Theoretical and experimental studies on uranium(VI) adsorption using phosphine oxide-coated magnetic nanoadsorbent

Zeinab F. Akl

In this study, novel Cyanex-923-coated magnetite nanoparticles (Fe₃O₄@Cyanex-923) were prepared, comprehensively characterized, and employed for uranium(VI) ion adsorption from aqueous solutions. FTIR and TGA data confirmed that Fe₃O₄ has successfully gained Cyanex-923 surface functionality. Particle size and morphological studies via DLS, HR-TEM, and SEM showed uniform-dispersed quasi-spherical nanoparticles with a mean diameter of ca. 44 nm. Magnetism measurement data revealed the superparamagnetic properties of the Fe₃O₄@Cyanex-923 nanoadsorbent. The effect of different experimental conditions on the adsorption efficiency was studied to determine the best operational conditions. The experimental results were analyzed using Langmuir, Freundlich, and Temkin isotherms; where the adsorption data obeyed the Langmuir model showing a theoretical adsorption capacity of 429.185 mg g⁻¹ at 298 K. Kinetics data analysis revealed a fast adsorption process that could reach equilibrium within 60 min and is well-fitted to the pseudo-2nd-order model. Temperature affected the adsorption process and the thermodynamic data indicated that uranium(VI) adsorption was spontaneous and exothermic. Fe₃O₄@Cyanex-923 nanoparticles displayed a good regeneration behavior over three sequential adsorption–desorption cycles. The Fe₃O₄@Cyanex-923 nanoadsorbent showed a high uranium adsorption capacity, fast equilibration time, economic nature, good reusability, and easy separation; making it a promising candidate for uranium(VI) removal from nuclear waste streams.

1. Introduction

The magnetic separation technique is one of the most recognized and widely used methods for water and wastewater treatment.¹ The process involves contaminant attachment onto a magnetic material’s surface followed by separation of the contaminant-laden material via an externally employed magnetic force.² Magnetic adsorbents have continuously received growing attention due to their numerous advantages including fabrication simplicity, cost-effectiveness, high adsorption capacities, rapidness, and convenience.³ Their facile and economic separation from the aqueous solutions via applying a magnetic field makes them feasible materials for efficient and sustainable adsorption processes.⁴ Thus, the utilization of magnetic adsorbents can lead to a simple, environmentally-friendly, time-saving, and cost-effective adsorption process as it evades the filtration and centrifugation steps while the magnetic adsorbent can be easily collected and reused.⁴

Among magnetic iron oxides, magnetite (Fe₃O₄) is widely investigated for the environmental remediation as well as other numerous applications including biomedicine, sensors, catalysis, energy storage devices, and magnetic resonance imaging.⁵ Owing to their inexpensive production strategy, availability, physiochemical properties, nontoxic character, ease of modification, biocompatibility, ecological suitability, stability, superparamagnetism, recoverability, and recyclability; Fe₃O₄-based adsorbents have a considerable potential for removing a wide range of organic and inorganic contaminants from water streams.⁶ The nanoscale dimension of Fe₃O₄ can be developed leading to an enhanced performance under various environmental circumstances.⁷ The high surface area of Fe₃O₄ nanoparticles along with their susceptibility to the magnetic fields; have made them attractive materials for efficient removal of water impurities.⁸

Uranium is the most common naturally occurring radionuclide that possesses different forms and oxidation states.⁹ Excessive uranium quantities are discharged to the environment from many anthropogenic activities e.g., mining, milling, spent fuel reprocessing, improper nuclear waste management, nuclear testing, nuclear accidents, and phosphate fertilizers industry.⁹ Such activities increase the potential of uranium contamination in natural waters (ground and surface water) that may be adsorbed and concentrated by plants and consequently reach the food chain.⁹ Accordingly, uranium would hand over to humans and could finally accumulate in various organs to cause acute or chronic health problems; such as
tubular necrosis, skin corrosion, leukemia, bone cancer, kidney failure, liver or brain damage, and even death. As a result, uranium removal from water streams has become one of the main environmental remediation issues nowadays.

