

ORIGINAL RESEARCH PAPER

## Carboxymethyl- $\beta$ -cyclodextrin Modified Magnetic Nanoparticles for Effective Removal of Arsenic from Drinking Water: Synthesis and Adsorption Studies

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### ABSTRACT

The  $\beta$ -cyclodextrin coated magnetic nanoparticles were prepared by the surface modification of  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles using carboxymethyl- $\beta$ -cyclodextrin. Prepared nanoparticles were characterized by X-ray diffraction analysis, transmission electron microscope, Fourier transform infrared spectroscopy, dynamic light scattering and vibrating sample magnetometer. The  $\beta$ -cyclodextrin modified  $\text{Fe}_3\text{O}_4$  nanoparticles have a narrow size distribution with mean diameter about 10 nm. They exhibit superparamagnetic properties at room temperature with saturation magnetization of 48 emu/g. Since, the most reported technologies for arsenic removal are more effective in removing As(V) rather than As(III), the adsorption ability of these nanoparticles was investigated for removing As (III) from aqueous solution. The adsorption behavior of this material can be influenced by various factors such as contact time, pH, adsorbent dosage and initial concentration of As(III), which their effects were studied. Equilibrium data were fitted by Langmuir isotherm and the maximum removal percentage was obtained about 85% at optimum conditions. Using these modified  $\text{Fe}_3\text{O}_4$  nanoparticles, the arsenic concentrations can be reduced to the allowed limits declared by the World Health Organization.

**KEYWORDS:** Arsenic removal; Magnetic nanoparticle;  $\beta$ -cyclodextrin; Adsorption; Drinking water treatment

### How to cite this article

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## INTRODUCTION

Arsenic contamination, which is present mainly as oxyanion compounds in drinking water and groundwater, is a serious environmental worldwide problem because of its toxicity and health hazards. The ingestion of arsenic can result in both cancerous and non-cancerous health effects such as disturbance of cardiovascular and nervous system function, pigmentation, depigmentation, skin cancer and cancer of internal organs [1].

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Arsenic exists in four oxidation states, +5 (arsenate), +3 (arsenite), 0 (arsenic), and -3 (arsine). The toxicity of arsenic depends on its speciation, For example, arsenite is significantly more toxic than arsenate. It is typically more difficult to remove arsenite than arsenate from contaminated water. Under normal pH conditions (in natural waters), arsenite is mostly found as an uncharged species ( $\text{H}_3\text{AsO}_3$ ), and negatively charged species ( $\text{H}_2\text{AsO}_3^-$ )

,  $\text{HAsO}_3^{2-}$  and  $\text{AsO}_3^{3-}$ ) are found only at high pH [2].

Arsenic contamination of water results from both natural and anthropogenic activities. Arsenic is present in water due to dissolution of minerals as well as human activities such as mining, smelting of metal ores and use of pesticides causing arsenic pollution [3]. Reports have indicated arsenic pollution in many regions of countries around the world including USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Japan, India and Islamic Republic of Iran [4,5]. Due to the negative impacts of arsenic on human health, the US Environmental Protection Agency, the World Health Organization (WHO), and the European Commission have reduced the maximum contaminant level of arsenic in drinking water from 50 to 10 ppb. However, some countries have kept the earlier WHO guideline of 50 ppb as their standard [3,6]. Many arsenic removal technologies such as precipitation [7], membrane separation [8,9], nanofiltration [10,11], coagulation [12], ion exchange [13], microbial transformation [14,15], and adsorption [16,17,18] have been developed. Most of these techniques are only effective in removing arsenate, and they require a pretreatment step for oxidation of arsenite to arsenate. These pretreatment chemical methods can be used easily; however, their applications are limited by producing large amount of toxic sludge, and they need further treatment before disposal into the environment [19].

Among the removal methods, adsorption from solution has received more attention due to its low cost and high efficiency for arsenic treatment [20]. Many adsorbent materials have been used including activated alumina, activated carbon, red mud, bauxsol, etc [21]. Therefore, one of the key factors in adsorption-based technologies is the development of highly effective and inexpensive adsorbents [22]. Recently, adsorption through  $\text{Fe}_3\text{O}_4$  magnetic nano-sized particles has been more popular because of the specific characteristics of these materials. Particular properties of them such as extreme small size, high surface-area-to-volume ratio and the absence of internal diffusion resistance, provides better kinetics for adsorption of arsenic from aqueous solution. Magnetic nano-adsorbents have the qualities of both magnetic separation techniques and nano-sized materials,

thus they can be easily separated with an external magnetic field [23, 24]. However, these adsorbents are not stable and hardly can be recycled because  $\text{Fe}_3\text{O}_4$  is highly susceptible to oxidation when it is exposed to the atmosphere due to its small size [25]. In order to improve the stability and functionality, the iron oxide nanoparticles are often modified with natural or synthetic polymers.

Cyclodextrins are polysaccharides produced through the degradation of starch by cyclodextrin glucanotransferase enzyme.  $\beta$ -cyclodextrin ( $\beta$ -CD) is a cyclic oligosaccharide consist of seven  $\alpha$ -D-glucose units connected through  $\alpha$ -(1,4) linkages. The structure of these molecules is like toroidal truncated cones containing a lipophilic cavity with two hydroxyl groups one lying on the outside and the other lying in the inside [26,25]. Cyclodextrins are available on a large scale. Their production is not costly, and most importantly they have the ability to form inclusion complexes (guest-host complexes) with a wide variety of organic and inorganic compounds in its hydrophobic cavity. In addition, metal ions can be complexed by cyclodextrins through hydroxyl groups [27].

