



Separation Science and Engineering

Influence of monovalent cations and CuO nanoparticles on X-nanozeolite in uranium anionic species separation from contaminated drinking water

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ABSTRACT

The main purpose of this work was the modification of NaX nanozeolite using copper oxide nanoparticles and various monovalent cations such as K^+ , Cs^+ , and Ag^+ in order to make the negatively charged zeolite surface accessible for anionic forms of uranium which are the most dominant species of uranium in the contaminated radioactive waters at natural pH. Various methods such as the X-ray fluorescence (XRF), X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and atomic absorption spectroscopy (AAS) were used to characterize the final synthesized adsorbents. Batch technique was used to study the adsorption behavior of uranium ions from polluted drinking water by NaX nanozeolite and its modified forms. In order to better understand the performance of them, the results were compared with those that were obtained for synthesizing bulk NaX zeolite and Na-form of clinoptilolite natural zeolite. Preliminary results indicated that uranium sorption increased as the loading level of CuO nanoparticles on NaX nanozeolite increased from 2.1 wt% to 11.2 wt%. In addition, from the obtained data, an increase in uranium removal efficiency resulted as charge/ionic radius ratio of exchanged cation decreased. Also, the effect of contact time, solid–liquid ratio, initial concentration and temperature on the adsorption process was studied. It is worth mentioning that, in this study, the sorption of uranium was performed under natural conditions of pH and the presence of competing cations and anions which are available in drinking waters.

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1. Introduction

Recent advances in nanotechnology have opened new horizons to develop next-generation of materials for water treatment. Due to their high specific surface area, nanoadsorbents show a considerably higher rate of adsorption compared with traditional granular or powdered adsorbents. They have great potential for novel, more efficient, and faster decontamination processes aimed at removal of organic and inorganic pollutants like heavy metals [1,2]. These advantages caused various nanoadsorbents including different kinds of metal oxide nanoparticles [3] and nanozeolites [4] to be extensively studied by researchers.

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations, with a microporous structure and high chemical and radiation stability. Due to special physicochemical properties, they are widely used as molecular sieves, ion-exchangers, adsorbents, catalysts, etc. [5]. However, due to the permanent negative charge on their surface, zeolites have no or little selectivity for anionic contaminants [6]. Therefore, studies have focused

on the preparation of new anion-selective zeolites by modification of their surface using metal oxides or surfactants [7]. Modifying the zeolites with cationic surfactants such as hexadecyltrimethylammonium (HDTMA), which yields surfactant modified zeolite (SMZ), leads to the occurrence of a charge reversal from negative to positive and enables them to adsorb also an anionic species form of various contaminants from aqueous media [8–14]. Over the last decades, increasing attention has been paid to metal oxide modified zeolites to prepare selective and efficient adsorbents for various types of contaminants [15–17]. In this method, the metal oxide clusters insert into zeolite channels. It caused the channels of zeolite to become narrower and the interested pore-size to be achieved. Therefore, various properties of zeolites such as acidity and basicity would change [18,19].

Uranium is known as one of the most hazardous pollutants due its chemical toxicity and radioactive nature [20]. Besides the natural sources, various human activities such as mining, nuclear power production, military activities, and using the uranium containing phosphate fertilizers are considered as major sources for uranium disseminated in the environment [21,22]. Uranium has four oxidation states which are usually represented by U^{3+} , U^{4+} , $UO_2^+(5+)$, and $UO_2^{2+}(6+)$. Uranium due to its high chemical reactivity, readily reacts with other elements and can

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form different types of complexes. The hexavalent uranium, which is mainly present as the uranyl cation, UO_2^{2+} , reacts easily with various anions such as carbonate, phosphate, sulfate, chloride and fluoride. In aqueous solutions with low pH ($\text{pH} < 5$), the uranyl ion is very stable while at pH near 7, the uranyl ion reacts with phosphate and carbonate anions and forms the stable complexes. Especially, for drinking water supplies with pH values ranging from 7 to 10, uranyl-carbonate-complexes including $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are the predominant anion species [23,24].

So far, various sorbents were used to remove cationic species of uranium from aqueous solutions [25–29]. However, only a few numbers of studies about the removal of uranium anionic species were reported. For example, Sarri *et al.* [24] investigated the uranium anionic species removal from alkaline aqueous solutions by two polyethylenimine–epichlorohydrin resins. In our previous work [30], we synthesized and modified the bulk NaX zeolite to remove uranium from drinking water, but in this study, we extend our previous work and synthesized the NaX nanozeolite and then modified it by CuO nanoparticles and various monovalent cations to improve its uranium removal efficiency from contaminated drinking water. The removal of uranium was performed under natural conditions of pH and the presence of the all competing cations and anions which are available in drinking waters. However, to the best of our knowledge, such study has been not reported in any previous work. The results of the present study provide insight into the heavy metal removal potential of metal oxides supported on zeolite.

2. Materials and Methods

2.1. Materials

The used chemical reagents contained sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} > 98\%$, Sigma-Aldrich), sodium aluminate (54.3% Al_2O_3 , 44.5% Na_2O , Riedel-de-Haën), sodium hydroxide pellets (99%, Sigma-Aldrich), and copper nitrate trihydrate (Sigma-Aldrich; puriss. p.a., 99%–104%). The natural clinoptilolite was collected from Semnan deposits in northeast of Iran, with chemical formula: $(\text{KNa}_2\text{Ca}_2)(\text{Si}_{29}\text{Al}_7)\text{O}_{72}24\text{H}_2\text{O}$ and $\text{Si}/\text{Al} = 5.69$. Potassium nitrate ($\geq 99.0\%$, Sigma-Aldrich), silver nitrate ($\geq 99.0\%$, Sigma-Aldrich), and cesium nitrate (99.999% trace metals basis, Sigma-Aldrich) were also used. Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ACS reagent, Sigma-Aldrich) was used to prepare a stock solution for the adsorption experiments. All chemicals without any purification were directly used.

2.2. Preparation of Na-clinoptilolite powder

The natural clinoptilolite zeolite was crushed and pulverized in a mortar and sieved to a particle size of 45–75 μm . To wash out fine impurities and salts from the zeolite, clinoptilolite was purified through a washing process using de-ionized water.

To prepare the Na form of clinoptilolite, the ammonium exchanged form (NH_4^+ -Clino) was firstly prepared. Approximately 10 g of the purified sample was shaken with 300 ml of $1 \text{ mol} \cdot \text{L}^{-1}$ NH_4NO_3 at 60°C with agitation speed $200 \text{ r} \cdot \text{min}^{-1}$ for 72 h. The solution was decanted and fresh solution was added. This procedure was repeated three times. The solid was filtered, washed and dried at 110°C . The H-form of clinoptilolite was prepared by heating the NH_4 -form at 450°C for 2 h to remove ammonia molecule. Na-exchanged form of clinoptilolite zeolites (Na-Clino) was prepared by shaking 10 g of an H-form of zeolite with 200 ml of $1 \text{ mol} \cdot \text{L}^{-1}$ solution of NaNO_3 at 60°C for 24 h. Again, the solution was decanted and fresh solution was added. This procedure was repeated three times. The solid was separated, washed with distilled water, dried at 110°C overnight, and stored in the desiccator until use.

2.3. Synthesis of bulk NaX zeolite

Bulk NaX zeolite was synthesized according to the method that was reported in our previous paper [30].

2.4. Synthesis of NaX nanozeolite

For synthesis of NaX nanozeolite, 5.34 g of sodium hydroxide (NaOH) was dissolved in 50 g of deionized water. Then, 2.42 g of NaAlO_2 was added to the solution. After stirring for 30 min, a solution of 3.43 g of SiO_2 and 50.0 g of H_2O was added to it. The formed hydrogel was stirred at 27°C for 30 min. The hydrogel was transferred to a 250 ml polypropylene bottle and hydrothermally treated for 96 h at a temperature of 60°C with an agitation speed of $200 \text{ r} \cdot \text{min}^{-1}$. The final product was washed with deionized water several times, until pH 8 was reached. The sample was dried at 70°C for 24 h.

