

Solvothermal synthesis and characterization of magnetic Fe_3O_4 nanoparticle by different sodium salt sources

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Four different magnetic Fe_3O_4 nanoparticles were synthesized and characterized by solvothermal method based on different sodium salts. Sodium salts which were used to synthesize the nanoparticles were NaOAc, Na_2CO_3 , a mixture of NaOAc and Na_3Cit , and a mixture of NaOAc and $\text{Na}_2\text{C}_2\text{O}_4$. The structural and optical properties of the synthesized nanoparticles were examined by XRF, XRD, SEM and FT-IR. The results estimated from XRD pattern and SEM image indicated that the second sample (Na_2CO_3) had the lowest average particle and crystallite size around 29 nm and 43 nm. It was also shown that the first (NaOAc) and second (Na_2CO_3) samples had the best FT-IR spectra, similar to the available commercial sample which was provided by Merck. At last, the prepared Fe_3O_4 nanoparticles were applied as sorbents to sorb uranium ions (U(VI)) from radioactive wastewater. The adsorption results showed that the highest U(VI) adsorption was obtained for the second sample in the solution with pH around 10.

Keywords: *magnetic Fe_3O_4 nanoparticle; solvothermal synthesis; sodium salt sources; uranium adsorption*

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1. Introduction

Magnetic Fe_3O_4 nanoparticles as a kind of magnetic nanoparticle material have attracted significant interest due to their unique magnetic properties and feasibility of preparation [1]. The preparation feasibility of Fe_3O_4 nanoparticles is one of the key advantages of the magnetic nanoparticles. Using an external magnetic field can lead to easy and rapid separation of the Fe_3O_4 particles from their matrix or solution [2, 3]. Other advantages of the magnetic Fe_3O_4 nanoparticles, including scalable and non-toxic synthesis and economical and efficient properties, are the other reason to consider Fe_3O_4 nanoparticles for potential applications and fundamental research [1, 4, 5]. Magnetic Fe_3O_4 nanoparticles are supposed to be the main potential adsorbent for toxic and radioactive heavy metals such as Cu, Cr, Cd, Ni, As, Pb, and U, because of their good chemical and mechanical stability, high surface area and the unique advantage of easy separation [1, 4, 6–9]. Today, these nanoparticles are frequently used for removing heavy-metals from

wastewater because of their high adsorption capacity for heavy-metal ions and organic pollutants [4]. The studies have shown that the higher adsorption capacity to remove metals can be achieved by the magnetic Fe_3O_4 nanoparticles with high ratio of surface-to-volume which is known as the finite-size effect [1, 4].

Although magnetite nanoparticles with different properties were prepared by many authors, they still inspire researchers to improve their characteristics by which a great significance in different fields can be obtained [10, 11]. There are several methods to synthesize nanostructured magnetic materials usually by co-precipitation, sol-gel method, thermal decomposition of organometallic compounds, hydrothermal synthesis, etc. [12–16]. The hydrothermal or solvothermal method is well-established to synthesize many nanoparticle materials such as magnetite Fe_3O_4 nanoparticles. However, the kinetics is typically slow because of relatively low temperatures which are used in the experiment [2]. The first magnetite Fe_3O_4 microspheres (200 nm to 800 nm) were synthesized by the solvothermal method in the ethylene glycol (MEG) in 2005 [17].

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Wang et al. [8] synthesized water-soluble Fe₃O₄ nanoparticles as adsorbents to remove heavy metals from waste water by a hydrothermal approach. The synthesized nanoparticles had high solubility and appropriate stability (at least for one month). They also showed excellent removal ability. Chen et al. [12] studied different parameters which influence the solvothermal synthesis of Fe₃O₄ microspheres in monoethylene glycol (MEG). They successfully synthesized 0.34 μm magnetic Fe₃O₄ microspheres. They also prepared EDTA-modified Fe₃O₄ microspheres as a potential magnetic adsorbent to remove heavy metals from waste water. Li et al. [2] used the microwave-solvothermal method to synthesize Fe₃O₄ magnetic nanoparticles in a simple reaction system. They succeeded in synthesizing Fe₃O₄ magnetic nanoparticles during a considerably shorter time than the other traditional methods such as solvothermal or hydrothermal methods. Also, Shen et al. [4] conducted research on the synthesis of magnetite Fe₃O₄ nanoparticles to remove Cd²⁺, Cr⁶⁺, Cu²⁺ and Ni²⁺ from waste water. They provided the magnetic Fe₃O₄ nanoparticles with different sizes.

