Arsenic Removal from contaminated water and its stabilization in soil using iron/copper nanoparticles

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ABSTRACT

Arsenic contamination of water has become a crucial water quality problem in many parts of the world considering the fact that the source of pollution is mostly contaminated soils. To overcome this problem many new technologies are being developed, among them using nanoparticles as a new class of adsorbents is becoming attractive because of their high specific surface area and higher surface reactivity due to their extremely small size. In this research, iron/copper bimetallic nanoparticles were used to remove arsenic from aqueous solutions as well as to stabilize arsenic in an industrial contaminated soil. Results of this study show that Fe/Cu nanoparticles are effective for removing arsenic from aqueous solutions and have the potential for developing a simple process for field applications to stabilize arsenic in soil.

RÉSUMÉ

La contamination à l'arsenic de l'eau est un problème critique par rapport à la qualité de l'eau mondiale compte tenu du fait que la source de pollution est essentiellement les sols contaminés. Pour surmonter ce problème, de nombreuses nouvelles technologies ont été développées. L'utilisation de nanoparticules comme nouvelle classe d'adsorbants a notamment reçu beaucoup d'attention en raison de leur surface spécifique élevée et de la réactivité de surface. Dans cette recherche, les nanoparticules bimétalliques (fer/cuivre) ont été utilisées pour éliminer l'arsenic de solutions aqueuses et pour stabiliser l'arsenic dans un sol contaminé industriel. Les résultats de cette étude montrent que les nanoparticules de Fe/Cu sont efficaces pour éliminer l'arsenic de solutions aqueuses et qu'elles ont le potentiel pour développer un processus simple pour éliminer l'arsenic dans les sols pour les applications sur le terrain.

1 INTRODUCTION

Arsenic as a heavy metal has been widely presented in soils and waters in many parts of the word. In some areas like in the Bengal Delta and western United States, elevated levels of arsenic have been reported (Berg et al., 2001;Welch et al., 2000). Arsenic and its associated compounds are known to be toxic and carcinogenic. Intake of inorganic arsenic may lead to skin lesions, cancers and other symptoms. The first route that arsenic enters into the body is ingestion. Generally contaminated ground water is the main source of ingestion of inorganic arsenic to the human population considering the fact that the source of pollution is mostly contaminated soils (Maharjan et al., 2005). Both natural and anthropogenic arsenic polluted soils can cause groundwater to become contaminated.

In Canada, industrial activities such as gold and base-metal processing, use of arsenical pesticides and wood preservatives, thermal and coal-fired power generation has doubled the release of arsenic in soil environment that previously had been just from natural weathering and erosion processes of arsenic-bearing rocks and soils (Wang & Mulligan, 2006). High levels of arsenic in soil up to 25,000 mg/kg have been reported from some regions in Canada which will require appropriate remediation (Newhook et al., 2003). In general, arsenic treatment technologies that are applicable to soil are: 1) Solidification and stabilization, 2) Vitrification, 3) Soil washing/acid extraction, 4) Pyrometallurgical recovery and 5) In situ soil flushing (EPA, 2002). Although all of these methods have been successful to remove arsenic, recently nanoparticles (due to their unique features) as a new class of adsorbents have been introduced for this purpose. Different types of nanoparticles have been tried to remove a variety of contaminants including arsenic from polluted environments. The extremely small size of nanomaterials, typically in the range of 1 to 100 nanometres, generates a large surface to volume ratio, providing them with an enhanced surface reactivity (Khin et al., 2012). Moreover nanoparticles due to their small size can move easily in porous media and reach to the target zone of contamination. Among different nanoparticles, nanoscale zero-valent iron (nZVI) is the most widely used nanoparticle that has been investigated as a new class of material for the remediation of contaminated water and soil (Liang et al., 2014). Over the past 10 years, there has been increased interest in developing iron bimetallic nanoparticles. It is hypothesized that through combining iron with a more noble metal (e.g., Pd, Pt, Ag, Ni, Cu), reactivity and also environmental longevity will improve the process by limiting aqueous corrosion (Altavilla & Ciliberto, 2011).

