06435</td>
<td>333.33</td>
<td>2.7434</td>
<td>-5.809</td>
<td>23.079.5</td>
<td>-8.5525</td>
</tr>
<tr>
<td>30</td>
<td>0.06</td>
<td>0.03333</td>
<td>16.6666</td>
<td>3.40119</td>
<td>-2.8134</td>
<td>6,380.18</td>
<td>-6.2146</td>
</tr>
<tr>
<td>47</td>
<td>0.22</td>
<td>0.021276</td>
<td>4.545</td>
<td>3.8501</td>
<td>-1.5141</td>
<td>2,630.26</td>
<td>-5.364</td>
</tr>
<tr>
<td>50.4</td>
<td>0.452</td>
<td>0.01984</td>
<td>2.21238</td>
<td>3.91999</td>
<td>-0.7941</td>
<td>2,290.59</td>
<td>-4.714</td>
</tr>
<tr>
<td>57</td>
<td>0.82</td>
<td>0.01754</td>
<td>1.2195</td>
<td>4.04305</td>
<td>-0.12783</td>
<td>1.041</td>
<td>-4.2415</td>
</tr>
</tbody>
</table>

#### 3.2.1. Langmuir isotherm plot

From Figure (6), the correlation coefficient (\( R^2 \)) is 0.9251. An indication of a good correlation.

![Figure 6. Langmuir isotherm plot for iron adsorption on GACCH](image)

#### 3.2.2. Freundlich isotherm plot

From Figure (7), the correlation coefficient (\( R^2 \)) is 0.9887. It is better fit than Langmuir is.
3.2.3. **Temkin isotherm plot**

From Figure (8), the correlation coefficient (R²) is 0.6248, an indication of a bad fit.

3.2.4. **Dubinin-Radushkevich isotherm plot**

From Figure (9), the correlation coefficient (R²) is 0.9374. It is good fit but less than Freundlich.
3.2.5. Elovich isotherm plot
From Figure (10), the correlation coefficient (R²) is 0.6722, an indication of a bad fit.

![Elovich isotherm plot](image)

**Figure 10.** Elovich isotherm plot for iron adsorption on GACCH

By comparison, conclude that Freundlich isotherm best fits experimental data;
\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]
y = 4.1902 x – 17.261
Slope was 4.1902, and n = 0.23865; while Intercept was –17.261, and \(K_F=3.1889 \times 10^{-8}\)

3.3. Estimation of isotherms for iron adsorption on GACD
The linear forms of Langmuir, Freundlich, Timken, Dubinin-Radushkevich, Elovich isotherms and constants for each one respectively are presented in Table (2). Adsorption isotherms calculations for iron on GACD are illustrated in Table (6).

### Table 6. Adsorption isotherms calculations for GACD

<table>
<thead>
<tr>
<th>(C_e)</th>
<th>(q_e)</th>
<th>(1/C_e)</th>
<th>(1/q_e)</th>
<th>(\ln (C_e))</th>
<th>(\ln (q_e))</th>
<th>(\xi^2)</th>
<th>(\ln(q_e/C_e))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.087</td>
<td>6.6666</td>
<td>11.49425</td>
<td>-1.897</td>
<td>-2.4418</td>
<td>24,619,940.02</td>
<td>-0.5447</td>
</tr>
<tr>
<td>4.55</td>
<td>0.221</td>
<td>0.21978</td>
<td>4.52488</td>
<td>1.5151</td>
<td>-1.50959</td>
<td>234,219.4</td>
<td>-3.02472</td>
</tr>
<tr>
<td>13.9</td>
<td>0.382</td>
<td>0.07194</td>
<td>2.6178</td>
<td>2.6318</td>
<td>-0.9623</td>
<td>32,590.05</td>
<td>-3.5942</td>
</tr>
<tr>
<td>35.8</td>
<td>0.444</td>
<td>0.02793</td>
<td>2.2522</td>
<td>3.5779</td>
<td>-0.8119</td>
<td>4,503.98</td>
<td>-4.3898</td>
</tr>
<tr>
<td>60</td>
<td>0.26</td>
<td>0.016666</td>
<td>3.8461</td>
<td>4.0943</td>
<td>-1.347</td>
<td>1,621.3</td>
<td>-5.4414</td>
</tr>
<tr>
<td>68</td>
<td>0.6</td>
<td>0.014705</td>
<td>1.6666</td>
<td>4.2195</td>
<td>-0.5108</td>
<td>1,264.7</td>
<td>-4.73033</td>
</tr>
</tbody>
</table>

3.3.1. Langmuir isotherm plot
From Figure (11), the correlation coefficient (R²) is 0.9267, an indication of a good correlation.
3.3.2. Freundlich isotherm plot
From Figure (12), the correlation coefficient ($R^2$) is 0.8124.

3.3.3. Temkin isotherm plot
From Figure (13), the correlation coefficient ($R^2$) is 0.6242, it is a bad fit.
3.3.4. Dubinin-Radushkevich isotherm plot

From Figure (14), the correlation coefficient ($R^2$) is 0.7239.

![Dubinin-Radushkevich isotherm plot for iron adsorption on GACD](image)

Figure 14. Dubinin-Radushkevich isotherm plot for iron adsorption on GACD

3.3.5. Elovich isotherm plot

From Figure (15), the correlation coefficient ($R^2$) is 0.4664, an indication of a bad fit.

![Elovich isotherm plot for iron adsorption on GACD](image)

Figure 15. Elovich isotherm plot for iron adsorption on GACD

By comparison, conclude that Langmuir isotherm best fits experimental data;

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

\[ y = 1.2974 x + 2.8829 \]

Intercept was 2.8829, and $q_m = 0.346873$, while Slope was 1.2974, and $K_L = 2.222$.

4. Conclusion

In this study, activated carbon adsorbents were prepared from charcoal and date stones in addition to a commercial active carbon bought from market and applied for the adsorption of iron metal from wastewater. Investigation of adsorption isotherms were carried out at 20 °C and pH 7. The collected adsorption data sets were fitted into different two parameter models namely Langmuir, Freundlich, Temkin, Dubunin – Radushkevich and Elovich isotherms.

Freundlich model was good model for adsorption of iron on GACM, and GACCH. On the other hand, Langmuir isotherm best fits experimental data of GACD.
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References