Herein, we synthesized and characterized magnetite Fe₃O₄ nanoparticles by solvothermal method based on different sodium salts. The prepared Fe₃O₄ nanoparticles were applied as sorbents to sorb U(VI) ions from radioactive wastewater. The batch sorption technique was used to assess the absorbability of magnetite Fe₃O₄ nanoparticles from the wastewater.

2. Experimental

2.1. Chemicals

Iron source and solvent which were used in this study, were FeCl₃·6H₂O and MEG, respectively. To study the effect of anions on the characteristics of the synthesized magnetite Fe₃O₄ nanoparticles, different sodium salts were used including CH₃COONa (NaOAc), Na₂CO₃, trisodium citrate dihydrate (Na₃Cit), sodium oxalate (Na₂C₂O₄). To study uranium adsorption, 1000 ppm uranium standard (UO₂(NO₃)₂) was also used to prepare a sample solution. All chemicals were purchased from

Merck Co. The uranium adsorption experiments were performed to perform a comparative study of uranium adsorption by different sodium salts based synthesized magnetite Fe₃O₄ nanoparticles. The adsorbent concentration in all adsorption test was 1g/L and uranium aqueous solution concentration was 50 ppm. A 50 ppm aqueous uranium solution was prepared by diluting 25 mL of 1000 ppm uranium standard (UO₂(NO₃)₂, 1000 ppm) in deionized water (500 mL). The adsorption experiments were carried out by using the batch method. Negligible volumes of diluted nitric acid or sodium hydroxide solution were used to adjust the solution pH.

2.2. Procedures of synthesizing magnetite Fe₃O₄ nanoparticles in MEG

Firstly, a yellow solution was prepared by dissolving 4 g FeCl₃·6H₂O in 10 mL MEG. The process was followed by adding an appropriate amount of each basic sodium salt or a mixture of two of them. Then, the resulted mixture was vigorously stirred for about 30 min to 60 min to homogenize it. After that, the final solution was transferred to a Teflon-lined autoclave with a stainless-steel cover. The solution was heated in the autoclave at temperature of 200 °C for 24 h. Then, the resultant product was cooled to room temperature (RT). The final black product was separated by centrifugation, washed in water and ethanol, and dried at 70 °C in vacuum environment for 4 h.

2.3. Characterization

Four available systems, XRF, XRD, SEM and FT-IR were used to characterize and compare the synthesized magnetite Fe₃O₄ nanoparticles. XRD, Bruker D8 Advance diffractometer was used to collect XRD patterns at 30 kV and 20 mA, and CuKα radiation (λ = 0.1540598 nm). The particle sizes of synthesized nanoparticles were measured by FE-SEM (HITACHI S-4160). The crystallite size of the synthesized magnetic Fe₃O₄ nanoparticles was estimated based on the Scherrer equation by using X-ray line broadening method [18]. Bruker Optics TENSOR 27 FT-IR spectrometer was also used to record FT-IR spectra of synthesized samples.

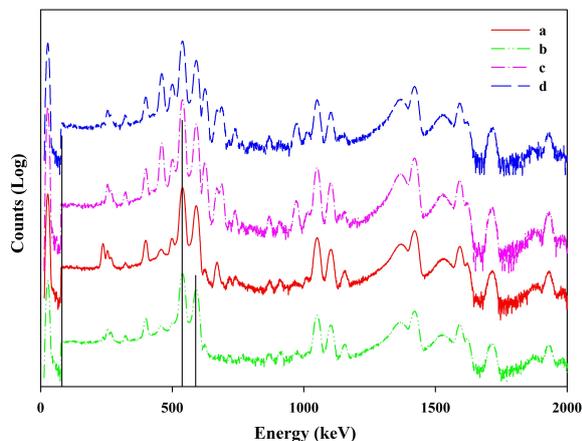


Fig. 1. XRF patterns of magnetite Fe_3O_4 nanoparticles synthesized by different sodium salts (a) Na_2CO_3 , (b) NaAc, (c) NaAc-CIT and (d) NaAc-oxallat.

