# Application of $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite for U(VI) removal

Zohreh Akbari-Jonoush[a], Simin Naseri[a,b], Mahdi Farzadkia[c,*],
Hamid-Reza Mohajerani[d], Mehdi Shirzad-Siboni[c,*], Jae-Kyu Yang[e]

[a]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran,
emails: z_akbari1229@yahoo.com (Z. Akbari-Jonoush), naserise@tums.ac.ir (S. Naseri)
[b]Center for Water Quality Research (CWOR), Institute for Environmental Research (IER), Tehran University of Medical Sciences,
Tehran, Iran
[c]Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran,
Tel. +98 9122588677; Fax: +98 2188607939; email: mahdifarzadkia@gmail.com (M. Farzadkia), Tel. +98 9112346428;
Fax: +98 2188607939; emails: mshirzadsiboni@yahoo.com, shirzad.m@iums.ac.ir (M. Shirzad-Siboni)
[d]Iran Radioactive Waste Management Company, Atomic Energy Organization of Iran, Tehran, Iran, email: hmohajerani@aeoi.org.ir
[e]Division of General Education, Kwangwoon University, Seoul 139-701, Korea, email: jkyang@kw.ac.kr

## ABSTRACT

In this study, $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite synthesized by co-precipitation method were used as adsorbents for the removal of U(VI) from aqueous solutions. The main compositions of AC–$Fe_3O_4$ and $C_{14}/SiO_2$–$Fe_3O_4$ were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. The removal efficiency of U(VI) was studied as a function of pH, contact time, ionic strength, temperature, adsorbent dose, initial U(VI) concentration, and initial benzamide concentration. Maximum adsorption of U(VI) was obtained at pH 6. The removal of U(VI) reached an equilibrium within 30 min by $C_{14}/SiO_2$–$Fe_3O_4$ and 90 min by AC–$Fe_3O_4$, respectively. Removal efficiency of U(VI) by both adsorbents was decreased with increasing ionic strength and initial U(VI) concentration, but was increased with increasing temperature and adsorbent dosage. Kinetic study revealed that the pseudo-second order model well described the adsorption of U(VI) onto two adsorbents. When adsorption data was analyzed by both Langmuir and Freundlich adsorption isotherms, it was better described by the Langmuir model. The maximum adsorption of U(VI) was 16.29 and 15.87 mg/g by $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite, respectively. The thermodynamic parameters of the adsorption process indicated that adsorption occurred through endothermic process. Overall, this work shows that $C_{14}/SiO_2$–$Fe_3O_4$ is a more effective adsorbent than AC–$Fe_3O_4$ for the removal of low concentration of U(VI).

*Keywords:* Adsorption; U(VI); $C_{14}/SiO_2$–$Fe_3O_4$; AC–$Fe_3O_4$; Kinetics and isotherm models

*Corresponding authors.

## 1. Introduction

In recent years, contamination of surface and ground waters is regarded as one of the most important environmental issues. Radionuclides having high toxicity and non-biodegradability cause several problems in environmental systems and public health [1–3]. Generally, uranium concentration in natural environment is very low [4,5]. But artificial use of uranium as nuclear fuel [2,6–8] is serious concern in environment and human health. Under aerobic condition, uranium exists predominantly as a hexavalent species [9,10], which is soluble and mobile [11–13]. So uranium contaminated in soils can be transferred to surface and groundwater. The inhalation and ingestion of uranium can cause irreversible lungs and kidney damage or even death [12,14,15] due to its long half-life as well as chemical and radiological toxicity [16,17]. Recently, a few studies have shown that the central nervous system is sensitive to uranium because it crosses the blood–brain barrier and accumulates in brain [18]. One of the sources of uranium accumulation in human body is ingestion of contaminated drinking water [19]. Thus, united states environmental protection agency (US-EPA) and World Health Organization (WHO) established a maximum contaminant level (MCL) for uranium in drinking water as 30 and 9 µg/L, respectively [20,21]. Due to the several problems mentioned above, finding a proper method for the treatment of water contaminated with uranium becomes an important research topic. Among several traditional methods such as adsorption, coagulation, precipitation, reverse osmosis, electrochemical treatments, ion exchange, membrane separation [2,22,23], adsorption is an effective method for the removal of moderate and low concentration of uranium due to its simplicity of design and operation, high capacity, and ease of regeneration [6,24–27]. In recent years, several kinds of adsorbents have been used for the removal of uranium. Among them, nano-sized adsorbents are more effective and attractive because of their high surface area to volume ratio and convenience in the modification of their surface functionality [28]. But separation of the nano-sized adsorbents is very difficult in practical application. Recently, many efforts have been devoted to synthesize super paramagnetic nanocomposites combined with iron oxide nanoparticles. These adsorbents can be easily separated by an external magnetic field without no costly process such as centrifugation or filtration [29,30]. Das et al. reported that $Fe_3O_4$ nanoparticles had approximately 5 mg/g adsorption capacity of U(VI) [31]. Therefore, modification of chemical and physical properties of $Fe_3O_4$ nanoparticles has much attention. $Fe_3O_4$–$SiO_2$ nanocomposite has an iron oxide core and a silica shell. Silica shell plays an important role in physical and chemical properties of the nanocomposite because it can prevent damage of physical and magnetic properties of the coated material [32] as well as aggregation of particles in solution [15]. There are several studies about modification of $Fe_3O_4$–$SiO_2$ nanocomposite. For example, Sha et al. and Wang et al. modified $Fe_3O_4$–$SiO_2$ nanocomposite by chlorodimethyl-n-octadecylsilan and (3-aminopropyl)trimethoxysilane (APTMS) [33,34]. Chang grafted hexadecyltrimethoxysilane (HTMOS) onto the surface of $Fe_3O_4$-$SiO_2$ nanocomposite [35]. Tan et al. used 1,6-hexanediamine for modification of $Fe_3O_4$-$SiO_2$ nanocomposite [1] and Ahangaran used vinyltriethoxysilane as a silane coupling agent for the modification of $Fe_3O_4$-$SiO_2$ nanocomposite [32]. Another way for increasing the adsorption capacity of $Fe_3O_4$ nanoparticles is coating of them on the effective and economic adsorbents. Activated carbon is widely used in the treatment of various industrial effluents because it has a higher thermal and radiation resistance, better acid–base stability, high surface area, and porosity [36].

