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Arsenic and chromium removal by mixed magnetite–maghemite nanoparticles and the effect of phosphate on removal

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A B S T R A C T

Adsorption of arsenic and chromium by mixed magnetite and maghemite nanoparticles from aqueous solution is a promising technology. In the present batch experimental study, a commercially grade nano-size 'magnetite', later identified in laboratory characterization to be mixed magnetite–maghemite nanoparticles, was used in the uptake of arsenic and chromium from different water samples. The intent was to identify or develop a practical method for future groundwater remediation. The results of the study showed 96–99% arsenic and chromium uptake under controlled pH conditions. The maximum arsenic adsorption occurred at pH 2 with values of 3.69 mg/g for arsenic(III) and 3.71 mg/g for arsenic(V) when the initial concentration was kept at 1.5 mg/L for both arsenic species, while chromium(VI) concentration was 2.4 mg/g at pH 2 with an initial chromium(VI) concentration of 1 mg/L. Thus magnetite–maghemite nanoparticles can readily adsorb arsenic and chromium in an acidic pH range. Redox potential and pH data helped to infer possible dominating species and oxidation states of arsenic and chromium in solution. The results also showed the limitation of arsenic and chromium uptake by the nano-size magnetite–maghemite mixture in the presence of a competing anion such as phosphate. At a fixed adsorbent concentration of 0.4 g/L, arsenic and chromium uptake decreased with increasing phosphate concentration. Nano-size magnetite–maghemite mixed particles adsorbed less than 50% arsenic from synthetic water containing more than 3 mg/L phosphate and 1.2 mg/L of initial arsenic concentration, and less than 50% chromium from synthetic water containing more than 5 mg/L phosphate and 1.0 mg/L of chromium(VI). In natural groundwater containing more than 5 mg/L phosphate and 1.13 mg/L of arsenic, less than 60% arsenic uptake was achieved. In this case, it is anticipated that an optimum design with magnetite–maghemite nanoparticles may achieve high arsenic uptake in field applications.

1. Introduction

Naturally occurring elemental arsenic exists in both inorganic and organic forms and ranks twentieth in abundance in the earth's crust, fourteenth in seawater and twelfth in the human body (Mandal and Suzuki, 2002). Although relatively wide-ranging in environmental sources such as air, water and soil, arsenic can also be found in plants and other organisms (Shih, 2005). Chromium, another common contaminant, is the twenty-first most abundant element in the earth's crust and it is used in diverse metal products and processes (Nriagu and Nieboer, 1988). At many sites, chromium has been entering the environment via leakage, poor storage, or unsafe disposal practices (Palmer and Wittbrodt, 1991). Cr(VI) is comparatively mobile in the environment. Naturally occurring chromium is mostly the result of dissolved minerals from weathering of chromites and other chromium-bearing minerals present in bedrock and soil (Nriagu and Nieboer, 1988).

Groundwater contamination by heavy metals is a key environmental concern in areas where the water supply system draws primarily on groundwater. Several methods of arsenic and chromium removal are already available including precipitation, electrochemical reduction, adsorption, ion exchange, solvent extraction, nano filtration and reverse osmosis (Mayo et al., 2007 and Hu et al., 2004). Adsorption of arsenic and chromium on different sorbents such as iron, iron oxide, iron coated sand, and iron coated activated carbon (Petrusevski et al., 2002), and granular ferric hydroxides (Driehaus and Jekel, 1998) have also been investigated. However, their use is limited due to high operation

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cost, sludge formation, and technical difficulties in preparation of materials. Naturally occurring ores and minerals, namely kaolinite (Guhab and Chaudhuri, 1990), feldspar (Prasad, 1994), magnetite (Shipley et al., 2009), hematite and maghemite (Tuutijärvi et al., 2009) have also been used for the adsorption of arsenic though not as extensively as other materials. Arsenic and chromium in groundwater can be removed using nanomaterials and, currently, a lot of research is being conducted in this field. Dixit and Hering (2003) showed that arsenite adsorption on iron oxide was independent of pH from 4 to 10. However, Raven et al. (1998) reported that arsenate adsorption on iron oxide decreased with increasing pH. Fendorf et al. (1997) showed that arsenic and chromium could form a monodentate complex, a bidentate–binuclear complex, and a bidentate–mononuclear complex with iron oxides. These authors noted that extended X-ray absorption fine structure spectroscopy (EXAFS) provided direct evidence for inner sphere adsorption of arsenate and chromate on goethite. Recently, Yean et al. (2005) showed that magnetite iron oxide adsorbed arsenic species at pH below 9 but the arsenic desorbed when pH was adjusted to more than 10. Undoubtedly, the surface properties of iron oxides are key factors in the adsorption of arsenic and chromium by magnetite–maghemite nanoparticles. According to Grosvenor et al. (2004), iron oxide films produced after short oxygen exposure times contained a mixture of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). According to Yavuz et al. (2006), the use of magnetite particles for arsenic decontamination of water has been proposed based on its magnetic properties. In acidic pH range, most arsenic and chromium species in aqueous solution are negatively charged. Thus electrostatic attraction between magnetite–maghemite nanoparticles and metal species leads to the removal of arsenic and chromium compounds from aqueous solution. According to Hu et al. (2004), chromium(VI) adsorption by magnetite was a combination of electrostatic attraction and ligand exchange at various pH conditions. According to Tuutijärvi et al. (2009) and Hu et al. (2005), maghemite (γ-Fe_2O_3) can also reduce arsenic and chromium concentration. These authors suggested that electrostatic attraction is the key mechanism of arsenic and chromium removal by maghemite from aqueous solutions and that the process is highly dependent on initial concentration, pH and temperature.

Previous studies have also shown competitive adsorption of arsenic or chromium with other anions (for example, phosphate and sulfate). Jackson and Miller (2000) studied the influence of phosphate concentration (i.e. 0.1 M and 0.5 M NaH_2PO_4) and pH (3–7) on arsenic extraction. They found that, in the presence of higher phosphate concentration, desorption of arsenic(III) and arsenic(V) from both ferrihydrite and goethite was greater. Su and Puls (2001) reported that phosphate severely inhibited the removal of arsenic(III) and arsenic(V) by zerovalent iron. Arsenate sorption on both goethite and gibbsite decreased with increasing initial phosphate to arsenate molar ratios (Violante and Pigna, 2002). Again, the presence of orthophosphate prevented the adsorption of chromium(VI), most likely by competition for adsorption sites. Consistent with this finding, KH_2PO_4 was found to be the best extracting agent for chromium(VI) (Bartlett and Kimble, 1976). According to Tzou et al. (2003), phosphate (P), organic ligands, and light sources, could influence chromium(VI) retention by the soil components. The existence of phosphate (P) or organic ligands not only competes with solution chromium(VI) for surface sites, but also results in releasing sorbed chromium(VI).

The objective of the present study was to investigate arsenic and chromium removal from different water samples using commercially available nano-size magnetite, which was subsequently identified from laboratory characterization to be a mixture of magnetite and maghemite, in batch experiments. This is one of the very few studies that have, to date, examined arsenic and chromium removal from stock solution as well as from natural groundwater by mixed magnetite–maghemite nanoparticles. Although magnetite and maghemite may separately remove greater amounts of arsenic or chromium from solution than the mixture (Hu et al., 2005; Shipley et al., 2009 and Lim et al., 2009), it is probably more realistic and practical to investigate the removal efficiency of the mixture because of the common association of the two minerals in nature.

