SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF Cu$_2$[Fe(CN)$_6$] NANOPARTICLE FOR THE ADSORPTION OF CESIUM ION (Cs$^+$)

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ABSTRACT

In this investigation, the sorptive removal of Cesium ions (Cs$^+$) from CsCl aqueous using Cu$_2$[Fe(CN)$_6$] nanoparticles was studied. The synthesis of Cu$_2$[Fe(CN)$_6$] nanoparticle was carried out, X-ray diffraction (XRD) was used to analyze the characteristics of Cu$_2$[Fe(CN)$_6$], and the total reflection X-ray fluorescence (TXRF) technique was applied to detect absorbent capacity. Some characteristics of Cu$_2$[Fe(CN)$_6$] including Miller indices (h, k, l), the spacing between the atomic planes (d), the lattice parameter (a), and volume of the unit cell (V) were calculated. All experiments in this research were studied at pH = 7 level and room temperature and change solute concentration. The Freundlich and the Langmuir isotherm model are applied to determine the heterogeneity factor (1/n) and the maximum adsorption capacity ($q_{max}$).

Keywords: Synthesis; Cu$_2$[Fe(CN)$_6$]; X-ray diffraction (XRD); Cesium ion (Cs$^+$)

1. Introduction

As a consequence of operating nuclear power plants, a huge amount of the radioactive wastes possibly will move to the sea, especially, fission products. Cesium is a heavy element emitted from the nuclear reaction in the nuclear reactor, which is the result of the fission reaction. Two radioisotopes, Cs-134 and Cs-137, have a long half-life (Eisenbud, 1997; Glasstone, & Sesonske, 1994). In the ocean, Cesium usually is in the salt forms, and CsCl is the popular form. They move freely in sea water, which are the main reasons the diffusion of radioisotopes increase in the water environment.

The previous work showed that the radioisotopes should be encased in concrete and stored underground (Walker et al., 1992). Nowadays, with the current development of science and technology in the world, especially, material technology, scientists produced more new materials which can collect much radiation waste. Normally, the collection of heavy metals such as radioisotopes requires some different techniques, such as precipitation, electrocoagulation, the solvent extraction, and the exchange of ions on resins.

The absorption techniques are well known to collect Cesium. Some nanoparticle materials are synthesized and applied to accumulate Cs\(^+\) (Borai et al., 2009; Yang et al., 2011; Sheha, 2012). This study was carried out with Cs\(^+\) on Cu\(_2\)[Fe(CN)\(_6\)] nanoparticles which were synthesized by the researchers.

2. Materials and methods

2.1. Materials

K\(_4\)[Fe(CN)\(_6\)].3H\(_2\)O, CuCl\(_2\).2H\(_2\)O, and standard solution Cs\(^+\) (CsCl, 1000 mg/L) which were produced by Merck Co., Ltd were used in our study. They have a high purity level of 99.99%.

- **Synthesis of Cu\(_2\)[Fe(CN)\(_6\)]**

For the synthesis of Cu\(_2\)[Fe(CN)\(_6\)], two separate solutions were prepared: a) 250 ml 0.05 M K\(_4\)[Fe(CN)\(_6\)].3H\(_2\)O (Merck) aqueous solution and b) 750 ml 0.15 M CuCl\(_2\).2H\(_2\)O (Merck) aqueous solution. The first solution was poured with 5 ml/mins into the second one with a vigorous stirring of 1200 rpm for four hrs. Cu\(_2\)[Fe(CN)\(_6\)] is brown. The chemical reaction between CuCl\(_2\) and K\(_4\)[Fe(CN)\(_6\)] happens as follows:

\[
2\text{CuCl}_2 + \text{K}_4[\text{Fe(CN)}_6] \rightarrow \text{Cu}_2[\text{Fe(CN)}_6] + 4\text{KCl}
\]

K\(_4\)[Fe(CN)\(_6\)] solid precipitate was filtered by a centrifuge machine, washed multiple times with distilled water until it reaches a neutral pH level, and dried at 70°C for 50 hrs. Finally, grinding with a mortar and pestle produced absorption material.