In this study, a magnetic nano-adsorbent was fabricated by surface modification of  $\text{Fe}_3\text{O}_4$  nanoparticles with  $\beta$ -CD for the adsorption of arsenic contamination. The size, morphology and properties of the  $\beta$ -CD modified magnetic nanoparticles were characterized using different analytical tools. The mean diameter of  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were  $\sim 10$  nm. These modified nanoparticles exhibit superparamagnetic properties at room temperature; therefore, they can be easily separated by applied magnetic field. They were evaluated as adsorbents to remove arsenic, and the effects of several factors such as, pH, initial arsenic concentration, contact time, and mechanism of arsenic adsorption onto  $\beta$ -CD modified magnetic nanoparticles were investigated in this report. In Iran, in western and north-western provinces especially in Kurdistan province arsenic contamination has been reported in groundwater sources [5,28]. Real water samples from Kurdistan villages were collected, and the ability of modified magnetic nanoparticles in removing arsenic in real samples was examined. Overall, the major end of the current research is ascertaining the capability of  $\beta$ -CD modified

magnetic nanoparticles to remove trivalent arsenic from water in a one-step operation with no pretreatment. The maximum removal efficiency of arsenic (III) at optimal conditions is about 85%.

## EXPERIMENTAL

### Materials

Iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, sodium hydroxide (NaOH), ammonium hydroxide (25%),  $\beta$ -cyclodextrin ( $\beta$ -CD), monochloroacetic acid, Carbodiimides (cyanamide,  $\text{CH}_2\text{N}_2$ ), arsenic trioxide ( $\text{As}_2\text{O}_3$ ) and methanol (99%) were purchased from Merck. All chemicals were the guaranteed or analytic grade reagents commercially available and used without further purification. Arsenic solutions that were used in different experiments were prepared by diluting a stock solution (1000 ppm of arsenic). The stock solution was prepared by solving 50 mg of  $\text{As}_2\text{O}_3$  salt in 100 ml deionized water. For preparing working solution from 1 up to 100 ppm of arsenic, 0.01 ml to 1 ml of the stock solution were diluted in 10 ml deionized water.

### Apparatus

In order to investigate the size and morphology of magnetic nanoparticles, transmission electron microscopy (CM10, Philips) was used.  $\beta$ -CD's grafting onto the surface of magnetic nanoparticles (MNPs) was monitored by Fourier transform infrared spectroscopy (RX1, Perkin-Elmer). The crystalline structure of  $\text{Fe}_3\text{O}_4$  nanoparticles was characterized by X-ray diffraction technique (D8 Advance, Bruker). The magnetic properties of the  $\text{Fe}_3\text{O}_4$  nanoparticles coated with  $\beta$ -cyclodextrin were investigated using a vibrating sample magnetometer (Megnatis Daghigh Kavir, Iran). The size and size distribution of nanoparticles were measured by particle size analyzer (L-550, HORIBA).

### Preparation of Naked $\text{Fe}_3\text{O}_4$ magnetic nanoparticles

$\text{Fe}_3\text{O}_4$  nanoparticles were prepared by chemical co-precipitation method. A complete precipitation of  $\text{Fe}_3\text{O}_4$  was achieved under alkaline condition, while maintaining a molar ratio 1:2 of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In a typical synthesis to obtain 1 g  $\text{Fe}_3\text{O}_4$  precipitate, 0.86 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 2.36 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 40 ml of distilled water with vigorous

stirring at a speed of 1000 rpm. 5 ml of  $\text{NH}_4\text{OH}$  (25%) was added after the solution was heated to 80 °C. The reaction was continued for 30 min at 80 °C under constant stirring to ensure the complete growth of the nanoparticle crystals. The resulting particles were then washed with Distilled water at least 5 times to remove any unreacted chemicals and dried [24].

### Preparation of Carboxymethyl $\beta$ -cyclodextrin

Carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ CD) was prepared following the previous procedure [29]. CM- $\beta$ CD was synthesized in the alkaline condition by reacting monochloroacetic acid with  $\beta$ -CD. A mixture of  $\beta$ -CD (2 g) and NaOH (1.86g) in water (7.4 ml) was treated with a 16.3% monochloroacetic acid solution (5.4 ml) at 50 °C for 5 h. The temperature of the reaction mixture was reduced to room temperature, and then the pH values were adjusted in the range of 6–7. The obtained neutral solution was added to methanol, and the produced white precipitate, carboxymethylated  $\beta$ -cyclodextrin, was filtered and dried in oven at 50 °C.

### Preparation of CM- $\beta$ CD Modified Magnetic Nanoparticles

$\beta$ -cyclodextrin modified magnetic nanoparticles can be prepared using one-step or two-step methods. By one-step co-precipitation method, in which iron precursors ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) and CM- $\beta$ CD were mixed together, the binding of CM- $\beta$ CD onto the  $\text{Fe}_3\text{O}_4$  surface was conducted. Briefly, 0.57 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 1.57 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1 g CM- $\beta$ CD were dissolved in 26.7 ml of distilled water with vigorous stirring at a speed of 1200 rpm. When the temperature of the reaction mixture reached 90 °C, 3.5 ml of  $\text{NH}_4\text{OH}$  (25%) was added in drop. The reaction was maintained at 90 °C under constant stirring for 1 h. The resulting nanoparticles were then washed with distilled water to remove any unreacted chemicals and then it was dried in oven at 70 °C. In this method, the carboxyl groups of CM- $\beta$ CD directly reacted with the surface OH groups on the magnetite to form Fe-carboxylate [29].