In this study iron-copper nanoparticles were synthesized and were used to investigate for their capacity for adsorption of arsenic in aqueous environment and the possibility of use in an industrial contaminated soil.

2 MATERIALS AND METHODS

2.1 Chemicals

Ferrous sulfate ($FeSO_4.7H_2O$) was purchased from Sigma Aldrich (St Louis, MO, USA), cupric sulfate ($CuSO_4.5H_2O$) was obtained from Fisher (Nazareth, PA, USA), potato starch, hydrochloric acid (HCl) and acetone (C_3H_6O) were purchased from Fisher Scientific (Lane Fair Lawn, New Jersey, USA) and sodium borohydride ($NaBH_4$, 98%) was obtained from Acros (Lane Fair Lawn, New Jersey, USA). Deionized (DI) water (Milli-Q water purification system, Millipore, Bedford, MA, USA) was used as the solvent for preparing all solutions.

2.2 Preparation of Fe-Cu nanoparticles

Synthesis of Fe–Cu bimetallic nanoparticles was carried out by reduction of $FeSO_4·7H_2O$ and $CuSO_4·5H_2O$ aqueous mixture using sodium borohydride. The reaction for synthesis can be described as follows (Morales-Luckie et al., 2008):

$$4Fe^{+2} +4Cu^{+2}+3BH_4+12H_2O \rightarrow 4Fe^0Cu^0+3B(OH)_4^- +24H^+ \quad [1]$$

First, a 5mM aqueous solution of $FeSO_4.7H_2O$ and a 5mM $CuSO_4.5\ H_2O$ aqueous solution were prepared using de-ionized water. Then 500 mL of each metal salt solution were mixed under nitrogen and vigorous stirring for 20 min. After that, pH was adjusted to 7.0 with 1 N and 0.1 N NaOH solutions; subsequently, 100 mL of a 10 mM aqueous solution of $NaBH_4$ were added drop wise to the metal salts solution in a 20 min period. A fine black precipitate of hybrid nanoparticles was obtained. The precipitates were then washed three times with de-ionized water, and finally, water was removed with acetone.

2.3 Arsenic adsorption tests

Batch adsorption experiments were conducted to determine arsenic sorption capacity of the Fe/Cu nanoparticles. These experiments were carried out in 50 mL centrifuge tubes at ambient temperature (20 ± 2◦C). Concentrations of 100 and 10 mg/L of trivalent and pentavalent arsenic solutions were prepared by dissolving an accurately weighed quantity of arsenic salts in 1 L of DI water. Solutions of desired concentration were obtained by successive dilution of the stock solutions.

First, in order to investigate the effect of contact time, a preliminary experiment was carried out for 48 hours with different initial concentrations of As (III) and 50 mg/L of nanoparticles. Fe/Cu nanoparticles suspensions were prepared by adding 50 mg of Fe/Cu NPs in 1 L DI water. For uniform dispersion of NPs, the suspensions were sonicated for 15 minutes with a probe sonicator (Branson model 102 C(CE), USA). For the first 6 hours, samples were taken every hour and after that sampling was performed at 12 hour intervals. As the result showed that the removal efficiency does not change from hour one to hour 48, other experiments were done for two hours.

In order to study the adsorption isotherms, 100 mg of nanoparticles were placed in arsenic solutions of different concentrations (100, 500, 1000, 2000, 3000, 4000 and 5000 µg/L) at pH 7 (adjusted by 0.1 M NaOH or 0.1 M HCl) for 2 h with constant shaking on a platform shaker (200 rpm) at ambient temperature of 20 ± 2◦C. The amount of arsenic adsorbed (mg/g) on the surface of the NPs was determined from the difference of the two concentrations. Duplicate experiments were carried out for all operating variables studied and only the average values were taken into consideration. Every hour, samples were taken, centrifuged and filtered (25 nm, Millipore, USA) to separate nanoparticles, leaving only dissolved arsenic in the solutions. The aliquots were then analyzed for arsenic remaining in the aqueous phase using ICP-MS (Agilent Technologies, 7700 Series, USA).