2. Materials and methods

2.1. Water and magnetite nanoparticle samples

All the solutions used in the experiments were prepared from certified reagent grade chemicals, which were used without further purification. Solutions were made with distilled, de-ionized water using Mega-pure Deionizing still. Glass volumetric flasks and reaction vessels were treated with 10% HNO_3 and rinsed several times with de-ionized water before they were used. Both arsenic(V) and arsenic(III) stock solutions were prepared by dissolving arsenic oxides (As_2O_5 and As_2O_3) powder in de-ionized water, by using 4 g/L NaOH since both oxides have enhanced solubility in NaOH solution. Chromium(VI) and chromium(III) stock solutions were prepared by dissolving the chromium oxides (CrO_3) and chromium nitrate ($Cr(NO_3)_3$) respectively in de-ionized water.

The commercially available 20–40 nm magnetite–maghemite mixture particles were obtained from Reade Advanced Materials (Rhode Island, U.S.A.). The surface area of the 20–40 nm magnetite–maghemite mixture particles were measured using the Brunauer, Emmett, Teller (BET) method and found to have average value of 49 m^2/g. The magnetite–maghemite nanopowder was received in an airtight plastic bag. Further examination of the as-received sample showed that the magnetite–maghemite mixture was dispersed. 99.5% purity of 20–40 nm magnetite–maghemite particles had black and spherical morphology, and bulk density was measured 0.8 g/cm^3. X-ray photoelectron spectroscopy analysis showed that the 'magnetite' was actually a mixed oxide Fe_3O_4-γ-Fe_2O_3, consisting of 30.8% maghemite and 69.2% magnetite (Chowdhury et al., submitted for publication). In addition, most commercial grade 'magnetite' nanoparticles used in field scale remediation of arsenic or chromium contamination would likely be a mixture of magnetite and maghemite because of slight oxidation during handling and sampling.

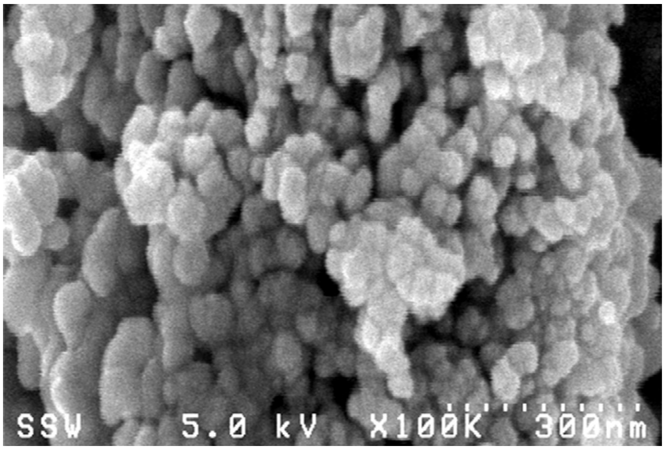

Fig. 1. Scanning electron photomicrograph of magnetite–maghemite nanoparticles (20–40 nm) at 100,000× magnification showing highly uniform sample.

The different initial concentrations of arsenic and chromium stock solution, synthetic solution as well as natural contaminated groundwater and spiked groundwater samples were added to 0.4 g/L amount of 20–40 nm magnetite–maghemite particles to evaluate the removal efficiency of arsenic and chromium. Fig. 1 shows 100,000× magnification image of mixed magnetite–maghemite nanoparticles using Hitachi S4500 scanning electron microscopy (SEM). A 100,000× magnification was also used to check surface porosity but the image did not show the presence of pores at 100,000× magnification and the mixture particles appeared to be highly uniform. The SEM photomicrograph (Fig. 1) also showed that the particles ranged from 20 to 40 nm.

2.2. Sample preparation

Known amounts (0.4 g/L) of magnetite–maghemite particles were added to a desired concentration of stock (As or Cr) solution in 2000 mL plastic bottles. Solutions were prepared with de-ionized water. Redox potential and pH data identified possible dominating species and oxidation states of arsenic and chromium in solution. Standard acid (0.1 M HNO_3) and base (0.1 M NaOH) solutions were used for pH adjustment. The pH of each solution was measured using an Orion combination electrode. In the batch test, both As and Cr concentrations were kept in the range of 0.5–4 mg/L. For each stock solution, redox potential was measured using a WTW Multi 340i ORP electrode (Wellheim, Germany) to confirm the targeted arsenic(V), arsenic(III) and chromium(VI) species. In addition, synthetic water is prepared by adding desired amounts of phosphate, sulfate, chloride and nitrate solutions with 0.4 g/L of magnetite particles in 2000 mL plastic bottles. Batch experiments were performed to investigate the influence of dissolved phosphate in arsenic and chromium uptake by magnetite–maghemite nanoparticles. In synthetic water, As and Cr concentrations were kept at 1.21 and 1.00 mg/L respectively. The adsorbent (magnetite–maghemite nanoparticles) concentration was always maintained at 0.4 g/L.

2.3. Natural groundwater and spiked groundwater samples

Arsenic contaminated groundwater collected from shallow aquifers in Bangladesh was used in the study. All samples were immediately acidified with 2% HNO_3 upon collection to prevent the precipitation of Fe–As compound and were kept in plastic bottles. Table 1 presents the physico-chemical characteristics of the groundwater samples (before acidification). Samples were collected from Srinagar, Munshiganj and Sylhet Golapganj in Bangladesh on October 5, 2007. Groundwater samples from three wells were spiked to check the quality of analytical methods. Known concentrations of arsenic stock solution were added to desired amount of groundwater to increase the initial concentration of arsenic. Different initial concentrations of arsenic in groundwater samples were prepared to investigate the adsorption capacity of 20–40 nm magnetite–maghemite particles in the removal of arsenic from contaminated groundwater. In addition, groundwater was also spiked with different known concentrations of a competing anion, namely PO_4^{3-}. Batch experiments were performed in the presence of this competing anion.

Table 1
Physico-chemical characteristics of groundwater samples (before acidification).

Parameters	Units	Measured concentration		
		Sample 1	Sample 2	Sample 3
Arsenic (As)	μg/L	282	439	55
pH		7.25	7.02	7
Electrical conductivity (E_c)	μS/cm	161.8 at 28.1 °C	190.1 at 28.1 °C	130 at 25 °C
Chloride (Cl^-)	mg/L	12	15	8
Nitrate (NO_3-N)	mg/L	0.2	< 0.1	1.2
Phosphate (PO_4^{3-})	mg/L	0.839	3.57	0.5
Sulfate (SO_4^{2-})	mg/L	<1.0	<1.0	<1

Notes: Samples were collected from Srinagar, Munshiganj and Sylhet Golapganj in Bangladesh on October 5, 2007.

2.4. Batch tests

2.4.1. Adsorption tests

Magnetite–maghemite was dispersed in solution by sonication in a sonication bath for 20 min. Magnetite–maghemite electrolyte mixtures were prepared and held in a slowly rotating rack of a shaker that provided a gentle end-over-end tumbling (28 rpm) for 24 h at room temperature. After shaking, the mixtures were centrifuged at 5000 rpm for 30 min. The supernatant solutions were then collected and filtered through 0.2 μm Nalgene Surfactant-Free Cellulose Acetate (SFCA) syringe filters. The pH of each solution was measured immediately after sampling. The filtrate was acidified with 1% nitric acid. Arsenic and chromium concentrations in the filtrate were measured using ICP-AES (inductively coupled plasma atomic emission spectroscopy). Every experiment was run in triplicate and average values were used in the graph. The minimum detection limit of ICP-AES for both metals was 0.01 mg/L.