### Adsorption Experiments

The adsorption experiments of As(III) by CM- $\beta$ CD modified magnetic nanoparticles (CM- $\beta$ CD-

MNPs) were investigated in aqueous solutions. For each treatment, 30 mg CM- $\beta$ CD-MNPs was added into 5 mL of arsenic solution. The solutions of As(III) were obtained by dissolving arsenic trioxide ( $\text{As}_2\text{O}_3$ ) into distilled water. The influence of experimental factors such as pH value, contact time, adsorbent dosage and initial arsenic concentration on the removal efficiency of As(III) was investigated. When equilibrium was achieved, magnetic nanoparticles were separated magnetically from arsenic solution using a magnet. The concentration values of As(III) were measured using the inductively coupled plasma spectroscopy (ICP) method. For comparison, the adsorption of As(III) by the naked  $\text{Fe}_3\text{O}_4$  nanoparticles (unmodified MNPs) was also investigated.

The adsorption isotherm experiments were performed using different initial As(III) concentrations. The adsorption capacity ( $q_e$ , mg/g) and removal efficiency (E) of the adsorbent were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where  $C_0$  and  $C_e$  are initial and equilibrium concentration (mg/L) of As(III) solution, respectively;  $V$  is the volume of the As(III) solution; and  $m$  is the weight of the  $\beta$ -CD modified magnetic nanoparticles.

## RESULTS AND DISCUSSIONS

One of the most important steps in magnetic nanoparticle preparation is their characterization. It means the investigation of their size, shape and size distribution and also, their magnetic properties. For this purpose different methods were used and the results were shown following.

### Characterizations of $\beta$ -cyclodextrin modified $\text{Fe}_3\text{O}_4$ nanoparticles

#### Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was utilized to investigate the size and morphology of magnetic nanoparticle samples. As shown in Fig. 1, the sample includes small nanoparticles that are relatively uniform in size and shape. The average size of the particles is about 10 nm. This reveals that

the binding process did not significantly result in changes in the size of the particles but it prevents agglomeration of nanoparticles which leads to lower distribution of modified nanoparticles rather than unmodified nanoparticles.

#### Dynamic Light Scattering (DLS)

In Fig. 2 the size distribution graphs for the naked and  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles obtained by DLS method are presented. The average diameters of the naked and  $\beta$ -CD modified magnetic nanoparticle were equal to 13.7 and 18.5 nm, respectively. It can be seen for Fig. 2 that, they are low-dispersed nanoparticles. As it evidence, the nanoparticles size observed by DLS is larger than those obtained by TEM because,  $\beta$ -CD coating increases the hydrodynamic diameter of nanoparticles [25].

#### FTIR analysis

The CM- $\beta$ -CD binding on the surface of magnetic nanoparticles was confirmed by FTIR spectroscopy. FTIR spectra of naked MNPs, CM- $\beta$ -CD-MNPs, and pure CM- $\beta$ -CD in the range of 350–4000  $\text{cm}^{-1}$  wavenumbers are shown in Fig. 3.

In the spectra of the  $\text{Fe}_3\text{O}_4$  nanoparticles, the absorption peak at 585 is the characteristic of Fe-O-Fe bond in  $\text{Fe}_3\text{O}_4$ . The broad band around 3426 is due to -OH stretching vibrations. The spectrum of CM- $\beta$ -CD shows the characteristic peaks at 948, 1031 and 1190. The peak at 948 is due to the R-1,4-bond skeleton vibration of  $\beta$ -CD, and the peaks at 1031 and 1190 corresponded to the asymmetric glycosidic (C-O-C) vibrations and coupled  $\nu(\text{C}-\text{C}/\text{C}-\text{O})$  stretch vibration [21]. All of these characteristic peaks in the spectrum of CM- $\beta$ -CD (900–1200) can also be seen in the spectrum of CM- $\beta$ -CD-MNPs with slight differences. The characteristic peak appeared at 1606 is due to bands of -COOM groups (M represents metal ions), indicates that the -COOH groups of CM- $\beta$ -CD reacted with the surface of  $\text{Fe}_3\text{O}_4$  particles [30]. These findings indicate that the binding of CM- $\beta$ -CD on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles were done successfully.