2.5. Preparation of NaX/CuO nanocomposite

NaX nanozeolite was modified by the impregnation method by mixing 1 g NaX zeolite with 50 ml of an aqueous solution of copper nitrate with different molarities (Table 1). The mixture was stirred strongly at ambient temperature for 4 h. The powders were centrifuged, washed with distilled water and dried at 110°C . The obtained samples were calcined at 450°C in air for 4 h.

Table 1

Preparation of NaX/CuO samples with different CuO concentrations

Samples	$\text{Cu}(\text{NO}_3)_2$ (aq)/ $\text{mol} \cdot \text{L}^{-1}$	CuO loading/wt%
CuO/NaX-1	0.01	2.1
CuO/NaX-2	0.05	3.5
CuO/NaX-3	0.1	9.1
CuO/NaX-4	0.2	11.2

2.6. Preparation of cation exchanged forms of NaX nanozeolite

Various monovalent cation exchanged forms of NaX nanozeolite were prepared by the wet impregnation method. To prepare (K^+ , Cs^+ , Ag^+)-exchanged form of NaX nanozeolite, 2 g of zeolite was shaken with 100 ml of $0.02 \text{ mol} \cdot \text{L}^{-1}$ solution of KNO_3 , CsNO_3 , and AgNO_3 for 4 h at room temperature respectively. Then, the solid was separated, washed with distilled water, dried at the 110°C overnight, and stored in the desiccator until use.

2.7. Uranium removal from water

All the experiments were carried out using a batch technique in polyethylene bottles under ambient conditions. The stock solutions of uranium prepared by dissolving an appropriate quantity of uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 500 ml of drinking water (Table 2). The pH was adjusted to desired values by adding HCl and NaOH ($0.01 \text{ mol} \cdot \text{L}^{-1}$) solutions. 0.1 g of various adsorbents was added into 50 ml uranium solution of the given concentration. After the suspensions were stirred for 1 h, the solid and liquid phases were separated by centrifugation. Effects of different relevant parameters such as contact time, initial concentrations, solid–liquid ratio, and temperature on adsorption of uranium ions also were investigated.

The removal efficiency (R) and distribution coefficient (K_d , $\text{L} \cdot \text{g}^{-1}$) are calculated from equations [31]:

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

Table 2
Various parameters of drinking water sample

Parameter	Value
pH	7.6
Total dissolved solids/mg·L ⁻¹	250
Turbidity/NTU	0.6
Hardness/mg·L ⁻¹ CaCO ₃	166.5
Conductivity/μS·cm ⁻¹	393
Aluminum/mg·L ⁻¹	0.08
Lead/mg·L ⁻¹	0.003
Zinc/mg·L ⁻¹	<0.04
Chloride/mg·L ⁻¹	23.04
Fluoride/mg·L ⁻¹	0.15
Sulfate/mg·L ⁻¹	35.32
Nitrate/mg·L ⁻¹	8.72
Magnesium/mg·L ⁻¹	17.99
Sodium/mg·L ⁻¹	15.7
Potassium/mg·L ⁻¹	0.81
Calcium/mg·L ⁻¹	37.07
Bicarbonate/mg·L ⁻¹ CaCO ₃	158.6
Uranium/μg·L ⁻¹	<20

$$K_d = \frac{(C_0 - C_e) V}{C_e m} \quad (2)$$

where C_0 is the initial concentration, C_e is the final concentration in the supernatant after centrifugation, m is the mass of adsorbent, and V is the batch volume.

The amount of adsorption at equilibrium time t , q_e (mg·g⁻¹), was calculated by [16]:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (3)$$

2.8. Characterization

Synthesized materials were characterized using different techniques of X-ray diffraction (XRD) (Bruker, D8ADVANCE) with CuK α radiation, X-ray fluorescence (XRF) (Bruker, S4 PIONEER), and field emission-scanning electron microscopy (FE-SEM) (TESCAN, VEGA II). A Philips EM208S transmission electron microscope was used to take transmission electron microscopy (TEM) images. The concentration of uranium in solutions was measured by inductively coupled plasma atomic emission spectroscopy (ICP-OES). An atomic absorption spectrometer (AAS) (Varian, 220SS) was used to measure the amount of copper in the samples. The infrared transmission spectrum of the samples was made by the KBr wafer technique. The spectrum was recorded on an FTIR Spectrometer System 2000 FT-IR (Perkin-Elmer).

3. Results and Discussion

3.1. XRD analysis

The Na-Clino and synthetic bulk NaX zeolite, NaX nanozeolite, NaX/CuO nanocomposite with various CuO nanoparticles concentrations and different monovalent cation exchanged-X nanozeolite were characterized by XRD (Fig. 1). The XRD patterns of Na-Clino are presented in Fig. 1a. This figure demonstrates that the major phase in zeolite is clinoptilolite [32]. In the pattern related to bulk NaX zeolite (Fig. 1a) the characteristic peaks are in good agreement with those of the face-centered cubic crystal structures of NaX zeolite (molecular formula: C₅H₄O₂·Na₂O·Al₂O₃·3.3SiO₂·7H₂O) with a lattice parameter of $a = 2.4960$ nm (pdf No. 41-118). Moreover, the NaX nanozeolite XRD pattern (Fig. 1a) showed that the NaX nanozeolite has a face-centered cubic

crystal structure (molecular formula: Na₂O·Al₂O₃·2.5SiO₂·6.2H₂O) (pdf No. 038-0237).

The broadening of the diffraction peaks which is the characteristic of a nanocrystal, is obvious in the XRD pattern corresponding to synthesized NaX nanozeolite. The mean crystallite size D was determined according to the Scherrer equation [33]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

where K is a constant (shape factor, about 0.9), λ is the X-ray wavelength (0.15405 nm), β is FWHM (full width at half maximum) of the diffraction line, and θ is the diffraction angle. Based on the full width at half maximum of the reflection from plane (1 1 1), the mean crystal size of the NaX nanozeolite was found to be 35.5 nm.

The concentration of copper in the NaX/CuO nanocomposites which, was measured by an atomic absorption spectrometer (AAS), varied from 2.1 wt% to 11.2 wt% (Table 1). The XRD patterns of the NaX/CuO nanocomposite samples (Fig. 1 b) were similar to that obtained from parent nano-NaX zeolite, which indicated that the morphology and crystalline structure of parent X-zeolite were retained during various stages of the CuO modification process. However, the intensity of some characteristic peaks clearly was decreased with increasing CuO concentration and even some other were disappeared. It can be seen from Fig. 1c which shows the expanded scale of the corresponding pattern for the NaX/CuO-3 sample, that six peaks appeared at 2θ values of 32.46°, 35.1°, 38.5°, 47.2°, 58.2° and 61.9°. These peaks are in good agreement with the monoclinic phase of CuO with lattice constants of $a = 4.6840$, $b = 3.4250$ nm and $c = 5.1290$ nm (pdf No. 005-0661). From these results it can be inferred that CuO particles are either amorphous, included inside the channels of the zeolite and are too small that were detected by XRD. This may be caused by the interaction of CuO with zeolites which results in copper oxide deaggregation and incorporation of single copper ions and/or Cu-O species in the cationic sites of zeolite through their exchange with the zeolite OH groups [34]. Similar results had already been observed by various authors in several cases [35,36]. For example, Nezamzadeh-Ejhieh and Karimi-Shamsabadi [37] reported the same phenomena for CuO modified X-nanozeolite. They observed that the intensity of most peaks of X-nanozeolite was decreased after incorporation of CuO into it. Also, they identified weak characteristic peaks corresponding to CuO phase in CuO/NaX sample. Moreover, the XRD patterns of various monovalent cation exchanged forms of NaX nanozeolite including KX, CsX, and AgX nanozeolites are shown in Fig. 1d. The similarity of XRD patterns of cation exchanged zeolites and parent zeolite showed that the structure of these zeolites is retained after the cation exchange process. However, the intensity of some peaks in the XRD patterns of the cation exchanged zeolites is lower than the parent zeolite which indicated that the crystallinity of zeolites decreased after their conversion into K, Cs, and Ag-exchanged forms. Kondru *et al.* also observed the same phenomena for the Y-zeolite and its iron-exchanged form. They reported that the intensity of some peaks of Y-zeolite was decreased in the Fe-exchanged form of Y-zeolite [38].

