Original Article

Removal of Hexavalent Chromium from Aqueous Solutions Using Magnetic Nanoparticles Coated with Alumina and Modified by Cetyl Trimethyl Ammonium Bromide

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Abstract

Introduction: The development of an effective method regarding chromium removal from the environment is of great importance. Therefore, the present study aimed to examiner magnetic nanoparticles coated with alumina modified by Cetyl Trimethyl Ammonium Bromide (CTAB) in the removal of Cr^{6+} through magnetic solid phase extraction method.

Materials & Methods: At first, iron oxide nanoparticles were synthesized, coated with alumina, modified with CTAB and characterized with suitable instruments. The factors affecting the process of chromium removal were investigated, including the concentration of CTAB, the pH, the amount of nanoparticles, the sample volume, a proper eluent, the adsorption and desorption time, and the effect of interfering ions. Moreover, the chromium concentration was determined by flame atomic absorption spectrometric (FAAS) technique. The adsorption isotherm, adsorption capacity, and recoverability of the adsorbent were further examined.

Results: The modified magnetic nanoparticles were demonstrated to be homogeneous, spherical, with a size lower than 20 nanometer having a magnetic property. The optimal conditions for chromium removal entailed $7*10^{-6}$ mol/L concentration of CTAB, pH range of 6-8, 0.1 g of the nanoparticles, 10 mL volume of the chromium sample (5 $\mu g\ mL^{-1}$), nitric acid 2 M as a suitable eluent, 15 minutes of adsorption and desorption, and no interference of interfering ions in the process of chromium separation. The process efficiency under optimal conditions was determined to be over 95%, which this process followed the Langmuir adsorption isotherm. The adsorption capacity proved to be 23.8 mg/g. Reusing after four times of adsorbent recovering was effective in the chromium removal (80%). The method accuracy for five measurement times was 4.155% and the method's LOD was 0.081 mg/L.

Conclusion: The method enjoys the benefits of convenient preparation of the adsorbent, high selectivity, high accuracy, short process time, and high-efficiency in chromium removal from aquatic environments, lending itself to be used in the real samples.

Keywords: Cationic surfactant; Hexavalent chromium; Magnetic nanoparticles; Magnetic solid phase extraction

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Introduction

Heavy metals are placed among the most important environmental pollutants that have changed into a global concern due to their toxicity and carcinogenetic properties. These metals, even in trace amounts, accumulate in the body of creatures and their food cycle [1-3]. These metals are not metabolized in the body and accumulate in the body tissues resulting in emergence of diseases and many complications including cancer. One of the most applicable heavy metals is chromium widely used in many industries including electroplating, dyeing, tannery, and fertilizer producing. As the wastewater of these industries enter the environment, this metal is spread throughout the environment [4]. American Environmental Protection Agency has reported chromium as one of the main toxic pollutants. This metal exists in the environment mainly in the form of trivalent and hexavalent forms. Hexavalent chromium is really toxic with its adsorption in potable water being nine times as much as the adsorption of trivalent chromium [5-7]. Moreover, the carcinogenicity of the hexavalent chromium has also been confirmed by the World Health Organization [8]. The international cancer research agency has placed hexavalent chromium in the first group of carcinogen substances [9]. Hexavalent chromium can cause serious problems in the performance of the liver, kidneys, and lungs. The short-term effects of exposure to chromium involves burning and inflammation in the upper respiratory tract and dermatological burning resulting in ulcers and scars. On the other hand, lung cancer and kidney damages can be mentioned as long-term effects of being exposed to chromium[10]. If the chromium concentration in the body exceeds 0.1 mg/kg, it can lead to death [11]. At high concentrations, all chromium compounds are toxic and thus it is required to treat wastewaters polluted with these compounds before being discharged into the environment. The maximum allowable limit for chromium in potable water is 0.05 mg/L [12]4 according to Iranian industrial standard and research Institute, while World Health Organization has specified it as 0.01 mg/L [8].

Various methods have been reported including electro dialysis, chemical deposition, ion exchange resins, reduction, and reverses osmosis in order to remove such heavy metals as chromium. However, their use seems to be limited due to relatively high costs, low removal efficiency, discharge of wastes produced by treatment, the need for regular monitoring of the system, the need for expending a great deal of energy, production of toxic sludge, and in general the need to high capital investment and high operational costs [13-17].

Nanoparticles and nanotechnology are also applied in the treatment of wastewaters as a novel method [18]. Adsorption by modified nanoparticles is an environmentally friendly technology that has been studied extensively in recent years as an effective agent to remove organic pollutants and the

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ions of heavy metals from water and wastewater [19]. The unique feature of nanoparticles in the removal of heavy metals includes their high-efficiency, reasonable costs, and high variety[20].