Various technologies have been applied to remove uranium from contaminated water, nevertheless; adsorption is considered an effective method that has gained wide interest among the nuclear industry scientists. Over the last decades, developing efficient uranium adsorbents has been a research focus. Numerous organic and inorganic materials have been developed and assessed for their affinity towards uranium such as amidoxime-based,\textsuperscript{16} carbon-based,\textsuperscript{17} biochar-based,\textsuperscript{18,19} metal organic frameworks-based,\textsuperscript{20} covalent organic frameworks-based composites\textsuperscript{21,22} and nanocomposites.\textsuperscript{23} Among them, nanometric scale adsorbents are of particular concern due to their inimitable properties, as they have high specific surface area, elevated reactivity, high adsorption efficiency and capacity, fast adsorption rate, and acceptable reusability. In this context, diverse nanomaterials have been developed to remove uranium from aqueous media, including carbon nanotubes,\textsuperscript{24} graphene nanocomposites,\textsuperscript{25} nanoscale zero-valent iron,\textsuperscript{26} and functionalized Fe\textsubscript{3}O\textsubscript{4} nanoparticles.\textsuperscript{27}

During the last decades, bare and coated Fe\textsubscript{3}O\textsubscript{4} nanoparticles have been widely investigated for uranium entrapment.\textsuperscript{28–31} Utilization of Fe\textsubscript{3}O\textsubscript{4} nanoparticles for uranium remediation conforms to the environmental and human safety considerations; as they can be easily and remotely controlled and separated and consequently reduces the radiation exposure.\textsuperscript{6} Fe\textsubscript{3}O\textsubscript{4} nanoparticles can be readily coated with a variety of functional groups, where their affinity towards uranium can be enhanced by their surface modification with materials having a good binding capability for uranium.\textsuperscript{24} Up to now, several studies have investigated the removal of uranium by Fe\textsubscript{3}O\textsubscript{4} nanoparticles coated with various organic and inorganic materials.\textsuperscript{22–28}

Organophosphorus compounds have good affinity and selectivity for actinides and were extensively tested for uranium extraction from nuclear waste streams.\textsuperscript{32–34} In particular, trialkylphosphine oxides are cost-effective neutral extractant with demonstrated high extraction capacity and high stability in strong acidic media, which makes them are excellent ligands to functionalize various adsorbents for uranium capture.\textsuperscript{31,32} Cyanex-923 is a promising phosphine oxide extractant which revealed high radiation stability, good hydrolysis resistance, poor water solubility, and non-corrosive nature;\textsuperscript{31,34} thus, it could be a potential candidate to be impregnated onto the Fe\textsubscript{3}O\textsubscript{4} surface for the efficient uranium adsorption.

Although coating of Fe\textsubscript{3}O\textsubscript{4} nanoparticles is a well-established method to enhance their adsorption efficiency, there is no work carried out on coating the surface of Fe\textsubscript{3}O\textsubscript{4} nanoparticles by Cyanex-923, to the author’s knowledge. While plentiful studies have been reported on uranium(\textit{vi}) adsorption \textit{via} various adsorbents, the feasibility of uranium(\textit{vi}) adsorption on Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 nanoadsorbent has not been tested yet. Thus, motivated by combining the features of simple magnetic separation and efficient uranium extraction; this work reports Cyanex-923 utilization for coating the Fe\textsubscript{3}O\textsubscript{4} nanoparticles in order to design a novel uranium(\textit{vi}) nanoadsorbent. Uranium remediation from water systems was investigated in relation to the medium acidity, Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 dose, initial concentration, and temperature. Besides, the adsorption isotherms, kinetics, and thermodynamics studies were conducted.

2. Experimental

2.1. Reagents

The reagents used throughout the experimental work were of analytical grade. Ferrous chloride, ferric chloride, and arsenazo-III were obtained from Sigma-Aldrich (Saint Louis, USA). Nitric acid, sodium hydroxide, ammonia solution, sodium carbonate, oleic acid, and ethanol were obtained from Merck (Darmstadt, Germany). Cyanex-923 was provided by Solvay/Cytec (Ontario, Canada). Uranium nitrate hexahydrate was used to prepare the working uranium(\textit{vi}) solutions.

2.2. Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 preparation

Fe\textsubscript{3}O\textsubscript{4} nanoparticles were first prepared according to the literature\textsuperscript{35} by mixing acidified ferric and ferrous chloride solutions in a 2:1 molar ratio, under vigorous stirring and nitrogen purging. Then, the pH was increased to 9 and the reaction was kept at 80 °C for 60 min using oleic acid as dispersant.\textsuperscript{35} The produced Fe\textsubscript{3}O\textsubscript{4} nanoparticles were separated by a magnet and washed with excessive ethanol.

Cyanex-923 coated Fe\textsubscript{3}O\textsubscript{4} nanoparticles were obtained by dispersing a known weight of the prepared Fe\textsubscript{3}O\textsubscript{4} nanoparticles in Cyanex-923 ethanolic solution (0.150 mol L\textsuperscript{−1}, 50 mL) followed by overnight shaking at room temperature. Then, the product was collected using an external magnet, washed with ethanol, and vacuum-dried to a fixed weight.