#### UV-Vis spectra

The UV-visible absorption spectra of the naked and  $\beta$ -CD modified nanoparticles are illustrated in Fig. 4. As can be seen in the absorption spectra

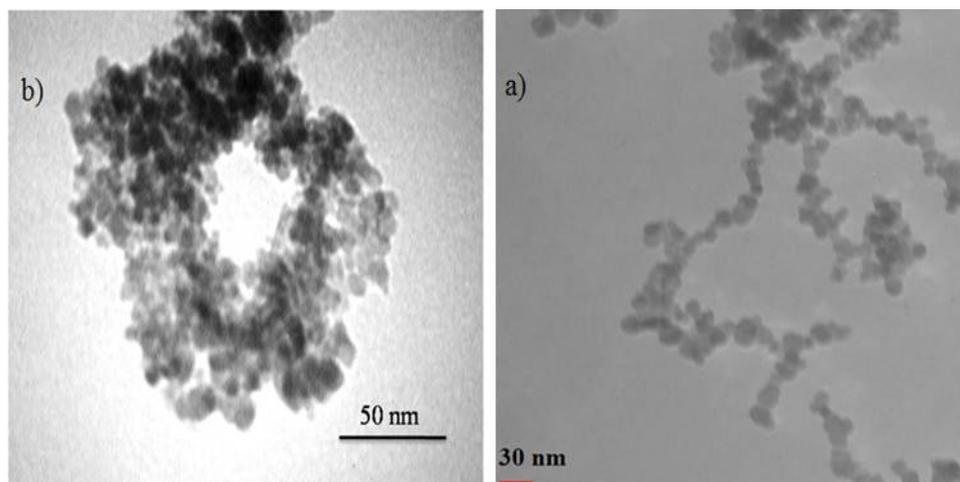


Fig. 1. TEM images of the (a) naked and (b) CM- $\beta$ CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles

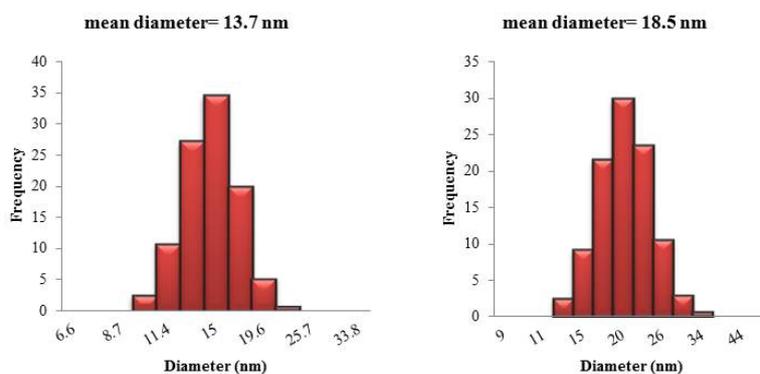


Fig. 2. DLS plots of the (a) naked and (b)  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles

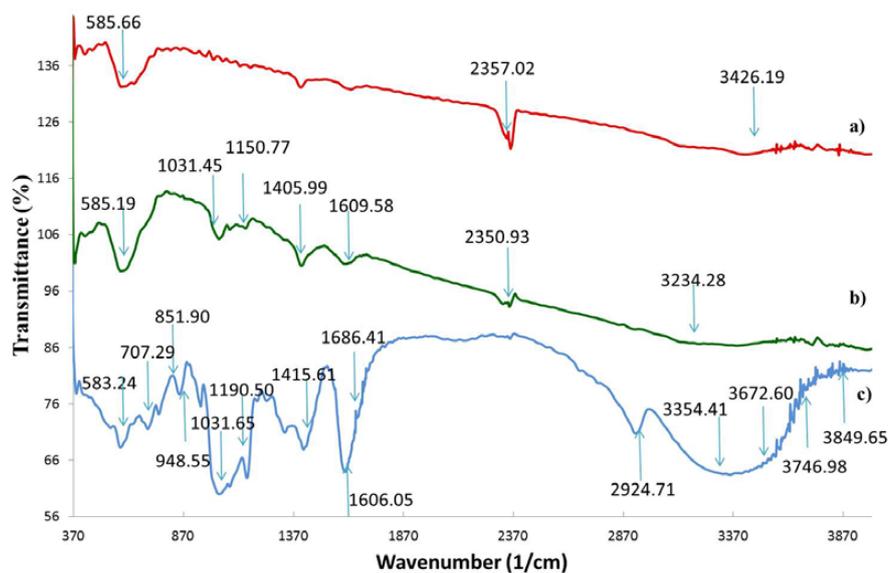


Fig. 3. FTIR spectra of (a) naked and (b)  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles and (c) pure CM- $\beta$ CD

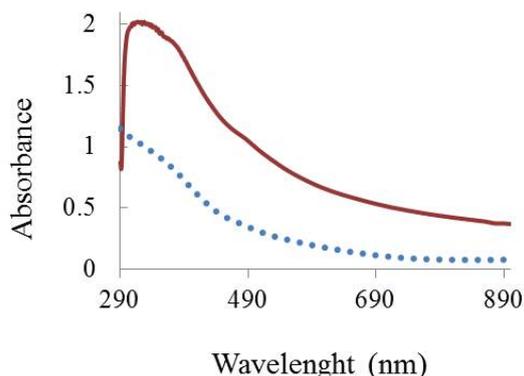


Fig. 4. UV-visible spectra of the naked (Dot line) and  $\beta$ -CD modified (Solid line)  $\text{Fe}_3\text{O}_4$  nanoparticles

reported in Fig. 4, after  $\beta$ -CD coating on the MNPs the UV-Vis spectrum of these nanoparticles was changed. This phenomenon can be also used as another confirmation for binding of  $\beta$ -CD on the  $\text{Fe}_3\text{O}_4$  nanoparticles' surface.