2.4. Adsorption tests

Uranium adsorption experiments were performed by preparing 50 ppm aqueous uranium solutions with various solution pH. The uranium concentrations were determined before treatment and after 2.5 hours. The percent of metal removal [%] was calculated using the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is the initial uranium concentration and C_e is the uranium concentration at equilibrium, after treatment with synthesized Fe_3O_4 nanoparticles [7].

3. Results and discussion

One of the important parameters which has a significant influence on the synthesis of magnetite Fe_3O_4 nanoparticles is the effect of anions of sodium salts [12]. In general, the synthesis of magnetite Fe_3O_4 nanoparticles from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is affected by coordination ability (e.g., CH_3COO^- , CO_3^{2-}) of sodium salts. The anions with the weaker coordination ability usually promote the synthesis. In order to synthesize magnetic Fe_3O_4 nanoparticles from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the adequate amount of OH^- ions should be provided to reduce Fe^{3+} by MEG. However, the anions with stronger

coordination ability, such as oxalate and citrate, are not appropriate for the synthesis of magnetite Fe_3O_4 nanoparticles in MEG. In this case, stable Fe^{3+} complexes are formed which inhibit $\text{Fe}(\text{OH})_3$ formation and reduce Fe^{3+} by MEG, and consequently prevent the formation of magnetite Fe_3O_4 nanoparticles in MEG. So, for the Fe_3O_4 nanoparticles, synthesis by the anions with stronger coordination ability, extra base, such as NaOH, and NaOAc, is still required [12]. In this study, different sodium sources, including CH_3COONa (NaOAc), Na_2CO_3 , trisodium citrate dihydrate (Na_3Cit), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) were used to synthesize magnetite Fe_3O_4 nanoparticles. The experimental results showed that the solution provided by trisodium citrate dihydrate (Na_3Cit) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) separately did not lead to the synthesis of magnetic Fe_3O_4 nanoparticles. Four types of magnetic Fe_3O_4 nanoparticles were synthesized by using different sodium additions, including (1) CH_3COONa (NaOAc), (2) Na_2CO_3 , (3) mixture of NaOAc and trisodium citrate dihydrate (Na_3Cit), and (4) mixture of NaOAc and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$). The XRF analysis of the four synthesized nanoparticle types indicated that Fe–O contribution in the samples was 85 % to 92 %. The XRF patterns of the four synthesized magnetic Fe_3O_4 nanoparticles are shown in the Fig. 1. As shown in the figure, the characteristic lines of Fe–O contributions are related to three important lines of Fe: K-Alpha, Fe, L-Alpha and Fe, K-Beta. The other peaks in the XRF patterns are related to the other X-ray fluorescence which comes from the X-ray source. The amounts of different sodium sources which were used to synthesize Fe_3O_4 in the four sample types were: (1) 3.642 g of NaOAc, (2) 2.35 g of Na_2CO_3 , (3) 2.73 g of NaOAc and 1.088 g of Na_3Cit , and (4) 2.73 g of NaOAc and 0.745 g of $\text{Na}_2\text{C}_2\text{O}_4$. The amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and MEG were 4 g and 10 mL in all the sample solutions, respectively. Their values were calculated based on optimum Na/Fe molar ratio, which was 3:1 [12]. The experimental results indicated that the sodium sources with anions of stronger coordination ability, such as oxalate and citrate, are not appropriate for the synthesis of magnetic Fe_3O_4 nanoparticles in MEG.

Fig. 2 shows the XRD patterns of the four synthesized magnetite Fe₃O₄ nanoparticles. The observed characteristic peaks are (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (6 2 2). These peaks are the most important peaks which confirm that the resultant particles are pure Fe₃O₄. They were observed for the Sample 1 (NaOAc) at the diffraction angles of $2\theta = 18.34^\circ, 30.15^\circ, 35.5^\circ, 43.13^\circ, 53.49^\circ, 56.99^\circ, 62.57^\circ, 70.97^\circ, 74.03^\circ$, respectively. The peak positions for the other samples are listed in the Table 1. As can be seen, their position and intensities of almost all of peaks are well matched to those of the other experimental results and the standard PDF Cards for Fe₃O₄ nanoparticles (JCPDS Card No. 19-0629) [19–22]. The synthesized samples are in a good agreement with the other experiments [16, 23, 24]. There is an additional peak between (1 1 1) and (2 2 0) in the XRD pattern of NaAc-oxalate, which can be due to the Fe₂O₃ or alpha-Fe₂O₃ particles in the synthesized magnetic Fe₃O₄ nanoparticles [21, 22]. It can be one of the most important reasons that the synthesized magnetic Fe₃O₄ nanoparticles based on NaAc-oxalate have the lowest uranium adsorption. The results show a slight variation in the peak positions for different samples which can be due to their structure formation.

