TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC SƯ PHẠM TP HỒ CHÍ MINH
Tập 17, Số 9 (2020): 1696-1702

HO CHI MINH CITY UNIVERSITY OF EDUCATION
JOURNAL OF SCIENCE
Vol. 17, No. 9 (2020): 1696-1702

ISSN:
1859-3100

Website: *http://journal.hcmue.edu.vn*

Research Article

SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF $Cu_2[Fe(CN)_6]$ NANOPARTICLE FOR THE ADSORPTION OF CESIUM ION (Cs^+)

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Received: February 07, 2020; Revised: September 04, 2020; Accepted: September 25, 2020

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.

Cite this article as: Le Thị Ha Lan, Nguyen An Son, Thach Thi Ngoc Tran, Nguyen Dinh Trung, Do Thi Le, & Nguyen Thi Phuc (2020). Synthesis, characterization, and application of $Cu_2[Fe(Cn)_6]$ nanoparticle for the adsorption of cesium ion (Cs^+). *Ho Chi Minh City University of Education Journal of Science, 17*(9), 1696-1702.

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 el at., 2009; Yang el 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

$K_4[Fe(CN)_6].3H_2O$, $CuCl_2.2H_2O$, 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 $K_4[Fe(CN)_6].3H_2O$ (Merck) aqueous solution and b) 750 ml 0.15 M $CuCl_2.2H_2O$ (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:

$2CuCl_2 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 4KCl$

$K_4[Fe(CN)_6]$ solid precipitate was filtered by a centrifuge machine, washed multiple times with distilled water until it reaches a neutral pH level, and dried at 70^0C 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 ^0C. The pH is maimed 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 (λ) of the reflected X-ray, the spacing between the atomic planes (d) and the angle of diffraction (θ) as follows:

$$2d sin\theta = k\lambda_{khl} \quad (1)$$

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*

Corresponding hkl	$h^2 + k^2 + l^2$
100	1
110	2
111	3
200	4
210	5
211	6
220	8
221, 300	9
310	10
311	11
222	12
320	13
321	14
400	16

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

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \qquad (2)$$

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

$$V = a^3 \qquad (4)$$

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, mg/L) and final concentration (C_e, mg/L) as follows (Dang et al., 2009; Tan. G. Q et al., 2009):

$$q_e = \frac{C_0 - C_e}{M} V \qquad (5)$$

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:

$$\log q_e = \log K_F + \frac{1}{N}\log C_e \rightarrow q_e = K_F {C_e}^{1/N} \qquad (6)$$

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

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:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \rightarrow q_e = \frac{K_L q_{max} C_e}{1+K_L C_e} \qquad (7)$$

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

3. Results and discussions

3.1. *The characteristics of $Cu_2[Fe(CN)_6]$*

The XRD pattern was recorded to determine the structure of $Cu_2[Fe(CN)_6]$ by using a Bruker D8 advance X-ray diffractometer with $\lambda_{CuK\alpha 1}$= 1.5406Å. Fig. 1 shows the XRD pattern of $Cu_2[Fe(CN)_6]$.

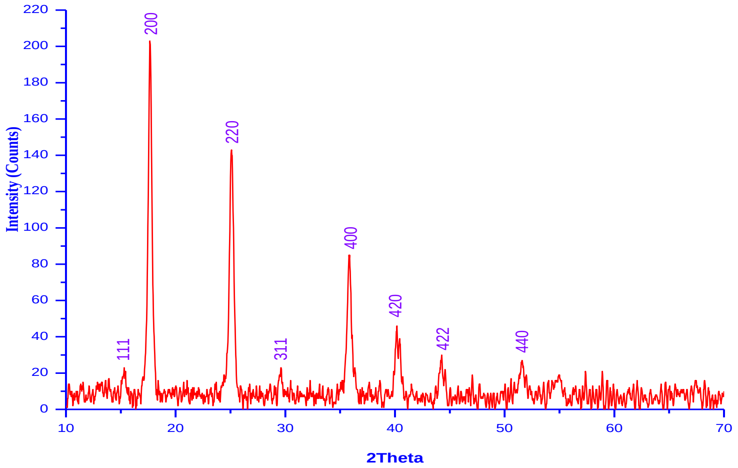

Fig. 1. *XRD pattern of $Cu_2[Fe(CN)_6]$ nanoparticle*

To calculate some characteristics of $Cu_2[Fe(CN)_6]$, the formulas (1) ÷(4) is used. Table 2 shows the results.