2.3. Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 characterization techniques

Fourier transmission infrared spectroscopy (FTIR, Nicolet iS10 FTIR spectrophotometer, Thermo Scientific, Japan) was used for detecting the functional groups of Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923. Dynamic light scattering (DLS) analysis was utilized to determine the particles diameter of Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 using PSS-NICOMP particle sizer (380ZLS, 40 mW, nominal wavelength 632.8 nm, PSS-NICOMP, Santa Barbara, CA, USA). The morphology of Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 was investigated by a high-resolution transmission electron microscope (HR-TEM, JEM 2100, JEOL, Japan) and scanning electron microscope (SEM, 6510 LA, JEOL, Japan). A thermogravimetric analyzer (TGA, Shimadzu TGA-50, Japan) was used to investigate the thermal stability of Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 within the temperature range 25–750 °C, at heating and nitrogen flow rates of 10 °C min\textsuperscript{−1} and 20 mL min\textsuperscript{−1}, respectively.

2.4. Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 adsorption performance

In a typical batch experiment, 30 mg of Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 was placed in a conical flask containing uranium(\textit{vi}) solution adjusted at pH 5 by a calibrated combination glass electrode (Sentek, UK). After shaking at 25 °C for 60 min, Fe\textsubscript{3}O\textsubscript{4}@Cyanex-923 was magnetically separated and the residual uranium
concentration was measured by a UV-Visible spectrophotometer (Thermo evolution 300, UK).

The adsorption efficiency of uranium(vi) on Fe3O4@Cyanex-923 (ΔE,%) was determined from the difference of the starting and equilibrium uranium(vi) concentrations according to the following equation:

\[ \Delta E = \frac{(C_0 - C_e)}{C_0} \times 100 \]  

(1) 

where, \( C_0 \) and \( C_e \) represent uranium starting and equilibrium concentrations (mg L\(^{-1}\)), respectively.

The uranium(vi) quantity adsorbed through Fe3O4@Cyanex-923 unit weight (qe, mg g\(^{-1}\)) was determined from the subsequent expression:

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

(2) 

where, \( V \) represents the solution volume (L) and \( W \) represents Fe3O4@Cyanex-923 weight (g).

To evaluate the pH effect on uranium adsorption, the adsorption experiments were carried out while varying the solution pH from 2 to 9. Briefly, aliquots of pH-adjusted uranium(vi) solutions with identical concentrations were added to a constant weight of Fe3O4@Cyanex-923 and stirred at 25 °C for a fixed time. Finally, the uranium content remaining in the solution was spectrophotometrically measured.

The adsorption behavior of bare Fe3O4 nanoparticles towards uranium(vi) was also investigated under the same conditions.

2.5. Adsorption kinetics

To investigate the contact time effect on uranium(vi) adsorption, the adsorbent (30 mg) was shaken with a series of uranium(vi) solutions of identical concentration and pH for different time intervals (0–200 min), then the uranium content in each solution was analyzed after separating the nanoadsorbent magnetically.

The experimental results were treated by the pseudo-1st-order and pseudo-2nd-order kinetics models given by the following formulas, respectively:\(^\text{17}\)

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  

(3) 

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  

(4) 

where \( q_e \) and \( q_t \) represent uranium(vi) quantities (mg g\(^{-1}\)) adsorbed at equilibrium and time \( t \) (min), respectively. While \( k_1 \) and \( k_2 \) are the pseudo-1st-order (min\(^{-1}\)) and pseudo-2nd-order (g mg\(^{-1}\) min\(^{-1}\)) rate constants, respectively.

The chi-square test (\( x^2 \)) was further used to validate the kinetic models fitting to the experimental data and was determined as follows:\(^\text{16}\)

\[ x^2 = \sum \frac{(q_{exp} - q_{cal})^2}{q_{cal}} \]  

(5) 

where \( q_{exp} \) and \( q_{cal} \) are quantities of adsorbed uranium(vi) at equilibrium (mg g\(^{-1}\)), experimentally determined and theoretically computed, respectively.

Moreover, the pseudo-2nd-order fitting data was used to compute the initial adsorption rate (h, mg g\(^{-1}\) min\(^{-1}\)) as follows:\(^\text{15}\)

\[ h = k_2 q_e^2 \]  

(6) 

2.6. Adsorption isotherms

Isotherms investigations were conducted by equilibrating the magnetic nanoadsorbent with uranium(vi) solutions of different concentrations (25–200 mg L\(^{-1}\)) while maintaining the experimental settings fixed and then treated as previously described.

The experimental results were analyzed by three adsorption isotherm models; namely Langmuir, Freundlich, and Temkin. The Langmuir isotherm model is expressed as:\(^\text{27}\)

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

(7) 

where \( C_e \) and \( q_e \) are as described earlier, \( q_{max} \) (mg g\(^{-1}\)) represents the maximal single-layer coverage capacity, and \( K_L \) is Langmuir parameter (L mg\(^{-1}\)). The linear plot of \( C_e/q_e \) vs. \( C_e \) has intercept and slope values equal to \( 1/q_{max} K_L \) and \( 1/q_{max} \), respectively.