The microstructures of the synthesized magnetic Fe₃O₄ particles were also characterized by SEM. Fig. 3 shows the SEM images for the four synthesized magnetic Fe₃O₄ particles. The SEM images show that the synthesized products are composed of spherical nanoparticles which have the minimum average diameter of about 45 nm for sample 2 (Na₂CO₃) and the maximum average diameter of about 190 nm for sample 1 (NaAc).

A comparative study which can be done on the basis of XRD patterns is determination of the average crystallite size of different synthesized samples. The average crystallite size (D_{hkl}) of magnetite Fe₃O₄ nanoparticles is estimated by the Scherrer equation as below:

$$D_{hkl} = 0.89\lambda / \beta \cos \theta \quad (2)$$

Here, β is the full-width at half-maximum (FWHM) of XRD diffraction lines, the wavelength

$\lambda = 0.1540598$ nm and θ is the half diffraction angle of 2θ [10, 17, 23]. The estimated average crystallite sizes of the synthesized magnetite Fe₃O₄ nanoparticles for the (3 1 1) diffraction peak are 48.42 nm, 29.06 nm, 29.61 nm, and 48.4 nm for sample 1 to sample 4, respectively. The average crystallite size for the other peaks have been calculated and summarized in Table 1. As can be seen, sample 2 (Na₂CO₃) has approximately the lowest average crystallite size in the almost all of the peaks. The XRD pattern of sample 2 is shown in the Fig. 2b.

Fig. 4(a) shows the FT-IR spectra for different synthesized magnetite Fe₃O₄ nanoparticles. The spectra illustrate a broad band around 580 cm⁻¹, which is associated with the stretching vibrations of F–O bond (ν_1) or the tetrahedral groups (Fe³⁺–O²⁻) in Fe₃O₄. Also the peak at about 390 cm⁻¹ is observed, which belongs to ν_2 of the Fe–O bond of the bulk magnetite. The results show that the FT-IR spectra of sample 1 and sample 2 are in a good agreement with the available commercial sample. The FT-IR spectrum of sample 2 is also shown in the Fig. 4(b). There are also the broad bands at around 1630 cm⁻¹ and 3436 cm⁻¹ in the spectrum, which correspond to the H₂O molecules or O–H adsorbed on the surface of Fe₃O₄ [8, 16, 25].

Uranium adsorption by different synthesized magnetite Fe₃O₄ nanoparticles as a function of the solution pH is shown in the Fig. 5a. As shown in this figure, the best uranium adsorption is obtained for sample 2 at the solution pH around 10. It can be due to its lowest average particle size. The adsorption of U(VI) by Fe₃O₄ was greatly affected by the solution pH. The adsorption increased from about 5 % to 85 % when the pH value increased from 2.0 to 10.0. The results also indicate that the optimum solution pH is different for various samples. Based on Fig. 5, the graph can be divided into three parts, (1) pH between 1 and 6, (2) pH between 6 and 10, (2) pH higher than 10. In part 1, in which the solution pH is lower than 6, UO₂²⁺ is the dominant species of uranium ions in the solution which have to compete with the high abundance of H⁺ and H₃O⁺ ions for the binding sites