Table 2. *Assignment of Miller indices, the lattice parameter and volume of the unit cell*

Peak #	2θ	d (Å)	$1/d^2$	$h^2+k^2+l^2$	h	k	l	a (Å)	$V = a^3$
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 $Cu_2[Fe(CN)_6]$ 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 $Cu_2[Fe(CN)_6]$*

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

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 $Cu_2[Fe(CN)_6]$*

Freundlich isotherm			
The conditions:	K_F (mg/g)	1/n	R^2
room temperature, pH = 7	3.950	0.635	0.989
Langmuir isotherm			
The conditions: room	q_{max} (mg/g)	K_L (L/mg)	R^2
temperature, pH = 7	270.48	0.00386	0.989

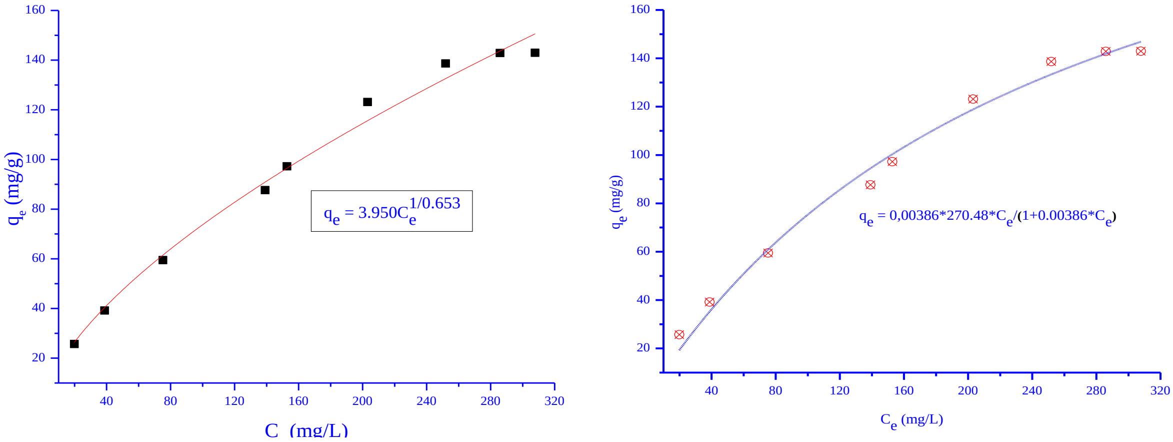

Fig. 2. *Freundlich isotherm (left) and Langmuir isotherm (right) for Cs^+ sorption onto $Cu_2[Fe\,(CN)_6]$ at room temperature and pH = 7*

The experimental data was fitted by Origin 8.5 software. This result shows that the maximum adsorption capacity ($q_{max\text{-}fit}$) is 207.48 mg/g. The experimental data were analyzed by TXRF technique, the maximum adsorption capacity ($q_{max\text{-}exp}$) 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 ($q_{max\text{-}fit}$) reaching 270.48 mg/g.

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

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TỔNG HỢP, ĐẶC TÍNH VÀ ỨNG DỤNG CỦA NANO $Cu_2[Fe(CN)_6]$ TRONG HẤP PHỤ ION CESIUM (Cs^+)

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Ngày nhận bài: 22-7-2020; ngày nhận bài sửa: 07-9-2020, ngày chấp nhận đăng: 25-09-2020

TÓM TẮT

Trong nghiên cứu này, khả năng hấp thụ ion Cs^+ từ dung dịch CsCl sử dụng hạt nano $Cu_2[Fe(CN)_6]$ được quan tâm. Vật liệu nano $Cu_2[Fe(CN)_6]$ đã được tổng hợp; phổ kế nhiễm xạ tia X (XRD) được dùng để phân tích các đặc trưng của $Cu_2[Fe(CN)_6]$; kĩ thuật huỳnh quang tia X phản xạ toàn phần được sử dụng để xác định khả năng hấp phụ. Một số đặc trưng của $Cu_2[Fe(CN)_6]$ như: khoảng cách giữa các nút mạng nguyên tử (d), tham số mạng (a), và thể tích của các hạt nano đã được tính toán rõ ràng. Tất 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 lí thuyết đẳng nhiệt Freundlich và Langmuir được sử dụng để xác định hệ số hỗn hợp của quá trình hấp thụ/ phản hấp thụ (1/n), và dung lượng hấp phụ cực đại của ion Cs^+ (q_{max}).

Từ khoá: tổng hợp; $Cu_2[Fe(CN)_6]$; nhiễm xạ tia X (XRD); ion Cesi (Cs^+)