The essential characteristics of Langmuir model are described through a non-dimensional parameter known as separation factor \( (R_L) \) that explains the favorability of the adsorption process and can be calculated from the subsequent formula:\(^\text{16}\)

\[ R_L = \frac{1}{1 + K_L C_0} \]  

(8) 

Freundlich isotherm model is given by the following equation:\(^\text{28}\)

\[ \log q_e = \log k_F + \frac{1}{n} \log C_e \]  

(9) 

where, \( K_F \) is Freundlich constant (mg g\(^{-1}\)) and \( n \) is an empirical parameter indicating the adsorption favorability (L g\(^{-1}\)), and their values are obtainable from plotting \( \log q_e \) vs. log \( C_e \).

Temkin isotherm model is expressed as:\(^\text{27}\)

\[ q_e = B \ln A_T + B \ln C_e \]  

(10) 

where, \( B \) is constant related to the adsorption heat (J mol\(^{-1}\)) and is expressed as \( B = \frac{RT}{b_T} \), \( b_T \) is Temkin constant, \( T \) is the absolute temperature (K), \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( A_T \) is Temkin equilibrium binding constant (L g\(^{-1}\)). Temkin constants can be calculated from plotting \( q_e \) vs. ln \( C_e \).

2.7. Adsorption thermodynamics

The variation of energy during the adsorption process was investigated through calculating the thermodynamic parameters. The linear regression plotting of \( \ln K_L \) vs. \( 1/T \) according to eqn (11) enables the calculation of enthalpy (\( \Delta H^0 \)) and entropy
\( \Delta S^\circ \) from the plot slope and the intercept, respectively. The Gibbs free energy (\( \Delta G^\circ \)) can be calculated using eqn (12):\(^\text{39,36}\)

\[
\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

\( \Delta G^\circ = RT \ln K_c \)

(11)

(12)

where, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (K), and \( K_c \) is the adsorption equilibrium constant expressed as \( K_c = \frac{q_e}{C_e} \).

2.8. Regeneration and reusability studies

Regeneration experiments were performed in batch mode for three consecutive cycles. Initially, the magnetic nanoadsorbent was added to uranium solution of 50 mg L\(^{-1}\) adjusted at pH 5 and then the solution was agitated at room temperature. When the adsorption equilibrium was attained the magnetic nanoadsorbent was magnetically isolated, washed with deionized water to remove the unbounded uranium, and dried to a fixed weight. Then, this nanoadsorbent was treated with various desorption agents (0.5 mol L\(^{-1}\) Na\(_2\)CO\(_3\) and 0.01 mol L\(^{-1}\) HNO\(_3\)) at room temperature for 120 min under shaking conditions. Afterward, the concentration of uranium released into the solution was determined spectrophotometrically. To assess the reusability of the magnetic nanoadsorbent, the described adsorption–desorption cycle was conducted three times using the same nanoadsorbent. The desorption efficiency (\( E_D \)) was determined according to the below formula:\(^\text{38}\)

\[
E_D\% = \frac{\text{quantity of desorbed uranium}}{\text{quantity of adsorbed uranium}} \times 100
\]

(13)

3. Results and discussions

3.1. Fe\(_3\)O\(_4\)@Cyanex-923 nanoadsorbent characterization

The size distribution and average particle size of Fe\(_3\)O\(_4\)@Cyanex-923 nanoadsorbent were determined by DLS analysis as displayed in Fig. 1(a). From the DLS graph, it can be noticed that Fe\(_3\)O\(_4\)@Cyanex-923 nanoparticles have a size distribution range of 15–95 nm with a mean particle size of 44.6 nm, as calculated by a Gaussian fit. The calculated polydispersity index (PI) of Fe\(_3\)O\(_4\)@Cyanex-923 nanoparticles is 0.199, which indicate a high homogeneity in the particles population.

TEM analysis was conducted to further investigate the particles size, structure, and surface morphology of Fe\(_3\)O\(_4\)@Cyanex-923. As is indicated from Fig. 1(b), Fe\(_3\)O\(_4\)@Cyanex-923 nanoparticles have a quasi-spherical structure of an average diameter of \( \sim 34.4 \) nm. The observed partial agglomeration in Fig. 1(b) could be due to the drying process and the tendency of the nanoparticles to aggregate resulting from their large surface-to-volume ratio.\(^\text{39}\) As can be noted, the average diameter observed by TEM measurement is relatively smaller than that obtained by DLS analysis. This is due to the fact that DLS calculates the particles diameter in liquid media, thus the hydrodynamic size measurements are usually greater than the actual nanoparticles size. This originates from the presence of extra solvent layers associated with the nanoparticles surface.\(^\text{40}\) The surface morphology of Fe\(_3\)O\(_4\)@Cyanex-923 nanoadsorbent was further observed by SEM. The micrograph of Fe\(_3\)O\(_4\)@Cyanex-923, Fig. 1(c), shows nearly homogeneous grains with a smooth surface where most of the nanoparticles are quasi-spherical in shape.

