Original Article

Applications of CTAB modified magnetic nanoparticles for removal of chromium (VI) from contaminated water

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ABSTRACT

This study investigated the elimination of Cr(VI) from aqueous solution utilizing a composite from magnetic nanoparticles (Fe3O4) capped with cetyltrimethylammonium bromide (CTAB). The structure of the prepared composite system was examined by Fourier Transform Infra Red Spectroscopy (FTIR), X-ray Diffractometry (XRD), and Transmission Electron Microscopy (TEM). Separation of the Fe3O4/CTAB composite from the wastewater can be achieved by application of an external magnetic field. Factors affecting the Cr(VI) expulsion from wastewater such as pH, competing ions, the dosage level of the nanoparticles, and contact time were studied. The results indicated that the maximum efficiency of the present system for removal of Cr(VI) (95.77%) was in acidic conditions (pH 4), contact time 12 h, and composite dosage of 12 mg/mL. The used Cr(VI) concentration was 100 mg/L. Considering results, the Fe3O4/CTAB system showed a high capability and selectivity for the treatment of water sullied with Cr(VI). This can recede the mutagenic and carcinogenic health risk caused by Cr(VI) water tainting.

Introduction

Study of water remediation from contaminants such as toxic heavy metals is one of the most important environmental issues. Contaminants can pose serious health and environmental problems [1]. The literature survey confirms that chromium has two
oxidation states, hexavalent Cr(VI) and trivalent Cr(III) [2]. The latter is essential in mammals life and it is concluded that Cr(VI) is more toxic, mutagenic, carcinogenic and hazardous than Cr(III) by 500 times. Cr(VI) can be found as chromate (CrO₄²⁻), hydrogen chromate (HCrO₄), dichromate (Cr₂O₇²⁻), and hydrogen dichromate (H₂Cr₂O₇) stable oxyanions in wastewater [3]. The highly toxic transition heavy metal Cr(VI) has a harmful and destroying effect on the human biological system. It is found in wastewater streams from mining, stainless steel production, textile industry, and dyes [4–6].

US Environmental Protection Agency (EPA) indicates that the allowed contamination level for chromium ion in potable water is 0.1 mg/L, while the concentration of the discharge to inland surface water is 0.5 mg/L [7]. Adsorption is the sufficient technique for Cr(VI) removal from industrial wastewater [8]. The guideline prescribed by the World Health Organization (WHO) for Cr(VI) in drinking water is 16 mg/L [9]. The effluent from industries containing Cr(VI) is considered by the International Agency for Research on Cancer (IARC) (1982) as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomal aberration [10].

Wastewater treatment using the adsorption techniques is more effective than using other techniques as precipitation, coagulation, chemical reduction, and ion exchange [11]. Magnetic nanoparticles are a good candidate for heavy metal adsorption from aqueous solution. Due to the four unpaired electrons in the 3d shell, an iron atom has a strong magnetic moment. Fe²⁺ ions have 4 unpaired electrons in their 3d shell and Fe³⁺ ions have 5 unpaired electrons in their 3d shell. Thus, the formed crystals from iron ions of Fe²⁺ or Fe³⁺, can be in ferromagnetic or ferrimagnetic states [12]. Magnetic nanoparticles are susceptible to air oxidation and can be easily aggregated in aqueous systems [13]. The stabilization of the iron oxide nanoparticles by adding surfactants as a type of surface modification is desirable. This can change in the surface layer properties to become more different from that in the core of the nanoparticles [14]. The properties of the nanocrystals strongly depend on the dimension of the nanoparticles [15,16]. Fe₃O₄ and Fe₇O₁₄ nanoparticles stabilized by Aloe Vera were successfully applied before for the elimination of mercury (70%) from a wastewater sample [17]. Fe₃O₄/talc nanocomposite was used for the removal of Cu(II), Ni(II), and Pb(II) ions from aqueous solutions. The results showed 72.15%, 50.23%, and 91.35% removal efficiency for Cu(II), Ni(II), and Pb(II), respectively [18]. Fe₇O₁₄ magnetic nanoparticles modified with Schiff base ligand were prepared to remove heavy metal ions from aqueous solutions. The maximum adsorption capacities were 97.2, 87, and 81.6 mg g⁻¹ for Cu(II), Zn(II), and Ni(II), respectively [19].