- **Investigation of Cesium adsorption using Cu\(_2\)[Fe(CN)\(_6\)]**

For safety, cesium (Cs\(^+\)) (CsCl) salt used for the research is the stable isotope. 0.1 g of Cu\(_2\)[Fe(CN)\(_6\)] was added into 100 ml of a Cs\(^+\) ion solution with different concentrations (ranging from 30 to 90 mg/L). The reactor was tightly closed, and the reaction mixture was shaken at 180 rpm for 24 hrs. to ensure that the absorption reaches equilibrium at 25 °C. The pH is mained at an appropriate pH. Upon the completion of adsorption, the material was magnetically separated. The supernatant solution was centrifuged (5 mins, 10,000 rpm) and filtered through a 0.24 μm filter.

2.2. Calculation methods

**Using X-ray diffraction technique (XRD) to determine nanomaterial characteristics**

The Bragg’s law relates the wavelength (\(\lambda\)) of the reflected X-ray, the spacing between the atomic planes (\(d\)) and the angle of diffraction (\(\theta\)) as follows:

\[
2dsin\theta = k\lambda_{kht}
\]
Miller indices the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes (Pearson, 1972): h, k, l. For a cubic class case, some integer values of the Miller indices h, k, and l are possible as presented in Table 1.

**Table 1. Some integral values of the Miller indices h, k, and l are possible**

<table>
<thead>
<tr>
<th>Corresponding hkl</th>
<th>( h^2 + k^2 + l^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>110</td>
<td>2</td>
</tr>
<tr>
<td>111</td>
<td>3</td>
</tr>
<tr>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>210</td>
<td>5</td>
</tr>
<tr>
<td>211</td>
<td>6</td>
</tr>
<tr>
<td>220</td>
<td>8</td>
</tr>
<tr>
<td>221, 300</td>
<td>9</td>
</tr>
<tr>
<td>310</td>
<td>10</td>
</tr>
<tr>
<td>311</td>
<td>11</td>
</tr>
<tr>
<td>322</td>
<td>12</td>
</tr>
<tr>
<td>320</td>
<td>13</td>
</tr>
<tr>
<td>321</td>
<td>14</td>
</tr>
<tr>
<td>400</td>
<td>16</td>
</tr>
</tbody>
</table>

For the cubic system, the spacing between the atomic planes (d) and Miller indices k, h, l as illustrated in the following functions:

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (2)
\]

\[
d = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \rightarrow k = \frac{2a \sin(\theta)}{\sqrt{h^2 + k^2 + l^2}} \rightarrow \sin^2(\theta) = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \quad (3)
\]

\[
V = a^3 \quad (4)
\]

where a is the lattice parameter and V is the volume of the unit cell.

**Calculation of the sorption**

The amount of the sorption was calculated based on the initial \((C_0, \text{mg/L})\) and final concentration \((C_e, \text{mg/L})\) as follows (Dang et al., 2009; Tan. G. Q et al., 2009):

\[
q_e = \frac{C_0 - C_e}{M} V \quad (5)
\]

where \(q_e\) is the metal uptake capacity (mg/g), \(V\) is the volume of the CsCl solution (L) and \(M\) is the dry sorbent mass (g).

**Freundlich isotherm**

The Freundlich isotherm model (Freundlich, 1939) shows the adsorption process. This isotherm is an empirical equation and is expressed as follows in the linear form:

\[
\log q_e = \log K_F + \frac{1}{N} \log C_e \rightarrow q_e = K_F C_e^{1/N} \quad (6)
\]

where \(K_F\) is the Freundlich constant related to the bonding energy, \(1/n\) is the heterogeneity factor, and \(n\) (g/L) is a measure of the deviation from linearity of adsorption.

**Langmuir isotherm**

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The Langmuir isotherm model (Langmuir, 1918) presumes that monolayer adsorption occurs on a uniform surface with a finite number of adsorption sites. Once a site is filled, no other sorption can take place at that site. The function is as follows:

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

where \(K_L\) is the Langmuir constant related to the energy of adsorption and \(q_{\text{max}}\) is the maximum adsorption capacity (mg/g).

3. Results and discussions

3.1. The characteristics of \(\text{Cu}_2[\text{Fe(CN)}_6]\)

The XRD pattern was recorded to determine the structure of \(\text{Cu}_2[\text{Fe(CN)}_6]\) by using a Bruker D8 advance X-ray diffractometer with \(\lambda_{\text{CuK}\alpha} = 1.5406\text{Å}\). Fig. 1 shows the XRD pattern of \(\text{Cu}_2[\text{Fe(CN)}_6]\).