The functional groups of Fe\(_3\)O\(_4\)@Cyanex-923 were identified by FTIR spectroscopy as shown in Fig. 2(a). The signals at 454 cm\(^{-1}\) and 588 cm\(^{-1}\) correspond to the characteristic Fe-O vibrations of the Fe\(_3\)O\(_4\) core.\(^\text{41}\) The signals at 1150 cm\(^{-1}\), 1289 cm\(^{-1}\), and 1460 cm\(^{-1}\) arise from P=O, O-P-O, and P-C stretching vibrations, respectively.\(^\text{42}\) The signals at 1378 cm\(^{-1}\) and 2954 cm\(^{-1}\) represent the \(-\text{CH}_3\) symmetric and dissymmetric stretching frequency, whereas the signals at 2854 cm\(^{-1}\) and 2924 cm\(^{-1}\) represent \(-\text{CH}_2\) symmetric and dissymmetric stretching vibrations, respectively.\(^\text{41}\) These results indicate that Cyanex-923 was successfully coated onto the Fe\(_3\)O\(_4\) surface. The appearance of a broad peak around 3400 cm\(^{-1}\) could result from the water molecules adsorbed from the atmospheric moisture.

To investigate the thermal stability and quantify the surface coating of the Fe\(_3\)O\(_4\) nanoparticles, TGA was performed and represented in Fig. 2(b). The TGA curve of Fe\(_3\)O\(_4\)@Cyanex-923 shows two-step degradation with a total mass loss of 35.5%,
Fig. 2  (a) FTIR spectrum, (b) TGA curve, and (c) magnetization curve of Fe$_3$O$_4$@Cyanex-923 nanoadsorbent.
starting at pH ~5.5, thus decreases the overall uranium(vi) concentration.\textsuperscript{28} As the pH moves beyond neutral, anionic uranium species such as UO\(_2\)(OH)\(_3\)\(^{2-}\), (UO\(_2\))(OH)\(_4\)\(^{2-}\), and (UO\(_2\))(OH)\(_5\)\(^3-\) dominate and their electrostatic repulsive interactions with the negatively charged surface of Fe\(_3\)O\(_4\)@Cyanex-923 cause a sharp decrease in the adsorption capacity.

The results of uranium adsorption on the bare magnetite nanoparticles demonstrate that the adsorption efficiency is dependent on the solution pH as shown in Fig. 3(a). This can be attributed to the influence of the medium acidity on the functional groups at the Fe\(_3\)O\(_4\) surface. Fe\(_3\)O\(_4\) is an amphoteric solid that is capable to develop charges via the protonation and deprotonation of –FeOH sites on its surface with the pH change as follows:\textsuperscript{47,48}

\[
\begin{align*}
\text{–FeOH} + \text{H}^+ & \leftrightarrow \text{–FeOH}_2^+ \quad (14) \\
\text{–FeOH}_2^+ - \text{H}_2\text{O} & \leftrightarrow \text{–Fe}^+ \quad (15) \\
\text{–FeOH}_2^+ & \leftrightarrow \text{–FeOH} + \text{H}^+ \quad (16) \\
\text{–FeOH} & \leftrightarrow \text{–FeO}^- + \text{H}^+ \quad (17)
\end{align*}
\]

At low pHs, the H\(^+\) ions exist in excess that causes the protonation of the –OH on the surface of Fe\(_3\)O\(_4\) and accordingly the –FeOH\(_2^+\) content increase, resulting in electrostatic repulsion with positively charged uranium(vi) ions.\textsuperscript{47} With the pH increase, more adsorption sites on the Fe\(_3\)O\(_4\) surface turn into the more reactive deprotonated and negatively charged forms, thereby leading to a higher uptake of uranium(vi) ions.\textsuperscript{48} With further pH value increase, the anionic uranium species are formed that do not tend to bind to the negatively charged Fe\(_3\)O\(_4\) surface.