Surfactants are used to lower the surface tension of liquids and have a structure that cannot easily be detected by conventional methods. Cetyltrimethylammonium bromide (CTAB) is a common surfactant used in nanoparticles synthesis. CTAB has a 16-carbon as a long tail and an ammonium head group with three methyl groups attached. Here CTAB can be used for the removal of heavy metals from wastewater [20]. CTAB is a positively charged surfactant, used as a coating agent. CTAB can appear as rod-like micelles with increasing its concentration [21–23]. Jin et al. had succeeded in preparing the Fe₃O₄ composite capped with CTAB for arsenate removal from water. Fe₃O₄/CTAB was prepared by a modified simple co-precipitation process using cheap and environmentally friendly iron salts and the cationic surfactant CTAB [24].

This work aims to develop magnetic nanoparticles (MNPs) coated with CTAB as an efficient composite for the removal of toxic Cr(VI) from wastewater. It is evident from literature survey that, this is the first time that Cr(VI) elimination and quantification from wastewater samples based on Fe₇O₁₄ and Fe₃O₄/CTAB is described. Schematic representation of Cr(VI) elimination by Fe₇O₁₄/CTAB is sketched in Scheme 1. The Fe₇O₁₄/CTAB has some advantages such as facile synthesis and simple regeneration in alkali solutions. Thus, favoring its reusing or recycling purposes. It also can be easily collected by external magnetic field for the regeneration process. Furthermore, this composite is cheap and effective in the removal of Cr(VI) from wastewater.

Material and methods

Reagents

All chemicals that used in this work are analytical grade reagents. Iron (III) chloride 97% (FeCl₃), iron (II) chloride tetrahydrate 98% (FeCl₂·4H₂O), potassium chromate (K₂CrO₄) 99%, Cetyltrimethylammonium bromide (CTAB) 95% and ammonium solution 25% were purchased from Sigma-Aldrich (Missouri, USA). Nitrite standard, sulfate standard, and phosphate standard were purchased from Ultracech (California, USA).

Preparation of Fe₃O₄ (magnetic) nanoparticles

Chemical co-precipitation method is a widely applicable method for synthesis of iron oxide nanoparticles. It involves mixing of ferric and ferrous salts in 2:1 (Fe³⁺/Fe²⁺) ratio in a basic aqueous medium (using 25% ammonium solution) [25]. Formation of Fe₃O₄ nanoparticles can be completed at a pH 8.0–10.0 [26].

The formed nanoparticles were washed with deionized water (DI), collected by applying an external magnetic field and dried under vacuum [27].
Preparation of Fe₃O₄/CTAB composite

Cationic surfactants have been used for anionic metal removal [28]. Iron (III) chloride (0.5 g), 0.4 g of iron (II) chloride tetrahydrate, and 0.4 g of CTAB was dissolved together in 100 mL DI, then 25% ammonium solution was added until the black precipitate was formed. The mixture was stirred for 2 h and the formed Fe₃O₄/CTAB was collected and washed as mentioned before [11].

Samples processing

DI was used for all preparations and throughout all experiments. Experiments were carried out at room temperature. Different dosages of Fe₃O₄ nanoparticles or Fe₃O₄/CTAB (4, 8, and 12 mg/mL) were added in 25 mL of DI containing Cr(VI) (100 mg/L) solution. The adsorption capacity of the adsorbents was determined according to Eq. (1) [29].

\[
Q_e = \frac{(C_0 - C_f) \times V}{W}
\]  

(1)

where \(Q_e\) is the equilibrium adsorption capacity of the adsorbent in mg (metal)/g (adsorbent), \(C_0\) is the concentration of metal ions before adsorption in mg/L, \(C_f\) is the equilibrium concentration of metal ions in mg/L (remained in solution after shaking), \(V\) is the volume of metal ions solution in liter scale, and \(W\) is the weight of the adsorbent in gram scale. The samples were shaken at a rate of 1.17 x 10⁻² g/cm² and different contact times (2, 4, 6, 8, 10, and 12 h) to estimate the best contact time for maximum adsorption. All adsorption experiments were conducted in triplicate and the mean of the three values was expressed as the result. After shaking, the adsorbent was collected by applying an external strong magnet. The concentration of Cr(VI) in the supernatant as well as in the control samples was determined by flame atomic absorption spectroscopy (FAAS) [30].