Nanoparticles are used as adsorbents because of their high surface-area-to-volume ratio and active sites for adsorption. Among nanoparticles, iron magnetic nanoparticles have gained more interest due to their abundance, inexpensiveness, non-toxicity, rapid reaction, high competence and efficiency in chemical and physical adsorption of organic and inorganic pollutants including heavy metals from polluted waters [21].

So far, numerous adsorbances have been used regarding removal of hexavalent chromium from aquatic solutions [22-26]. Sun et al. (2014) removed chromium from aquatic solutions using magnetic cellulose nano composite functionalized with amine groups in China [27]. Hao et al. (2014) indicated that use of iron oxide nanoparticles can be regarded as an effective method for chromium removal [28]. Zhang et al. (2014) observed that modified bentonite has a reasonable efficiency in the chromium removal from aquatic solutions [29]. Bhaumik et al. (2014) removed hexavalent chromium using avocado grains modified with sulfuric acid [30]. Moreover, Linnikov et al. (2014) synthesized crystal magnetite nanoparticles in various sizes and applied them in the chromium removalfrom aquatic environments [31]. In another study, Srivastava et al. (2014) used magnetic nanoparticles coated with silica in the removal of chromium from aquatic environments in India [32]. Farokhi et al. (2014) revealed that the modified sawdust of alder tree is able to remove chromium from aquatic environments [33]. Likewise, Ghaneian et al. (2014) managed to remove chromium from aquatic environments using carbon nanotubes [34]. Ehrampoosh et al. (2013) were able to remove hexavalent chromium from aquatic environments using alumina nanoparticles modified with Schiff Base ligand under acidic conditions [35].

Based on the conducted studies on the chromium removal, magnetic nanoparticles coated with alumina, which were modified by Cetyl Trimethyl Ammonium Bromide (CTAB) as the adsorbent, have not yet been used in chromium removal. This study aimed to synthesize magnetic nanoparticles coated with alumina modified by CTAB and investigate the efficiency of these nanoparticles in the removal of hexavalent chromium from aquatic environments using the simple and sensitive methods of magnetic solid phase extraction.

Materials and Methods

This experimental study was conducted in the environmental health engineering research Center of Kerman University of medical sciences in cooperation with nanotechnology research laboratory of Sirjan Payam Noor University. First, the magnetic nanoparticles were prepared and coated with alumina. The magnetic nanoparticles were synthesized using chemical co-precipitation method. 2 g of iron (II) chloride, 5.2 g of iron (III) chloride together with 0.85 mL of concentrated

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hydrochloric acid were dissolved in 25 mL of distilled water. This solution was then dropwise added to 250 mL of NaOH solution 1.5 M using Burette, while being stirred vigorously using a mechanical stirrer. Nitrogen gas was also constantly being passed through the solution. After the completion of the reaction, the formed deposit was held using a magnet and the top solution was overflowed. The formed nanoparticles were washed four times (each time with 200 mL pure distilled water), and further dried at 80°C. Nanoparticles coating with alumina was performed through Karimi et al's method [36,37]. First, 1 g of aluminum isoperoxide was dissolved into 60 mL of ethanol using ultrasonic. Then, 0.1 g of Fe_3O_4 nanoparticles was added to it and stirred in ultrasonic bath for five minutes. Thereafter, 50 ml of water and ethanol solution was gradually added to this solution under mechanical stirring with a high speed. The resulting solution was stirred for half an hour and then was remained constant for one hour. At the next stage, the deposit was separated from the solution using a magnet, which was washed five times with ethanol. It was eventually dried in an oven and calcined in a kiln for 3 hours. Next, 0.1 g of the magnetic nanoparticles coated with alumina was washed by 10 mL of pure water. A total of 10 mL of Cetyl Trimethyl Ammonium Bromide solution with a concentration of $7*10^{-6}$ mg/L was added into the magnetic nanoparticles coated with alumina. The solution's pH was brought to 7 using a phosphate buffer (Na_2HPO_4/NaH_2PO_4). The solution was then stirred with a stirrer for five minutes, finally overflowed using a magnet. After being washed by pure distilled water, 10 mL of chromium VI solution 5 μg mL^{-1} was added and the solution's pH was brought to 7 using phosphate buffer. After 10 minutes of stirring, the top solution was separated using a magnet. The chromium adsorbed by nanoparticles was then washed with 5 ml of nitric acid 2 M, and its value was determined by FAAS technique. All the stages of the experiment are demonstrated in Fig. 1. The factors affecting the chromium removal process were examined such as CTAB concentration, the solution's pH, the amount of nanoparticles, the sample volume, proper eluent , the adsorption and desorption time as well as the effect of disturbing ions. Furthermore, adsorption isotherm, adsorption capacity, and reusability of the adsorbent were also examined. Based on the obtained results, the method accuracy, the linear calibration range, and the limit of detection were determined. By adding certain amounts of chromium to the synthetic and real samples as well as recovery, the method validity was examined.