Fig. 3  Effect of (a) pH and (b) sorbent dose on uranium adsorption.
3.3. Dosage effect on the adsorption performance of Fe₃O₄@Cyanex-923

To maximize the interaction between uranium(VI) ions and the active sites of magnetic nanoadsorbent, the nanoadsorbent mass was varied from 1 to 50 mg while maintaining all other factors fixed. The corresponding adsorption efficiency was determined and presented in Fig. 3(b). As can be noticed the adsorption efficiency of Fe₃O₄@Cyanex-923 and bare Fe₃O₄ nanoparticles first increases with the adsorbent dose increment reaching its maximum at 30 mg. Further increase of nanoadsorbent dose doesn’t cause a significant increase of the adsorption efficiency. Initially, the higher nanoadsorbent dose provides a larger surface area and more adsorption sites for uranium(VI) ions till a plateau is reached. At this point, the uranium(VI) quantity adsorbed per nanoadsorbent unit weight keeps constant where more unoccupied active sites would no longer contribute to the adsorption process. Considering factors of adsorption efficiency and economic cost, 30 mg was considered as the optimal dose in next experiments.

3.4. Adsorption kinetics

When optimizing the adsorption systems design, particularly for industrial applications, it is of paramount importance to explore the adsorption kinetics. Thus, the adsorption efficiency
was monitored over time to examine how the contact time affects the adsorption process. Fig. 4(a) reveals that the adsorption efficiency of uranium(VI) first increases sharply with contact time by virtue of the presence of available abundant adsorption sites at the magnetic nanoadsorbent surface. This behavior indicates the increase of driving force for mass transfer and thus further uranium(VI) ions reach the surface of the magnetic nanoadsorbent within a short time. Afterwards, the adsorption efficiency continues to increase at a slower rate, and eventually reaches equilibrium and then remains steady for the rest of the time as the vacant binding sites on the magnetic nanoadsorbent surface are almost consumed.

As can be noticed from Fig. 4(a), Fe₃O₄@Cyanex-923 shows a faster equilibrium time (60 min) compared to bare Fe₃O₄ (180 min). The fast equilibrium state achieved by Fe₃O₄@Cyanex-923 is caused by the strong chelation of uranium ions with phosphine oxide functional groups. Additionally, the adsorbent nanoscale structure gives a share in the fast diffusion. According to the kinetic results, Fe₃O₄@Cyanex-923 could have real-world applications potential for uranium removal from sizable amounts of water.

To describe the rate-controlling step of uranium(VI) adsorption on the prepared nanoadsorbent, the pseudo-1st-order and pseudo-2nd-order models were employed and the corresponding fitting curves were illustrated in Fig. 4(b) and (c), respectively. The related kinetic parameters calculated from these models were summarized in Table 1. According to the results, the pseudo-2nd-order model reveals a better regression analysis for Fe₃O₄@Cyanex-923 experimental data \( R^2 = 0.997 \), thus the uranium(VI) adsorption process on Fe₃O₄@Cyanex-923 obeys the pseudo-2nd-order kinetic equation. Additionally, the adsorption capacity obtained from the pseudo-2nd-order model \( (108.695 \text{ mg g}^{-1}) \) is nearer to the experimental value \( (99.862 \text{ mg g}^{-1}) \) compared to that obtained from the pseudo-1st-order model \( (127.938 \text{ mg g}^{-1}) \). The lower \( c_2 \) value obtained for the pseudo-2nd-order model further validates that this model is ideal for explaining the uranium(VI) adsorption behavior on Fe₃O₄@Cyanex-923. These results indicate that the dominant interaction of uranium(VI) ions with the active sites on the

![Image](https://example.com/image.png)

### Table 1 Kinetic parameters of pseudo-1st-order and pseudo-2nd-order models

| Adsorbent               | \( q_{\text{e,exp}} \) \( (\text{mg g}^{-1}) \) | \( q_{\text{e,cal}} \) \( (\text{mg g}^{-1}) \) | \( k_1 \) \( (\text{min}^{-1}) \) | \( R^2 \) | \( \chi^2 \) | \( k_2 \times 10^{-3} \) \( (\text{g mg}^{-1} \text{ min}^{-1}) \) | \( R^2 \) | \( \chi^2 \) | \( h \) \( (\text{mg g}^{-1} \text{ min}^{-1}) \) |
|-------------------------|---------------------------------------------|---------------------------------------------|-----------------|---------|---------|-----------------------------|---------|---------|---------|
| Fe₃O₄@Cyanex-923        | 99.862                                      | 127.938                                    | 0.052           | 0.974   | 8.453   | 108.695                     | 0.719   | 0.997   | 0.949   | 8.503   |
| Fe₃O₄ nanoparticles     | 13.601                                      | 13.365                                     | 0.025           | 0.996   | 0.063   | 16.666                      | 1.534   | 0.981   | 0.691   | 0.427   |

![Fig. 5](https://example.com/image.png)