Hence, in this study, $Fe_3O_4$–$SiO_2$ nanocomposite modified by triethoxyoctylsilane($C_{14}/SiO_2$–$Fe_3O_4$) and AC–$Fe_3O_4$ nanocomposite was used to remove U(VI) from aqueous solutions. Benzamide ($C_7H_7ON$), which is a derivative of benzoic acid, was used as medium solution because it has donor atoms (N, O) that can form complexes with uranyl ions [16,37]. The adsorption behavior of these adsorbents toward U(VI) was investigated with respect to different experimental conditions such as initial solution pH, contact time, ionic strength, temperature, adsorbent dose, concentration of U(VI), and concentration of benzamide. The adsorption kinetics, isotherms, and thermodynamics were conducted to evaluate the adsorption capacity of $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite.

## 2. Materials and methods

### 2.1. Chemicals

Triethoxyoctylsilane, tetraethylorthosilicate (98%), benzamide, pyridine, toluene, ethanol, arsenazo(III), ammonium solution, iron(II) chloride, iron(III) chloride (97%), zinc (99%), and activated carbon, which were of analytical grade, were purchased from Merck, Germany. The initial pH of solution was adjusted by the addition of 0.1 M NaOH or HCl and was measured by pH meter (HQ40d HACH, US). The experiments were carried out at constant temperature in a shaking incubator (Labcon, Afrika). Uranium stock solution (1,000 mg/L) was prepared by dissolving

appropriate amounts of $C_4H_6O_6U \cdot 2H_2O$ with 99% purity (Merck, Germany) in distilled water.

## 2.2. Preparation of magnetic adsorbents

### 2.2.1. Synthesis of $C_{14}/SiO_2$–$Fe_3O_4$ nanocomposite

First, $Fe_3O_4$ nanoparticles were synthesized by co-precipitaion of $Fe^{2+}$ and $Fe^{3+}$ ions in an ammonia solution [38]. Typically, 8.48 g $FeCl_3 \cdot 6H_2O$ and 2.25 g $FeCl_2 \cdot 4H_2O$ were dissolved in 400-mL distilled water for 1 h at 80°C under $N_2$ atmosphere with vigorous mechanical stirring. Then, 20-mL ammonium solution was added into the reaction mixture, which resulted in black precipitate of $Fe_3O_4$ nanoparticles. After 30 min, the nanoparticles were separated from the suspension using a permanent magnet and repeatedly washed with distilled water. Then, the nanoparticles were dried at 50°C for 4 h.

To prepare silica-coated $Fe_3O_4$ nanoparticles, 2.5 g of $Fe_3O_4$ nanoparticles were dispersed for 10 min in a three-necked round bottom flask with ultrasonic irradiation. One hundred and fifty milliliters of ethanol and 40 mL of ammonium solution were then added to the $Fe_3O_4$ suspension. The mixture of ethanol and tetraethylorthosilicate (TEOS) (89.2 and 10.8 mL) was slowly added to the $Fe_3O_4$ suspension within 8 h. Then, the $Fe_3O_4$–$SiO_2$ nanocomposite was separated from the supernatant with a permanent magnet and thoroughly washed with distilled water. And then it was dried at 50°C for 12 h. $C_{14}/SiO_2$–$Fe_3O_4$ nanocomposite was prepared by surface functionalization of $Fe_3O_4$–$SiO_2$ nanocomposite using triethoxyoctylsilane as a silylation agent. Two grams of $Fe_3O_4$-$SiO_2$ nanocomposite and 100 mL of toluene were dispersed by ultrasonic irradiation. Ten milliliter of pyridine and 2 mL of triethoxyoctylsilane were then added into the mixture solution under vigorous mechanical stirring at room temperature for 10 h. The modified $Fe_3O_4$–$SiO_2$ nanocomposite was collected with a permanent magnet and washed with ethanol several times. And then it was dried at 50°C for 12 h [33].

### 2.2.2. Synthesis of AC–$Fe_3O_4$ nanocomposite

AC–$Fe_3O_4$ nanocomposite was prepared by the co-precipitation method [39,40]. First, 8 g of $FeCl_3 \cdot 6H_2O$ and 2.5 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 400 mL of distilled water at 80°C under nitrogen atmosphere and intense mechanical stirring for 1 h. Then, 10 g of powder-type activated carbon was added into the reaction mixture and stirred for 30 min. After mixing, 25 mL of 25% ammonia solution was added into the mixture.

Finally, the formed suspension was separated with a permanent magnet and washed several times with distilled water. The AC–$Fe_3O_4$ nanocomposite was dried at 50°C for 12 h.

## 2.3. Characterization instruments

For characterization of the functional groups on the surface of the samples, Fourier transform infrared spectroscopy (FT-IR) analysis (Tensor 27, Bruker, Germany) was performed in the range of 400–4,000 $cm^{-1}$. To determine the crystal phase composition of the prepared samples, X-ray diffraction (XRD) was carried out at room temperature using a D8 Advance diffractometer (Bruker, Germany) with monochromatic high-intensity Cu Kα radiation (l = 1.5406 Å), the accelerating voltage of 40 kV, and the emission current of 30 mA. The Debye–Scherrer formula was used to measure the average crystalline size of the catalysts [41]. The surface morphology of both $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite was examined by field emission scanning electron microscope (FE-SEM, Hitachi S4160 Japan). The point of zero charge ($pH_{pzc}$) was determined to investigate the surface charge properties of the adsorbents. The $pH_{ZPC}$ of samples was determined adopting the method previously used [42,43].

## 2.4. Adsorption experiments

Batch adsorption experiments were performed in 1,000 mL Erlenmeyer flask containing 5 mg/L U(VI) solution and 2 g of adsorbent. The flasks were shaken at 250 rpm and at specified temperature in different contact time (5–120 min). After adsorption process, the adsorbent was separated from solution with an external magnet. The concentration of U(VI) was measured using a spectrophotometric method (UV–visible Spectrometer, Cintra 6, Australia) based on the formation of colored complex with Arsenazo(III) at 665 nm [7,44]. To evaluate various parameters on the adsorption efficiency, adsorption experiments were conducted at different initial pH (2–10), initial benzamide concentration (0–60 mg/L), contact time (5–120 min), ionic strength (0.01–1.5 M), temperature (288–333 K), initial U(VI) concentration (1–30 mg/L), and adsorbent amounts (0.4–4 g/L). The equations for obtaining removal efficiency and adsorption capacity of U(VI) are shown in Table 1. All experiments were performed in duplicate or triplicate and averaged values were reported.