Effect of pH

Three pH values, including acidic, neutral and basic pH were tested to assess the adsorption capacity of the adsorbent in the different media. The pH of the samples was adjusted to 4.0, 7.0, and 9.0 using 0.01 N NaOH or 0.01 N HCl. The percentage of removal was calculated from the Eq. (2)

\[
\% \text{ Removal} = \left(\frac{C_0 - C_f}{C_0}\right) \times 100
\]  

(2)

where \(C_0\) and \(C_f\) are the initial and final concentration of heavy metals in the solution, respectively [31]. Additionally, the association between the initial concentration of Cr(VI) and the adsorption capacity was explored. 8 mg/mL of Fe₃O₄/CTAB nanoparticles was added into each flask containing 25 mL of Cr(VI) ion solutions with various initial metal ion concentrations (from 10 mg/L to 200 mg/L). All the flasks were shaken at 1.17 x 10⁻² g/cm² for 80 min. The adsorbed amount of metal ions onto the Fe₃O₄/CTAB was calculated according to Eqs. (1) and (2).

Effect of interfering ions

A series of different concentrations (1, 10, 15 and 20 mg/L) of interfering anions (nitrite, sulfate, and phosphate) was prepared. Each anion was applied separately in a binary system to investigate its interference with the Cr(VI) (100 mg/L) adsorption by Fe₃O₄/CTAB composite at pH 4 and 12 h contact time.

Field sample

The real field samples were collected from (Ternaries area, Fom El-Khaleg, Cairo Governorate-Egypt). The real field experiment was performed using 12 mg/mL Fe₃O₄/CTAB composite and 25 mL wastewater sample volume. The contact time was 12 h at pH 4 and shaking rate 1.17 x 10⁻².

Instruments

Atomic absorption spectroscopy of Cr(VI) was measured using a Perkin-Elmer flame atomic absorption spectrometer model 2380 (Perkin-Elmer, Norwalk, Connecticut, USA). The hollow cathode lamp used as a radiation source was operated at a wavelength of 425.4 nm and the slit width was adjusted to 0.2 nm. The flow of acetylene and air was 4.5 and 15.0 L/min, respectively. The infrared spectra (4000.6–399.1 cm⁻¹) were recorded on a Fourier Transform Infra Red spectrometer JASCO FT/IR-4100 (Jasco, Tokyo, Japan). X-ray diffraction (XRD) pattern was performed using a PANalytical’s X’Pert PRO diffractometer (PANalytical, Almelo, Netherlands) with Cu Kα radiation. The morphology of the Fe₃O₄ nanoparticles was observed by the transmission electron microscope (FEI Tecnai G2 20, 200 kV TEM, Oregon, USA). JENWAY 3010 digital pH/mV meter (JENWAY, Staffordshire, UK) was used for pH measurement. Millipore Elix S (Automatic Sanitization Module, Millipore, Massachusetts, USA) was used for the preparation of deionized water.

Results

Characterization of the prepared magnetic nanoparticles

XRD

The crystal structure and phase purity of the prepared iron oxide nanoparticles were identified by measuring the XRD pattern as shown in Fig. 1.

All the peaks of XRD pattern were analyzed and indexed comparing with magnetite standards. The lattice constants are equal (\(a = b = c = 8.3778 \text{ Å}\) confirming the formation of a cubic structure. The diffraction peaks at 30, 35.4, 43, 53.4, 56.9, and 62.5° are indexed to planes (220), (311), (400), (422), (511) and (440) of the cubic unit cell. The average Fe₃O₄ crystal size estimated from the plane (311) at 2θ=35.5° using the Scherrer formula (Eq. (3)) is 16.25 nm [32].

\[
d = \frac{K \lambda}{\beta \cos \theta}
\]  

(3)

Fig. 1. XRD pattern for Fe₃O₄ nanoparticles.
where d is the crystal size, K is the Scherrer constant (0.89), λ is the wavelength of the X-ray radiation (0.15418 nm for Cu Kα), and β is the full width at half maximum of a diffraction peak measured at 2θ.

**FTIR**

The IR spectrum of CTAB (Fig. 2a) consists of a band at 3420 cm⁻¹ that could be assigned to the vibrations of the ammonium moiety in CTAB. Peaks at 2918 and 2848 cm⁻¹ are attributed to two different CH bands vibration of the −CH₂ group in CTAB. The bands at 1630 and 1467 cm⁻¹ belong to asymmetric and symmetric stretching vibration of N⁺−CH₃, while the band at 960 cm⁻¹ corresponds to the out-of-plane −CH vibration of CH₃ [33]. The band at 720 cm⁻¹ could be assigned to Br⁻. The FTIR spectrum of Fe₃O₄/CTAB nanoparticles (Fig. 2b) displays a peak at 566 cm⁻¹ that represents Fe-O of Fe₃O₄. The broadband at 3430 cm⁻¹ might be assigned to the electrostatic interaction between Fe₃O₄ surface hydroxyl groups and the ammonium moiety in CTAB (OH ··· N⁺).