3. Results and discussion

3.1. Effect of pH on arsenic and chromium

The pH of the solution determines the concentration distribution of the ionic forms of the arsenic(III) and arsenic(V). The effect of pH on arsenic(III) and arsenic(V) adsorption by magnetite–maghemite nanoparticles was studied in the pH range of 1–14 at the contact time of 24 h and all measurements were made at room temperature. The change in pH through the experiments was monitored for each run, and was found to be within ±0.1 of the initial values. Hu et al., 2005 and Shipley et al. (2009) reported that, at room temperature, chromium and arsenic adsorption by maghemite or magnetite nanoparticles was not significantly affected by ionic strength in the acidic pH range. In this study, no noticeable changes were observed in magnetite–maghemite electrolyte at a very low pH. Arsenite [As(III)] is the dominant form of inorganic arsenic at E_h values lower than approximately -170 mV, while arsenate [As(V)] is predominant at higher E_h values (Ryu et al., 2002). In the present study, the observed average redox potentials for arsenic(III) and arsenic(V) stock solutions were -145 mV and -10 mV, respectively, at pH 10 which indicated the desired types of arsenic species (oxidation state) in each solution. The ionic strength of the stock solution was measured to be 0.05 M.

Figs. 2 and 3 show that, at room temperature, the uptake of As(V) by 20–40 nm magnetite–maghemite particles was more highly pH dependent (at least up to pH 8) than arsenic(III). Maximum uptake efficiencies of 99% and 96% were found at pH 2 and adsorbed amounts of As(V) species were 3.71 and 7.2 mg/g for initial arsenic(V) concentrations of 1.5 and 3 mg/L, respectively. With initial arsenic(III) concentrations of 1.5 and 3 mg/L, the maximum uptake efficiencies at pH 2 were 98.5% and 94%, and adsorbed amounts of arsenic(III) species were 3.69 and 7.1 mg/g, respectively. Surface coverage on magnetite–maghemite nanoparticles was found to be almost 2 $\mu mol/m^2$ when initial concentrations for both arsenic(III) and arsenic(V) were kept at 3 mg/L. These results clearly show that magnetite–maghemite nanoparticles can adsorb arsenic (III) and arsenic(V) more readily in an acidic pH range. After

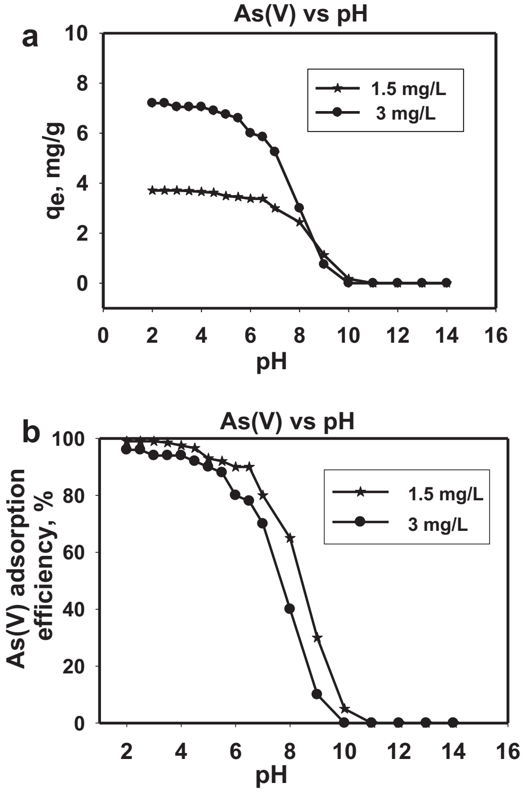

Fig. 2. (a) q_e (mg of As(V)/g) vs pH and (b) effect of pH on As(V) adsorption efficiency (%) from stock solutions. (adsorbent conc: 0.4 g/L, contact time: 24 h).

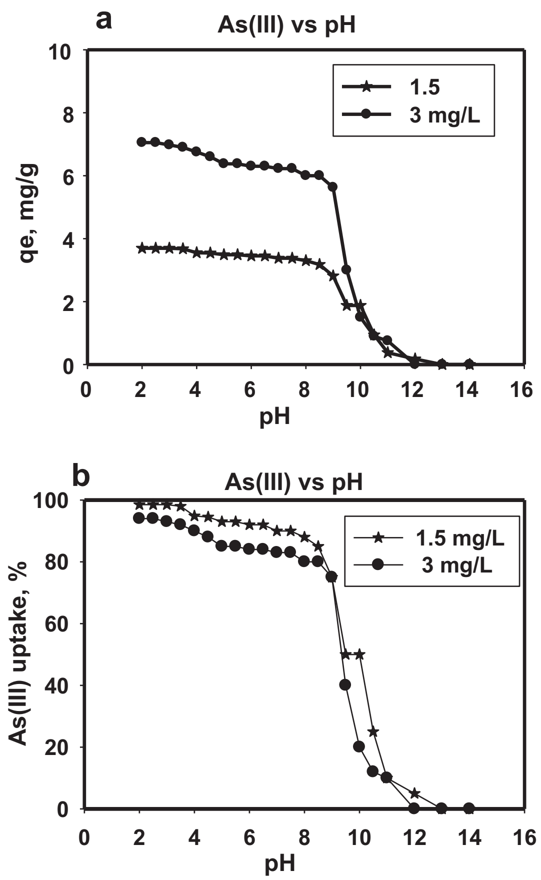

Fig. 3. (a) q_e (mg of As(III)/g) vs pH (b) effect of pH on As(III) species adsorption efficiency(%) from stock solution (adsorbent conc: 0.4 g/L, contact time: 24 h).

adsorption and filtration, Fe concentration in solution was determined to be less than 0.05 mg/L in every sample. The amount of arsenic(III) and arsenic(V) uptake decreased with increasing pH. Arsenic(V) uptake efficiency was less than 10% when pH was adjusted to a value of more than 10. The variation in uptake efficiency at different pH values may be attributed to the affinities of the mixture of magnetite and maghemite for the different species of arsenic(III) and arsenic(V) existing at different pH values, namely AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4, AsO_3^{3-}, $HAsO_3^{2-}$, $H_2AsO_3^-$, and H_3AsO_3. At pH 2.3–6.9, the predominant species of arsenic(V) is $H_2AsO_4^-$ (Nordstrom and Archer, 2003). The adsorption free energy of $H_2AsO_4^-$ ion may be lower than that of $HAsO_4^{2-}$ and AsO_4^{3-}, and this would explain why $H_2AsO_4^-$ is more favorably adsorbed than $HAsO_4^{2-}$ and AsO_4^{3-}.

From measured zeta potential of magnetite solution at different pH values, it is apparent that magnetite surface contains positive charge at pH below 8.3 and negative charge when pH is adjusted to more than 8.3 (Hu et al., 2004). In addition, optimum adsorption occurs at pH below 7. Yean et al. (2005) reported from potentiometric titrations that the surface of magnetite particles had a positive surface charge in the pH range 4–6.8, a point of zero charge of 6.8 and a negative surface charge in the pH range 6.8–9.5. According to Tuutijärvi et al., 2009, maghemite had a point of zero charge at pH_{pzc} 7.5 and the more acidic the condition the more positive was the surface charge of the adsorbent and, accordingly, the more attractive to arsenic(V) species, namely $H_2AsO_4^-$ or $HAsO_4^{2-}$. Thus magnetite–maghemite particles may adsorb either negatively or positively charged species by electrostatic attraction depending on pH.

The percentage of arsenic(III) removed from solution decreased sharply when the solution pH was 9 or higher. More than 80% uptake efficiency was found up to pH 9 for both initial arsenic(III) concentrations of 1.5 and 3 mg/L. From literature, the first pK value for arsenic(III) in aqueous solution is 9.17 (Nordstrom and Archer, 2003). The nonionic form of arsenic(III) to magnetite surface did not change sharply with pH. However, arsenic(III) uptake decreased slowly because of the higher concentration of OH^- ion present in the reaction mixtures.