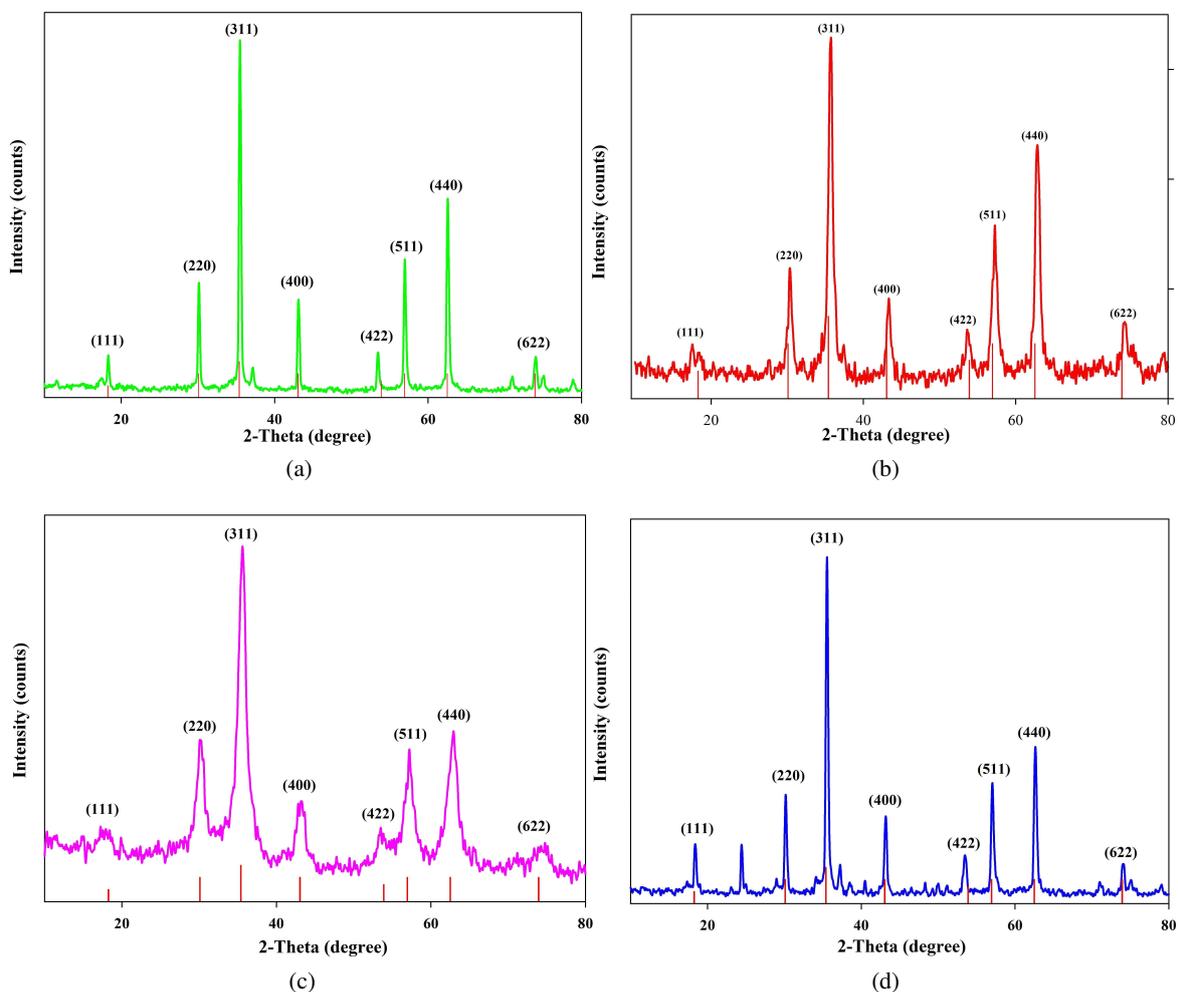


Fig. 2. Powder X-ray diffraction (XRD) patterns of magnetite Fe_3O_4 nanoparticles: (a) NaAc as sodium salt, (b) Na_2CO_3 which shows the lowest average crystallite size, (c) NaAc-Cit and (d) NaAc-oxallat. The red bars represent the standard pattern of Fe_3O_4 (PDF Card No. 19-0629).

Table 1. Crystallite size values of magnetite Fe_3O_4 nanoparticles synthesized by different sodium salts for different peaks.