3.2. FT-IR studies

The FT-IR spectra of Na-Clino, bulk NaX, NaX nanozeolite, and NaX/CuO nanocomposite with various CuO nanoparticles concentrations are shown in Fig. 2a. Infrared spectra of bulk NaX and NaX nanozeolite have absorption bands at 1200–450 cm⁻¹ which are known to be assigned to Si–O–Al, Si–O–Si, Al–O and Si–O–Na species. The absorption band at 462 cm⁻¹ is due to internal vibrations of (Si, Al)O₄ tetrahedral of zeolite X, whereas the bands at 569 and 755 cm⁻¹ are due to vibrations related to external linkages between tetrahedral and hence sensitive to framework structure. The band at 671 cm⁻¹ is due to the internal vibration of (Si, Al)–O symmetric stretching. Vibration in the

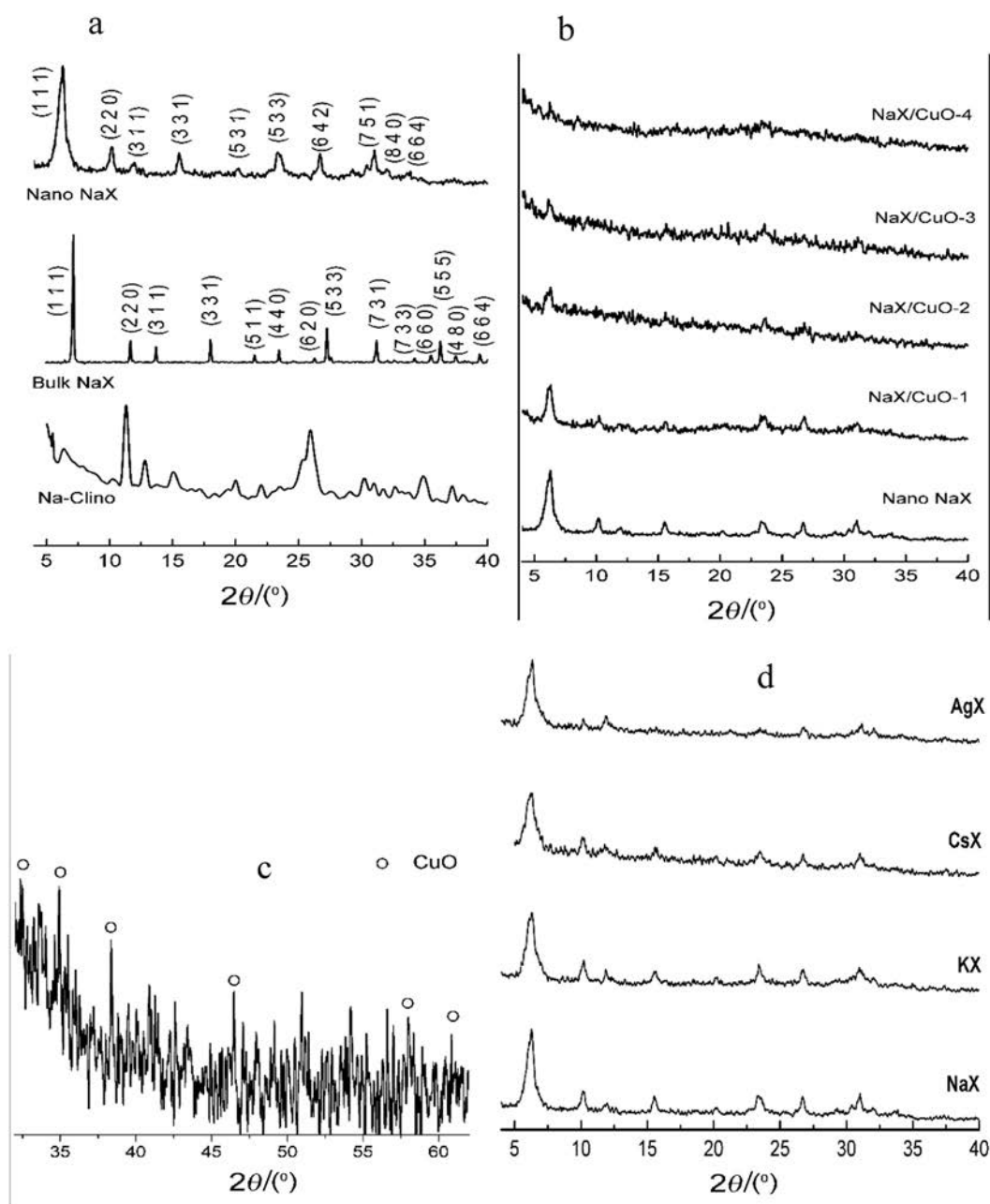


Fig. 1. XRD pattern of synthesized (a) Na-Clino, bulk NaX and NaX nanozeolite, (b) NaX/CuO nanocomposites, (c) expanded scale of the pattern of NaX/CuO-3 sample, and (d) cation exchanged forms of parent NaX nanozeolite.

978 cm^{-1} region is assigned to a T–O stretch involving primary motion associated with oxygen atoms. Usually, the bands in the wave number range 2500–3800 cm^{-1} and near 1650 cm^{-1} are attributed to different kinds of hydroxyl groups [39–45].

The FT-IR spectra of all NaX/CuO nanocomposite samples showed no presence of characteristic peaks of crystalline CuO phase and showed similar spectra with those given by NaX nanozeolite. This is due to low CuO content at NaX/CuO nanocomposite that caused the lower CuO vibration intensity than that in the NaX. These results show that the addition of CuO does not affect the structure of NaX zeolite. However, the intensity of some characteristic peaks decreases with increasing amount of CuO content [46]. On the other side, dealumination of NaX nanozeolite during the cation exchange process which changes the Si/Al ratio in the zeolite, causes a shift in bands at 978 cm^{-1} and 671 cm^{-1} towards higher frequencies [47] (Fig. 3b). The Si/Al ratio can be determined

using IR double-ring vibration frequency (ω_{DR}) by the following relation [48]:

$$r_{\text{Si/Al}} = \frac{1-x}{x}, \text{ and } x = 3.857 - 0.00619\omega_{\text{DR}} \quad (5)$$

where ω_{DR} is IR double-ring vibration frequency (cm^{-1}) and x is the Al molar fraction. The value of the calculated Si/Al ratio for parent NaX nanozeolite, KX, CsX, and AgX is 1.64, 1.73, 1.80, and 1.88 respectively. It is obvious that the Si/Al ratio parameter increases due to removal of aluminum as mentioned before. XRF analysis also was used to determine the Si/Al ratio of parent NaX nanozeolite. Major element compositions of the NaX nanozeolite are summarized in Table 3. From this table, the Si/Al ratio parameter is 1.78 for parent NaX nanozeolite which is in good agreement with the value determined by FT-IR spectrum.

