

Application of Cobalt Hexacyanoferrate Coated Fe_3O_4 Nanoparticle for Cs^+ Adsorption

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1. Introduction

The nuclear industry has produced a lot of radioactive waste, which has a long half-life. ^{137}Cs is the main radioactive material derived from nuclear accidents and nuclear waste, accounting for 6.3% of the fission product.

Previous works have demonstrated zeolite, ammonium molybdophosphate (AMP), silicotitanate (CST), and ferrocyanide complexes to be a good cesium absorbent. In particular, ferrocyanide - transition metal complexes have been known as high selective absorbent for cesium. Dwivedi et al. used a gel composed of Cobalt hexacyanoferrate attached to Alginate with a micrometer size as an absorber to separate cesium from water.

Although ferrocyanide-transition metal complexes (FTMC) are selective towards cesium, the recovery and reusability of ferrocyanide-transition metal complexes are difficult in practical due to the dispersion of the particles in the solution. The deposition of ferrocyanide-transition metal complexes on different substrates is a promising method to solve this problem. Recently, nanoparticles for environmental monitoring and treatment have been used extensively. For example, Fe_3O_4 nanoparticle was exploited to remove toxic elements from the aqueous solution.

In this paper, the process of synthesis nanocomposite comprising cobalt hexacyanoferrate deposited on the surface of Fe_3O_4 nanoparticles is reported. The obtained nanocomposite is applied as cesium absorbent, and its adsorption capacity and mechanism are discussed.

2. Experiment Descriptions

2.1. Materials

In this study, standard solutions (Cs^+ (1000 mg/L), CsCl, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ of 99.99% purity (Merck) were mainly used, and also used are $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 25% NH_4OH solution, HNO_3 (0.01-0.1N), NaOH (0.01-0.1 N), among others.

2.2. Synthesis of Iron oxide nanoparticles (Fe_3O_4)

An aqueous solution containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with a molar ratio of 2:1 (filter out the solution if it precipitated) was added into a flask, bubbled by N_2 for 10 min, and heated up to 70°C in a ultra-sonifier. The above solution was dropwisely added to 25 mL of NH_4OH (25%). The temperature of the chemical reaction was maintained at 70°C with stirring speed of 1200 rpm. The reaction solution became dark green. After the products were separated by a magnet machine and rinsed several times by distilled water until neutral pH was obtained reaction completion.

2.3. Synthesis of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$

4g of as-prepared Fe_3O_4 nanoparticles were dispersed in 500 ml of CoCl_2 solution (0.01 M), which was dropwisely added by 250 mL of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution (0.1 M). The temperature of the reaction was maintained at 25°C and stirring speed of 1200 rpm was applied. After reaction, the dark brown product was separated from the reaction solution by a magnet machine, rinsed with distilled water, and dried at 600°C .

2.4. Analyses of synthetic materials

The elements in the materials were determined by total reflection X-ray fluorescence spectroscopy analysis (TXRF).

2.5. Determination of cesium adsorption capacity of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$

The pH of the solution (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0) was adjusted by using HNO_3 (0.01-0.1M) or NaOH (0.01-0.1M). After 24 hours of reaction, the absorbent material was separated by a magnet. The supernatant was centrifuged, filtered, and detected by TXRF.

2.6. Investigation on the reaction rate

The absorbed cesium content was based on the original and residual concentration of cesium in the solution with following formular:

$$q = \frac{V(C_i - C_e)}{B} \quad (1)$$

q is the amount of cesium absorbed (mg/g absorbent); C_i and C_e are Cs^+ concentrations before and after absorption, respectively; V is the volume of solution, and B is the mass of absorbent used.

Langmuir adsorption isotherm equation is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

q_e is the amount of Cs^+ absorbed by the material (mg/g absorbent), q_m is the maximum absorption capacity (MAC) of the Cs^+ , C_e is the initial concentration of the adsorption at time, b is the constant of the adsorption/desorption ratio.

Freundlich adsorption isotherm equation is given by:

$$q_e = K C_e^{1/n} \quad (3)$$

All samples of the absorbent material after adsorption experiments were washed several times by distilled water, dried at 60°C , were then detected by TXRF method. The Cs^+ concentration change in the solution can reveal the adsorption mechanism.

3. Results and discussion

The characterizations of materials were determined by PXRD and TEM. PXRD patterns of Fe_3O_4 , $\text{Co}_2[\text{Fe}(\text{CN})_6]$, and $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ are shown in Fig. 1.