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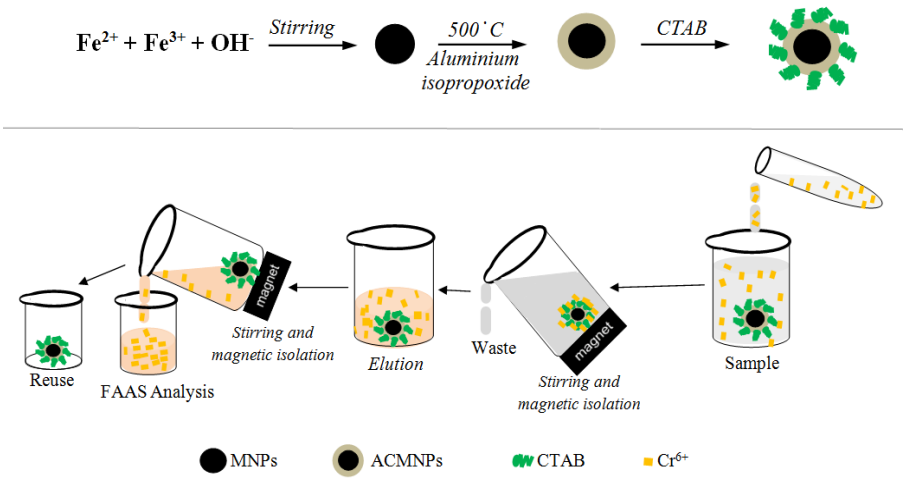


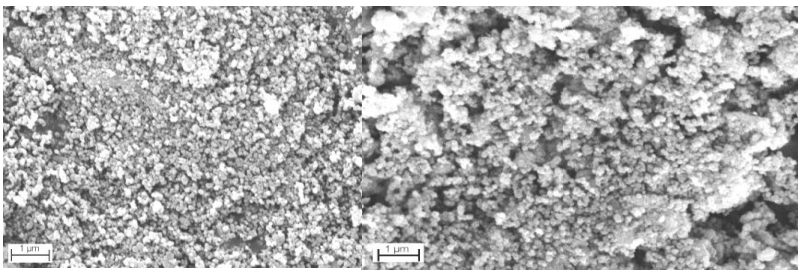
Fig. 1. The general process of synthesis of magnetic nanoparticles coated with alumina modified by Cetyl Trimethyl Ammonium Bromide and separation of chromium from aquatic solutions through magnetic solid phase extraction method

The prepared nanoparticles were investigated in order to study the effect of their nature, size, morphology, presence of coatings, and magnetic properties using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Vibrating Sample Magnetometer (VSM). Measuring chromium concentration was performed by Atomic Absorption Spectrophotometer made by PG Instruments, England, Model: PG 990. PH of the solutions were Adjused and measured were carried out using a pH-meter, Model: Metrohm 780. A piece of magnet with the dimensions of 2*5*10 cm and magnetic field power of 1.2 Tesla were used to exert magnetic field as well as to separate the nanoparticles from the solution. Other employed devices consisted of ultrasonic bath (S60H,Germany), mechanical stirrer(Heidolph RZR202), scanning electron microscope with the composition device to prepare three-dimensional images of the nanoparticles(VP Leo1455) X-ray diffraction device (Bruker D8ADVANCE, Germany), Fourier Transform Infrared spectroscopy to prepare infrared spectrum of nanoparticles and the associated compounds (FT/IR 4200). The magnetic properties of the nanoparticles were measured by Lake-Shore 7400 vibrating sample magnetometer. All the materials and chemical reagents used in this study were purchased from Merck Co, Germany with a high purity degree. In order to analyze the study data, SPSS software (ver.18) was utilized applying descriptive statistics.

Results

SEM images related to Fe_3O_4 nanoparticles as well as the nanoparticles coated with alumina are demonstrated in Fig. 2.

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(a) (b)

Fig. 2. SEM images of Fe_eO_4 nanoparticles (a) and nanoparticles coated with alumina (b)

The X-ray diffraction spectrum of Fe_3O_4 nanoparticles and the nanoparticles coated with alumina are revealed in Fig. 3.