Table 1
All equations used in this study (The kinetics, isotherms and thermodynamics) [1,6,15,16,28,58,59]

|  | Kinetic models | Thermodynamic equations | Isotherm equations |
|---|---|---|---|
| Removal efficiency $\frac{C_0 - C_e}{C_0} \times 100$ | Pseudo-first-order $\ln(q_e - q_t) = \ln q_e - K_1 t$ | Van't Hoff $\ln(K_1) = \frac{\Delta S}{R} - \frac{\Delta G}{RT}$ | Langmuir isotherm $\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$ |
| Adsorption capacity $\frac{C_0 - C_e}{W} \times V$ | Pseudo-second-order $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$ | Distribution coefficient ($K_d$) $\frac{q_e}{C_e}$ | Freundlich isotherm $\log q_e = \log K_F + \frac{1}{n} \log C_e$ |
|  | Intraparticle diffusion models $q_t = K_p \times t^{0.5} + C$ | Standard free energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ | Separation factor ($R_L$) $\frac{1}{1 + bC_0}$ |

Notes: Parameters: $C_0$ and $C_e$ is initial and equilibrium concentrations of uranium (mg/L), $V$ is the volume of solution (L), $W$ is the mass of adsorbent (g), $q_e$ (mg/g), $q_t$ (mg/g), $k_1$ (1/min), $k_2$ (g/mg min), $K_L$ (L/mg), $q_m$ (mg/g), $K_F$ (mg$^{1-1/n}$ L$^{1/n}$ g$^{-1}$), $K_p$ (mg/g min$^{-0.5}$), $C_0$ (mg/g), $\Delta S$ (J/mol K), $\Delta H$ (kJ/mol), $R$ (8.314 J/mol K), $T$ (K).

# 3. Results and discussion

## 3.1. Characterization of the adsorbent

FT-IR spectra of $Fe_3O_4$, $Fe_3O_4$–$SiO_2$, $C_{14}$/$SiO_2$–$Fe_3O_4$, and AC–$Fe_3O_4$ nanocomposite are shown in Fig. 1. For the case of $Fe_3O_4$ nanoparticles, a single absorption peak observed at 586 cm$^{-1}$ is related to Fe–O–Fe bond vibration [45,46]. Two FT-IR spectra of $Fe_3O_4$–$SiO_2$ and $C_{14}$/$SiO_2$–$Fe_3O_4$ nanocomposite are very similar except peaks observed at 2,914, 2,201, and 2,232 cm$^{-1}$. The absorption peak at 2,914 cm$^{-1}$ in the modified $Fe_3O_4$–$SiO_2$ nanocomposite is approximately twice taller than that in unmodified nanocomposite.



Fig. 2. XRD spectra of the samples.
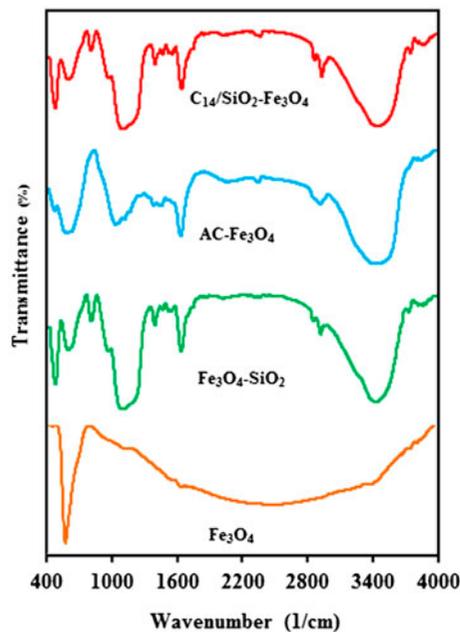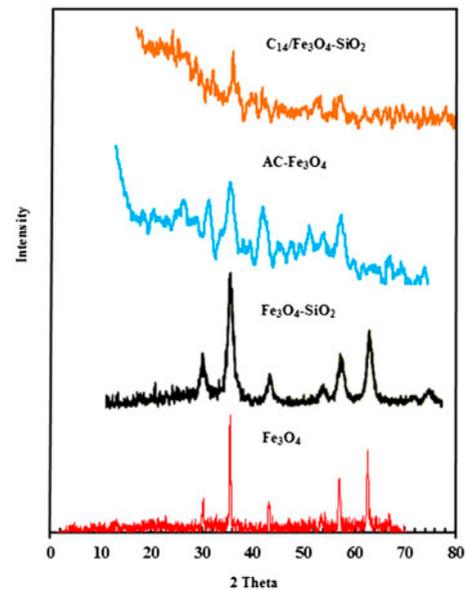
This peak is related to $CH_2$ group which originates from silane coupling agent [33]. The two peaks observed at 2,201 and 2,232 cm$^{-1}$ are corresponding to C≡N stretching vibration [47]. This result indicates successful modification of $Fe_3O_4$–$SiO_2$ by triethoxyoctylsilane. Other absorption peaks observed at 460 and 800 cm$^{-1}$ in $Fe_3O_4$–$SiO_2$ and $C_{14}$/$SiO_2$–$Fe_3O_4$ nanocomposite are related to Si–O–Si stretching vibration and Si-O vibration, respectively [45]. The absorption peak at 3,401 cm$^{-1}$ is related to O–H stretching vibration of the silanol group [35]. The band at 1,540 cm$^{-1}$ is corresponding to asymmetric C=O stretching of carboxylate [48]. The peak at 1,384, 1,634, and 1,458 cm$^{-1}$ is attributed to the vibration of –CH=CH– double bond,
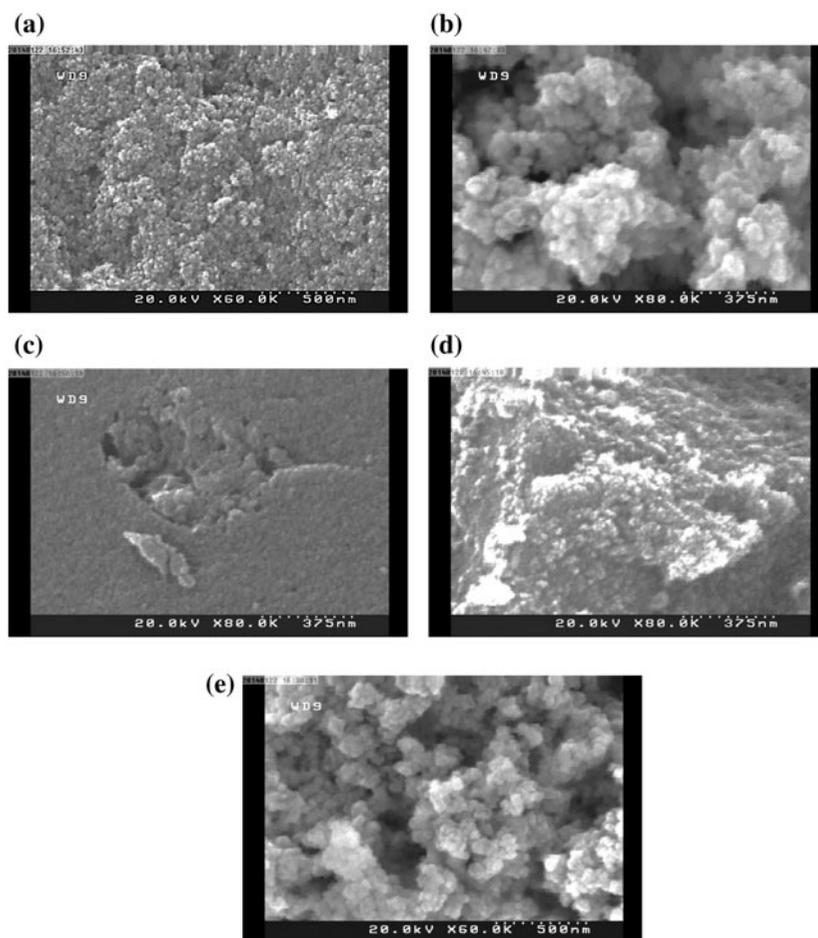