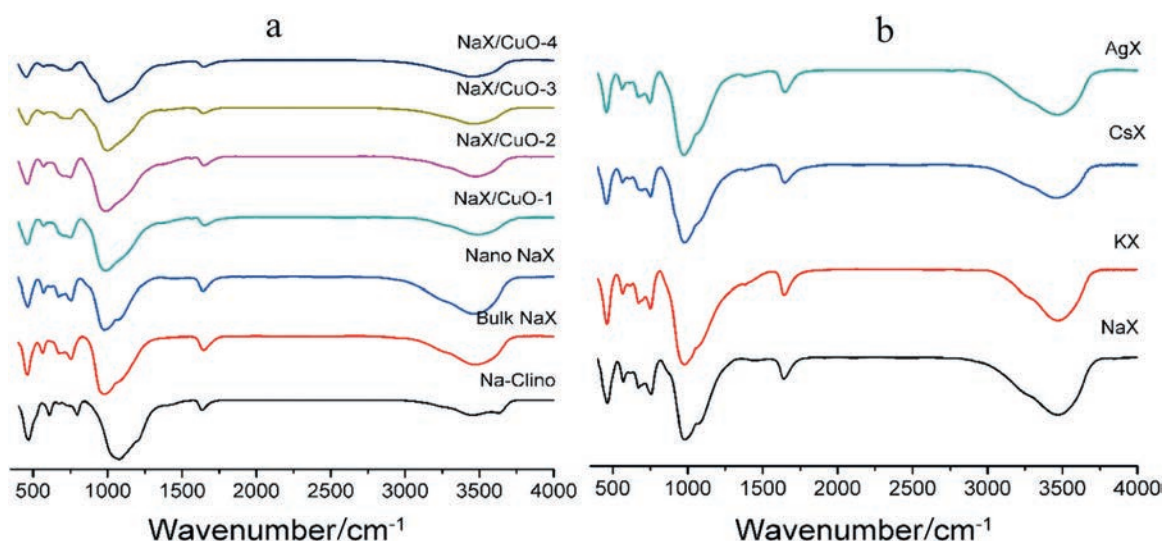


Fig. 2. FT-IR spectra of (a) Na-Clino, bulk NaX, NaX nanozeolite, and NaX/CuO nanocomposite with various CuO nanoparticles concentration and (b) cation exchanged forms of parent NaX nanozeolite.

3.3. FE-SEM and TEM images

FE-SEM microphotographs of the synthesized bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolite are presented in Fig. 3. From these images one can see that NaX nanozeolite and its modified

forms including AgX and NaX/CuO nanocomposite have the petal-like form. Moreover, comparison of NaX nanozeolite morphology with NaX/CuO nanocomposite and AgX nanozeolite shows that morphology and crystallite size are retained on samples. Also, one can see that the bulk NaX zeolite has a well-defined cubic structure. TEM images of

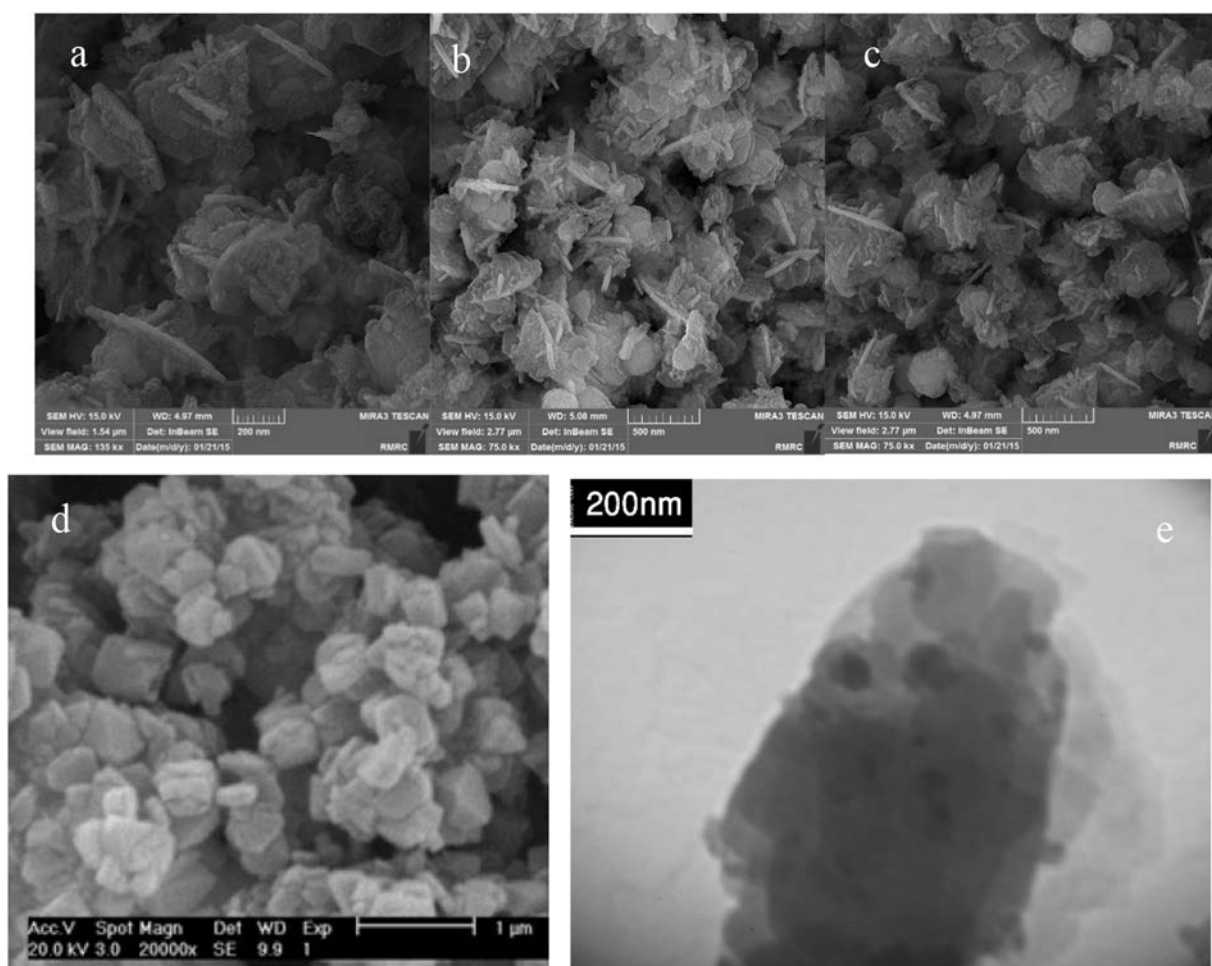


Fig. 3. FE-SEM micrograph of (a) NaX nanozeolite, (b) NaX/CuO nanocomposite, (c) AgX nanozeolite, (d) bulk NaX and (e) TEM images of NaX/CuO nanocomposite.

Table 3
Elemental analysis of parent NaX nanozeolite

Compound	Si	Al	Na	Cl	Ca	S	Fe	Cu	Ba	K	Sr	Zn	LOI ^①	Total
Concentration/wt%	41.55	23.40	11.60	6.10	5.38	0.375	0.159	0.117	0.110	0.092	0.65	0.32	12.42	101.4

^① Loss on Ignition (1000 °C, 2 h).

NaX/CuO nanocomposite are shown in Fig. 3e. It can be seen that CuO is well distributed on the external surface of the zeolite.