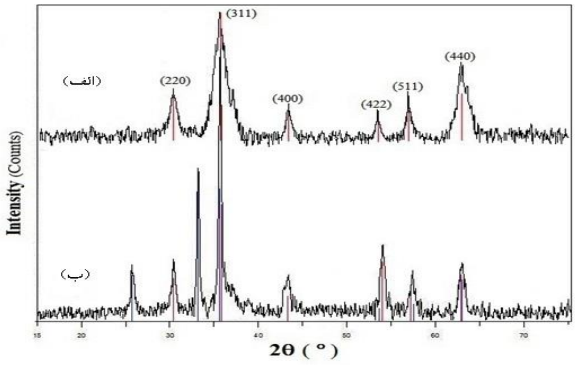


Fig. 3. XRD spectrum of Fe_3O_4 nanoparticles (a) and nanoparticles coated with alumina (b)

VSM spectra of Fe_3O_4 nanoparticles and the nanoparticles coated with alumina are shown in Fig. 4.

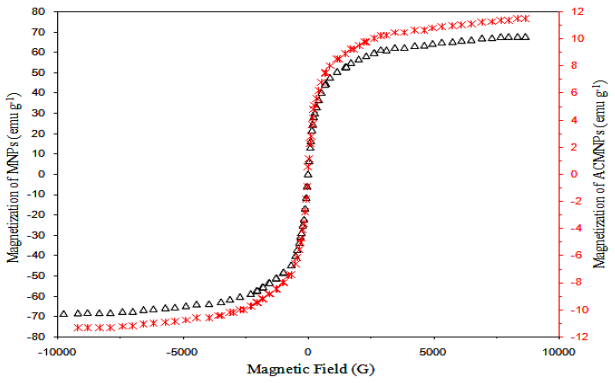


Fig. 4. VSM spectrum related to Fe_3O_4 nanoparticles (Δ) and nanoparticles coated with alumina(*)

As it is shown in Fig. 5, Fourier Transform Infrared spectrometry (FTIR) was performed to confirm existence of coatings on the surface of Fe_3O_4, Fe_3O_4/Al_2O_3 and Fe_3O_4/Al_2O_3/CTAB. .

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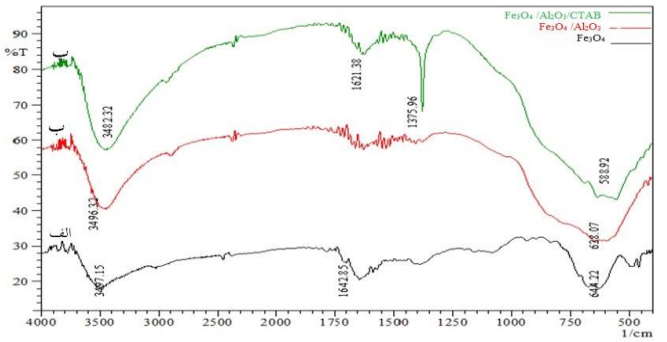


Fig. 5. FTIR spectra of Fe_3O_4 nanoparticles (a) and Fe_3O_4/Al_2O_3 nanoparticles (b), and Fe_3O_4 $/Al_2O_3/CTAB$ (c)

The results obtained from evaluation of different concentrations of Cetyl Trimethyl Ammonium Bromide on the level of chromium adsorption are shown in Fig. 6.

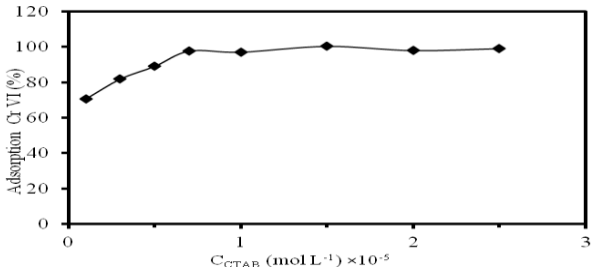


Fig. 6. The effect of the concentration of Cetyl Trimethyl Ammonium Bromide on the level of chromium adsorption

The results obtained from evaluations ofng different pH of chromium solutions and Cetyl Trimethyl Ammonium Bromide on the level of chromium adsorption are reported in Fig. 7.

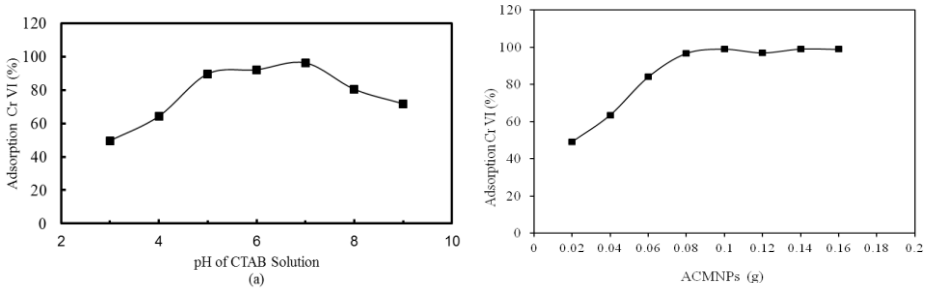


Fig. 7. The effect of pH on the chromium adsorption in Cetyl Trimethyl Ammonium Bromide (a) and chromium (b) solutions

The results obtained from examination of different amounts of nanoparticles on the level of chromium adsorption are indicated in Fig. 8.