**TEM**

The TEM image in Fig. 3a showed particles with spherical-like shapes and size range from 10 to 20 nm. There is a good correspondence between Fe₃O₄ size shown in the TEM and that calculated from XRD spectrum by Scherrer formula.

The HRTEM image in Fig. 3b shows Fe₃O₄ crystal with a well-aligned and single crystalline structure (the d spacing is 0.22 nm).

**Factors affecting the adsorption process**

**Effect of pH**

The pH of the sample influences the adsorption progress by protonation and deprotonation of adsorbent surface functional groups. The effect of different pH values (4, 7, and 9) on the adsorption of Cr(VI) by nanoparticles (4 and 12 mg/mL) for 8 h contact time was investigated.

Table 1 showed that the maximum adsorption of Cr(VI) was observed at pH 4 for both adsorbents after 8 h contact time. From Table 1 it is obvious that the composite of Fe₃O₄/CTAB adsorption efficiency is higher than Fe₃O₄ in acidic pH 4. For example, the same dose (12 mg/mL) results in 72.47% Cr(VI) removal when applying Fe₃O₄ nanoparticles whereas it removes 94.19% after using Fe₃O₄/CTAB.

**Effect of nanocomposite dosage**

As evident from studying the effect of pH, removal of Cr(VI) was more proficient in pH 4 for both adsorbents. Therefore, the effect of nanocomposite dosage will be investigated at this pH value. Different dosages from both adsorbents (4, 8, and 12 mg/mL) were applied for the removal of Cr(VI) ions (100 mg/L) at room temperature (25.0 °C ± 1.0 °C) and at different contact times. From Fig. 4a and b it was noted that the removal of the Cr(VI) ions increases as the concentration of both adsorbents increases.
optimum dosage (12 mg/mL) of the composite Fe₃O₄/CTAB could stamp out 95.77% from Cr(VI) while an equivalent amount from Fe₃O₄ adsorbs 74.49% of Cr(VI) after 12 h contact time. The intermediate amount (8 mg/mL) from both Fe₃O₄/CTAB and Fe₃O₄ nanoparticles wipes out 84.4% and 57.4% Cr(VI), respectively.

The maximum adsorption capacity was achieved for both adsorbents at 8 mg/mL dosage level using 100 mg/L Cr(VI) concentration. It was 6.74 mg/g (Fig. 5-a) and 10.05 mg/g (Fig. 5b) for Fe₃O₄ and Fe₃O₄/CTAB, respectively.

From the adsorption capacity values, it appears that Fe₃O₄/CTAB has a better adsorption than bare Fe₃O₄.

**Adsorption kinetic study**

The metal adsorption mechanism can be explored by applying the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model equation assumes that the binding is originated from a physical adsorption as follows [34].

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

where \(q_e\) and \(q_t\) are the amount of heavy metal ions adsorbed on the adsorbent in mg (metal)/g (adsorbent) at equilibrium and at time \(t\), respectively. \(K_1\) is the constant of first-order kinetics in min⁻¹.

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While the pseudo-second-order kinetic model is based on chemical adsorption (chemisorption) as follows [29].

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) and \(q_t\) are the amount of heavy metal ions adsorbed by the adsorbent in mg (metal)/g (adsorbent) at equilibrium and at time \(t\), respectively. \(K_2\) is the rate constant of second-order kinetics in g/(mg min).

The values of \(K_1\) and \(K_2\) for Fe₃O₄/CTAB were experimentally determined from Eqs. (4) and (5), respectively. The fitting curves obtained from the linear plots of log \((q_t - q_e)\) versus time and \(t/q_e\) versus time are plotted in Fig. 6a and b respectively. From Fig. 6 it appears that the second order model seems to be more favorable for the Cr(VI) sorption process indicating its chemical adsorption by Fe₃O₄/CTAB nanocomposite.

The obtained \(K_1\) and \(K_2\) values for Fe₃O₄ and Fe₃O₄/CTAB nanocomposite plus other parameters obtained from the linear form of pseudo-first-order and pseudo-second-order are listed in the Table 2.
The common isotherm models (Langmuir and Freundlich), were used to describe the adsorption of Cr(VI) ion on the Fe₃O₄/CTAB nanocomposite. Langmuir model supposed that all the adsorption sites of the adsorbent have the same binding energy and every site joins to only one adsorbate [35].