#### XRD analysis

Fig.5 shows the XRD pattern of the CM- $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles. There are six characteristic peaks for  $\text{Fe}_3\text{O}_4$  at  $2\theta$  values of  $30.3^\circ$ ,  $35.6^\circ$ ,  $43.25^\circ$ ,  $53.65^\circ$ ,  $57.15^\circ$ , and  $62.85^\circ$  marked by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0), respectively. These observations confirm the presence of inverse cubic spinel structure of the resultant nanoparticles [29]. It is also clear that the coating did not lead any phase change of  $\text{Fe}_3\text{O}_4$  nanoparticles. The average size of the CM- $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  can be calculated from Scherrer equation:

$$d = 0.9\lambda/\beta\cos\theta \quad (3)$$

Where  $d$  is particle diameter,  $\lambda$  is X-ray wavelength,  $\beta$  is the peak width of half-maximum, and  $\theta$  is Bragg's diffraction angle in degree. The obtained size of CM- $\beta$ -CD modified MNPs using strongest peak (3 1 1) at  $2\theta=35.6^\circ$  and  $\lambda=1.54 \text{ \AA}$  was about 8.8 nm, which is in consistent with the results of TEM.

#### Vibrating sample magnetometer (VSM) analysis

In order to examine the magnetic properties of prepared nanoparticles, they were analyzed by vibrating sample magnetometer (VSM) at room temperature. The magnetization hysteresis loops of naked and CM- $\beta$ -CD-MNPs were shown in Fig.

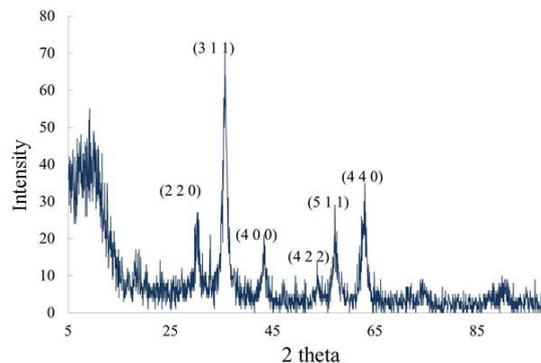


Fig. 5. XRD pattern of the  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles synthesized

6. The saturated magnetizations for naked MNPs and CM- $\beta$ -CD-MNPs are 54 and 48 emu. This demonstrates that all samples are superparamagnetic which can responsive to an applied magnetic field and retain no permanent magnetization after removing the applied magnetic field. The saturated magnetization of the  $\text{Fe}_3\text{O}_4$  nanoparticles decreased after coating with CM- $\beta$ -CD (Fig. 6). This is mainly attributed to the existence of non-magnetic materials on the surface of nanoparticles. Similar results are reported by Badruddoza et. al. [29]. Materials with superparamagnetic properties can be easily separated from the solution with the aid of an external magnetic field within several minutes.

#### Adsorption of arsenic onto $\beta$ -CD modified MNP

The adsorption process can be influenced by some experimental parameters. The effects of these parameters should be investigated and the optimal conditions should be used for real samples analysis.

#### Effects of initial pH on arsenic adsorption

One of the most important parameters in arsenic removal process is the pH value of the sample. Since the pH variation can influence on the ionic state of the surface functional groups of nanoparticles, it can be effective on the adsorption process. On the other hand, the arsenic chemistry in water also highly depends on pH values. Therefore, arsenic adsorption ability of CM- $\beta$ -CD-MNPs was investigated at room temperature by varying pH values in the range of 8 to 11 (Fig. 7). The removal efficiency of arsenic improved by increasing pH values and then remains almost constant at pH 9 -11 because of the pH-dependency of As (III).

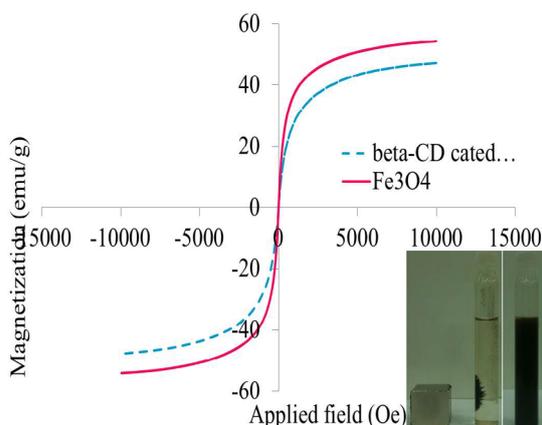


Fig. 6. Magnetic hysteresis curves of naked (solid line) and  $\beta$ -CD modified (dot line)  $\text{Fe}_3\text{O}_4$  nanoparticles

However, pH 9 was selected as the optimal value since no significant improvement in arsenic removal was observed between 9 to 11 pH values.

#### Effect of Magnetic Nanoparticles Dosage

The effect of adsorbent dosage on arsenite adsorption capacity and removal efficiency was investigated and the results were shown in Fig. 8. It is evident that the removal efficiencies of arsenite increase with increasing adsorbent dosage, while the amount of adsorption capacity ( $q_e$ ) decreases. The increase in the removal efficiency is due to an increase in the adsorbent amount which provides more adsorbent surface for the solute to be adsorbed.

#### Effect of Initial Concentration

As mentioned above, CM- $\beta$ CD-MNPs provided good adsorption capacity for As(III) at pH 9 and 6 mg/ml adsorbent amount by applying 30 minutes contact time. The adsorption isotherm of arsenic was obtained by changing the initial concentration of As(III) at values ranging from 1 to 100 ppm. The removal efficiency of As(III) decreases with an increase in initial As(III) concentration (Fig. 9). This behavior was due to the fact that the total available adsorption sites for a fixed amount of adsorbent are limited, which leads to a decrease in removal percentage corresponding to an increased initial adsorbate concentration.