Fig. 5 (a) Effect of initial uranium concentration on the adsorption capacity, (b) Langmuir, (c) Freundlich, and (d) Temkin isotherms fitting curves.
Freundlich kinetics of uranium(VI) on bare Fe₃O₄ nanoparticles could be exchanging electrons at the solid/solution interface. Langmuir and Freundlich models gave $R²$ values of 0.997 and 0.958, respectively. It can be noted that Freundlich model showed a lower $R²$ value compared to the Langmuir model, suggesting that Langmuir model is better fitted with the Fe₃O₄@Cyanex-923 adsorption data and a homogenous single-layered adsorption dominates the process. On the contrary, the fitting coefficient for bare magnetite nanoparticles is greater for Freundlich isotherm than Langmuir isotherm, suggesting the suitability of Freundlich model to the adsorption data of bare Fe₃O₄ and the existence of heterogeneous adsorption sites.

Table 2: Isotherm parameters of Langmuir, Freundlich, and Temkin models

| Adsorption isotherm          | Fe₃O₄@Cyanex-923 | Fe₃O₄ nanoparticles |
|------------------------------|------------------|---------------------|
| Langmuir                     | $R² = 0.997$     | $R² = 0.927$        |
|                              | $q_{max} = 429.185$ (mg g⁻¹) | $q_{max} = 29.850$ (mg g⁻¹) |
|                              | $K_L = 0.099$ (L mg⁻¹) | $K_L = 0.041$ (L mg⁻¹) |
| Freundlich                   | $R² = 0.958$     | $R² = 0.994$        |
|                              | $K_F = 57.003$ (mg g⁻¹) | $K_F = 4.611$ (mg g⁻¹) |
|                              | $n = 2.402$ (L mg⁻¹) | $n = 2.792$ (L mg⁻¹) |
|                              | $1/n = 0.416$   | $1/n = 0.358$      |
| Temkin                       | $R² = 0.988$     | $R² = 0.805$        |
|                              | $A_F = 2.559$ (L g⁻¹) | $A_F = 1.496$ (L g⁻¹) |
|                              | $B = 52.849$ (J mol⁻¹) | $B = 4.580$ (J mol⁻¹) |

Fig. 5(a) displays how the adsorption capacity of Fe₃O₄@Cyanex-923 towards uranium(VI) ions, hence it could be considered as a promising material for uranium(VI) adsorption from aqueous solutions. The $R_L$ values were less than unity for both Fe₃O₄@Cyanex-923 and bare Fe₃O₄ (0.048–0.993), indicating that the adsorption process is suitable for both magnetic nanoabsorbents. The higher value of Freundlich constant for Fe₃O₄@Cyanex-923 ($K_F = 57.003$ L g⁻¹) compared to bare Fe₃O₄ ($K_F = 4.611$ L g⁻¹) indicates the higher adsorption capacity of Fe₃O₄@Cyanex-923 that results from the strong affinity of Fe₃O₄@Cyanex-923 to uranium(VI) ions. The $n$ values of Fe₃O₄@Cyanex-923 and bare Fe₃O₄ lies between 1 and 10, indicating a favorable adsorption process. The $n$ value is slightly higher for bare Fe₃O₄.
nanoparticles, denoting the increased heterogeneity of the adsorption.

Temkin isotherm is another model that assumes the dependence of the adsorption free energy on the adsorbent surface coverage, as the adsorption heat linearly decreases because of the adsorbent–adsorbate interactions. The plot of Temkin isotherm fitted quite well to the experimental data obtained for Fe₃O₄@Cyanex-923 ($R^2 = 0.988$) which further elucidates the chemisorption adsorption process. The poor-fit of the uranium(VI) adsorption data on bare Fe₃O₄ nanoparticles to Temkin model indicates the unsuitability of this model to describe the uranium(VI) interaction with bare Fe₃O₄. The $B$ value calculated for Fe₃O₄@Cyanex-923 is 52.849 J mol⁻¹ which confirmed that the uranium(VI) adsorption process onto Fe₃O₄@Cyanex-923 is a chemisorption one. The positive value of $B$ made it clear that the adsorption is exothermic for Fe₃O₄@Cyanex-923 supporting the obtained thermodynamics results.

### 3.6. Adsorption thermodynamics

To foresee the effect of the uranium(VI) adsorption on the solution temperature, adsorption experiments were carried out under a temperature range of 298 to 328 K. The results revealed that the adsorption capacity of Fe₃O₄@Cyanex-923 and bare Fe₃O₄ nanoparticles gradually decreases upon increasing the temperature; signifying the exothermic nature of the adsorption process. Such behavior is attributed to the equilibrium shift toward desorption accompanied by weaker uranium–adsorbent interactions resulted from the increased molecular mobility and lower chemical affinity when the temperature is raised.