The linearized Langmuir isotherm is given by Eq. (6):

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}
\]

where \(q_e\) is the equilibrium adsorption capacity of the adsorbent in mg (metal)/g (adsorbent), \(C_e\) is the equilibrium concentration of metal ions in mg/L, \(q_m\) is the maximum amount of metal adsorbed in mg (metal)/g (adsorbent), and \(b\) is the constant that belongs to the bonding energy of adsorption in L/mg.

On the other hand, Freundlich isotherm assumes heterogeneity of binding energies of adsorption sites [35]. The linearized Freundlich isotherm is given by Eq. (7):

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

where \(q_e\) is the equilibrium adsorption capacity of the adsorbent in mg (metal)/g (adsorbent), \(C_e\) is the equilibrium concentration of heavy metal ions in mg/L, \(K_f\) is the constant refers to the adsorption capacity of the adsorbent in mg/L, and \(n\) is the constant linked to the adsorption intensity.

Usually, for the valuation of preeminent fit, values of correlation coefficients \((R^2)\) of linear plots of the two models are compared. The correlation coefficient is higher \((R^2 = 0.99)\) in the case of applying a Langmuir model (Fig. 7a) than Freundlich model \((R^2 = 0.95)\) as

Table 2

| Parameters                      | Fe₃O₄     | Fe₃O₄/CTAB |
|--------------------------------|-----------|------------|
| Qe (mg/g)                      | 6.74      | 10.05      |
| SE                             | 0.006     | 0.004      |
| Pseudo first order model       |           |            |
| \(K_1\) (min⁻¹)                | 0.012     | 0.064      |
| \(R^2\) (correlation coefficient) | 0.95      | 0.98       |
| SE                             | 0.0009    | 0.003      |
| Pseudo second order model      |           |            |
| \(K_2\) (g mg⁻¹min⁻¹)          | 0.002     | 0.001      |
| \(R^2\) (correlation coefficient) | 0.96      | 0.99       |
| SE                             | 0.007     | 0.003      |

Equilibrium modeling

The common isotherm models (Langmuir and Freundlich), were used to describe the adsorption of Cr(VI) ion on the Fe₃O₄/CTAB nanocomposite. Langmuir model supposed that all the adsorption sites of the adsorbent have the same binding energy and every site joints to only one adsorbate [35].

The linearized Langmuir isotherm is given by Eq. (6):

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}
\]

Fig. 7. Adsorption isotherm of Cr(VI) ion onto the Fe₃O₄/CTAB nanocomposite plotted by (a) Langmuir model and (b) Freundlich model.
shown in Fig. 7 (b). The correlation coefficients and other parameters for both models are presented in Table 3.

**Effect of interfering ions**

Some anions can compete with Cr(VI) at the adsorption process by the nanoparticles. As Fe₃O₄/CTAB nanocomposite gives a better adsorption results, it was applied to investigate the effect of competitive anions at a pH 4 and at a contact time 12 h. As can be seen from Fig. 8 the Cr(VI) ions abolition percentage was 94.89, 93.56, and 90.68% in the existence of SO₄²⁻, NO₂⁻ or PO₄³⁻ (20 mg/mL), respectively. These values are very close to the obtained results without competitive ions under the same conditions (95.77%).

**Wastewater field sample test**

Real samples (three replicates) were collected from Ternaries area, Fom El-Khaleg, Cairo Governorate-Egypt. The test was performed to investigate the nanocomposite efficiency in the field applications. The Fe₃O₄/CTAB composite was chosen for field application at the optimized conditions (12 mg/mL dosage at pH 4) that was used in the model sample. The results in Fig. 9 reveal a high removal % of Cr(VI) (94.636%) from the field samples compared with the model samples (95.77%).

**Discussion**

Since the XRD analysis is used for phase identification of a crystalline material, the strongest reflection in Fig. 1 that proceeds from the 311 plane is characteristic of the crystal cubic phase. Zhao et al. obtained similar XRD planes when they have prepared Fe₃O₄ nanocomposite [36].