#### Adsorption Kinetics

Another important parameter in the arsenic wastewater treatment process is equilibrium

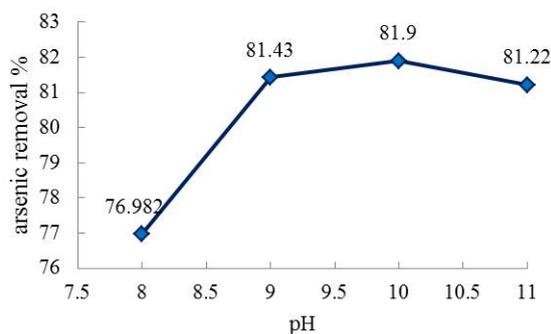


Fig. 7. The effect of pH on the arsenic removal efficiency by the  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticle. The removal studies were carried out by applying 6mg/ml  $\beta$ -CD-modified  $\text{Fe}_3\text{O}_4$  on the As(III) solution with 10 ppm concentration, during 10 min contact time at room temperature)

contact time. The effect of contact time of CM- $\beta$ -CD-MNPs with arsenic solution on the removal efficiencies was shown in Fig. 10. More than 75% of the arsenite was adsorbed during the first 5 min. There is no significant change from 30 to 45 min, and then equilibrium reached during only 90 min. Therefore, 30 min was considered as the optimal contact time for adsorption. The fast adsorption in the beginning of operation is due to the greater concentration gradient and more available sites for adsorption; however, as the process continues, the rate of As(III) adsorption becomes slower. This phenomenon may be attributed to decreasing of the binding sites on the surface of nanoparticles. Such behavior is common in adsorption processes and has been reported [22].

In order to investigate adsorption kinetics mechanism, pseudo-first order and pseudo-second order models were applied to fit the experimental data [20]. The correlation coefficient  $R^2$  was used to express the uniformity between the experimental and model-predicted data. The equation used at pseudo-first order kinetic model is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where  $q_e$  and  $q_t$  are the amounts of arsenic adsorbed by each unit of CM- $\beta$ -CD-MNPs at equilibrium state and time  $t$ , respectively (mg/g),  $k_1$  is the pseudo-first order rate constant for the adsorption process and can be obtained from the plots of  $\ln(q_e - q_t)$  against  $t$ . The corresponding kinetic parameters are shown in Table. 1. Low value of correlation coefficient ( $R^2$ ) and large difference between  $q_{e,cal}$  and  $q_{e,exp}$  indicated poor fit of the

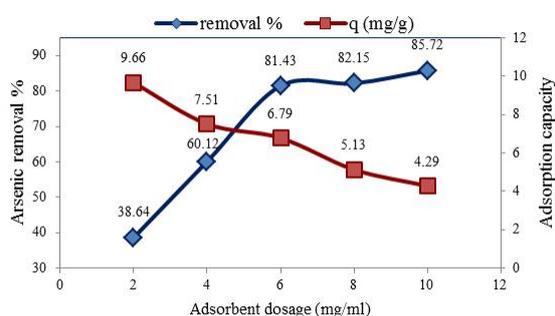


Fig. 8. The effect of  $\beta$ -CD-modified  $\text{Fe}_3\text{O}_4$  nanoparticle adsorbent dosage on arsenic efficiencies and adsorption capacity

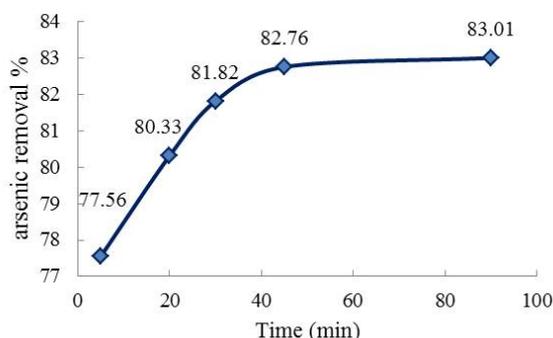


Fig. 10. The effect of contact time on the arsenic removal efficiency by the  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticle. The initial concentration of arsenic was 50 ppm here

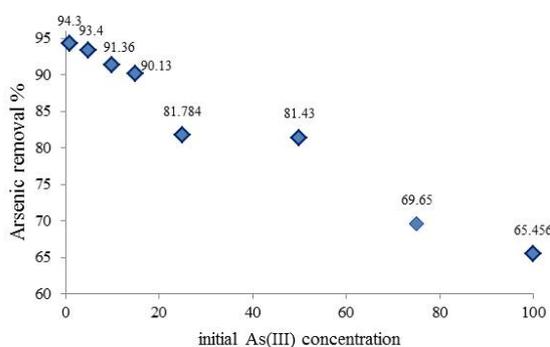


Fig. 9. The effect of initial As(III) concentration on arsenic efficiencies

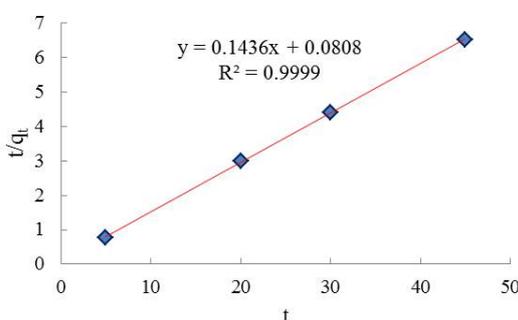


Fig. 11. plot of  $t/q_t$  against  $t$  that can show pseudo second-order kinetics for adsorption of As(III)