![XRD pattern of Cu_2[Fe(CN)_6] nanoparticle](image)

**Fig. 1.** XRD pattern of \(\text{Cu}_2[\text{Fe(CN)}_6]\) nanoparticle

To calculate some characteristics of \(\text{Cu}_2[\text{Fe(CN)}_6]\), the formulas (1) ÷ (4) is used. Table 2 shows the results.

| Peak # | 2θ  | d (Å) | 1/d² | h²+k²+l² | h | k | l | a (Å) | V = a³ |
|--------|-----|-------|------|---------|---|--|--|--|-------|-------|
| 1      | 15.27| 5.798 | 0.0297| 3       | 1 | 1 | 1 | 10.042| 1012.65|
| 2      | 17.65| 5.021 | 0.0397| 4       | 2 | 0 | 0 | 10.042| 1012.63|
| 3      | 25.06| 3.551 | 0.0793| 8       | 2 | 2 | 0 | 10.043| 1012.82|
| 4      | 29.59| 3.017 | 0.1099| 11      | 3 | 1 | 1 | 10.005| 1001.39|
| 5      | 35.77| 2.508 | 0.1590| 16      | 4 | 0 | 0 | 10.033| 1009.92|
| 6      | 40.12| 2.246 | 0.1983| 20      | 4 | 2 | 0 | 10.043| 1013.04|
| 7      | 44.17| 2.049 | 0.2382| 24      | 4 | 2 | 2 | 10.037| 1011.11|
| 8      | 51.61| 1.770 | 0.3194| 32      | 4 | 4 | 0 | 10.010| 1003.02|

For a cubic structure (Pearson, 1972), the result shows that \(\sin^2(\theta)\) follows in a ratio of 1, 2, 3, 4, 5, 6…, then the unit cell is likely primitive cubic. In this study, Table 2 shows that \(\text{Cu}_2[\text{Fe(CN)}_6]\) nanoparticle structures are primitive cubic.
3.2. The adsorption capacity

The total reflection X-ray fluorescence (TXRF) technique was carried out. This technique is popularly used in a qualitative and quantitative analysis of element compositions in solid, liquid, and gas samples. This study aimed to determine the concentration of Cs$^+$ before and after being absorbed in Cu$_2$[Fe(CN)$_6$] nanoparticles. The data obtained from Cs$^+$ ions onto Cu$_2$[Fe(CN)$_6$] nanoparticles shows that the contact time of 24 hrs. was sufficient to achieve the equilibrium. Therefore, the adsorbed Cs$^+$ concentrations ($C_e$, mg/L) and the uptake ($q_e$, mg/g) at the end of 24 hrs. are given as the equilibrium values. The volume of all samples is 0.05 liters, and the dry sorbent mass is 0.1g. Table 3 presents the results.

### Table 3. The ion Cs$^+$ absorbent by Cu$_2$[Fe(CN)$_6$]

<table>
<thead>
<tr>
<th>No.</th>
<th>Cs$^+$ ion initial concentrations (in mg/L), $C_0$</th>
<th>Cs$^+$ ion adsorbed concentrations (in mg/L), $C_e$</th>
<th>Cs$^+$ ion uptake capacity (in mg/g), $q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71.244</td>
<td>19.882</td>
<td>25.68</td>
</tr>
<tr>
<td>2</td>
<td>117.142</td>
<td>38.810</td>
<td>39.17</td>
</tr>
<tr>
<td>3</td>
<td>194.137</td>
<td>75.215</td>
<td>59.46</td>
</tr>
<tr>
<td>4</td>
<td>314.451</td>
<td>139.135</td>
<td>87.66</td>
</tr>
<tr>
<td>5</td>
<td>338.701</td>
<td>152.748</td>
<td>97.24</td>
</tr>
<tr>
<td>6</td>
<td>425.649</td>
<td>203.084</td>
<td>123.14</td>
</tr>
<tr>
<td>7</td>
<td>506.764</td>
<td>251.835</td>
<td>138.67</td>
</tr>
<tr>
<td>8</td>
<td>562.118</td>
<td>285.926</td>
<td>142.87</td>
</tr>
<tr>
<td>9</td>
<td>597.133</td>
<td>307.794</td>
<td>142.97</td>
</tr>
</tbody>
</table>

The present result shows that the effect of adsorbent concentration on the Cs$^+$ (%) removal at equilibrium conditions was investigated. The amount of Cs$^+$ varied with the adsorbent concentration. The amount of Cs$^+$ adsorbed increases with an increase in Cu$_2$[Fe(CN)$_6$] concentration from 71 to 560 mg/g, and the amount of Cs$^+$ was simply stable with Cu$_2$[Fe(CN)$_6$] concentration in the aqueous solution reaching over 560 mg/g.