3.4. Adsorption experiments

3.4.1. Effect of adsorption time and kinetic models

Fig. 4 shows the variation of removal efficiency of uranium from water by different synthesized absorbents including Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites with a contact time from 5 to 120 min. For this, 0.1 g of each absorbent contacts with 20 ml uranium solution with an initial uranium concentration of 4 mg·L⁻¹ and pH 7.56 at 27 °C. As one can see in Fig. 4, adsorption of uranium rapidly increased at the initial contact time for all absorbents except AgX nanozeolite during the first 30 min and then, slowly increased with time reaching a plateau. The uranium adsorption by AgX nanozeolite is fast and attains equilibrium before 5 min. Therefore, a contact time of 60 min was selected as the optimum contact time for

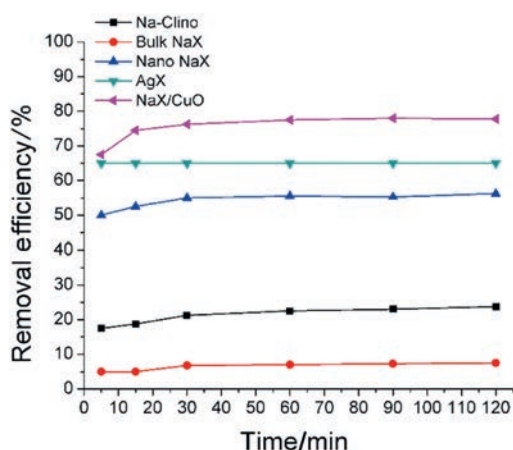
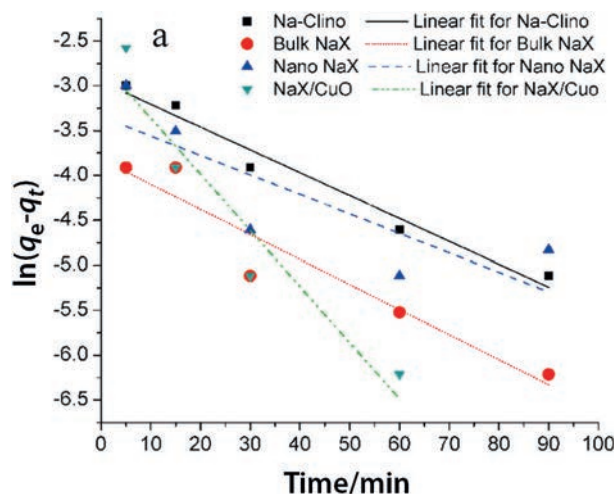


Fig. 4. Effect of contact time on the sorption of uranium at 27 °C, initial concentration of 4 mg·L⁻¹, initial pH = 7.56, and solid-liquid ratio is 5 g·L⁻¹.



the next experiments. In addition, it is clear that the uranium removal efficiency of NaX nanozeolite is higher than bulk NaX zeolite and Na-Clino zeolite. Reduction of particle size, which causes an increase in the specific surface area, leads to better performance of nanozeolite compared with bulk NaX zeolite and Na-Clino natural zeolite. However, modification of NaX nanozeolite with CuO nanoparticles and Ag⁺ resulted in a further increment of removal efficiency for NaX/CuO nanocomposite and AgX nanozeolite, respectively.

Two kinetics models including pseudo-first- and the pseudo-second-order which are expressed via Eqs. (5) and (6) respectively, were used to study the mechanism and rate of the uranium ion adsorption process by all absorbents [49]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (7)$$

$$h = K_2 q_e^2 \quad (8)$$

where q_e is the amount of ion adsorbed at equilibrium (mg·g⁻¹), q_t is the amount of ion adsorbed at time t (mg·g⁻¹), K_1 is the rate constant of the pseudo-first-order sorption (min⁻¹), K_2 is the rate constant of the pseudo-second-order kinetics (g·mg⁻¹·min⁻¹), and h is the initial sorption rate (mg·g⁻¹·min⁻¹). From the intercept and slope of the linear fitting of Eqs. (6) and (7) (Fig. 5) the value of the constants of these two models could be determined (Table 4).

As can be seen, for all synthesized absorbents including Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites the correlation coefficients (Adj.R²) are 0.99 for the pseudo-second-order model and have higher value than the pseudo-first-order adsorption model, indicating a better fit with the pseudo-second-order model. Also, the best fit of this model to the experimental data is seen in the better agreement between the experimental values for $q_{e,exp}$ and those from the second-order model. These results show that the pseudo-second-order sorption model is predominant in all performed sorption experiments. This means that, the overall sorption process is dependent on the amount of uranium ions which exist in solution and the number of adsorption sites on the adsorbents. On the other hand,

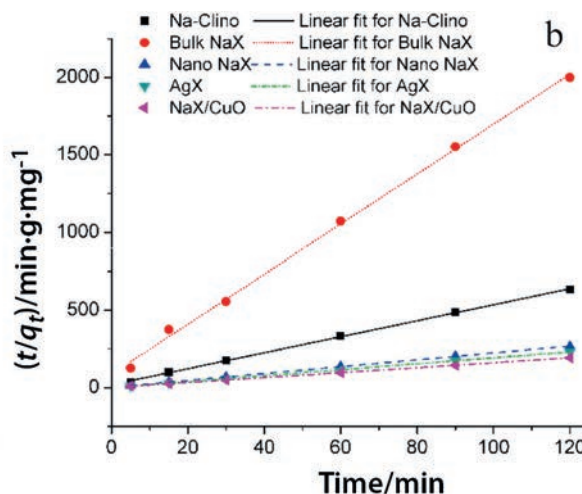


Fig. 5. a) Pseudo-first and b) pseudo-second-order kinetics plots of sorption of uranium at 27 °C, initial concentration of 4 mg·L⁻¹, initial pH = 7.56, and solid-liquid ratio is 5 g·L⁻¹.

Table 4

Kinetic parameters of pseudo-first-order and pseudo-second-order kinetic models for adsorption of uranium at 27 °C, initial concentration of 4 mg·L⁻¹, initial pH = 7.56, and solid-liquid ratio is 5 g·L⁻¹

Absorbent	$q_{e,exp}/\text{mg}\cdot\text{g}^{-1}$	Pseudo-first-order model			Pseudo-second-order model			
		K_1/min^{-1}	$q_e/\text{mg}\cdot\text{g}^{-1}$	Adj. R^2	$K_2/\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$q_e/\text{mg}\cdot\text{g}^{-1}$	$h/\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$	Adj. R^2
Na-Clino	0.19	0.026	–	0.96	1.38	0.19	0.05	0.9999
Bulk NaX	0.06	0.028	–	0.89	2.97	0.06	0.01	0.9993
Nano-NaX	0.45	0.022	–	0.58	2.39	0.45	0.49	0.9998
AgX	0.52	–	–	–	–	0.52	–	0.9998
NaX/CuO	0.62	0.063	–	0.88	2.07	0.63	0.82	0.9999

this model and quick adsorption of uranium ions on all the absorbents under study confirm that the chemical reactions such as complexation and ion-exchange are rate limiting steps for the process [50]. Moreover, one can see that the initial sorption rate of nano-NaX zeolite is higher than bulk NaX zeolite. This could be attributed to the smaller size and larger surface area of the nano-NaX zeolite. In addition, modification of NaX nanozeolite using CuO nanoparticles caused the initial sorption rate of NaX/CuO nanocomposite to be higher than the initial sorption rate of both bulk and nano-sized NaX zeolites.

3.4.2. Effect of initial uranium concentration and isotherm studies

The adsorption of uranium ions onto all synthesized absorbents including Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites as a function of the initial uranium concentrations was studied at 27 °C by varying the metal concentration from 4 to 20 mg·L⁻¹ (Fig. 6). The results showed that the removal efficiency of NaX nanozeolite decreases with solution concentration increasing which indicates that less favorable sites become involved when solution concentration rises. In the case of Na-Clino and NaX/CuO nanocomposite, this parameter rose with the initial uranium concentration increasing up to 12 mg·L⁻¹ and 16 mg·L⁻¹ respectively and then it dropped-off. A fast rise up to 8 mg·L⁻¹ and reaching a plateau after that were observed for both bulk NaX zeolite and AgX nanozeolite. Therefore, it can be concluded that modification of NaX nanozeolite by CuO nanoparticles and Ag⁺ created new adsorption sites on its surface so that saturation of absorbent occurred at higher initial uranium concentrations.