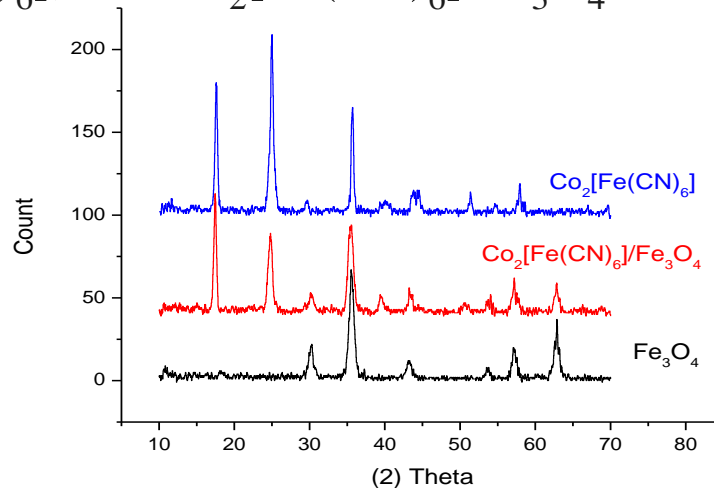


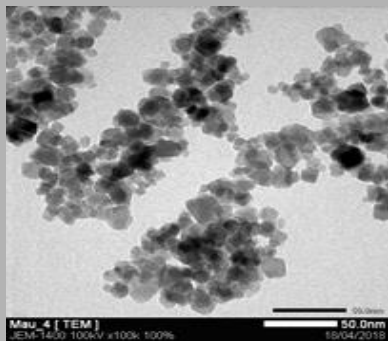
Fig. 1. PXRD patterns of Fe_3O_4 , $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$, and $\text{Co}_2[\text{Fe}(\text{CN})_6]$

The PXRD pattern of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ is clearly composed of both crystalline phases, illustrated by $\text{Co}_2[\text{Fe}(\text{CN})_6]$ ($2\theta = 18, 25, 37, 41, \text{ and } 44^\circ$) and Fe_3O_4 ($2\theta = 65^\circ$), which confirm the successful formation of the composite materials.

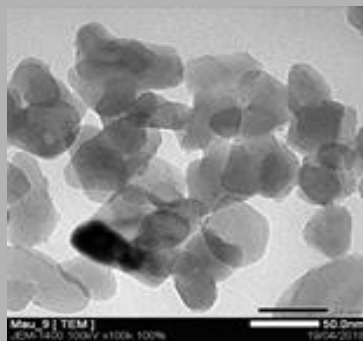
Determination of Fe_3O_4 and $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ by TXRF confirms that $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ is composed of several Fe_3O_4 nanoparticles. The molecular weight of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ is 329.8158 g/mol, and the elemental composition is shown in Table 1.

Table 1. Theoretical element composition of $\text{Co}_2[\text{Fe}(\text{CN})_6]$

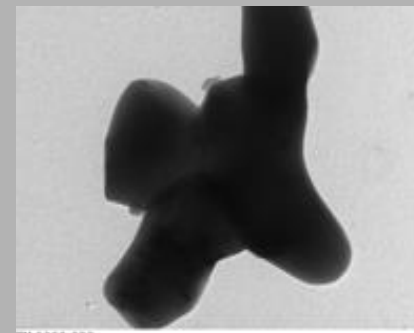
Elements	Molecular weigh	Stoichiometry	Weight percent (%)
Co	58.93	2	35.73
Fe	55.84	1	16.93
C	12.01	6	21.84
N	14.01	6	25.48



(a)



(b)



(c)

Fig. 2. TEM images of (a) Fe_3O_4 ; (b) $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$; (c) a high-magnification TEM image of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$

Based on the TEM image in Fig. 2, the increase in particle size upon the deposition of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ onto Fe_3O_4 nanoparticles is attributed to the aggregate of several Fe_3O_4 nanoparticles, and $\text{Co}_2[\text{Fe}(\text{CN})_6]$ plays a role as an outer covering layer. The $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ nano composite with the mean size of around 50 nm is used for further Cs^+ absorption studies.

The adsorption happened at 25°C and $\text{pH} = 5.0$, the results of the Cs^+ adsorbent on the materials are shown in Table 2. When the reaction reached the balance condition, the amount of Cs^+ absorbed in the solution was calculated by the formulas (1, 2, 3). The results showed that the process of the balance condition depended on the concentration of the original solution.