Fig. 1. FTIR spectra of the samples.

Fig. 3. SEM image of the sample: (a) $Fe_3O_4$, (b) $Fe_3O_4$–$SiO_2$, (c) AC, (d) AC–$Fe_3O_4$, and (e) $C_{14}$/$SiO_2$–$Fe_3O_4$.

the stretching vibrations of OH and vibrations of CH, respectively [49,50]. Also, the absorption peaks at 3,423 and 1,640 cm$^{-1}$ can be assigned to the adsorbed water on the silica shell or the silanol groups of the silica [32]. The absorption band at 1,000–1,300 cm$^{-1}$ of AC–$Fe_3O_4$ nanocomposite is related to C–O stretching [51].

The crystalline structures of the $Fe_3O_4$, $Fe_3O_4$–$SiO_2$, AC–$Fe_3O_4$, and $C_{14}$/$SiO_2$–$Fe_3O_4$ nanocomposite were identified by XRD analysis (Fig. 2). Diffraction peaks observed at 30.02°, 35.42°, 36.62°, 43.14°, 57.05°, and 62.75° as 2$\theta$ values were well matched with the standard patterns of $Fe_3O_4$ [34,52]. Quite similar diffraction peaks were observed for $C_{14}$/$SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite, indicating the presence of crystalline phase of $Fe_3O_4$ nanoparticles in both $C_{14}$/$SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite. The weak peaks appeared at low angles correspond to amorphous structure of $SiO_2$ [35].

SEM images of $Fe_3O_4$, $Fe_3O_4$–$SiO_2$, activated carbon, AC–$Fe_3O_4$ and modified $Fe_3O_4$–$SiO_2$ nanocomposite are shown in Fig. 3(a–e), respectively. As shown in Fig. 3(a–b) and (d–e), the morphology of nanoparticles is spherical. The SEM image in Fig. 3(a) reveals that $Fe_3O_4$ nanoparticles have very small particle size about 16 nm. Likewise, the diameter of $Fe_3O_4$–$SiO_2$ nanocomposite is in the range of 30–60 nm as shown in Fig. 3(b). After covering the $Fe_3O_4$ core by silica shell, the size of $Fe_3O_4$–$SiO_2$ nanocomposite is increased and the rough surface becomes smooth. Fig. 3(e) shows the morphology of $Fe_3O_4$–$SiO_2$ nanocomposite after modification with triethoxyoctylsilane. The particle sizes of this nanocomposite are larger and smoother than unmodified nanocomposite. These results showed that the $Fe_3O_4$–$SiO_2$ nanocomposite was completely coated by the triethoxyoctylsilane. In Fig. 3(c) and (d), it can be seen that the surface of activated carbon is completely covered by $Fe_3O_4$ nanoparticles in size about 20–30 nm after coating of $Fe_3O_4$ on the activated carbon.
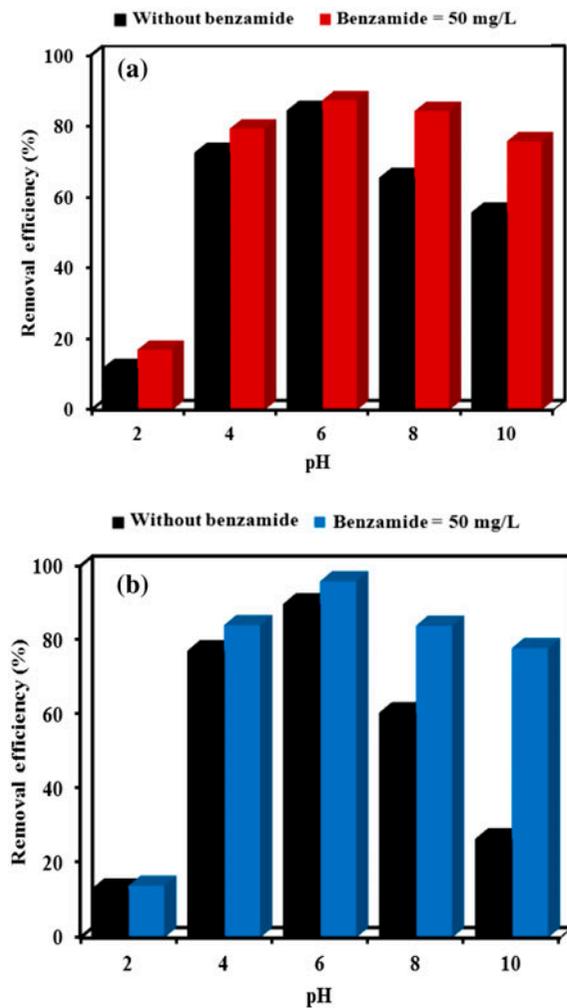
Fig. 4. Effect of pH and benzamide on the adsorption of U (VI) by (a) $C_{14}/SiO_2$–$Fe_3O_4$ and (b) AC–$Fe_3O_4$ nanocomposite (Time = 120 min, $T$ = 303 K, adsorbent dosage = 2 g/L, U(VI) = 5 mg/L, benzamide = 50 mg/L).