h k l	$D_{hkl} = \text{Calculated crystallite size [nm]}$											
	Sample 1			Sample 2			Sample 3			Sample 4		
	2 θ	FWHM	D_{hkl}	2 θ	FWHM	D_{hkl}	2 θ	FWHM	D_{hkl}	2 θ	FWHM	D_{hkl}
(1 1 1)	18.34	0.18	46.72	17.52	0.30	28	17.35	0.30	27.99	18.41	0.18	46.72
(2 2 0)	30.15	0.12	71.64	30.36	0.24	35.84	30.19	0.24	35.82	30.18	0.12	71.65
(3 1 1)	35.50	0.18	48.42	35.60	0.30	29.06	35.61	0.30	29.61	35.55	0.18	48.43
(4 0 0)	43.13	0.18	49.59	43.32	0.30	29.77	43.20	0.30	29.76	43.19	0.30	29.76
(4 2 2)	53.49	0.18	51.64	53.68	0.18	51.67	53.52	0.18	51.64	53.52	0.30	30.99
(5 1 1)	56.99	0.12	78.7	57.27	0.24	39.40	57.24	0.24	39.40	57.06	0.12	78.73
(4 4 0)	62.57	0.12	80.93	62.86	0.24	40.53	62.90	0.24	40.54	62.65	0.24	40.48
(6 2 0)	70.97	0.18	56.63	71.39	0.30	34.06	71.18	0.12	85.05	71.03	0.18	56.65
(6 2 2)	74.03	0.24	43.31	74.33	0.24	43.39	74.56	0.24	43.46	74.08	0.12	86.64

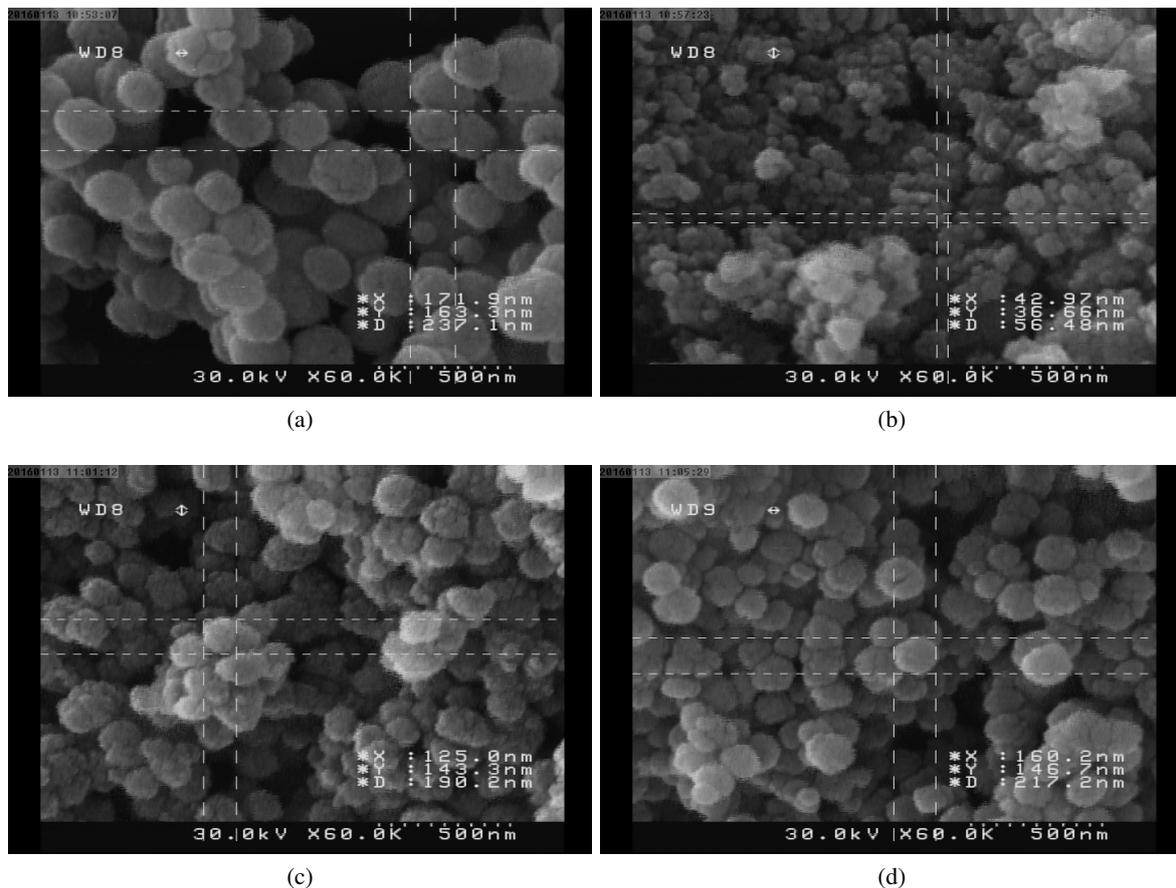


Fig. 3. SEM images of the synthesized magnetic Fe₃O₄ particles: (a) NaAc, (b) Na₂CO₃, (c) NaAc-CIT, and (d) NaAc-oxallat.