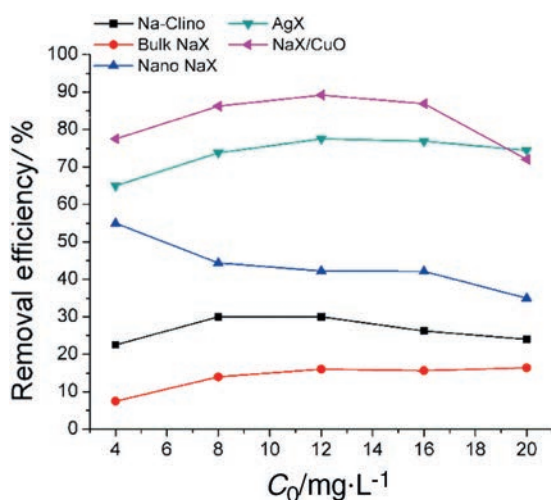


Fig. 6. Removal efficiency of sorption of uranium at 27 °C, adsorption time of 60 min, initial pH = 7.56, and solid-liquid ratio is 5 g·L⁻¹.

Moreover, in this study, four isotherm models including Langmuir, Freundlich, Sips, and C-isotherm were used to describe the equilibrium experimental data. The Freundlich isotherm, which is an empirical equation encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. This model is used to model the multilayer adsorption and for the adsorption on heterogeneous

surface. The Freundlich isotherm can be explained by the following equation [51]:

$$q_e = K_F C_e^{1/n} \quad (9)$$

where K_F and n are the Freundlich constant related to the adsorbent capacity and the intensity of the adsorption process respectively.

The Sips isotherm represents a combination of the Freundlich and Langmuir models. This model at low ion concentrations reduces to the Freundlich isotherm while a monolayer adsorption capacity, which is the characteristic of the Langmuir isotherm, is predicted at high concentrations by it. The Sips isotherm is expressed as follows [52]:

$$q_e = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}} \quad (10)$$

where q_m is relevant with adsorption capacity, b constant related to the energy of adsorption, and n is the exponent.

In C-isotherm, the parameter of distribution coefficient or K_d (L·g⁻¹), which is the concentration of the ions remaining in solution/the concentration of the ions adsorbed on the solid ratio, is constant at any concentration. The C-isotherm can be expressed by the following equation [53]:

$$q_e = K_d \times C_e \quad (11)$$

The Langmuir model did not fit to the experimental data and is hence not reported here. Freundlich, Sips, and C-isotherm plots for uranium adsorption onto Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites are shown in Fig. 7 and calculated parameters from fitting processes for each absorbent are listed in Table 5. Considering the value of correlation coefficients, Adj. R^2 , and amount of errors, it can be seen that the synthesized bulk NaX zeolite was well described by C-isotherm. Also, the best fit of this model to the experimental data is seen in the good agreement between the experimental values for $K_{d,exp}$ (0.04 L·g⁻¹) and those from this model (0.044 L·g⁻¹). For NaX nanozeolite the Freundlich isotherm was correlated to the experimental data well. Moreover, for this absorbent, n is greater than unity indicating that even at high uranium ion concentrations a significant adsorption occurs. On the other hand, for Na-Clino, AgX nanozeolite, and NaX/CuO nanocomposite the Sips isotherm well matched to the experimental data. The Sips model at high concentrations shows a monolayer adsorption capacity characteristic of the Langmuir isotherm. Therefore, at high initial uranium concentration sorption capacity must be decreased. This result is in good agreement with previous result obtained for the effect of initial uranium concentration for these three absorbents (Fig. 6).

3.4.3. Effect of temperature

The effect of temperature on uranium adsorption onto Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites from contaminated drinking water was studied and the results were shown in Fig. 8. Adsorption experiments were done at an initial uranium concentration of 20 mg·L⁻¹, contact time of 60 min, solid-liquid ratio is 5 g·L⁻¹, and pH 7.56. As temperature increases from 300 to 335 K, the adsorption capacity of all mentioned absorbent was increased. These results implicate

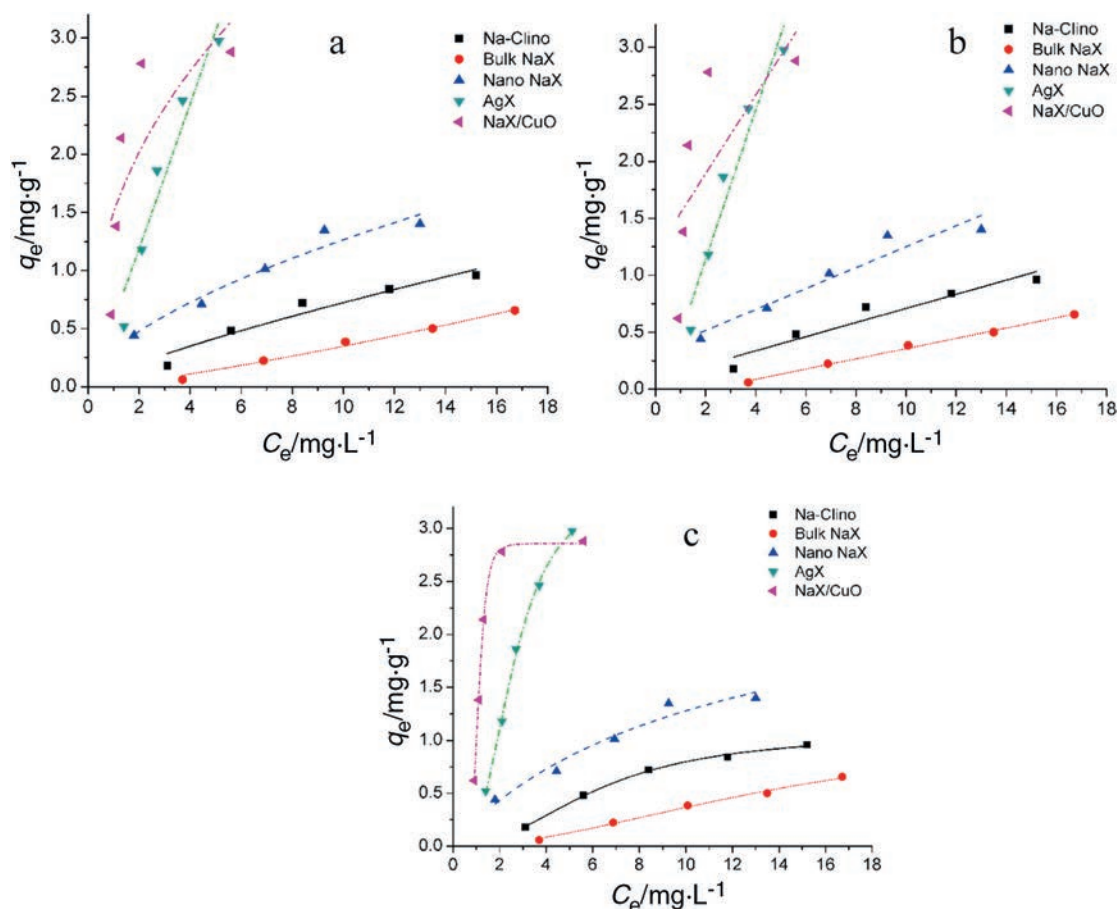


Fig. 7. (a) Freundlich, (b) C-isotherm, and (c) Sips sorption isotherm of U ions at 27 °C, adsorption time of 60 min, initial pH = 7.56, and solid-liquid ratio is 5 g·L⁻¹.

that the uranium adsorption process for these absorbents is an endothermic process and is utilitarian at higher temperatures.

In addition, various thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°), and free energy change, ΔG° , for the sorption of U ions onto all understudy absorbents were calculated using the following equations [26]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), K_d is the distribution coefficient, and T is the absolute temperature (K). The values of ΔH° and ΔS° are obtained from the slope and the intercept of the plot of $\ln K_d$ against $1/T$ for Na-Clino, bulk NaX, NaX/CuO nanocomposite, NaX and AgX nanozeolites (Fig. 9 and Table 6).