The FTIR analysis helps in interpreting reaction products. The decrease in the intensity of CTAB IR bands in Fig. 2b could be due to the dilution of CTAB during the functionalization process. The existence of CTAB IR bands (Fig. 2b) at 3420, 2918, 2855, and 1630 cm⁻¹ prove the capping of Fe₃O₄ by CTAB [37]. While the disappearing of N⁺-CH₃ absorption band at 1467 cm⁻¹ (Fig. 2b) showed that the ammonium moiety of CTAB interacted with Fe₃O₄ nanoparticles.

In the TEM image (Fig. 3) there are few particles (upright corner) with a large diameter observed faceted particles. This is probably related to the high crystallinity of the particles and reflecting the cubic phase of the Fe₃O₄ crystal, which agreed with the data obtained from the XRD analysis.

In Fig. 4 the augmentation of Cr(VI) adsorption at the high adsorbent dosage could be owing to the enhanced total surface area and adsorption sites of the adsorbent at high dosages. Similar results were obtained by Mahmodi et al. when they applied zinc ferrite nanoparticles and CTAB as an adsorbent for Direct Green (DG6) and Direct Red dyes (DR31) and (DR23) [38].

From Table 1 it is evident that the acidic medium was superior in Cr(VI) elimination than the basic medium. This may be due to in acidic medium a positively charged composite by the action of the protonated amino group (N⁺) of CTAB (zeta potentials of Fe₃O₄/CTAB are positive at pH < 6.4) easily adsorb negative HCrO₄⁻ ions through electrostatic attraction [24]. On the other side at basic pH, the excess of OH⁻ ions in the alkaline solution can compete with the metal ions in binding with anion-exchange sites of the Fe₃O₄/CTAB composite and cause a repulsion force between the adsorbent surface and the Cr(VI) metal ion [8]. Moreover, it was reported that electrons can transfer from the Fe²⁺ (located in the core of Fe₃O₄ MNPs) to Cr(VI). This resulting in the reduction of Cr(VI) which can precipitate as insoluble Cr(III) hydroxide on the magnetite surface [39]. Free radical electrons can be formed due to the magnetic field generated by MNPs around themselves. This is visible from the removal results of composite nanoparticles in alkaline pH 9. The same amount of the nanoparticles (4 mg/mL) eliminates 13.5% when applying Fe₃O₄/CTAB, which is less than that of the bare Fe₃O₄ nanoparticles (19.57%).

It is supposed that there is an electrostatic attraction between CTAB on the surface and Cr(VI) ions in the solution. This can

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**Table 3**

| Langmuir model | Freundlich model |
|----------------|-----------------|
| qₑ (mg/g)      | Kᵢ n r² SE      |
| 18.5           | 0.87 1.64 0.95 0.06 |
| b (L/mg)       | 0.001 SE        |
| r²             | 0.99             |
| SE             | 0.001            |

---

Fig. 8. The removal% of Cr(VI) using Fe₃O₄/CTAB nanocomposite (12 mg/mL) at pH 4 and 12 h contact time in the presence of SO₄²⁻, NO₂⁻ or PO₄³⁻ as interfering anions in a binary system.

Fig. 9. Comparison between the removal% of Cr(VI) in the model sample and real field sample using the Fe₃O₄/CTAB nanocomposite (12 mg/mL) at pH 4.
enhance the chemical adsorption of HCrO₄⁻ ions in the solution by iron cations in the core of MNP's. Chemical adsorption of Cr (VI) was reported before by Huang et al. when they are applying magnetic nanoparticles-multi-wall carbon nanotubes composite for adsorption of Cr(VI) in wastewater [40]. The adsorption isotherm models (Fig. 7) suggest the homogeneous metal ion adsorption activity. It may result from the similar adsorption sites of CTAB on the surface of Fe₃O₄ nanoparticles that have identical metal-binding energies.

The presence of the competitive ions such as sulfate, phosphate or nitrite at concentrations ranged from 1.0 to 20.0 mg/L does not give a significant effect on the adsorption of Cr(VI) ions. Thus, competitive adsorption of these metal ions from their binary solutions showed significant indication of high selectivity of Fe₃O₄/CTAB to Cr(VI) ion.

Applying Fe₃O₄/CTAB to wastewater field sample showed comparable Cr(VI) removal efficiency to that obtained in the model sample. Thus Fe₃O₄/CTAB can be introduced for real implementation in field application with high Cr(VI) elimination aptitude.