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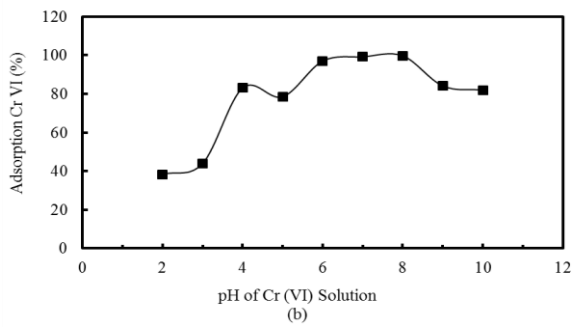


Fig. 8. The effect of the amount of nanoparticles on the chromium adsorption

In order to select the proper amount of nanoparticles coated with modified alumina for chromium adsorption available in 10 mL of the solution 5 µg mL $^{-1}$ under optimal conditions, the adsorption process was carried out on various amounts of nanoparticles culminating in the selection of 0.1 g as the proper amount.

The results obtained from evaluation of the sample volume on the level of chromium adsorption are shown in Fig. 9.

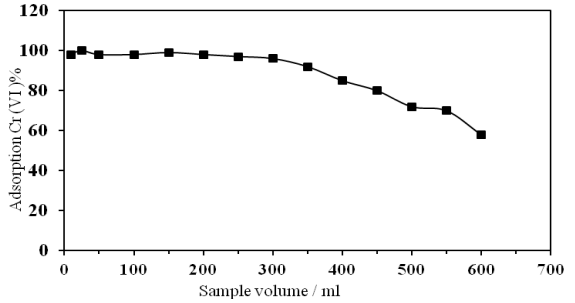


Fig. 9. The effect of the volume of the sample on chromium adsorption

In order to recover chromium from the nanoparticles surface, different eluents such as HCl, sulfuric acid, nitric acid, ethanol, and ammonium were studied at different concentrations. Eventually, 5 mL of nitric acid 2 M was chosen as the proper eluents with an efficiency of over 97%.

Separation time is introduced as a key variable in solid phase extraction processes. In this method, when compared with other methods, due to lack of need to columns and special equipment used in typical methods, less time is spent for the separation. In order to determine the required time for chromium adsorption, 10 mL of the 5-mg/L chromium solution was exposed to specific amounts of nanoparticles under the optimal conditions, where at various times, the level of adsorbed chromium was measured by Atomic Absorption Spectrometry. It was observed that 5 minutes is suitable for chromium adsorption (above 95%) and 10 minutes is adequate for chromium desorption. In addition, the total time required for one time of full separation and measurement was specified to be around 15 min.

In order to explore the disruption caused by potential ions, dual solutions of chromium together with the studied ions were prepared with different ratios. Following

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the extraction process, its effect on chromium desorption was studied and the disruption limit of every ion was further detected. The results are provided in Table 1, indicating no disruption caused by potential ions within the samples.

Table 1. The effect of interfering ions in the recovering of chromium

Entry	Ione	Mole ratio	Recovering of Cr^{6+} (%)	Entry	Ione	Mole ratio	Recovering of Cr^{6+} (%)
1	Ca^{2+}	1000	96	12	Cd^{2+}	500	94
2	Mg^{2+}	1000	97	13	Co^{2+}	500	98
3	Na^{+}	1000	94	14	NH_4^{+}	500	96
4	K^{+}	1000	98	15	Ag^{+}	500	95
5	Ni^{2+}	1000	96	16	NO_3^{-}	500	97
6	Ba^{2+}	1000	99	17	CH_3COO^{-}	500	99
7	Mn^{2+}	1000	94	18	SO_4^{2-}	100	95
8	Pb^{2+}	500	99	19	F^{-}	100	98
9	Fe^{2+}	500	98	20	Br	100	97
10	Bi^{3+}	500	95	21	I^{-}	100	96
11	Hg^{2+}	500	93	22	$C_2O_4^{2-}$	100	98

The method validity was investigated by adding certain amounts of chromium to water samples and real samples and retrieval. . The chromium solutions were prepared with concentrations of 5.0 and 10.0 mg/L out of the two types of studied water, previously collected from the tap water of Sirjan and spring water in Rabor in Kerman, IRAN. The chromium available in either solutions was concentrated and measured according to the proposed method. The results obtained from the adsorption measurement of the recovered solutions are provided in Table 2.