Applying the equations (6) and (7), using data in Table 3, the Origin 8.5 software was employed for fitting. Table 4 shows the Freundlich constant, the heterogeneity factor, the Langmuir constant, and the maximum adsorption capacity.

### Table 4. $K_F$, $1/n$, $K_L$ and $q_{max}$ for Cs$^+$ sorption by Cu$_2$[Fe(CN)$_6$]

<table>
<thead>
<tr>
<th></th>
<th>$K_F$ (mg/g)</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich isotherm</td>
<td>3.950</td>
<td>0.635</td>
<td>0.989</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>270.48</td>
<td>0.00386</td>
<td>0.989</td>
</tr>
</tbody>
</table>
The experimental data was fitted by Origin 8.5 software. This result shows that the maximum adsorption capacity (q_{max-fit}) is 207.48 mg/g. The experimental data were analyzed by TXRF technique, the maximum adsorption capacity (q_{max-exp}) is 281.71 mg/g. The experimental data confirms the Langmuir isotherm model.

4. Conclusion
In this research, Cu_{2}[Fe(CN)_{6}] nanoparticle was synthesized. Cu_{2}[Fe(CN)_{6}] has the spacing the atomic plane (d) forms are between 1.770 to and 5.798 Å. The lattice parameter is around 10.040 Å. The analysis of Cu_{2}[Fe(CN)_{6}] of XRD pattern shows that Cu_{2}[Fe(CN)_{6}] has the primitive cubic structure. The integral values of the Miller indices h, k, and l are (111), (200), (220), (311), (400), (420), (422) and (440) respectively. This study also investigated Cu_{2}[Fe(CN)_{6}] nanoparticle to absorb Cs^{+} at room temperature and pH = 7 conditions. The effect of adsorbent concentration on the Cs^{+} (%) removal at equilibrium conditions was Cu_{2}[Fe(CN)_{6}] concentrated in the aqueous solution of over 560 mg/g, and the maximum adsorption capacity (q_{max-fit}) reaching 270.48 mg/g.

\[ q_e = 3.950C_e^{1/0.653} \]

\[ q_e = 0.00386*270.48*C_e/(1+0.00386*C_e) \]

**Conflict of Interest:** Authors have no conflict of interest to declare.

**REFERENCES**


TỔNG HỢP, ĐẠC TÍNH VÀ ỨNG DỤNG CỦA NANO Cu₂[Fe(CN)_6] TRONG HẤP PHỤ ION CESIUM (Cs⁺)
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TÓM TÂT
Trong nghiên cứu này, khả năng hấp thụ ion Cs⁺ từ dung dịch CsCl sử dụng hạt nano Cu₂[Fe(CN)_6] được quan tâm. Vật liệu nano Cu₂[Fe(CN)_6] đã được tổng hợp; phổ kếp hấp thụ của ion X (XRD) được dùng để phân tích các đặc trưng của Cu₂[Fe(CN)_6]; kỹ thuật huỳnh quang tia X phân xạ toàn phần được sử dụng để xác định khả năng hấp phụ. Một số đặc trưng của Cu₂[Fe(CN)_6] như: khoảng cách giữa các nút mảng nguyên tử (d), tham số mặt (a), và thế tích của các hạt nano đã được tính toán rõ ràng. Tắt cả các thực nghiệm thực hiện ở điều kiện pH = 7 và nhiệt độ phòng, đồng thời thay đổi nồng độ chất bị hấp phụ. Mô hình li thuyết dùng nhiệt Freundlich và Langmuir được sử dụng để xác định hệ số hỗn hợp của quá trình hấp thụ phần hấp thụ (1/n), và dùng phương pháp cực đại của ion Cs⁺ (q_max).

Từ khóa: tổng hợp; Cu₂[Fe(CN)_6]; nhiệt xạ tia X (XRD); ion Cesı (Cs⁺)