Conclusions

The removal of Cr(VI) from wastewater is strongly pH dependent. It was also influenced by the Fe₃O₄/CTAB composite or the Fe₃O₄ nanoparticles amount. Contact time after 2 h or the competitive anions (20 mg/L) does not have a great effect on the adsorption of Cr(VI). For Cr(VI), the maximum adsorption was achieved at pH 4 and contact time 12 h using 12 mg/mL Fe₃O₄/CTAB. From this study, it can be concluded that the composite of Fe₃O₄/CTAB has high efficiency in remediation of wastewater with the advantage of low-cost and easy collection from the Cr(VI) contaminated wastewater. In future, this composite will be supported on a polymer thin film for easier reusing or recycling purposes without loss.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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References

[1] Ayangbenro AS, Babalola OO. A New strategy for heavy metal polluted environments: a review of microbial biosorbents. Int J Environ Res Public Health 2017;14:94. http://dx.doi.org/10.3390/ijerph14010094.

[2] Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. Environ Pollut 2000;107:263–83.

[3] Zhao Y-C, Shen H-Y, Pan S-D, Hu M-Q, Xie Q-H. Preparation and characterization of amino-functionalized nano-Fe₃O₄ magnetic polymer adsorbents for removal of chromium (VI) ions. J Mater Sci 2010;45:3291–301.

[4] Khan TA, Nazir M, Ali I, Kumar A. Removal of chromium (VI) from aqueous solution using guar gum-nano zine oxide biocomposite adsorbent. Arab J Chem 2013. http://dx.doi.org/10.1016/j.arabjc.2013.08.019.

[5] Burks T, Uhdeia A, Saleemi M, Elia M, Toprak MS, Muhammed M. Removal of chromium (VI) using surface modified superparamagnetic iron oxide nanoparticles. Sepa Sci Technol 2013;48:1243–51.

[6] Palanisamy KL, Devabharathi V, Meenakshi Sundaram N. The utility of magnetic iron oxide nanoparticles stabilized by carrier oils in removal of heavy metals from wastewater. Int J Res Appl Nat Sci 2013;1:15–22.

[7] Methods for chemical analysis of water and wastes. United States Environmental Protection Agency; March 1983. http://www.state.in.us/dnr/fishwild/files/Methods_Analysis_Water_Wastes_USEPA_March1983.pdf.

[8] Raduch P, Golab Z, Szczesniak MR, Rahman MT, Hao KW, Hidayat K, Uddin MS. Iron oxide nanoparticles for the removal of heavy metals from aqueous solution by adsorption process. Int J Environ Res 2015;6:1197–212.

[9] Grissi M, Kaykoglu G, Belgeniorn V, Lofrano G. Removal of emerging contaminants from water and wastewater by adsorption process. In: Lofrano G, Giuse, editor. Emerging compounds from wastewater treatment. New York: Elsevier; 2012. p. 15–37.

[10] Teja AS, Koh P-Y. Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Progr Cryst Growth Charact Mater 2009;55:22–45.

[11] Maity D, Agrawal DC. Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media. J Magn Mater 2007;308:46–55.

[12] Zhang L, He R, Gu HC. Oleic acid coating on the monodisperse magnetic nanoparticles. Appl Surf Sci 2006;253:2611–7.

[13] Zhou Y-T, Nie H-L, Branford-White C, He Z-Y, Zhu L-M. Removal of Cu from aqueous solution by chitosan-coated magnetic nanoparticles modified with α-lactoglobulin. J Colloid Interface Sci 2009;330:29–37.

[14] Vantasee W, Warner CL, Sangvanich T, Addleman RS, Carter TG, Wiacek RJ, et al. Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. Environ Sci Technol 2007;41:5114–9.

[15] Vattanavej C, Campillo GE, Morales G, Hincapié C, Osorio J, Arnache O, et al. Mercury removal in wastewater by iron oxide nanoparticles. J Phys: Conf Ser 2016;687:012050.

[16] Kalantari K, Ahmadv M, Masoumi HBE, Shami K, Basri M, Khandanlou R. Adsorption of heavy metals by Fe₃O₄/CTAB magnetic nanocomposites and optimization study using response surface methodology. Int J Mol Sci 2014;15(7):12913–27.

[17] Moradian S, Madhi B. Removal of heavy metals from aqueous solution using Fe₃O₄ nanoparticles coated with Schiff base ligand. Desalination Water Treat 2016;57(9):4028–36.

[18] Schachtner D. The source of toxicity in CTAB and CTAB-stabilized gold nanoparticles. University of New Jersey; 2013.