Table 2. Recovering of the chromium added to the real samples

Real samples	Cr^{6+} Recovering	Cr^{6+} (mg mL^{-1})	
	(%)	Determined	Added
Tap water	-	-	0
(Sirjan)	100.4	5.02	5
	101.0	10.10	10
Spring Water	-	-	0
(Rabor)	100.8	5.04	5
	98.3	9.83	10

Discussion

As it was observed in the SEM images, the nanoparticles were spherical and almost homogeneous in terms of size. This homogeneity and size were preserved well after coaching with alumina.

In the X-ray diffraction spectrum, there were six index peaks along with their

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characteristic numbers. Based on the information related to the database of the X-ray device's software (PDF No. 03-862), it can confirm the nature of particles as Fe_3O_4. Furthermore, in this spectrum (b), alumina presence was confirmed by the X-ray device. The lack of change in the structure of nanoparticles after being coated with alumina was also confirmed. The particles sizes of 7±4 and 18±5 nanometer were determined for the Fe_3O_4 and Fe_3O_4 coated with alumina, respectively.

As it can be seen in VSM spectra of Fe_3O_4 nanoparticles, the two diagrams have a uniform shape indicating similar magnetic properties before and after being coated with alumina. Lack of hysteresis loop reveals particle size of less than 20 nm and their supra-magnetism. High magnetic saturation is indicative of their high magnetization [28], where its value for Fe_3O_4 nanoparticles and the nanoparticles coated with alumina is 56.72 and 9.34 respectively, which is a suitable value regarding the separation with a typical magnet.

In the FTIR spectrum related to Fe_3O_4, a broad peak was observed at 644.22 cm^{-1}, related to the stretching bond of Fe-O-Fe. The peaks at 1642.85 and 3497.15 cm^{-1} can be related to the nitrogen stretching vibrating bond absorbed onto the surface of nanoparticles and the vibrating bond of hydroxyl group respectively. This spectrum also confirms the nature of Fe_3O_4 [39]. In the Spectrum (b), related to the nanoparticles after being coated with alumina, a broadening can be observed in the Fe-O peak, which is the result of its overlapping with the peak associated with Al-O bond (638.07 cm^{-1}), while indicating the alumina coating. In spectrum (c), related to the nanoparticles coated with alumina modified with Cetyl Trimethyl Ammonium Bromide, a sharp peak is observed at 1375 cm^{-1}, associated with the stretching bond of C-N within the structure of Cetyl Trimethyl Ammonium Bromide, demonstrating its existence on the surface of nanoparticles.

The magnetic nanoparticles coated with alumina and in general active alumina have a positive superficial charge in acidic conditions and are well able to adsorb negatively charged particles particularly anionic surfactants in aquatic environments [40]. In the present study, Cetyl Trimethyl Ammonium Bromide was used at a concentration lower than critical micellar concentration (CMC). The concentrations larger than Cetyl Trimethyl Ammonium Bromide resulted in the formation of micelle in aquatic solutions, inhibiting its adsorption within the surface of nanoparticles. According to micelle concentration at lower concentrations of critical point may be form hemimicelle and admicelle on the nanoparticles. As it is evident in Fig. 6, an increase in the concentration of Cetyl Trimethyl Ammonium Bromide boosts the level of adsorption, peaking at $0.8*10^{-5}$ M and continuing until the CMC concentration range. After CMC, due to micelles formation, the adsorption level in the solution declines. Therefore, the concentration of $0.7*10^{-5}$ M was chosen as the optimal concentration.

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As it can be seen, the highest adsorption of Cetyl Trimethyl Ammonium Bromide on the nanoparticles coated with alumina has occurred within the pH of 6-8 (Fig. 7a). Furthermore, the highest level of chromium adsorption on the nanoparticles modified with Cetyl Trimethyl Ammonium Bromide has also occurred within this range of pH (Fig. 7b). At pHs lower than 6 the level of adsorption diminishes due to the competition of H^+ with chromium ions. At pHs higher than 8, , the level of adsorption drops. Therefore, pH range of 6-8 was selected as the optimal range, which can be related to the formation of metal hydroxide deposit and ion separation from the nanoparticles surface due to the development of negative superficial charge in the nanoparticles.

The solid phase extraction method is recognized as a known process in regard with extraction and concentration of metal ions from samples with large volumes to achieve high pre-concentration factors. In this section, recovering was investigated as a function of the sample volume. It was observed that at volumes above 600 mL, recovering percentage decreases. As a result, the pre-concentration factor of approximately 80 was determined for the sample with initial volume of 400 mL and final volume of 5 mL (after recovering) with a desorption over 95%.