Generally, the thermodynamic parameters offer in-depth data concerning the spontaneity and feasibility of the adsorption process. Thus, the van’t Hoff plot, Fig. 6, was used to calculate the thermodynamic parameters of uranium adsorption on Fe₃O₄@Cyanex-923 and bare Fe₃O₄ nanoparticles and the data was listed in Table 3. It is clear that low temperature is favorable for uranium adsorption on Fe₃O₄@Cyanex-923 and bare Fe₃O₄, as interpreted from the decrease of $\Delta G^\circ$ values with temperature increasing. It is noticed that the $K_v$ values decrease with the temperature rise, signifying an exothermic process. The negative $\Delta G^\circ$ values indicate the spontaneity and feasibility of uranium adsorption on Fe₃O₄@Cyanex-923 and bare Fe₃O₄ under the studied temperatures. The negative $\Delta H^\circ$ values further affirm the exothermic character of the adsorption process. $\Delta S^\circ$ positive values suggest the increase of randomness at the solid/solution interface resulting from the decrease in molecular orderliness during the adsorption process.

#### 3.7. Desorption and reusability

Generally, the adsorbent regeneration and recycling are desirable to attain a feasible and economic adsorption process. Thus, to investigate the reusability of the magnetic nano-adsorbent, Fe₃O₄@Cyanex-923 and bare Fe₃O₄ were subjected to repetitive adsorption and desorption experiments in three consecutive cycles. Both nitric acid and sodium carbonate were tested for their effectiveness as eluent reagents. The results illustrated in Fig. 7 clearly show that uranium ions could be desorbed from Fe₃O₄@Cyanex-923 and bare Fe₃O₄ by 0.01 mol L⁻¹ HNO₃ and 0.5 mol L⁻¹ Na₂CO₃ solution. A desorption efficiency of 95–90% and 98–95.5% was obtained over 3 cycles by HNO₃ and Na₂CO₃, respectively, for Fe₃O₄@Cyanex-923. On the other hand, a lower desorption efficiency was observed for bare Fe₃O₄ nanoparticles (88–71 and 95–85% for HNO₃ and Na₂CO₃, respectively).

![Effect of desorption agents on the desorption efficiency of U(VI) from Fe₃O₄@Cyanex-923 and bare Fe₃O₄ for three continues cycles.](image)
It can be indicated from the results that higher recovery of U(VI) species from the loaded Fe₃O₄@Cyanex-923 and bare Fe₃O₄ could be obtained using 0.5 mol L⁻¹ Na₂CO₃ solution.

3.8. Comparison of Fe₃O₄@Cyanex-923 performance with other magnetic adsorbents

The literature reveals that a number of reagents were immobilized onto Fe₃O₄ core and used for uranium removal from different matrices. Table 4 shows the adsorption behavior of Fe₃O₄@Cyanex-923 towards uranium compared to the previously reported magnetic adsorbents in terms of adsorption capacity, experimental conditions, and equilibrium time. It can be noted that the q_max value of Fe₃O₄@Cyanex-923 is excellent compared to the listed magnetic adsorbents. The high adsorption capacity of Fe₃O₄@Cyanex-923 mainly results from the phosphine oxide groups distributed on the surface of Fe₃O₄ nanoparticles, thus uranium ions could have access to the adsorption sites easily during the adsorption process. It can be observed that Fe₃O₄@Cyanex-923 reveals the advantage of lower equilibration time which is essential in large volume samples and at an industrial scale. Table 4 suggests that Fe₃O₄@Cyanex-923 has a great potential as a uranium(VI) adsorbent.

4. Conclusions

The results of this work demonstrated that Fe₃O₄@Cyanex-923 nanoadsorbent is especially conceived for efficient removal of uranium(VI) ions from aqueous solutions. The optimal conditions for uranium(VI) adsorption were as follows: adsorption temperature = 25 °C, adsorption time = 60 min, Fe₃O₄@Cyanex-923 weight = 30 mg, and solution pH value = 5. Treating the experimental data with various kinetics and isotherms models indicated that the adsorption of uranium on Fe₃O₄@Cyanex-923 is a monolayer chemisorption process that is well-correlated to pseudo-2nd-order and Langmuir equations. Fe₃O₄@Cyanex-923 can be as easily separated by applying an external magnetic field and after three cycles the adsorption and desorption capacities of the magnetic adsorbent were still high. Fe₃O₄@Cyanex-923 adsorption capacity for uranium(VI) almost matched or exceeded that of reported magnetic adsorbents in the literature. Compared to bare Fe₃O₄ nanoparticles, the adsorption capacity and stability of Fe₃O₄@Cyanex-923 were greatly enhanced upon modification.

Conflicts of interest

There are no conflicts to declare.

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