[19] Imae T, Ibeda S. Characteristics of rod like micelles of cetyltrimethylammonium chloride in aqueous NaCl solutions: their flexibly and the scaling laws in dilute and semi dilute regimes. Colloid Polym Sci 1987;265:1090–8.

[20] Modaresi A, Sifaoi H, Grzesiak B, Solimando R, Domanska U, Rogalski M. CTAB aggregation in aqueous solutions of ammonium based ionic liquids: conductimetric studies. Colloid Surf 2007;296:104–8.

[21] Azarov SV, Danov KS. Micellar elongation and micelles from the stepwise thinning of foam films. Adv Colloid Interf Sci 2012;183–184:55–67.

[22] Liu Y, Liu F, Tng M, Hou Y. Removal of arsenate by cetyltrimethylammonium bromide modified magnetic nanoparticles. J Hazard Mater 2012;227–228:461–8.

[23] Bibi A, Abo-El-Rehim, Farag K, El-Saeed M, Abdel-Raouf M. Modified starch iron oxide nanoparticles. Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. Chem Eng J 2013;225:607–15.

[24] Abdul-Rehaim A, Farag K, El-Saeed M, Abdel-Raouf M. Modified starch iron oxide nanoparticles as low cost absorbents for selective removal of some heavy metals from aqueous solutions. Res J Pharm Biomed Sci 2015;6:1197–212.

[25] Shen YF, Tang J, Nie ZH, Wang YD, Ren Y, Zuo L. Preparation and application of magnetic Fe₃O₄ nanoparticles for wastewater purification. Sep Purif Technol 2009;68:312–9.

[26] Dave PN, Chopda NV. Application of iron oxide nanomaterials for the removal of heavy metals: Nanotechnol 2014;1–14.

[27] Bade R, Lee SH. A review of studies on micellar enhanced ultrafiltration for heavy metals removal from wastewater. J Water Supply 2011;1:85–102.

[28] Song J, Kong H, Jiang J. Adsorption of heavy metal ions from aqueous solution by poly rhodanine-encapsulated magnetic nanoparticles. J Colloid Interface Sci 2011;359:505–11.

[29] Vijay Kumar S, NarayanaSwamy WR, Sripathy M, Pai KV. Comparative study of removal of chromium (VI) ion from aqueous solution using eucalyptus, neem and mango leaves. Int J Eng Res Dev 2013;8:55–61.

[30] Abdel-Ghani N, Helmy M, Chaghably G. Removal of lead from aqueous solution using low cost abundantly available adsorbents. Int J Environ Sci Technol 2007;4(1):67–73.

[31] Finch LV. Elements of X-ray crystallography. New York: McGraw-Hill Book Co.; 1968.

[32] Guivar JAR, Sanches EA, Margon CJ, Fernandes EGR. Preparation and characterization of cetyltrimethylammonium bromide (CTAB)-stabilized Fe₃O₄ nanoparticles for electrochemistry detection of citric acid. J Electro Anal Chem 2015;755:158–66.

[33] Wu F-C, Tseng R-L, Jiang R-S. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. Water Res 2001;35(3):613–8.

[34] Bhat SA, Sakaria LP, Vasudevan M, Pawar RR, Sudheesh N, Bajaj CH, et al. Adsorption of anionic dye from aqueous medium by organoclays.
equilibrium modeling, kinetic and thermodynamic exploration. RSC Adv 2012;2:8663–71.

[36] Zhao Y, Tao C, Xiao G, Wei G, Li L, Liu C, et al. Controlled synthesis and photocatalysis of sea urchin-like Fe3O4@TiO2@Ag nanocomposites. Nanoscale 2016;8:5313–26.

[37] Kyzas GZ, Peleka EN, Deliyanni EA. Nanocrystalline magnetite as adsorbent for surfactant removal from aqueous solutions. Materials 2013;6:184–97.

[38] Mahmoodi NM, Abdi J, Bastani D. Direct dyes removal using modified magnetic ferrite nanoparticle. J Environ Health Sci Eng 2014;12:96.

[39] Simeonidis K, Kaprara E, Samaras T, Angelakeris M, Pliatsikas N, Vourlias G, et al. Optimizing magnetic nanoparticles for drinking water technology: the case of Cr(VI). Sci Total Environ 2015;535:61–8.

[40] Huang Z-N, Wang X-L, Yang D-S. Adsorption of Cr(VI) in wastewater using magnetic multi-wall carbon nanotubes. Water Sci Eng 2015;8(3):226–32.