The adsorption equilibrium isotherm of chromium ions was investigated by Langmuir adsorption isotherm model in phosphate buffer solution at pH=7 at 25 °C, with the results being provided in Fig. 10.

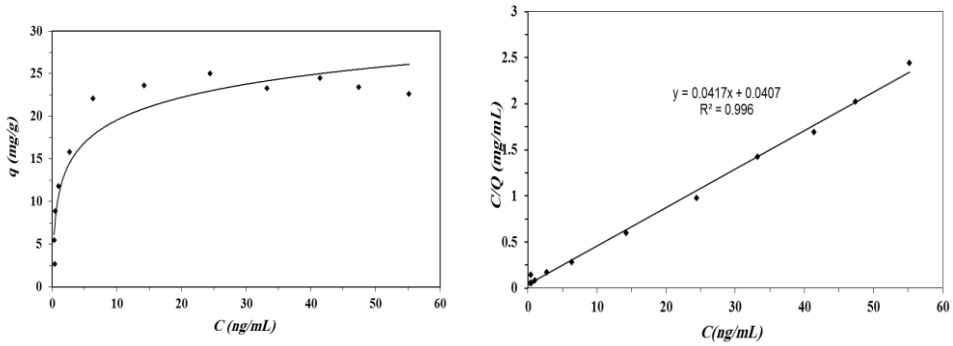


Fig. 10. The chromium adsorption isotherm on the nanoparticles coated with alumina modified by Cetyl Trimethyl Ammonium Bromide

The Langmuir isotherm model is mainly used in order to analyze the experimental data as well as to describe equilibrium in the adsorption. Langmuir isotherm indicates monolayer and homogeneous adsorption with removal of the interactive effects of the adsorbed molecules, shown in Eq. (1).

$$\mathbf{C_e/Q_e = (1/Kq_m)+(Ce/q_m)} \qquad \text{(Eq.1)}$$

Where, Q_e is the equilibrium adsorption of chromium (mg/g), C_e is the equilibrium concentration of chromium in the solution (mg/mL), q_m is the maximum level of chromium adsorption per gram of the adsorbent (mg/g), and K is the equilibrium constant of Langmuir adsorption isotherm (L/mg). According to Relation 2, the separation factor (R_L) can determine whether the adsorption process has acted satisfactorily .

$$\mathbf{R_L = 1/(1+KC_e)} \qquad \text{(Eq.2)}$$

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Where, if $R_L>1$, $R_L=1$, $o<R_L<1$, and $R_L=0$, the adsorption was demonstrated to be unsatisfactory, linear, satisfactory, and irreversible, respectively. R_L was revealed to be $0<R_L<1$ in the present study, and thus, it was determined to be satisfactory.

In order to investigate the adsorbent capacity, 1 g of the nanoparticles were subjected to 100 mL of chromium solution 300 μg mL^{-1} for 5 hours in the optimal conditions. Next, the amount of adsorbed chromium was measured, as a result of which 23.8 mg chromium per 1 g of nanoparticles was determined.

Reusing and recovering the adsorbent is regarded as a key parameter in the application of an adsorbent as the solid phase extraction. The adsorbent in this method is used up to 4 times with a recovering of over 80% for adsorption in the chromium desorption through the proposed method. In addition, in a production process, it is possible to prepare 4 g of nanoparticles coated with alumina, while only 0.1 g is required for the extraction process.

To examine the method replicability, the solid phase extraction was carried out according to the proposed method on five sample chromium solutions (10 mL) with a concentration of 5 mg/L. The adsorption of the solution was then measured by atomic absorption spectrometry, presented in Table 3.

Table 3. The atomic absorption results obtained from five times of measurement of chromium with a concentration of 5 mg/L

	No. of Sample					**Average**	**Standard deviation**	**Relative standard deviation (%)**
	1	2	3	4	5			
Absorption	0.268	0.251	0.270	0.258	0.245	0.258	0.010	4.155

The linear calibration range for chromium was 0.5-10 mg/L according to atomic absorption spectrometry, where out of this concentration range, it deviates from linearity due to decreased sensitivity of the standardization diagram. To plot the standardization diagram, solutions with concentrations of 0.5, 1, 2, 5, 8, and 10 mg/L were prepared, with the adsorption related to the standard samples, which the results are provided in Table 4.

Table 4. Standard solutions to plot calibration diagram

chromium concentration (mg/L)	**0.5**	**1**	**2**	**5**	**8**	**10**	**R^2**
Absorption	0.027	0.049	0.108	0.258	0.332	0.444	0.988

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The linear calibration diagram of chromium is shown in Fig. 11.