Table 2. The absorbed capacity of Cs⁺ by Co₂[Fe(CN)₆]/Fe₃O₄

(1)	30	35	40	45	50	55	60	65	70	75	80	85	90
(2)	46.52	48.11	49.04	50.11	50.24	51.70	51.57	52.10	52.90	53.30	53.43	53.29	53.37
(3)	0.35	0.36	0.37	0.37	0.38	0.39	0.39	0.39	0.4	0.4	0.4	0.4	0.4

(1): Cs⁺ concentration (mg/g)

(2): The absorbed capacity of Cs⁺ material (mg/g)

(3): The absorbed mili-equivalent of Cs⁺ material (meq/g)

Table 2 shows the experimental results, which are appropriate for the Langmuir and Freundlich adsorption isotherm models.

Table 3 and Fig. 3 show the parameters of the isothermal adsorption of Cs⁺ on Co₂[Fe(CN)₆]/Fe₃O₄ which are based on Langmuir and Freundlich adsorption isotherm models. MAC of materials based on Langmuir adsorption isotherm model was $q_m = 58.18$ mg/g, $R = 0.97$, and $b = 0.13$.

Table 3. The parameters of the Langmuir and Freundlich adsorption isotherm models for Cs^+ on $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ adsorption

The Langmuir adsorption isotherm model			
Ion adsorption	Q_m (mg/g)	b	R^2
Cs^+	58.18	0.13	0.97
The Freundlich adsorption isotherm model			
Ion adsorption	K(L/mg)	1/n	R
Cs^+	9.88	0.12	0.95

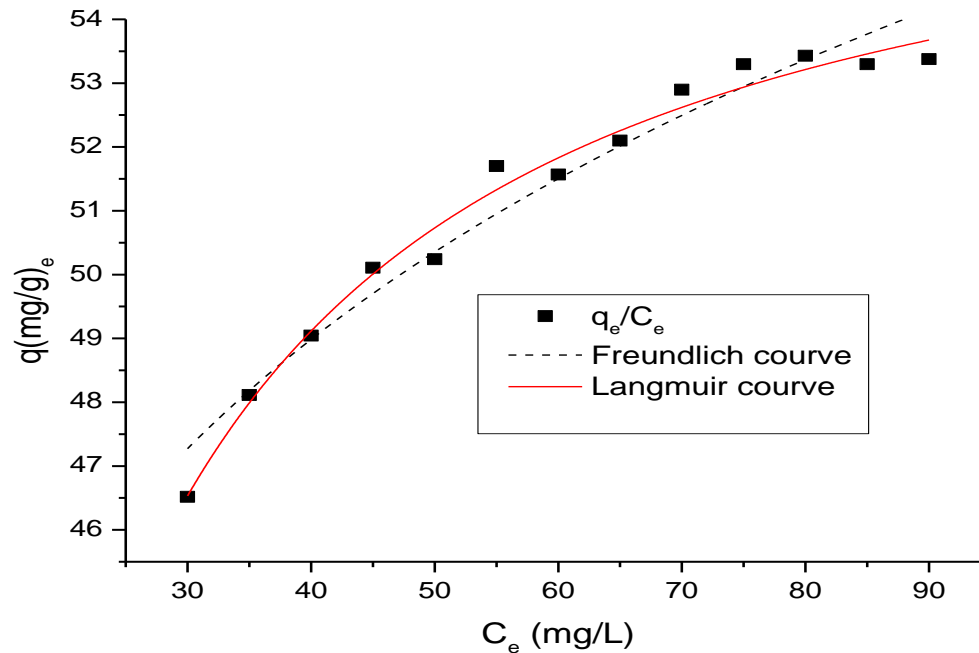


Fig. 3. Cs^+ adsorption isotherm by $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$

TXRF method was used for the analysis of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ sample which adsorbed Cs^+ . MAC reached 53.42 mg/g. MAC based on the Langmuir adsorption isotherm model is $q_{\text{max}} = 58.18$ mg/g, that is 4 units higher than the practical value ($q_{\text{exp}} = 53.42$ mg/g). The results show that Co^{2+} after adsorption decreased more than the original sample, and the reaction happened on the surface of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$.