Fig. 5. The zero point charge of samples.



Fig. 6. Effect of initial concentration of benzamide on the adsorption of U(VI) by $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite (Time = 120 min, $T$ = 303 K, adsorbent dosage = 2 g/L, U(VI) = 5 mg/L).

## 3.2. The effect of operational parameters on the U(VI) removal efficiency

### 3.2.1. The effect of solution pH

The effect of pH on the U(VI) adsorption was studied between pH 2 and 10 by 2 g/L of $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite with U(VI) solutions (5 mg/L) in the presence and absence of benzamide (50 mg/L). According to Fig. 4(a) and (b), the solution pH was identified as a very important parameter in adsorption process. Removal efficiency of U(VI) by two adsorbents was increased with increasing solution pH from 2 to 6 while it was decreased above pH 6. Percentage removal of U(VI) was maximum at pH 6. It may be due to the formation of various U(VI) species and structural features of the each adsorbent at different pHs [53]. Wang et al. reported distribution of U(VI) species in aqueous solution from pH 0–14 using a Medusa program [14]. Zero point charge of $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ was 4.8 and 5.7, respectively (Fig. 5). In pH > $pH_{zpc}$, the surface is negatively charged, whereas at pH < $pH_{zpc}$, it is positively charged. In acidic solution, the $UO_2^{2+}$ is a dominant U (VI) species [9,30]. Therefore, removal efficiency was very low at acidic conditions in two adsorbents because of electrostatic repulsion between protonated surface of each adsorbent and positive charges U(VI). The formation of trinuclearuranyle species began at pH 4 and was dominant at pH > 4.5 [9]. Removal

Fig. 7. Effect of contact time on the adsorption of U(VI) by $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposite (pH 6, $T$ = 303 K, adsorbent dosage = 2 g/L, U(VI) = 5 mg/L, benzamide = 50 mg/L).
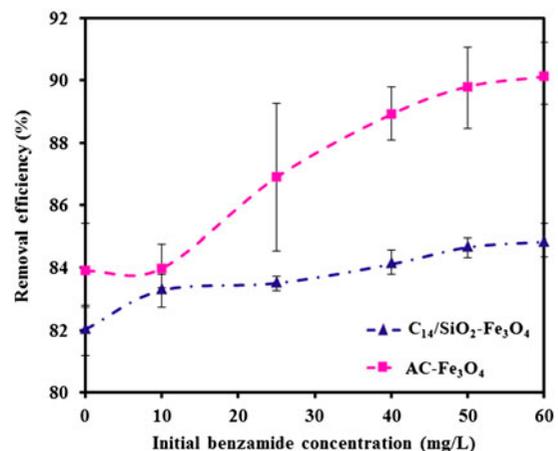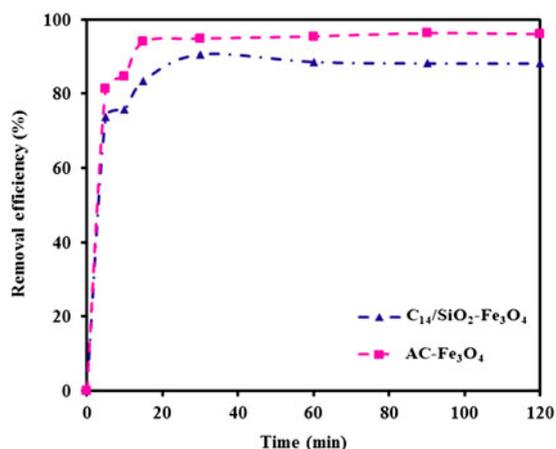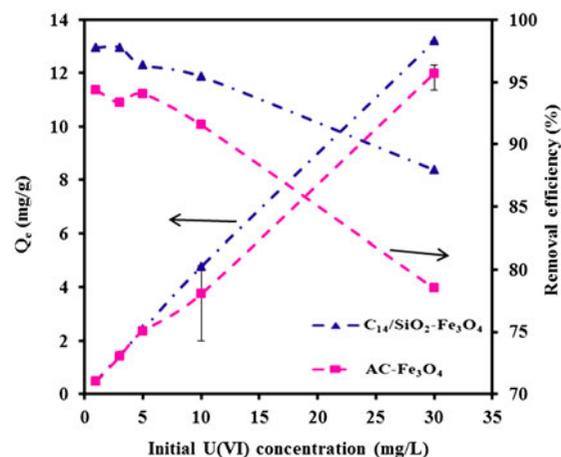


Fig. 9. Effect of initial U(VI) concentration on the adsorption of U(VI) by $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposite (pH 6, time = 30 min, $T$ = 318 K ($C_{14}/SiO_2–Fe_3O_4$), 303 K ($AC–Fe_3O_4$), adsorbent dosage = 2 g/L, benzamide = 50 mg/L).
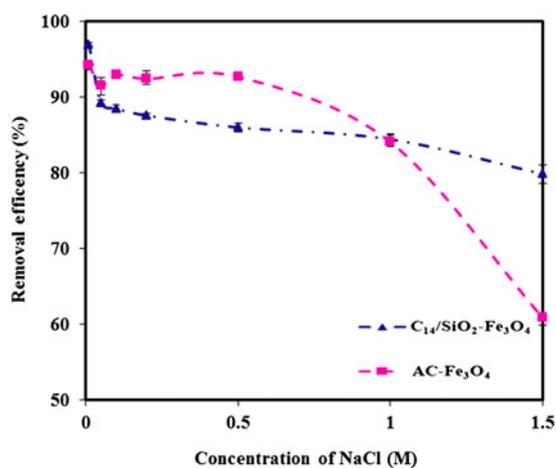


Fig. 8. Effect of ionic strength on the adsorption of U(VI) by $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposite (pH 6, time = 30 min, $T$ = 303 K, adsorbent dosage = 2 g/L, U(VI) = 5 mg/L, benzamide = 50 mg/L).