Fig. 4 shows that the uptake of chromium(VI) by magnetite–maghemite was highly pH dependent. Maximum adsorption efficiencies of 96% and 85% were found at pH 2 and adsorbed amounts were 2.4 and 4.45 mg/g for initial chromium(VI) concentrations of 1 and 2 mg/L, respectively. The surface coverage on magnetite–maghemite by chromium(VI) was found to be 1.9 μmol/m^2 at 2 mg/L of initial Cr(VI) concentration. The amount of chromium(VI) removed from solution decreased with increasing pH and the removal efficiency was less than 65% at pH greater than 6 indicating more readily adsorption in lower acidic pH range. The variation in removal efficiency at different pH values may be attributed to the affinities of the magnetite–maghemite for the different species of chromium(VI) existing at acidic pH values, namely $H_2CrO_4^0$, $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ (Manuel et al., 1995). Optimum adsorption occurred at pH below 4 (Fig. 4). chromium(VI) uptake decreased slowly because of the higher concentration of OH^- ions present in the reaction mixtures. A comparison of the arsenic uptake and chromium uptake shows that the uptake efficiency of arsenic was more than that of chromium in the groundwater pH range (6.5–8.5). Thus, the efficiency of adsorption of arsenic by magnetite–maghemite particles from contaminated groundwater is more favorable than chromium in groundwater pH range.

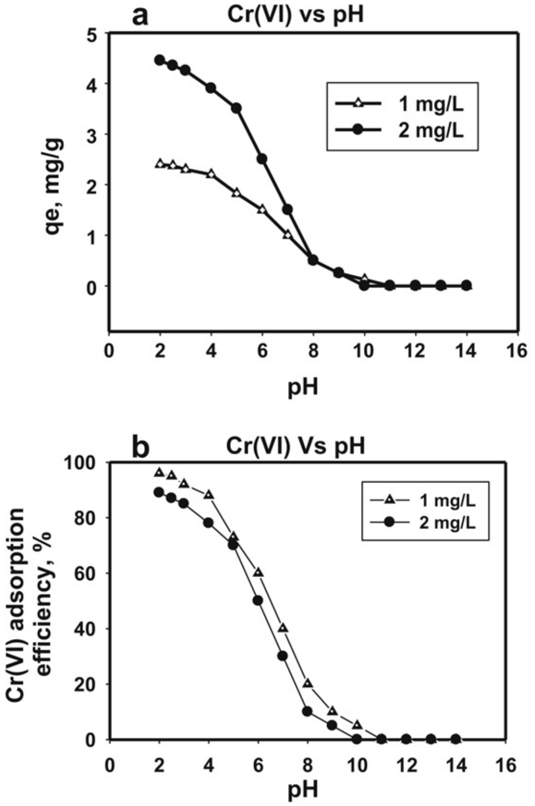

Fig. 4. (a) q_e (mg of Cr(VI)/g) vs pH (b) effect of pH on Cr(VI) species adsorption efficiency(%) from stock solution (adsorbent conc: 0.4 g/L, contact time: 24 h).

3.2. Contact time

The kinetics of arsenic(V) and arsenic(III) adsorption were studied by varying the contact time between magnetite–maghemite and solutions from 10 to 240 min using 0.4 g/L adsorbent at initial metal concentrations of 1 and 2 mg/L. The observed removal rates of As(V) and As(III) at different initial concentration are shown in Fig. 5(a and b). The removal seemed to take place in two phases. The first phase involved rapid metal uptake within 10 min of contact time and was followed by the subsequent slower uptake. The rapid adsorption of arsenic by mixed magnetite–maghemite mixture may be attributed to the external surface adsorption, and it is easy for arsenic to access active adsorption sites, thus resulting in a rapid uptake of arsenic. For different initial arsenic(V) and arsenic(III) concentrations, equilibrium was achieved in almost 3 h when experiments were run at pH 6.5. At equilibrium, the removal efficiency of As(V) and As (III) at initial concentrations of 1 and 2 mg/L was 98% and 92%, respectively. According to Shipley et al. (2009), adsorption equilibrium was achieved in almost 1 h when experiments were run with magnetite nanoparticles in the acidic pH range. It is noted that the percentage removal of As(V) and As(III) was lower at the higher initial concentration, for a given amount of adsorbent.

The removal rates of chromium(VI) at different initial concentrations are shown in Fig. 5c. For two different initial chromium(VI) concentrations (1 and 2 mg/L), equilibrium was achieved in 2 h when experiments were run at pH 3. According to Hu et al. (2004), adsorption equilibrium was achieved in 1 h in the case of magnetite. At equilibrium, the removal efficiency of chromium(VI) by magnetite–maghemite nanoparticles, at initial concentrations of 1 and 2 mg/L, were 92% and 85%, respectively. Again, the percentage removal of chromium(VI) decreased with increased initial concentration.

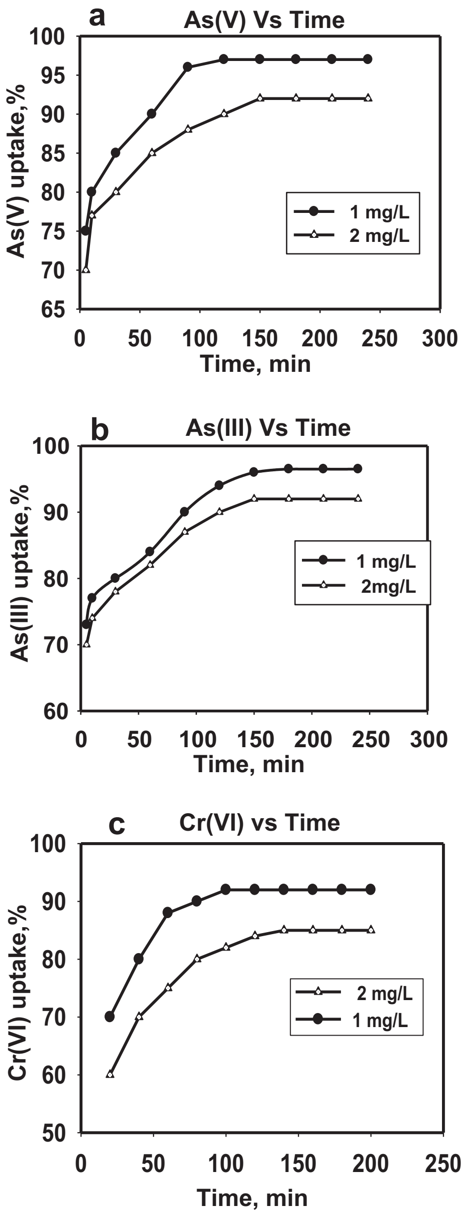

Fig. 5. (a) Effect of time (min) on As (V) uptake (%) at pH 6.5 (b) Effect of time (min) on As (III) uptake (%) at pH 6.5 (c) Effect of time (min) on Cr(VI) uptake (%) at pH 3. (Mixed magnetite–maghemite conc: 0.4 g/L).

3.3. Adsorption isotherm

Freundlich adsorption isotherm equations were used to interpret the nature of arsenic adsorption on magnetite–maghemite nanoparticles (Hu et al., 2004; Yean et al., 2005; Hu et al., 2005 and Mayo et al., 2007). The adsorption data were fitted with the Freundlich adsorption equation to identify adsorption parameters for future modeling and scale up.