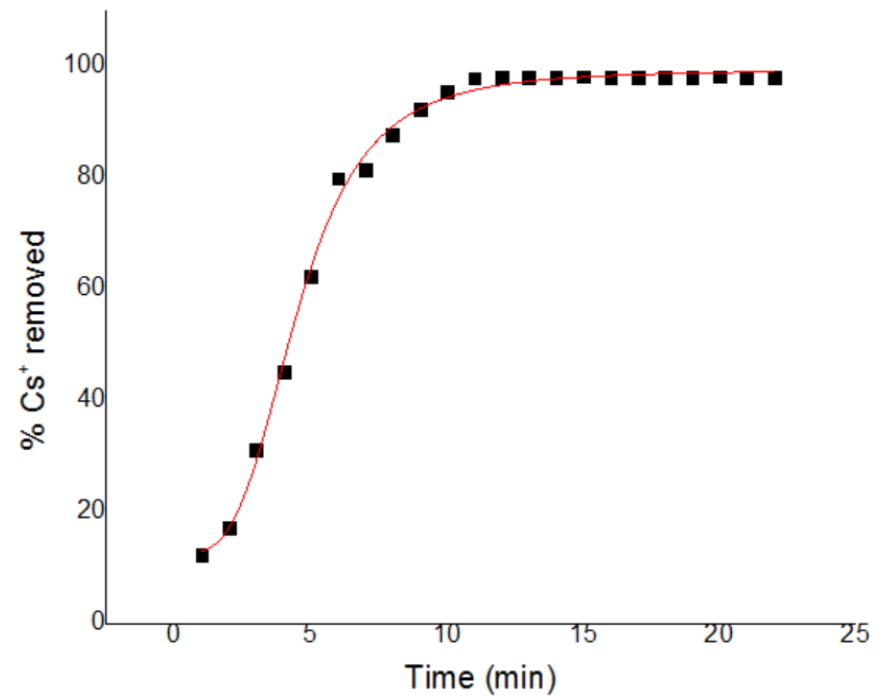
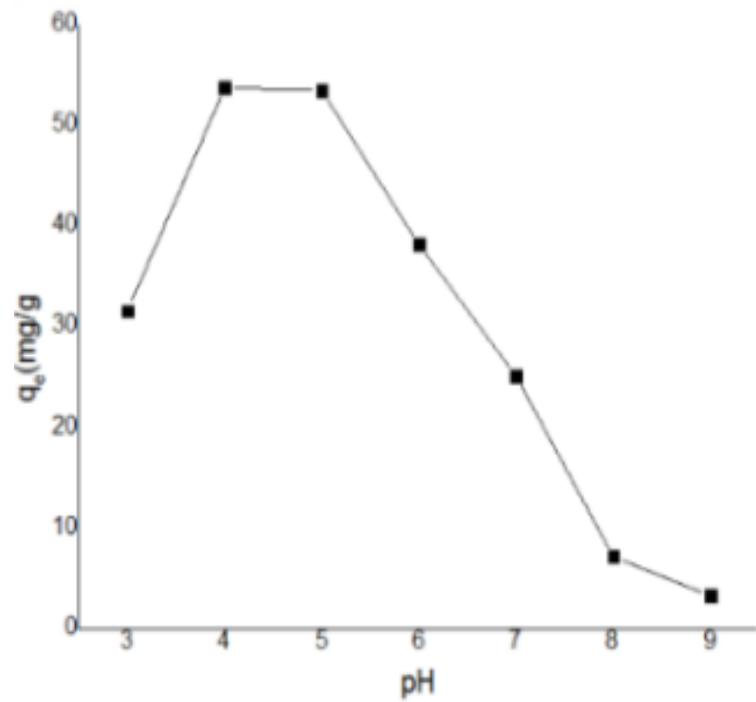


Fig. 4. The effective of pH and time on the absorption capacity of Cs^+ on $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$

After the reaction reached the balance condition, there were a corresponding change in the material of Cs^+ and Co^{2+} in the reaction. The absorbed mili-equivalent of Co^{2+} was created in solution $0.2 \text{ m}_{\text{eq}}/\text{mL}$. As we can see, there changed the appearance of Fe ion because it was diluted by the surface of the absorbent. The amount of Co^{2+} appeared in the solution corresponding to the losing of Cs^+ after the reaction while there weren't any Co^{2+} in the solution before the reaction.

4. Conclusions

The achievement of this study is successfully synthesize the $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$ material in nano size which can effectively absorb Cs^+ ion. $\text{Co}_2[\text{Fe}(\text{CN})_6]$ constitutes 20.56 % of the weight of $\text{Co}_2[\text{Fe}(\text{CN})_6]/\text{Fe}_3\text{O}_4$, which is paramagnetic material and easily separated from the solution by using magnet. The Cs^+ adsorption process of this material based on the ion structure exchange. The ion exchange process of this material occurred effectively at $\text{pH} = 4.0$. The maximum absorption capacity of the material at $\text{pH} = 4.0$ for ion Cs^+ was 0.40 meq/g, and around 98% of initial Cs^+ concentration was removed.

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