For all understudy absorbents including Na-Clino, bulk NaX zeolite, NaX/CuO nanocomposite, NaX and AgX nanozeolite, an endothermic process can be inferred from the positive amount of enthalpy change (ΔH°), which erewhile was shown by increasing of adsorption of uranium with temperature increasing (Fig. 8). For all understudy absorbents, ΔG° is negative which shows that the binding energy of uranium-sorbent is stronger than the uranium-solvent. Then uranium ion redistribution in the system and spontaneously sorption of uranium on the sorbent are due to this difference between energetic potentials of the system components. A chemical sorption occurs when high values of negative Gibbs free energies are obtained [54,55]. Moreover, the quantity of entropy change, (ΔS°), has a positive value for all synthesized absorbents indicating an increment in system randomness during the sorption process [26].

3.4.4. Effect of the solid-liquid ratio

As shown in Fig. 10, the removal efficiency of uranium ions for all synthesized absorbents including Na-Clino, bulk NaX zeolite, NaX/CuO

Table 5
Freundlich, Sips, and C-isotherm constant values for the adsorption of uranium ions

		Na-Clino	Bulk NaX	Nano-NaX	AgX	NaX/CuO
C-isotherm	K_d	0.06 ± 0.01	0.044 ± 0.001	0.09 ± 0.01	0.66 ± 0.090	0.34 ± 0.20
	Adj. R^2	0.90	0.99	0.90	0.93	0.32
Freundlich isotherm	K_F	0.12 ± 0.04	0.02 ± 0.01	0.31 ± 0.06	0.58 ± 0.14	1.50 ± 0.38
	$1/n$	0.80 ± 0.14	1.25 ± 0.10	0.61 ± 0.09	1.03 ± 0.18	0.43 ± 0.21
	Adj. R^2	0.92	0.98	0.94	0.92	0.46
Sips isotherm	q_m	1.07 ± 0.06	1.19 ± 0.49	2.84 ± 3.08	3.38 ± 0.15	2.86 ± 0.03
	b	0.02 ± 0.01	0.01 ± 0.00	0.09 ± 0.08	0.07 ± 0.01	0.53 ± 0.03
	$1/n$	2.25 ± 0.25	1.89 ± 0.44	0.94 ± 0.56	2.84 ± 0.23	6.42 ± 0.32
	Adj. R^2	0.99	0.988	0.92	0.997	0.998

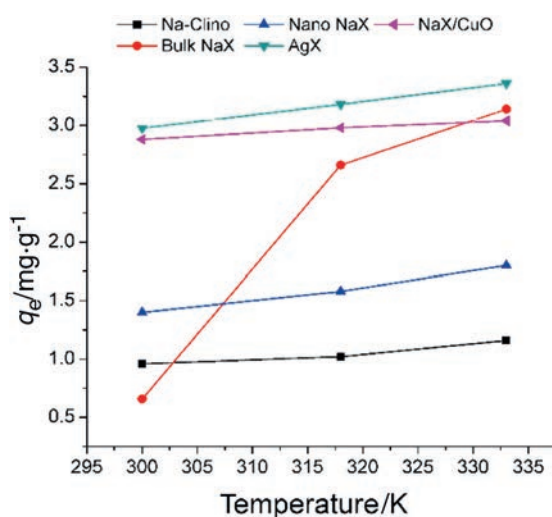


Fig. 8. Effect of temperature on sorption of U ions at initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, adsorption time of 60 min, initial pH = 7.56, and solid-liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$.

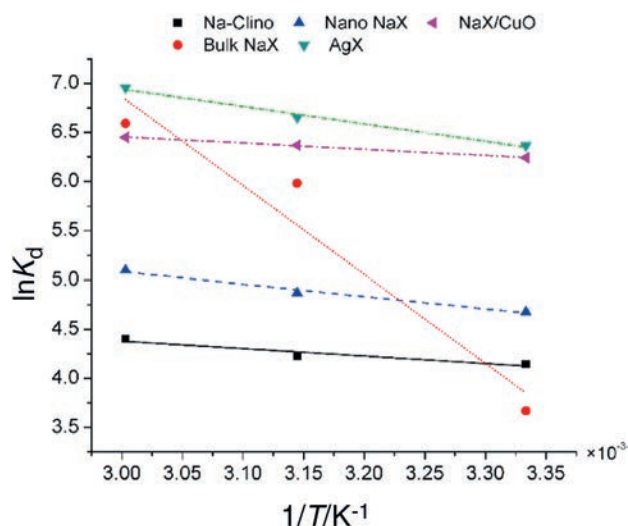


Fig. 9. The plot of $\ln K_d$ against $1/T$ at initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, adsorption time of 60 min, initial pH = 7.56, and solid-liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$.

nanocomposite, NaX and AgX nanozeolite enhanced when solid-liquid ratio was increased from $5 \text{ g} \cdot \text{L}^{-1}$ to $50 \text{ g} \cdot \text{L}^{-1}$. Adsorption experiments were done at 27°C , initial uranium concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, contact time of 60 min, and pH 7.56. For NaX nanozeolite and Na-Clino, the removal efficiency rapidly increases up to $20 \text{ g} \cdot \text{L}^{-1}$ and then maintains a high level up to $50 \text{ g} \cdot \text{L}^{-1}$. A rapid increase up to $10 \text{ mg} \cdot \text{L}^{-1}$ followed by a steady increase up to $50 \text{ mg} \cdot \text{L}^{-1}$ was observed for both bulk NaX zeolite and AgX nanozeolite. Removal efficiency for NaX/CuO

Table 6

Thermodynamic parameters for the adsorption of uranium ions at initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, adsorption time of 60 min, initial pH = 7.56, and solid-liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$

Absorbent	$\Delta H^\circ / \text{J} \cdot \text{mol}^{-1}$	$\Delta S^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta G^\circ / \text{kJ} \cdot \text{mol}^{-1}$		
			300 K	318 K	333 K
Na-Clino	6.32	55.37	−16.60	−17.60	−18.43
Bulk NaX	75.12	282.43	−84.65	−89.74	−93.97
Nano-NaX	10.39	73.50	−22.04	−23.36	−24.46
AgX	14.80	102.01	−30.59	−32.42	−33.95
NaX/CuO	5.24	69.42	−20.82	−22.07	−23.11

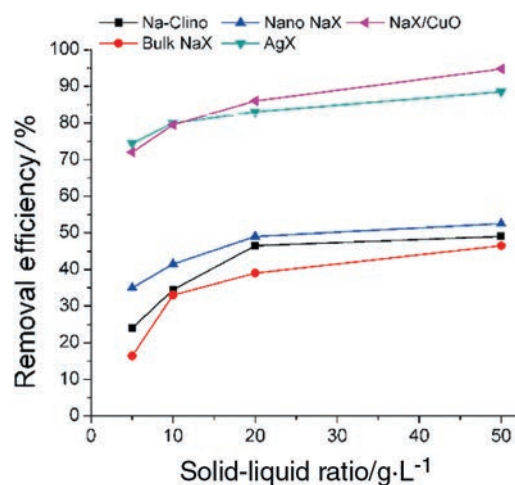


Fig. 10. Effect of solid-liquid ratio on the removal of uranium at 27°C , initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, adsorption time of 60 min, and initial pH = 7.56.

nanocomposite increases steadily with increasing solid-liquid ratio up to $50 \text{ g} \cdot \text{L}^{-1}$ and reaches the 94.75% removal efficiency at a solid-liquid ratio of $50 \text{ g} \cdot \text{L}^{-1}$. With increasing solid-liquid ratio, the number of adsorption sites in the system enhances, thereby, more exchangeable surface sites are available to adsorb uranium ions [27].