The Freundlich isotherm is represented as follows:

$$q_e = K \times C_e^{1/n} \tag{1}$$

where C_e is the concentration of solute at equilibrium or after adsorption, q_e is the mass of contaminant adsorbed per unit weight of the adsorbent and K and n are constants which must be evaluated for each solute and temperature and are related to adsorption capacity and energy of adsorption. Equation (1) may be expressed in the logarithmic form:

$$\log q_e = \log K + (1/n^{*}\log C_e) \tag{2}$$

Adsorption data, when plotted according to Equation (2), yield a straight line. To determine the adsorption characteristics of arsenic (III), arsenic(V), chromium(III) and chromium(VI) species on 20–40 nm magnetite–maghemite particles using the Freundlich adsorption isotherm, the adsorbent concentration in the solutions was fixed for the same pH.

Fig. 6 shows arsenic(III) and arsenic(V) adsorption, and Fig. 7 shows chromium(VI) and chromium(III) adsorption on 20–40 nm magnetite–maghemite nanoparticles using 0.4 g/L adsorbent concentration. The fit of the Freundlich isotherm to the experimental data shows that the adsorption on magnetite–maghemite nanoparticles is well described by the Freundlich equation. The plot of log q_e vs log C_e for various initial concentrations is found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate–adsorbent system. The calculated linear regression coefficient (R^2) values for the logarithmic plots in Figs. 6 and 7 are all greater than 0.95 suggesting a strong linear relationship between log q_e and log C_e. The higher value for K indicates the higher affinity for arsenic and chromium and the values of n lie between 1 and 10 indicating favorable adsorption (McKay et al., 1982). The parameters n and k are almost 2.1 and 9.4 for arsenic(III), 2 and 10.6 for arsenic(V), and for chromium(VI) 1.6 and 5.5. Tables 2 and 3 present Freundlich constants for Cr and As adsorption by magnetite–maghemite nanoparticles and other adsorbents. Experimental conditions (i.e. laboratory temperature) in the other referenced studies were similar to those used in the present work. Even though some experimental conditions, such as solution: adsorbent ratio and amount of adsorbent used varied from one study to another in Tables 2 and 3, the data show that As and Cr adsorption was favorable in all the studies cited. From the tables, it is apparent that magnetite–maghemite nanoparticles are very useful adsorbent for arsenic and chromium uptake from aqueous solution. More precisely, arsenic(III) and arsenic(V) have more affinity to magnetite–maghemite mixture and more favorable for adsorption than chromium(VI).

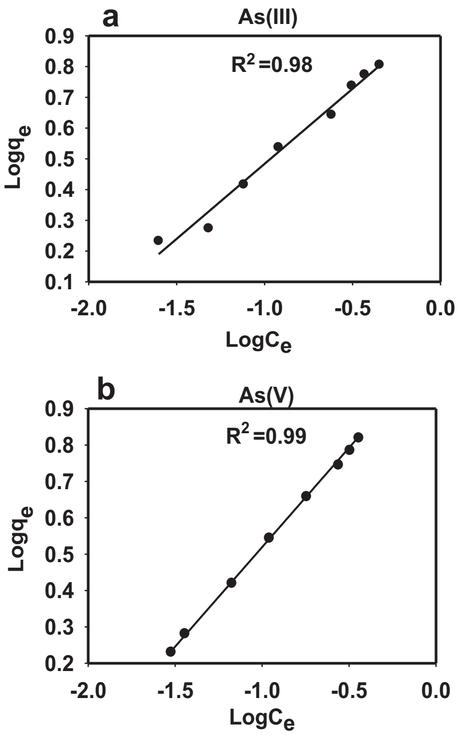

Fig. 6. (a) Arsenic(III) adsorption and (b) arsenic(V) adsorption on 20–40 nm magnetite–maghemite particles at pH 5 at room temperature (fitted by linearized Freundlich isotherm).

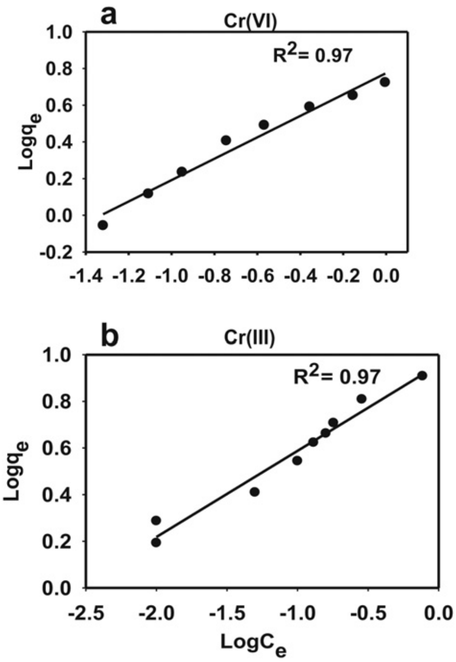

Fig. 7. (a) chromium(VI) adsorption at pH 4.5 and (b) chromium(III) adsorption at pH 9 on 20–40 nm magnetite–maghemite nanoparticles in stock solution at room temperature (fitted by linearized Freundlich isotherm).

Chromium(III) is commonly found in large quantities in textile and tannery waste waters. Though chromium(III) is not toxic, it can oxidize to the toxic form, chromium(VI), in natural water. Thus the removal and recovery of chromium(III) is necessary for environmental protection. Another significant finding from the present study is that chromium(III) could be removed from solution by magnetite–maghemite nanoparticles. There is very little work published on chromium(III) removal by iron oxide. From the Freundlich isotherm, it is clear that magnetite–maghemite nanoparticles can remove chromium(III) when the pH is kept between 8.5 and 9. In this pH range, the dominant chromium(III) species is $Cr_3(OH)_4^{5+}$(Sevgi and Akcin, 2002) and the magnetite–maghemite has a negative surface charge, as explained by Yean et al. (2005). Thus the magnetite–maghemite nanoparticles can adsorb the

Table 2
Comparisons of magnetite–maghemite nanoparticles with other adsorbents for Cr (VI) adsorption at room temperature.

Adsorbents	Freundlich parameters		References
	K (mg/g)	n	
Magnetite–maghemite nanoparticles	6	1.71	This study
Activated groundnut carbon	5.61	4.76	Periasam et al., 1991
Activated coconut jute carbon	1.55	2.72	Ramos et al., 1994
Commercial activated carbon	5.09	1.76	Chand et al., 1994
Sawdust	8.5	2.1	Raji and Anirudhan, 1998
Magnetite	11.23	3	Hu et al., 2004
Maghemite	3.4	6	Hu et al., 2005

Table 3
Comparisons of magnetite–maghemite nanoparticles with other adsorbents for As (III) and As(V) adsorption at room temperature.

Adsorbents	Freundlich parameters		References
	K (mg/g)	*n*	
As(V) to magnetite–maghemite nanoparticles	10.6	2.00	This study
As(III) to magnetite–maghemite nanoparticles	9.4	2.1	This study
As(III) to activated alumina	0.2249	2.22	Singh and Pant, 2004
As(V) to TiO_2 at pH 9	16	3.1	Paritam et al., 2004
As(III) to TiO_2 at pH 9	13	1.8	Paritam et al., 2004
As(V) to akaganeite	69.7	2.5	Deliyanni and Lazaridis, 2005
As(III) to akaganeite	10.42	1.16	Deliyanni and Lazaridis, 2005
As(V) to Ce(IV)-doped iron oxide	60.4	16.1	Zhang et al., 2003
As(V) to Laterite soil	0.055	4.23	Maji et al., 2007
As(III) to Laterite soil	0.476	1.01	Maji et al., 2007
As(V) to granular ferric hydroxide (GFH)	10.3	1.5	Thirunavukkarasu et al., 2003
As(III) granular ferric hydroxide (GFH)	18	2.3	Thirunavukkarasu et al., 2003
Magnetite	10	2.5	Mayo et al., 2007

positively charged chromium(III) species or $Cr_3(OH)_4^{5+}$ by electrostatic attraction.