experimental data to pseudo-first order model. The equation of pseudo-second order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where  $k_2$  is the pseudo-second order rate constant for the adsorption process and can be calculated from the intercept of plot of  $t/q_t$  against  $t$  and shown in Fig. 11. Table 1 summarizes adsorption capacities determined by this model. A linear relationship ( $R^2 = 0.9992$ ) obtained between  $t/q_t$  and  $t$  indicates that pseudo-second order model is better to describe the adsorption process than the other. The equilibrium adsorption capacity ( $q_{e,cal}$ ) by CM- $\beta$ CD-MNP was 6.99 mg/g, which is consistent with the experimental data. Also, it was found that the rate of the arsenic adsorption to be controlled by the chemisorption process [29].

#### Adsorption Isotherms

In order to examine the adsorption mechanism

and calculate the adsorption capacity of CM- $\beta$ CD-MNPs, adsorption isotherms were investigated at room temperature by changing the initial concentration of As(III). The adsorption isotherms are important in describing the adsorption mechanism and yield certain constant values which express the surface properties and affinity of the adsorbent [30]. The equilibrium isotherms for the adsorption of arsenic ions by CM- $\beta$ CD-MNPs at pH 9 are shown in Fig. 12. Generally, Langmuir and Freundlich adsorption isotherm models were used to describe the equilibrium data at a constant temperature. Langmuir model which is used widely assumes that adsorption takes place at specific homogeneous sites within the adsorbent and is applied to monolayer adsorption processes. The linear form of the Langmuir isotherm can be expressed as:

$$\frac{C_m}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (6)$$

The Freundlich model is based on a multilayer adsorption. In this model the adsorption energy

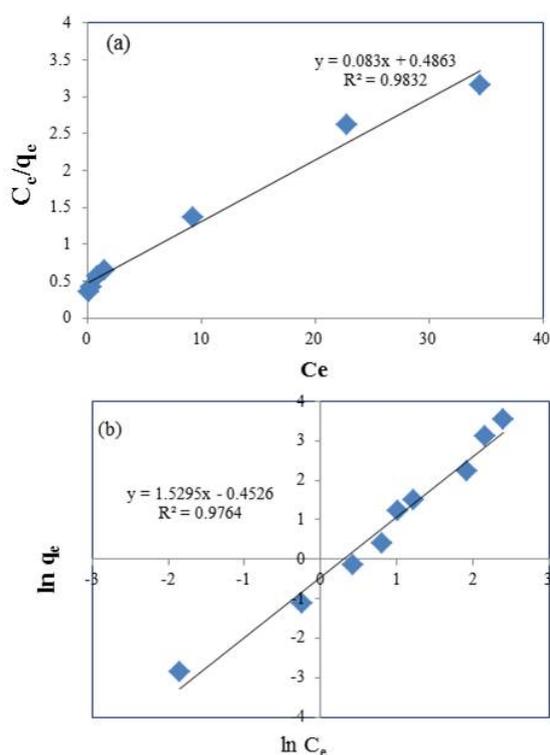


Fig. 12 The (a) Langmuir and (b) Freundlich isotherm plots for As(III) adsorption by CM- $\beta$ CD-MNPs at pH 9

decreases with the surface coverage. It is an empirical equation used to describe heterogeneous adsorption systems which can be represented as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (7)$$

Where  $q_e$  is the equilibrium adsorbate loading on the adsorbent in mg/g,  $C_e$  is the solute equilibrium concentration in mg/L,  $q_m$  the maximum capacity of adsorbent (mg/g), and  $K$  and  $1/n$  are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. The values of  $q_m$  and  $K_1$  were determined from the slope and intercept of the linear plots of  $C_e/q_e$  versus  $C_e$  (Fig. 12a) and the values of  $K$  and  $1/n$  were determined from the slope and intercept of the linear plot of  $\ln q_e$  versus  $\ln C_e$  (Fig. 12b). The isotherm parameters are shown in Table 2. The higher value of correlation coefficients indicates that the equilibrium data can be fitted better to Langmuir equation. Also, the maximum adsorption capacity obtained from the Langmuir isotherm was 12.33 mg/g. This result is comparable with the adsorption capacity of the other similar adsorbents reported in literature [25,

Table 1. Adsorption kinetic parameters of As(III) onto CM- $\beta$ CD-MNPs.

	Parameters	
Pseudo-first-order	$K_1(\text{min}^{-1})$	0.077
	$Q_{e,\text{cal}}(\text{mg/g})$	0.834
	$R^2$	0.964
Pseudo-second-order	$Q_{e,\text{exp}}(\text{mg/g})$	6.917
	$K_2(\text{g}/(\text{mg min}))$	0.256
	$Q_{e,\text{cal}}(\text{mg/g})$	6.993
	$R^2$	0.999

Table 2. Adsorption isotherm parameters for As(III) adsorption on  $\beta$ -CD modified magnetic nanoparticles at pH 9.