on the adsorbent surface. In part 2, in which solution pH is between 6 and 10, the uranium adsorption increases greatly due to fewer H⁺ and H₃O⁺ ions, and also higher number of adsorptive sites for uranium ions. However, when pH values are higher than 10 (part 3), the amount of uranium ions adsorbed decreases with increasing pH. This is due to the repulsion of the anions (UO₂(OH)₃⁻ and UO₃(OH)₇⁻, which is caused by the hydrolysis of U(VI) to the negatively charged surface of Fe₃O₄ at high pH [1, 26]. Fig. 5b shows the main extraction of Fe₃O₄ nanoparticles dispersion in the solution and separation by an external magnetic field.

The sorption isotherms of uranium ions onto magnetite Fe₃O₄ nanoparticles synthesized based on Na₂CO₃ as the selected sodium salt, are shown in the Fig. 6. The experimental results were

simulated by the Langmuir and Freundlich models. Langmuir model:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{C_e} \quad (3)$$

where q_e is the equilibrium adsorption of uranium ions, in mg/g, C_e is the equilibrium concentration of ions, in mg/L, q_m is the maximum adsorption capacity, in mg/g and K_L is the Langmuir constant which is related to the energy of adsorption.

Freundlich model:

$$\ln(q_e) = \ln(K_F) + \left(\frac{1}{n}\right) \ln(C_e) \quad (4)$$

where q_e is the amount of uranium sorbed on Fe₃O₄, in mg/g, C_e is the equilibrium concentration of uranium ions in mg/L, K_F (mg¹⁻ⁿ·Lⁿ/g)

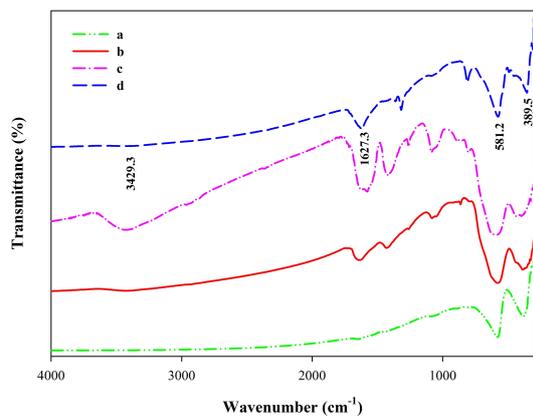
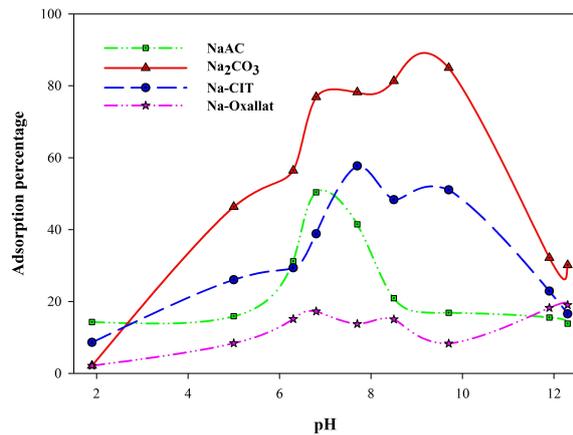
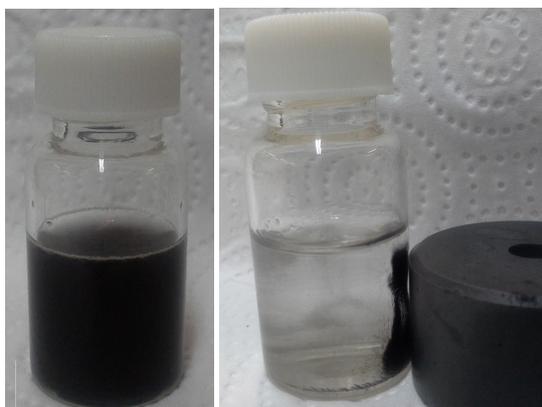


Fig. 4. FT-IR spectra of magnetite Fe_3O_4 nanoparticles: (a) NaAc sodium salts, (b) Na_2CO_3 , (c) NaAc-Cit, (d) NaAc-oxallat.