3.4. *Effect of phosphate on arsenic and chromium removal*

Other studies (Zhang et al., 2004 and Gao and Mucci, 2001) have shown that high concentrations of phosphate (PO_4^{3-}) in synthetic water decrease sorption capacity of iron oxide. Zhang et al. (2004) reported that the presence of phosphate significantly lowers the ability of iron ores to remove arsenic by adsorption and initial addition of 6.5 mg/L phosphate can lower the arsenic(V) adsorption on 5 g/L iron ore dose by 30–50% at pH 7. According to Gao and Mucci (2001), the surface complexation of arsenate on goethite is greatly reduced in competitive adsorption experiments and the decrease is proportional to the amount of phosphate present in solution. Hingston et al. (1971) reported that the amount of arsenate adsorbed on goethite from a 0.1 mol/L NaCl solution decreased with increasing phosphate concentrations. Likewise, Manning and Goldberg (1996) reported that phosphate and arsenate adsorption on goethite from a 0.1 mol/L NaCl solution is reduced in competitive experiments relative to their behavior in single anion subsystems.

The resulting percentage removal of arsenic and chromium in the presence of PO_4^{3-} is presented in Fig. 8. The results show that at the fixed adsorbent concentration of 0.4 g/L, arsenic and chromium removal (%) decreases with increasing phosphate concentration.

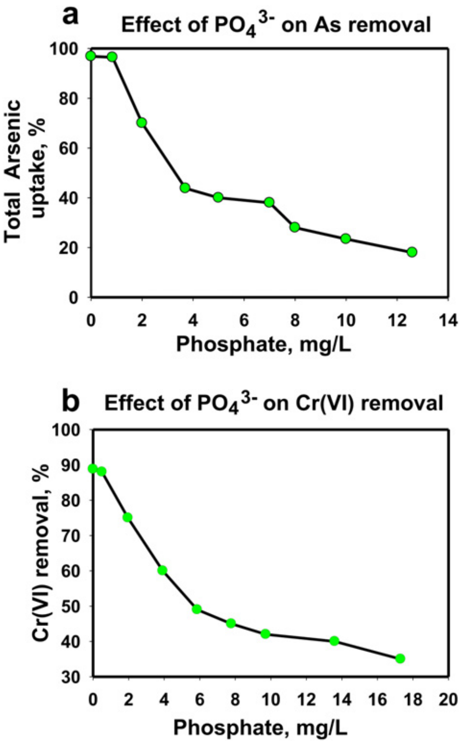

Fig. 8. Phosphate effect on (a) total arsenic uptake (%) at pH 6.5 and (b) chromium(VI) uptake (%) at pH 4. (Mixed magnetite–maghemite conc: 0.4 g/L).

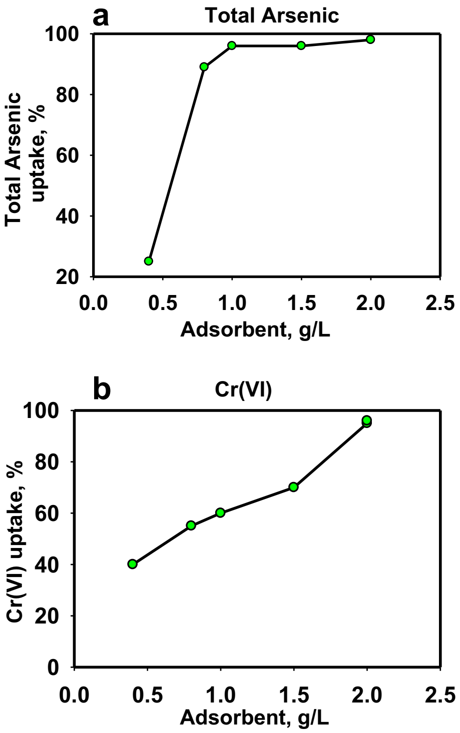

Fig. 9. (a) Total arsenic uptake at different adsorbent (g/L) concentration (b) chromium (VI) uptake at different adsorbent (g/L) concentration (PO_4^{3-} conc: 10 mg/L; total arsenic conc: 1 mg/L).

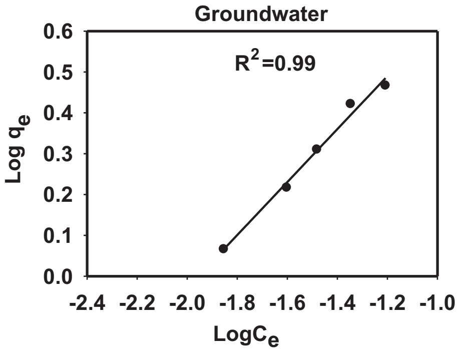

Fig. 10. Arsenic contaminated site samples' adsorption on 20–40 nm magnetite–maghemite nanoparticles at pH 2 (fitted by the linearized Freundlich isotherm).

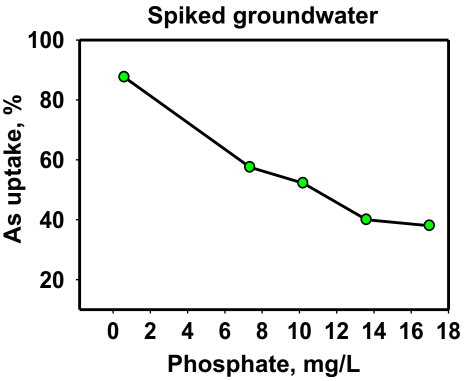

Fig. 11. Effect of phosphate on total arsenic uptake (%) from spiked groundwater at pH 6.5. (Total arsenic conc: 1.13 mg/L).

Magnetite–maghemite nanoparticles can remove less than 50% of total arsenic from synthetic water containing more than 3 mg/L PO_4^{3-} concentration and less than 50% of chromium from water containing more than 5 mg/L. Total arsenic or chromium(VI) and phosphate surface complexation on iron oxide may be one of the causes for the reduced removal of arsenic or chromium(VI) in the presence of high PO_4^{3-}. At the same time, no significant changes (data not shown) were observed in the case of elevated concentrations of Cl^-, SO_4^{2-}, and NO_3^- in solution.

Tejedor-Tejedor and Anderson (1990) reported that phosphate produces three different types of complexes on iron oxide (i.e. goethite, hematite, etc) surface: protonated ($(FeO)_2(OH)PO$), nonprotonated bridging bidentate ($(FeO)_2PO_2$) and a nonprotonated monodentate ($(FeO)PO_3$). Daou et al. (2007) also observed that $H_2PO_4^-$ formed monoprotonated binuclear phosphate complex on magnetite surface at pH 3. Similar dominant dissociation species (Pourbaix, 1974) and comparable intrinsic affinity for iron oxide surface (Pierce and Moore, 1982; Manning and Goldberg, 1996; Jain and Loeppert, 2000) may be another reason for less removal of arsenic and chromium in the presence of high PO_4^{3-}. Stumm and Morgan (1970) have reported that the extent of complex formation between Fe(III) and phosphates (PO_4^{3-} or HPO_4^{2-}) depends on the ratio $[OH^-]/[PO_4^{3-}]$ or $[HPO_4^{2-}]$. Therefore, by decreasing the pH, phosphate will have an increasing tendency to enter into the coordination sheath of Fe(III) ion, presenting a similar behavior with arsenic and chromium. Furthermore, the equilibrium constants of $FePO_4$ ($\log K = 20.8$) and of $FeAsO_4$ ($\log K = 20.1$) indicate that both anions present similar affinities for Fe(III) cations and hence there would be tendency for the formation of the respective complexes (Ioannis and Zouboulis, 2002).