Isotherm models	Parameters	
Langmuir	$q_m$	12.330
	$k_L$	0.171
	$R^2$	0.983
Freundlich	$n$	0.654
	$K_F$	1.572
	$R^2$	0.976

32, 33]. The result of this study indicated that the magnetic nanoparticles could be one of the best adsorbents for the removal of As(III) from aqueous solutions.

#### Effect of $\beta$ -CD Coating on Arsenic Adsorption

To investigate the effect of coating on adsorption of trivalent arsenic, the adsorption capacity of CM- $\beta$ CD modified and naked MNPs were compared. In Table 3, it can be seen that, the removal efficiency of As(III) by CM- $\beta$ CD-MNPs are higher than the naked ones. Hereby the use of  $\beta$ -CD for coated magnetic nanoparticles can effectively enhance the arsenic removal. The reason is that the coating can prevent MNPs from aggregating in adsorption process, and this increases the effective adsorption area. Also  $\beta$ -CD can form inclusion complexes with arsenic oxyanions in its hydrophobic cavity through host-guest interactions. Hence, the adsorption capacity of CM- $\beta$ CD-MNPs was enhanced through inclusion complex formation.

#### Desorption Experiments

Desorption experiments were conducted to evaluate the possibility of regeneration of the adsorbent. Desorption of As(III) from the surface of CM- $\beta$ CD-MNPs was conducted using 0.1 M

Table 3. Comparison of removal efficiency of As(III) by the (a) naked and (b)  $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles

Adsorbent	Concentration (ppm)	% Removal
Unmodified $\text{Fe}_3\text{O}_4$ nanoparticles	10	74.60
$\beta$ -CD modified $\text{Fe}_3\text{O}_4$ nanoparticles	10	91.36

Table 4. Results of desorption and recovery of  $\beta$ -CD modified magnetic nanoparticles

	Time	% Adsorption	% Desorption	% Recovery
$\text{H}_2\text{SO}_4$	3 h	85.01	37.91	81.09
$\text{NaOH}$	3 h	82.80	33.71	68.13
Hot water (60 °C)	30 min	81.78	3.1	-

Table 5. Removal efficiency of As(III) in real samples by CM- $\beta$ CD-MNPs

Real sample	Initial As(III) (ppm)	Spiked As(III) (ppm)	% Removal
Gavandak	0.578	-	99.13
Ghochagh	0.186	10 ppm	92.97
Babagorgor	0.133	10 ppm	91.93
Industrial water	0.005	10 ppm	94.57

$\text{NaOH}$  and 0.1 M  $\text{H}_2\text{SO}_4$  solutions as eluent. The corresponding results are shown in Table 4. It can be seen that the eluents could desorb As(III) from the surface of nanoparticles lower than 40%. For examining the recovery of one time used nanoparticles, they were used again in another adsorption cycle using fresh arsenic solutions. The results in the last column of Table 4 indicate that they can be efficient in arsenic removal again. Desorption of As(III) from the surface of CM- $\beta$ CD-MNPs was also carried out using heating at 60 °C in water. Since desorption efficiency of As(III) by heating was very low, it was indicated that arsenic adsorption process is chemisorption. Therefore, it can be hypothesized that  $\beta$ -CD modified magnetic nanoparticles remove As(III) through inclusion complex formation.

#### Real Samples

The ability of CM- $\beta$ CD-MNPs in the adsorption of arsenic from real samples was investigated. Several experiments with CM- $\beta$ CD-MNPs were conducted to remove arsenic from three surface water samples and one industrial water sample. The natural water samples were obtained from the villages of Kurdistan province, and industrial sample was collected from petroleum industrial waste water. To determine As(III) concentration in real samples, inductively coupled plasma mass spectrometry (ICP-MS) was utilized. Table 5 lists the

initial concentration and the removal efficiencies of As(III) after treatment with CM- $\beta$ CD-MNP. In the observed samples, the obtained removals of As(III) were above 98%, and they were rarely affected by the commonly coexisted ions in real water samples. The arsenic concentration reached below WHO's drinking water standards through adsorption process using CM- $\beta$ CD-MNPs.

#### CONCLUSIONS

In this study,  $\beta$ -cyclodextrin coated magnetic nanoparticles as novel adsorbents were prepared and characterized to remove As(III) from aqueous solution. These magnetic nano-adsorbents were fabricated by co-precipitation method which have the magnetic properties of  $\text{Fe}_3\text{O}_4$  nanoparticles and adsorption properties of CM- $\beta$ -CD. The TEM analysis indicated that the CM- $\beta$ -CD modified  $\text{Fe}_3\text{O}_4$  nanoparticles were monodisperse with a mean diameter of ~10 nm. These magnetic nano-adsorbents can effectively be used to remove As(III) from aqueous solution because the modification of  $\text{Fe}_3\text{O}_4$  by CM- $\beta$ CD enhances the arsenic adsorption. Various factors affecting the uptake behavior such as contact time, pH, amount of CM- $\beta$ -CD-MNPs, and initial concentration of As(III) were evaluated. The equilibrium data for CM- $\beta$ -CD-MNPs fitted well the Langmuir isotherm model. The maximum monolayer adsorption capacity of CM- $\beta$ -CD-MNPs was 12.33 mg/g at room temperature. Results

of this work suggest that the CM- $\beta$ -CD coated magnetic nanoparticles can have wide applications in the removal of hazardous species from water samples, and can be used instead of conventional adsorbents.

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#### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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