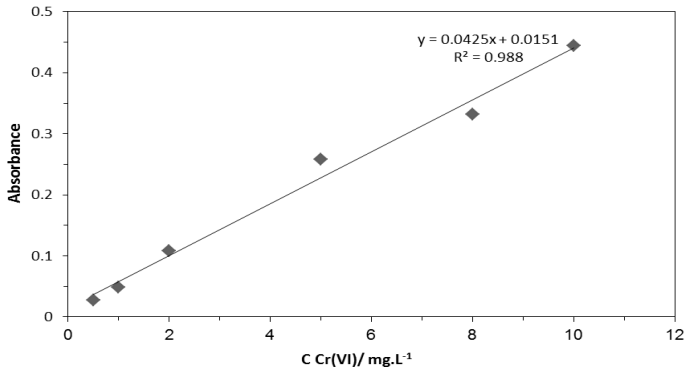


Fig. 11. The curve of absorption variations in terms of chromium concentration

Limit of detection (LOD) of a method is a concentration of the sample whose instrumental response is significantly different from that of the control sample. According to Eq. (3), it is defined as a concentration of the experimental sample whose signal is equivalent to the control signal plus standard deviation multiplied by three, which is obtained from the control solution.

$$\mathbf{Y_{LOD}=S_b+3S_B} \quad (3)$$

In the above relation, S_B is the standard deviation associated with the control solution, S_b is the signal related to the control solution, and Y_{LOD} is a signal related to the limit of detection. By putting the value of Y_{LOD} in Relation 4, the concentration equivalent to the limit of detection can be calculated.

$$\mathbf{Y_{LOD}= mC + S_b} \quad (4)$$

Where, m is the line slope, C is the concentration, and S_b is the signal associated with the control solution (the standardization of line equation). In order to determine the limit of detection of chromium, twice distilled water was exposed to the adsorbent according to the proposed method. After recovering, its adsorption was measured by flame atomic absorption spectrometer. In addition to limit of detection of the device, the limit of the detection of the method was also identified. The results obtained from these measurements are as follows:

0.007, 0.012, 0.010, 0.011 and 0.014

$$\mathbf{SD = 2.5\times10^{-3}\ ,\ \bar{X} = 1.08\times10^{-2}}$$

$$\mathbf{Y_{LOD} = \bar{X} + 3SD = 1.85\times10^{-2}}$$

After calculating Y_{LOD} and the calibration line equation, C_{LOD} was also calculated:

$$\mathbf{C_{LOD}= 0.0815\ mg/L}$$

Table 5 shows a comparison of the proposed method with other reported methods of SPE.It can be stated that some obtained values for the proposed method are as or better than some of the previously reported methods.

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Table 5. Comparative data from some recent studies on SPE

Adsorbent	Detection method	Enrichment factor	Sorbent capacity (mg g^{-1})	RSD (%)	Linear range (ng mL-1)	Detection limit (ng mL- 1)	Reference
Chelating resin of MAM	FAAS	200	34.3	1.2	1-12	0.01	[41]
Chromosorb 108 resin/dithizone	FAAS	71	4.5	<9	N.R.[a]	0.75	[42]
Ni_Al layered double hydroxide as nano-sorbent	FAAS	100	6.5	2.5	1-100	0.51	[43]
MWCNTs-APDC	FAAS	100	9.5	<9	N.R.	0.90	[44]
Amberlite XAD-1180 resin/1,5-Diphenylcarbazide	FAAS	75	N.R.	N.R.	0-250	7.7	[45]
Dowex M 4195 resin	FAAS	31	29.7	<10	N.R.	1.94	[46]
Nanometer TiO2	ICP-AES	50	7.6	2.4	N.R.	0.32	[47]
Amberlite XAD-2000 resin/APDC	FAAS	80	8.0	<6	N.R.	0.6	[48]
CTAB@ACMNPs	FAAS	80	23.8	4.15	0.2-10.0	0.081	This work

[a] Not Reported.

Conclusion

Magnetic solid phase extraction of chromium using iron oxide nanoparticles coated with alumina, whose surface is modified by Cetyl Trimethyl Ammonium Bromide, has advantages, including convenient preparation of the adsorbent, high selectivity, high accuracy, short process time, and high efficiency in removing chromium. The synthesized nanoparticles have had super-paramagentic properties with a size below 20 nm. This method was used successfully for chromium extraction in real samples. In this method, due to lack of the need to columns and special equipment using conventional methods, Spend less time to once isolated, revealing better results in comparison with other conventional solid phase extraction methods.

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