More sorption sites or greater quantity of nano-size magnetite particles should be applied to remove arsenic and chromium from contaminated water having elevated concentration of PO_4^{3-}. Fig. 9 shows arsenic and chromium removal at different adsorbent (g/L) concentration. In this test, PO_4^{3-} and total arsenic concentration was always kept at 10 and 1 mg/L respectively in synthetic water. The pH of the arsenic and chromium solutions was 6.5 and 4, respectively. Results showed that in the presence of elevated concentration of PO_4^{3-} (10 mg/L), 98% of total arsenic and 95% of chromium removal could be achieved when adsorbent concentration (magnetite–maghemite nanoparticles) was kept at 2 g/L. Thus, more sorption sites or greater quantity of nano-size magnetite–maghemite particles can reduce the effect of phosphate on total arsenic or chromium(VI) removal by magnetite–maghemite mixture nanoparticles.

3.5. Adsorption from groundwater

Groundwater was collected from three wells (Samples 1–3) in Bangladesh where most basins and aquifers contain higher concentrations of arsenic (>0.05 mg/L). The samples (1–3) were acidified upon collection to prevent metal precipitation. Groundwater samples were also spiked with arsenic. Bangladesh is severely affected by arsenic contamination. Total arsenic concentrations ranging from 0.0003 to more than 1.6 mg/L are found in different groundwater resources in Bangladesh (BGS, 2001). To investigate the ability of magnetite–maghemite particles to remove these levels of arsenic from Bangladesh groundwater by sorption, samples (1–3) were spiked to those concentration ranges. At the same time, some groundwater samples were kept at their natural arsenic concentrations. Thus spiked groundwater samples containing different initial concentrations of arsenic were added to 20–40 nm magnetite–maghemite in batch experiments to assess arsenic removal. Fig. 10 shows arsenic adsorption on 20–40 nm magnetite–maghemite nanoparticles using 0.4 g/L adsorbent concentration in samples (1–3) and at pH 2. As indicated, Freundlich isotherm provides a reasonable fit to the experimental data, indicating favorable adsorption (Fig. 10).

In Bangladesh, phosphate fertilizer such as triple super phosphate (TSP) and muriate of potash (MOP) are widely used. Arsenic pollution may be caused by the displacement of arsenic from sorption sites on aquifer minerals as a result of competitive (anion) exchange by fertilizer-phosphate, which may leach from soils after excessive use of fertilizer (Acharyya, 1999) supplied from surface application. Furthermore, concentrations of phosphorus increase with depth in Bangladesh groundwater (DPHE, 2000). On the other hand, septic tanks are also used largely in rural areas. Septic tanks can leach phosphorous into shallow aquifers. Domestic use of detergents, municipal waste disposal and poor storm water management practices also leach phosphorus into groundwater. These activities lead to increased concentration of dissolved phosphorus in groundwater. To investigate phosphate effects on arsenic removal from contaminated groundwater by magnetite–maghemite particles, a known concentration of phosphate stock solution was added to desired amount of groundwater (Samples 1–3 in Table 1). Samples were spiked with phosphate to investigate arsenic removal in the presence of high phosphate concentration in groundwater. The natural phosphate concentration in the groundwater was 0.6 mg/L. The initial concentration of arsenic was always kept at 1.13 mg/L by spiking. After 24 h adsorption, it was observed that the sample with the natural phosphate content (0.5 mg/L) showed higher arsenic removal (88%)

Table 4
Approximate cost of different nano-scale adsorbents.

Adsorbents	Size (nm)	Purity (%)	Cost (/kg)	References
Hematite (Fe_2O_3)	20	98+	$225	Reade Advance Materials, 2007
Magnetite (Fe_3O_4)	20	98.5+	$225	Reade Advance Materials, 2007
Iron(III) hydroxide (FeOOH)	30	99+	$990	Nanostructured & Amorphous Materials, Inc., 2007
Zerovalent Iron (Fe^0)	25	99	$2255	Nanostructured & Amorphous Materials, Inc., 2007.
Magnetite–maghemite mixture	20–40	98.5	$225	Reade Advance Materials, 2007
Maghemite	20–40	99	$225	Reade Advance Materials, 2007

than others. Magnetite–maghemite particle can remove less than 60% of arsenic from groundwater having more than 5 mg/L phosphate concentration (Fig. 11). The results presented here indicate that a decrease in arsenic removal by magnetite–maghemite may occur. Thus the proposed use of magnetite–maghemite nanoparticles to remove arsenic from contaminated groundwater could be less effective in the presence of phosphate. In this case, an optimum design for achieving high arsenic removal by magnetite–maghemite nanoparticles may be required.

3.6. *Cost analysis*

Table 4 shows the approximate cost of different nano-scale adsorbents. The nano zerovalent iron is more expensive than the other adsorbents. The magnetite and magnetite–maghemite mixture have similar costs. To develop a decision framework for helping utilities determine the most appropriate adsorbent based on cost and performance, more research and investigation are necessary. The results from the present work show that 0.4 g/L of 20–40 nm mixed magnetite–maghemite particles removed up to 3 and 2 mg/L arsenic and chromium, respectively. Thus the cost of using nano magnetite–maghemite adsorbent would be \$0.09/L.

4. Conclusions

The application of magnetite–maghemite nanoparticles for arsenic and chromium removal has a great potential in water and waste water engineering. Electrostatic attraction between heavy metals and magnetite–maghemite is a key concept for the removal of arsenic and chromium from aqueous solutions. To capitalize on this advantage, magnetite–maghemite nanoparticles could be used in water treatment and site remediation. Magnetite–maghemite particles may be applied in the design of permeable reactive barrier for groundwater remediation. The present study has shown that the removal of arsenic and chromium from contaminated water depends on pH, contact time, initial concentration of arsenic or chromium, PO_4^{3-} concentration in water, and adsorbent concentration. A comparison of the arsenic and chromium uptakes shows that the removal efficiency of arsenic was more than that of chromium in the groundwater pH range (6.5–8.5). Thus, arsenic removal by magnetite–maghemite particles from contaminated groundwater is more favorable than chromium in groundwater pH range. The Freundlich isotherm was fitted to the experimental data and the resulting isotherm parameters, were $n = 2.0$ and $k = 9.4–10.6$ for both arsenic(III) and arsenic(V), and $n = 1.7$ and $k = 6$ for Cr(VI). As the value of n is a measure of the energy of adsorption and k that of the adsorption capacity, it can be inferred that arsenic has greater affinity and is more favorable for adsorption on magnetite–maghemite nanoparticles than chromium(VI).

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References

Acharyya, S.K., 1999. Arsenic poisoning of Bangladesh groundwater. Nature 401, 545.

Bartlett, R.J., Kimble, J.M., 1976. Behavior of chromium in soils: II. Hexavalent forms. J. Environ. Qual. 5, 383–386.

British Geological Survey (BGS) and Government of the People's Republic of Bangladesh, 2001. Arsenic Contamination of Groundwater in Bangladesh. Technical report. WC/00/19,1.

Chand, S., Agarwai, V.K., Pavankumar, C., 1994. Removal of Cr(VI) from waste water by adsorption. Indian J. Environ. Health 36 (3), 151–158.

Chowdhury, S.R, Yanful, E.K., Pratt, Allen R. Arsenic removal from aqueous solutions by mixed magnetite–maghemite nanoparticles. Environ. Earth Sci., submitted for publication.

Daou, T.J., Begin, C.S., Greneche, J.M., Thomas, F., Derory, A., Bernhardt, P., Legare, P., Pourroy, G., 2007. Phosphate adsorption properties of magnetite-based nanoparticles. Chem. Mater. 19, 4494–4505.

Deliyanni, E.A., Lazaridis, N.K., 2005. Sorption of arsenites and arsenates onto surfactant-mediated akaganeite. In: 9th International Conference on Environmental Science and Technology, Rhodes Island, Greece.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182.