3.4.5. Effect of CuO nanoparticle concentration

The effect of various CuO nanoparticle concentrations from 2.1 wt% to 11.2 wt% on removal efficiency and distribution coefficient of NaX/CuO nanocomposite also was studied at 27°C , initial uranium concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, contact time of 60 min, solid-liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$ and pH = 7.56 (Fig. 11). From Fig. 11, clearly observed that both removal efficiency and distribution coefficient parameters increase by increasing in the CuO nanoparticle concentration. As mentioned before, at a pH close to 7, uranyl speciation distribution in the water media indicated that $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are the predominant anion species. On the other hand, zeolites have low affinity for inorganic anions due to the presence of uncompensated negative charge of their crystal lattice. Coating the zeolite with CuO led to a change in the negative external surface charge of it and an increase in its anion exchange capacity. Previous studies showed that due to the occurrence of an ion

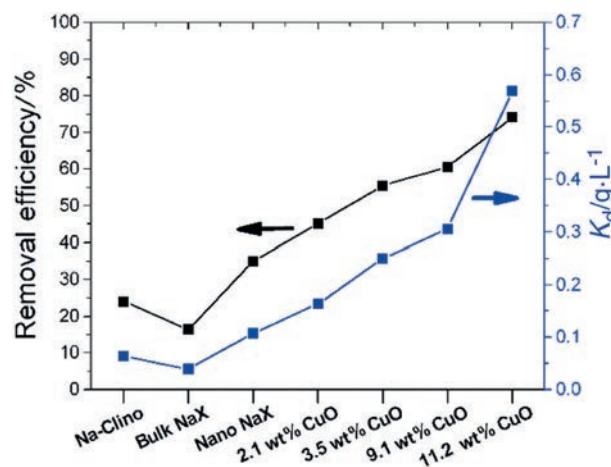


Fig. 11. Effects of CuO nanoparticles concentration on removal efficiency and distribution coefficient of uranium on NaX/CuO nanocomposite at 27°C , initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, solid-liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$, adsorption time of 60 min, and initial pH = 7.56.

exchange reaction between a metal oxide and OH groups of zeolite during the calcination process, a number of Brønsted and Lewis acid sites were generated in the zeolite. When zeolite was added to the copper nitrate solution, an ion exchange process occurs between Na^+ cations and $\text{Cu}(\text{OH})^{3+}$, $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2^{2+}$, or $\text{Cu}(\text{OH})_4^{2+}$ at specific pH values. Heating cause that $[\text{M}_i\text{O}_m(\text{OH})_n]^{p+}$ oxyhydroxide clusters generate in zeolites with di- or trivalent cations through hydrolysis. For example, Kazansky *et al.* resulted that in ZnO/NaY zeolite due to dehydration, the stability of $[\text{Zn}(\text{H}_2\text{O})_n]^{2+}$ species which insert in the supercages of NaY zeolite after zinc ion exchange process, is decreased during vacuum treatment at 300 °C. Therefore, the acidic bridging hydroxyl groups and nanozinc hydroxide cluster can be formed due to hydrolyzation of Zn^{2+} cations by water molecules. Nanozinc hydroxide clusters further were decomposed to zinc oxide. Using a diffuse reflectance IR and UV–Vis absorption spectra, the resulting acidic protons and the zinc oxide clusters were observed, respectively [56]. In addition, both capabilities of CuO nanoparticles [57] and NaX zeolite provide a dual active site system for removal of uranium ions from drinking water. Therefore, with the increasing concentration of CuO nanoparticles removal efficiency and distribution coefficient increase as shown in Fig. 11.

3.4.6. Effect of cation exchange

The removal efficiency and distribution coefficient for the adsorption of uranium ions on parent NaX nanozeolite and potassium, cesium, and silver exchanged forms of it have been determined and shown in Fig. 12. The all experiments were performed at 27 °C with 20 ml of the uranium initial concentration solution, contact time of 60 min, solid–liquid of $5 \text{ g} \cdot \text{L}^{-1}$, and $\text{pH} = 7.56$. Framework structure properties of X-zeolite and the location of the cations which affects the electric field in the zeolite framework may be reasons for the observed differences in the adsorption properties of various kinds of X-zeolite. Many factors such as a Si/Al ratio, cation charge, charge/radius ratio, cation density and water content can impress the effect of a single cation within the framework of zeolite [58]. As shown in Fig. 13 which shows the effect of the charge/radius ratio of exchanged cations on the uranium removal efficiency, monovalent cations with lower charge/radius ratio show better performance as absorbent for removal of uranium ions from contaminated waters. However, a difference between Ag-exchanged form and the other cation exchanged forms was observed. The d orbitals of silver ion give it much more intense directional properties than alkali and alkaline earth cations which have the stable noble gas electronic configuration. Silver ion has stronger polarizing power than ions with the same charge and similar size such as sodium ion. Furthermore, Ag^+ is monovalent and half of them will be in the exposed position on the cavity surface where their polarizing power can be most strongly exerted [59].

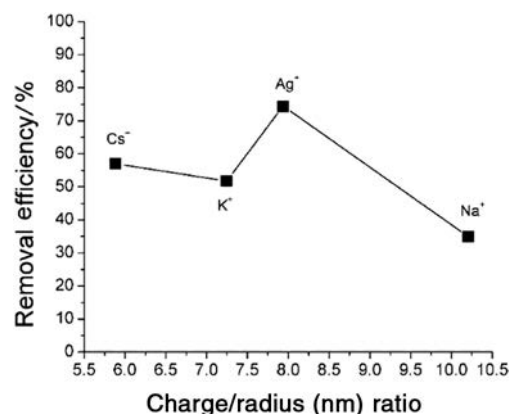


Fig. 13. Effects of charge/radius ratio of exchanged cations on uranium removal efficiency.

4. Conclusions

NaX nanozeolite synthesized by the hydrothermal method was modified using various concentrations of CuO nanoparticles and monovalent cations. Parent NaX nanozeolite and its modified forms were characterized by various techniques such as XRD, FE-SEM, TEM, AAS, and FT-IR. The uranium adsorption properties of the zeolites were determined using a batch technique by studying the effect of relevant parameters such as initial uranium concentration, contact time, temperature, solid–liquid ratio, CuO nanoparticle concentration, and charge/radius ratio of exchanged monovalent cations. Comparison of results obtained for NaX nanozeolite and its modified forms with those that were obtained in bulk NaX zeolite and Na-form of clinoptilolite natural zeolite showed that modification of NaX zeolite by CuO nanoparticles and various monovalent cations can effectively improve uranium absorption capacity of it. Moreover, an increase in adsorption capacity was observed by CuO nanoparticle concentration increasing and charge/radius ratio decreasing. Finally, the results showed that under optimum condition of $\text{pH} = 7.56$, contact time of 60 min at 27 °C with solid–liquid ratio of $50 \text{ g} \cdot \text{L}^{-1}$ a uranium removal efficiency of 94.75% can be obtained in the presence of all anions and cations which are available in drinking water by NaX/CuO nanocomposite.

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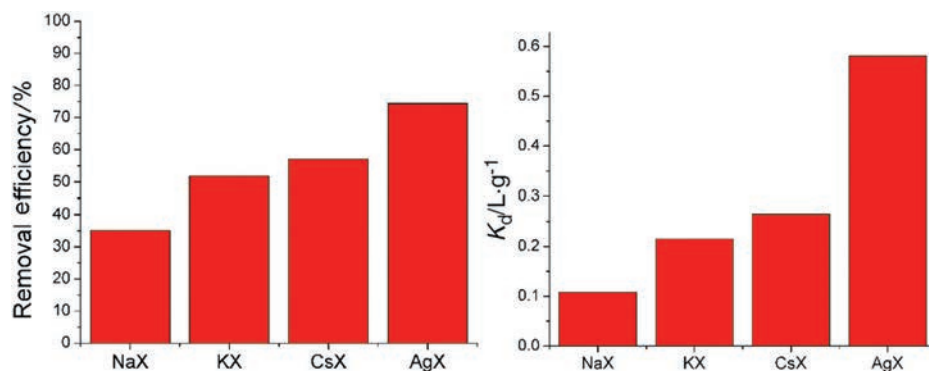


Fig. 12. Effects of cation exchange modification on removal efficiency and distribution coefficient of uranium at 27 °C, initial concentration of $20 \text{ mg} \cdot \text{L}^{-1}$, solid–liquid ratio is $5 \text{ g} \cdot \text{L}^{-1}$, adsorption time of 60 min, and initial $\text{pH} = 7.56$.

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