Fig. 10. Effect of adsorbent dosage on the adsorption of U(VI) by $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposite (pH 6, time = 30 min and $T$ = 318 K ($C_{14}/SiO_2–Fe_3O_4$), 303 K ($AC–Fe_3O_4$), ion strength = 0.01 M, U(VI) = 5 mg/L, benzamide = 50 mg/L).

efficiency of U(VI) reached to maximum around pH 6 because of the greatest electrostatic attraction between negative surface and positive species of U(VI). From pH > 7, the predominant U(VI) species has neutral and negative charge [24,54]. So, it can be expected that the adsorption of U(VI) become low above neutral pH. Also it could be seen from Fig. 4(a) and (b) that more positive effect of benzamide on the removal efficiency of U(VI) was observed in basic solution pH compared to that in acidic solution pH. It may be explained by the electrostatic attraction between surface of adsorbents and uranium–benzamide complex which was formed between uranium and benzamide in basic pH.

### 3.2.2. The effect of initial benzamide concentration

The effect of initial benzamide concentration on the removal efficiency of U(VI) was investigated at 5 mg/L uranium solution with variation of benzamide concentration from 0 to 60 mg/L, at 2 g/L of adsorbent and at pH 6 for 120 min. Fig. 6 indicated that the removal of U(VI) was increased in two adsorbents by adding benzamide up to 50 mg/L, but little increase was observed after 50 mg/L. The reason for the increased removal of U(VI) by adding the benzamide is related to the creation of uranium–benzamide

complex. This complex was created completely in 5 mg/L U(VI) and 50 mg/L benzamide. Similar results have been reported by other researchers [55–57].

### 3.2.3. The effect of contact time and kinetic studies

The effect of contact time on the U(VI) removal by $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposites was investigated with variation of reaction time from 5 to 120 min at constant concentration of U(VI) (5 mg/L), benzamide (50 mg/L) and at constant amount of adsorbent (2 g/L) at pH 6 (Fig. 7). Removal of U(VI) onto two adsorbents was quite rapid and 73.6 and 81.23% removal was observed within the first 5 min by $C_{14}/SiO_2$–$Fe_3O_4$ and by AC–$Fe_3O_4$ nanocomposite, respectively. Removal of U(VI) by $C_{14}/SiO_2$–$Fe_3O_4$ nanocomposite reached to maximum in 30 min (90.58%). And the removal of U(VI) by AC–$Fe_3O_4$ nanocomposite reached to 94.82% in 30 min. These results indicate that the adsorption of U(VI) onto two adsorbents occurred in two phase. In the first phase, adsorption occurs rapidly due to an abundant availability of active sites on the adsorbent [1,6]. Following this phase, adsorption rate is decreased and reached to an equilibrium. The reason for this trend is due to an intraparticle diffusion of U(VI) into inner surface of adsorbents and causing decrease of active sites [6,25].

The adsorption kinetic depicts valuable data about efficiency of adsorption, solute uptake rate and pathway. Adsorption kinetic experiments were performed by shaking U(VI) solution (5 mg/L) containing 2 g/L adsorbent for various contact times (5–120 min) at pH 6 and 303 K. The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were chosen in order to investigate the controlling mechanism of the adsorption. The linear forms of these models are expressed in Table 1. It is obvious from Table 2 that the pseudo-second-order adsorption kinetic model has higher correlation coefficients ($R^2$) in $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite. Therefore, the adsorption kinetic of U(VI) onto $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite was better described by the pseudo-second-order model than the pseudo-first-order and intra-particle diffusion models. These results indicate that the rate-determining step may be a chemisorption process, which involves strong interaction through sharing or exchanging of electrons between adsorbents and U(VI) [1,14].

### 3.2.4. The effect of ionic strength

The effect of ionic strength on the removal efficiency of U(VI) by $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite was investigated at varying concentration of NaCl (0.01–1.5 M) at 5 mg/L U(VI), 50 mg/L benzamide and 2 g/L adsorbent at pH 6 for 30 min. The effect of ionic strength on the U(VI) removal was shown in Fig. 8. According to this Figure, the removal of U(VI) was decreased from 96.98 to 79.82% by the $C_{14}/SiO_2$–$Fe_3O_4$ nanocomposite and was decreased from 94.24 to 60.82% by the AC–$Fe_3O_4$ nanocomposite when the ionic strength increased from 0.01 to 1.5 M. A plausible reason for the decreased U(VI) removal by two adsorbents can be related to the competition between $Na^+$ ions and U(VI) ions for the active sites of adsorbent [36,60]. According to this result, the increased ionic strength has negative effect on the removal of U(VI) by the $C_{14}/SiO_2$–$Fe_3O_4$ nanocomposite. It can be related to the modification of $Fe_3O_4$-$SiO_2$ nanocomposite with triethoxyoctylsilane. Other researchers also reported similar trends. For example, U(VI) removal onto carboxylate-functionalized poly (hydroxyethylmethacrylate)-grafted lignocellulosics was decreased from 99.3 to 80.6% when the ionic strength increased from 0.001 to 0.1 M [6]. Wang also reported 20% decrease in the removal of U(VI) with increasing ionic strength from 0 to 1 M [14].