DPHE, 2000. Groundwater Studies for Arsenic Contamination in Bangladesh. Supplemental data to Final Report, Rapid Investigation Phase. Department of Public Health Engineering, Government of Bangladesh. Mott MacDonald and British Geological Survey.

Driehaus, W., Jekel, M., 1998. Granular ferric hydroxide — a new adsorbent for the removal of arsenic from natural water. J. Water SRT-Aqua 47, 1–6.

Fendorf, S., Eick, M.J., Grossl, P., 1997. Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. Environ. Sci. Technol. 31, 315.

Gao, Y., Mucci, A., 2001. Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution. Geochim. Cosmochim. Acta 65 (14), 2361–2378.

Grosvenor, A.P., Kobe, B.A., McIntyr, N.S., 2004. Examination of the oxidation of iron by oxygen using X-ray photoelectron spectroscopy and QUASES. Surf. Sci. 565, 151–162.

Guhab, S., Chaudhuri, M., 1990. Removal of As(III) from groundwater by low cost materials. Asian Environ. 12, 42.

Hingston, F.J., Posner, A.M., Quirk, J.P., 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. Discuss. Faraday Soc. 52, 334–342.

Hu, J., Lo, I.M.C., Chen, G., 2004. Removal of Cr(VI) by magnetite nanoparticle. Water Sci. Technol. 50 (12), 139–146.

Hu, J., Guohua Chen, G., Lo, I.M.C., 2005. Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. Water Res. 39, 4528–4536.

Ioannis, A.K., Zouboulis, A.I., 2002. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. Water Res. 36, 5141–5155.

Jackson, B.P., Miller, W.P., 2000. Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides. Soil Sci. Soc. Am. J. 64, 1616.

Jain, A., Loeppert, R.H., 2000. Effect of competing anions on the adsorption of arsenate and arsenite ferrihydrite. J. Environ. Qual. 29, 1422–1430.

Lim, S.F., Zheng, Y.M., Chen, J.P., 2009. Organic arsenic adsorption onto a magnetite sorbent. Langmuir 25 (9), 4973–4978.

Maji, S.K., Pal, M., Pal, T., Adak, A., 2007. Adsorption thermodynamic of As on laterite soil. J. Surf. Sci. Technol. 22 (3–4), 161–176.

Manning, B.A., Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Sci. Soc. Am. J. 60, 121–131.

Manuel, P.C., et al., 1995. Chromium removal with activated carbons. Water Res. 29, 2174–2180.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58, 201–235.

Mayo, J.T., et al., 2007. The effect of nanocrystalline magnetite size on arsenic removal. Sci. Technol. Adv. Mater. 8, 71–75.

McKay, G., Blair, H.S., Garden, J.R., 1982. Adsorption of dyes on chitin-I. Equilibrium study. J. Appl. Polym. Sci. 127, 3034.

Nordstrom, D.K., Archer, D.G., 2003. Arsenic thermodynamic data and environmental geochemistry. In: Cai, Y., Braids, O.C. (Eds.), Biogeochemistry of Environmentally Important Trace Elements. Oxford University Press, pp. 1–25 (Chapter 1).

Nriagu, J.O., Nieboer, E., 1988. Historical Perspectives. IN: Chromium in the Natural and Human Environments, vol. 20. John Wiley & Sons, New York, pp. 1–20.

Palmer, C.D., Wittbrodt, P.R., 1991. Processes affecting the remediation of chromium-contaminated sites. Environ. Health Perspect. 92, 25–40.

Paritam, K.D., Ray, A.K., Sharma, V.K., Millero, F.J., 2004. Adsorption of arsenate and arsenite on titanium dioxide suspensions. J. Colloid Interface Sci. 278 (2004), 270–275.

Periasam, K., Srinivasan, K., Murugan, P.R., 1991. Studies on chromium(VI) removal by activated ground-nut husk carbon. Indian J. Environ. Health 33 (4), 433–439.

Petrusevski, B., Boere, J., Shahidullah, S.M., Sharma, S.K., Schippers, J.C., 2002. Adsorbent-based point-of-use system for arsenic removal in rural areas". J. Water SRT-Aqua 51, 135–144.

Pierce, M.L., Moore, C.B., 1982. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. Environ. Sci. Technol. 14, 214–216.

Prasad, G., 1994. Arsenic in the Environment. Part 1, New York p. 33.

Pourbaix, M., 1974. Atlas of Electrochemical Equilibria in Aqueous Solutions. National Association of Corrosion Engineers, Houston, TX, USA.

Ramos, R.L., Martinez, A.J., Coronado, R.M.G., 1994. Adsorption of chromium(VI) from aqueous solutions on activated carbon. Water Sci. Technol. 30 (9), 191–197.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32, 344–349.

Raji, C., Anirudhan, T.S., 1998. Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. Water Res. 32 (12), 3772–3780.

Ryu, J.H., Gao, S., Dahlgren, R.A., Zierenberg, R.A., 2002. Arsenic distribution, speciation and solubility in shallow groundwater of Owens Dry Lake, California. Geochim. Cosmochim. Acta 66 (17), 2981–2994.

Sevgi, K., Akcin, G.K., 2002. Removal and recovery of chromium and chromium speciation with MINTEQA2. Talanta 57, 23–30.

Shipley, H.J., Yean, S., Kan, A.T., Tomson, M.B., 2009. Adsorption of arsenic to magnetite nanoparticles: effect of particle concentration, pH, ionic strength, and temperature. Environ. Toxicol. Chem. 28 (3), 509–515.

Shih, M., 2005. An overview of arsenic removal by pressure-driven membrane processes. Desalination 172 (1), 85–97.

Singh, T.S., Pant, K.K., 2004. Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. Separ. Purif. Technol. 36, 139–147.

Stumm, W., Morgan, J., 1970. Aquatic Chemistry: an Introduction Emphasizing Chemical Equilibria in Natural Waters, vol. 39. Wiley, New York, pp. 481–482.

Su, C.M., Puls, R.W., 2001. Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate relative to chloride. Environ. Sci. Technol. 35, 4562.

Tejedor-Tejedor, M.I., Anderson, M.A., 1990. Protonation of phosphate on the surface of goethite as studied by CTR-FTIR and electrophoretic mobility. Langmuir 6, 602–611.

Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., 2003. Arsenic removal from drinking water using granular ferric hydroxide. Water SA 29 (2).

Tuutijärvi, T., Sillanpää, M., Lu, J., Chenb, G., 2009. As(V) adsorption on maghemite nanoparticles. J. Hazard. Mater. 166, 1415–1420.

Tzou, Y.M., Wang, M.K., Loeppert, R.H., 2003. Effects of phosphate, HEDTA, and light sources on Cr(VI) retention by goethite. Soil Sediment Contam. Int. J. 12 (1), 69–84.

Violante, A., Pigna, M., 2002. Competitve sorption of arsenate and phosphate on different clay minerals and soils. Soil Sci. Soc. Am. J. 66, 1788.

Yavuz, C.T., Mayo, J.T., Yu, W.W., Prakash, A., Falkner, J.C., Yean, S., Cong, L., Shipley, H.J., Kan, A., Tomson, M., Natelson, D., Colvin, V.L., 2006. Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals. Science 314 (5801), 964–967.

Yean, S., Cong, L., Yavuz, C.T., Mayo, J.T., Yu, W.W., 2005. Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate. J. Mater. Res. 20 (12) Materials Research Society.

Zhang, W., Singh, P., Paling, E., Delides, S., 2004. Arsenic removal from contaminated water by natural iron ores. Minerals Eng. 17, 517–524.

Zhang, Y., Yang, M., Huang, X., 2003. Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent. Chemosphere 51, 945–952.