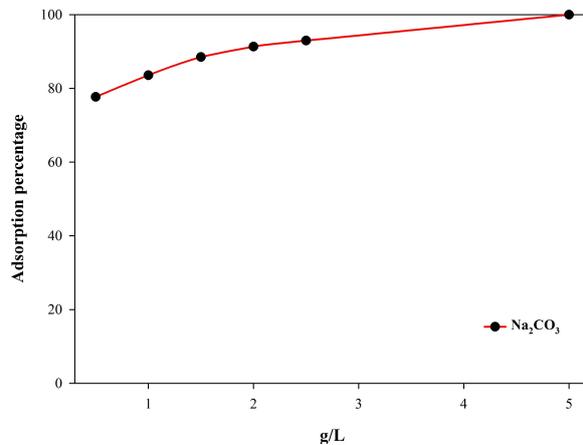


(a)

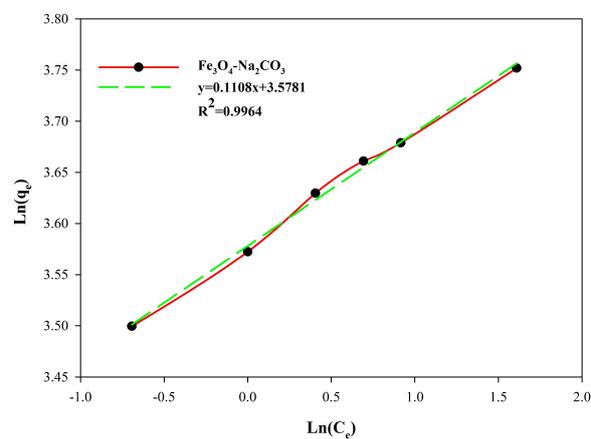


(b)

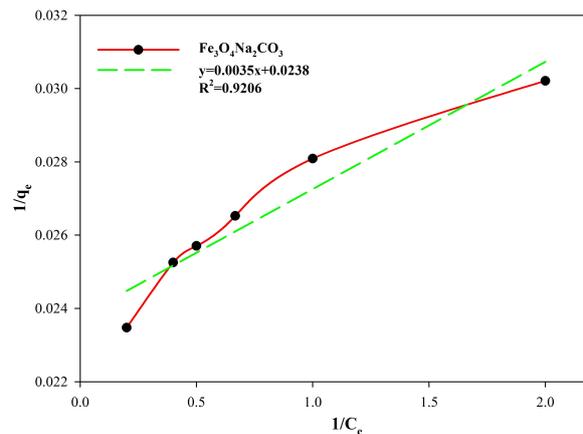
Fig. 5. (a) Effect of solution pH on uranium adsorption efficiency by different magnetite Fe_3O_4 nanoparticles, and (b) photographs of Fe_3O_4 dispersion and magnetic separation.



(a)



(b)



(c)

Fig. 6. (a) Adsorption percentages, (b) Freundlich and (c) Langmuir isotherms for the adsorption of uranium ions onto magnetite Fe_3O_4 nanoparticles synthesized based on the Na_2CO_3 as the selected sodium salt.

is the sorption capacity of the equilibrium concentration of ions when it equals 1, and n is the degree of dependence of sorption on equilibrium concentration. The results show that the Freundlich model fits the uranium ion sorption isotherms better than Langmuir model, which indicates that multilayer sorption occurred. This model has the best fit for the aqueous solution with low uranium concentration [16, 27].

4. Conclusions

In this study, the magnetic Fe₃O₄ nanoparticles were synthesized successfully by the solvothermal method. The nanoparticles were synthesized by four different sodium sources including (1) CH₃COONa (NaOAc), (2) Na₂CO₃, (3) mixture of NaOAc and trisodium citrate dihydrate (Na₃Cit), and (4) mixture of NaOAc and sodium oxalate (Na₂C₂O₄). The structural and optical properties of the synthesized magnetic Fe₃O₄ nanoparticles were examined by XRF, XRD, SEM and FT-IR at room temperature. The SEM and XRD patterns indicated that using Na₂CO₃ as sodium salt lead to obtaining the lowest average particle and crystallite size around 43 nm and 29 nm, respectively. The adsorption test showed that magnetic Fe₃O₄ nanoparticles are a suitable adsorbent for removal U(VI) from aqueous solutions and the best adsorption result was achieved for sample 2 at solution pH around 10.

Acknowledgements

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