### 3.2.5. The effect of temperature and adsorption thermodynamics

The effect of temperature on the removal of U(VI) was investigated at 288, 303, 318, and 333 K by contacting 2 g/L adsorbent at pH 6 for 30 min. Removal efficiency of U(VI) onto $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite was increased with an increase in the reaction temperature. This indicates that the adsorption process onto $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite is endothermic process. The Van't Hoff equation is expressed in Table 1. The thermodynamic parameters such as enthalpy ($\Delta H°$), entropy ($\Delta S°$) for the adsorption process were calculated from the slope and intercept of the linear plot between ln $K_d$ and $1/T$. All thermodynamic parameters are shown in Table 2. The positive value of $\Delta H°$ in Table 2 indicates endothermic nature of adsorption process. The positive value of $\Delta S°$ suggests the increased randomness at the solid/liquid interface during the adsorption of U(VI) on $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite. The standard free energy values at different temperatures, those are calculated from the equation in Table 1, became negative. It demonstrates that the adsorption process of U(VI) onto $C_{14}/SiO_2$–$Fe_3O_4$ and AC–$Fe_3O_4$ nanocomposite is spontaneous. In addition, more negative values of $\Delta G°$ at higher temperature suggest that adsorption process

Table 2
The comparison of kinetic, thermodynamic and isotherms parameters for the adsorption of U(VI)

**Kinetic parameters**

| Adsorbent | $q_e$ | Pseudo-first-order | | | Pseudo-second-order | | | Intraparticle diffusion | | | Ref[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_1$ | $q_{e,cal}$ | $R^2$ | $K_2$ | $q_{e,cal}$ | $R^2$ | $K_p$ | $C$ | $R^2$ | |
| Activated carbon | 24.44 | 0.02 | 12.23 | 0.98 | 0.004 | 25.51 | 0.99 | – | – | – | [68] |
| NaA zeolite | – | 0.04 | 1.08 | 0.99 | 0.0005 | 2.04 | 0.997 | 0.004 | 0.95 | 0.69 | [64] |
| Hematite | – | 0.011 | 3.82 | 0.93 | 0.003 | 4.1 | 0.99 | 0.186 | 0.25 | 0.97 | [66] |
| Natural Diatomite | – | 1.18 | 8.28 | 0.63 | 0.04 | 7.99 | 0.66 | – | – | – | [9] |
| HDTMA-Diatomite | – | 0.68 | – | 0.95 | 0.01 | – | 0.97 | – | – | – | [9] |
| Fe$_3$O$_4$@SiO$_2$-AO | 38.08 | 0.01 | 18.32 | 0.94 | 0.001 | 38.32 | 0.99 | – | – | – | [47] |
| magnetic oxine | 93.07 | 0.001 | 10.80 | 0.8059 | 0.004 | 93.46 | 0.9999 | – | – | – | [69] |
| Fe$_3$O$_4$@TiO$_2$ | – | 0.035 | 218.54 | 0.90 | 0.0002 | 101.2 | 0.99 | – | – | – | [70] |
| C$_{14}$/SiO$_2$-Fe$_3$O$_4$ | 2.26 | 1.45 | 0.7644 | 0.66 | 0.54 | 2.22 | 0.9997 | 1.18 | 1.09 | 0.478 | p[a] |
| AC-Fe$_3$O$_4$ | 2.41 | 2.6 | 0.661 | 0.74 | 0.45 | 2.42 | 0.9999 | 1.46 | 1.21 | 0.459 | p[a] |

**Thermodynamic parameters**

| Adsorbent | $C_0$ (mg/L) | pH | $\Delta H°$ (kj/mol) | $\Delta S°$ (j/mol K) | $\Delta G°$ (kj/mol) | | | | Ref[a] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 288 K | 303 K | 318 K | 333 K | |
| Activated carbon | 100 | 3 | –50.53 | –98.76 | – | –21.61 | –19.62 | –17.64 | [68] |
| Activated carbon[a] | 100 | 4.5 | –46.2 | –98 | –17.5 | –16.5 | –15.3 | –13.6 | [56] |
| Fe$_3$O$_4$@SiO$_2$-AO | 23.8 | 5 | 14.85 | 114.40 | –18.43 | – | –20.38 | –22.91 | [47] |
| magnetic oxine | 50 | 7 | 39.27 | 141.2 | –2.81 | –4.22 | –5.63 | – | [69] |
| Fe$_3$O$_4$@TiO$_2$ | – | 6 | 23.82 | 87.41 | –1.80 | –3.12 | –3.99 | –4.86 | [70] |
| C$_{14}$/SiO$_2$-Fe$_3$O$_4$ | 5 | 6 | 26.05 | 157.5 | –19.34 | –21.71 | –24.07 | –26.43 | p[a] |
| AC-Fe$_3$O$_4$ | 5 | 6 | 23.49 | 149.60 | –19.61 | –21.86 | –24.1 | –26.34 | p[a] |

**Isotherm models**

| Adsorbent | $T$ (K) | $q_e$ (mg/g) | Langmuir constants | | | Freundlich constants | | | Ref[a] |
|---|---|---|---|---|---|---|---|---|---|
| | | | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_f^a$ | $n$ | $R^2$ | |
| Activated carbon | 293.15 | – | 10.47 | 0.05 | 0.47 | 3.69 | 2.72 | 0.97 | [68] |
| Activated carbon[a] | 293.15 | – | 13.76 | 0.01 | 0.99 | 2.63 | 1.57 | 0.98 | [16] |
| Talc | – | – | 41.49 | 0.006 | 0.97 | 2.196 | 0.44 | 0.98 | [54] |
| NaA zeolite | 298.15 | – | 1.02 | 0.0002 | 0.99 | 0.52 | 6.51 | 0.95 | [64] |
| Silica-coated magnetic NPs[a] | 298.15 | 10 | 12.3 | 0.088 | 0.9 | – | – | – | [15] |
| Hematite | 293.15 | – | 3.36 | 1.01 | 0.99 | 1.56 | 3.84 | 0.89 | [66] |
| Fe$_3$O$_4$@SiO$_2$-AO | 298.15 | – | 105 | 0.01 | 0.99 | 0.463[a] | 1.89 | 0.98 | [47] |
| Fe$_3$O$_4$@SiO$_2$ | 298.15 | – | 52.36 | 0.103 | 0.99 | 8.49 | 2.39 | 0.98 | [67] |
| P(4-vinyl pyridine) hydrogel | 303.15 | – | 147.06 | 0.47 | 0.98 | 3.15 | 1.93 | 0.97 | [2] |

(Continued)

Table 2 (Continued)

Isotherm models

| | $T$ (K) | $q_e$ (mg/g) | Langmuir constants | | | Freundlich constants | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_f^a$ | $n$ | $R^2$ | |
| Natural Diatomite | 294.15 | – | 25.63 | 0.03 | 0.90 | 8.11 | 0.16 | 0.82 | [9] |
| HDTMA-Diatomite | 294.15 | – | 667.4 | 0.009 | 0.91 | 45.21 | 0.38 | 0.85 | [9] |
| magnetic oxine | 298.15 | – | 125 | 0.0103 | 0.9886 | 22.35 | 2.333 | 0.9040 | [69] |
| $Fe_3O_4@TiO_2$ | 298.15 | – | 91.1 | 0.845 | 0.99 | 33.1 | 0.30 | 0.91 | [70] |
| Modified diatomite | 298.15 | – | 86.78 | 0.0056 | 0.9954 | 2.980 | 0.586 | 0.9994 | [71] |
| $C_{14}/SiO_2$-$Fe_3O_4$ | 318 | 13.19 | 16.286 | 1.13 | 0.98 | 6.762 | 1.58 | 0.9792 | p[a] |
| AC-$Fe_3O_4$ | 303 | 11.99 | 15.87 | 0.48 | 0.98 | 3.98 | 1.50 | 0.9731 | p[a] |

[a]P: Present work.

Table 3
Separation factor $R_L$

| Initial uranium concentration (mg/L) | $R_L$ value C$_{14}$/SiO$_2$–Fe$_3$O$_4$ | $R_L$ value AC–Fe$_3$O$_4$ |
|---|---|---|
| 1 | 0.469 | 0.67 |
| 3 | 0.227 | 0.4 |
| 5 | 0.15 | 0.29 |
| 10 | 0.081 | 0.17 |
| 30 | 0.028 | 0.06 |

of U(VI) onto two adsorbents becomes more favorable at high temperature due to a more stable bonding between U(VI) ions and active sites on the adsorbent.

### 3.2.6. The effect of initial U(VI) concentration

The effect of the initial U(VI) concentration on the adsorption capacity was studied by varying initial U(VI) concentrations (1, 3, 5, 10, and 30 mg/L) at pH 6 for 30 min (Fig. 9). At the same adsorbent doses, U(VI) removal efficiency was decreased as the initial U(VI) concentration increased. The reason for the decreased removal of U(VI) at high U(VI) concentration can be explained by the limited active sites on the adsorbent [61]. To investigate the adsorption equilibrium isotherm, experiments were performed with variation of initial concentration ranging from 1 to 30 mg/L at 2 g/L adsorbent and at pH 6 for 30 min. The Langmuir and Freundlich isotherm equations were used to fit the experimental data. The linear equations of the Langmuir and Freundlich sorption model are expressed in Table 1. The Langmuir model assumes that the removal of adsorbate occurs on an energetically homogenous surface through monolayer adsorption assuming no interactions and steric hindrance between the adsorbed molecules [62]. The basic characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor ($R_L$), which is defined in Table 1. $R_L$ values between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption isotherm, respectively [63,64]. The Freundlich model is derived by assuming multilayer adsorption with a non-uniform distribution of adsorption heat and affinity over the heterogeneous surface [65,66]. The Langmuir and Freundlich models were analyzed by plotting $C_e/q_e$ vs. $C_e$ and log $q_e$ vs. log $C_e$, respectively. Langmuir and Freundlich constants as well as related correlation coefficients are given in Table 2. The high correlation coefficients confirmed the applicability of the Langmuir isotherm for the U(VI) adsorption process onto C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$

nanocomposite. In addition, the theoretical saturated adsorption capacities of Langmuir isotherms are very close to experimental data. It suggests that monolayer adsorption is dominated in the adsorption of U(VI) onto C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposite. The value of $R_L$ shown in Table 3 indicates that the adsorption process by C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposite is favorable. The removal capacity of C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposites is compared in Table 2. According to this comparison, C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposite has a higher adsorption capacity compared to NaA zeolite, hematite, activated carbon, and silica-coated magnetic NPs. Maximum adsorption capacity of C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposite was obtained as 16.29 and 15.87 mg/g at pH 6, respectively.

### 3.2.7. The effect of adsorbent dosage

The influence of adsorbent dosage on the removal efficiency of the U(VI) was tested at different amount of C$_{14}$/SiO$_2$–Fe$_3$O$_4$ and AC–Fe$_3$O$_4$ nanocomposite from 0.4 to 4 g/L at pH 6 for 30 min (Fig. 10). The results revealed that U(VI) removal efficiency was increased by increasing the adsorbent dosage from 0.4 to 2 g/L. The increased removal efficiency of U(VI) at higher adsorbent dosage can be attributed to the increased surface area and the availability of adsorption sites [61,67]. But as shown in Fig. 10, the removal efficiency of U(VI) was little increased beyond 1.2 g/L. According to Fig. 10, C$_{14}$/SiO$_2$–Fe$_3$O$_4$ nanocomposite has more removal capacity ($q_e$ = 16.29 mg/g) for U(VI) compared to AC–Fe$_3$O$_4$ nanocomposite ($q_e$ = 15.87 mg/g).

## 4. Conclusions

In the present research, Fe$_3$O$_4$-SiO$_2$ modified with triethoxyoctylsilane and AC–Fe$_3$O$_4$ nanocomposite were used as adsorbents in the removal of U(VI) with aid of benzamide as a medium agent in aqueous solutions. The prepared adsorbents were characterized

by FT-IR, XRD, and SEM analyses. The removal efficiency depended on experimental parameters like pH, contact time, ionic strength, temperature, U(VI) concentration, benzamide concentration, and adsorbent dosage. In two adsorbents, the removal efficiency was increased with increasing contact time, temperature, and adsorbent dose but was decreased with increasing ionic strength and initial U(VI) concentration. Pseudo-second-order model was better described the adsorption kinetics of U(VI) onto $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposites than pseudo-first-order model. The thermodynamic parameters indicated that the adsorption process by $C_{14}/SiO_2–Fe_3O_4$ and $AC–Fe_3O_4$ nanocomposite was endothermic and spontaneous. The high value of correlation coefficient for the Langmuir isotherms in two adsorbents suggests that adsorption occurs through homogeneous and monolayer adsorption. $C_{14}/SiO_2–Fe_3O_4$ nanocomposite had more adsorption capacity for U(VI) (16.29 mg/g) and was less influence by increased ionic strength. This result suggests that $C_{14}/SiO_2–Fe_3O_4$ nanocomposite is a good adsorbent for the removal of low concentration of U(VI) from aqueous solution.

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