The adsorption kinetics of As(III) and As(V) at pH 7.0 were also studied. The initial concentration of arsenic was fixed at 0.5, 1, 2 and 4 mg/L. The dosage of adsorbent was 0.1 g/L, and the total reaction time was 1h. The solutions were sampled at 1, 4, 7, 10, 15, 20, 30, 45 and 60 minutes.

2.4 Immobilization of arsenic in soil

To study the effect of nanoparticles on arsenic immobilization in a soil matrix, an arsenic contaminated soil from an industrial site was transferred to the lab. Batch kinetic tests of arsenic leaching from the soil were carried out in the presence and absence of the starch-stabilized nanoparticles. To stabilize the nanoparticles, a stock solution of 0.2 g/L of nanoparticles was prepared by probe sonicating nanoparticles in DI water for 15 minutes. Then, Fe/Cu suspensions (0.1 g/L) were prepared in 0.1 g/L starch solution. The mixtures were shaken at 200 rpm for 1 hour to promote interactions between starch and nanoparticles.

The tests were conducted using a batch of Corning plastic centrifuge tubes (15.5 mL).Typically, 1.5 g of As polluted soil (sieved through a standard sieve of 2-mm opening), were added to the centrifuge tubes each containing 15 mL of the nanoparticle suspension containing 0.1 g /L of the nanoparticles, resulting in a soil-to-liquid ratio (SLR) of 0.1. The tubes were then capped and equilibrated on an end-to end rotator operated at room temperature (20 ± 2◦C). The solution pH was initially adjusted to 7 ± 0.1. The first sample was taken after 6 hours and then every 12 hours, the tubes were sacrificially sampled up to 4 days. Then by centrifuging the mixtures at 10000 rpm for 20 minutes and passing the supernatant through a 25-nm Millipore membrane filters, samples were prepared for total arsenic analysis.

3. RESULTS AND DISCUSSION

3.1 Sorption Isotherms

The adsorption capacity is indicated by the adsorption isotherms. Over the years, in order to correlate the equilibrium adsorption data, various models like Langmuir and Freundlich have been developed. In this research in order to study the dominant adsorption mechanisms and to compute various adsorption parameters, these two models have been evaluated.

In Langmuir empirical model, it is assumed that the adsorption is monolayer (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite number of definite localized sites, that are identical and equivalent (Vijayaraghavan et al., 2006). The Langmuir model considers that the sorption energy of each molecule is the same. This isotherm has the following form:

$q_e=q_0bC_e/(1+bC_e)$ [2]

which may be written in linearized form as follows:

$C_e/q_e=1/q_0b \quad +1/q_0 \quad C_e$ [3]

where q_0 is the maximum adsorption capacity of the adsorbent, Ce is the liquid phase equilibrium concentration, qe is the amount of arsenic adsorbed, and b is the constant related to the energy or net enthalpy of adsorption.

The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of a monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption affinities over the heterogeneous surface.

Freundlich equation has the following form:

$q_e=K_FC_e^{1/n}$ [4]

which may be written in linearized form as follows:

$\log q_e=\log K_F+ 1/n \log C_e$ [5]

where q_e is the amount of arsenic adsorbed, Ce is the equilibrium concentration of arsenic in solution, K_F can be taken as a relative indicator of adsorption capacity, and 1/n is indicative of energy or intensity of the reaction ranges between 0 and 1. As the adsorption isotherms follow the Langmuir model (Fig. 1), Freundlich isotherms have not been plotted, although the isotherm parameters have been presented in Table 1.

3.2 Kinetic models

The adsorption kinetics on the adsorbent is very important for designing the appropriate adsorption technologies. To study the reaction kinetics, pseudo-first-order and pseudo second-order models were used. A simple pseudo-first-order kinetic model also known as the Lagergren equation is represented as (Lagergren, 1898):

$dq/dt = k_a (q_e - q_t)$ [6]

where q_e and q_t are the amounts of arsenic adsorbed per unit weight (mg/g) of adsorbent at equilibrium and at any time t, respectively, and k_a is the rate constant of pseudo-first order sorption. The linearized plots of log (q_e-q_t) versus t give the rate constants.

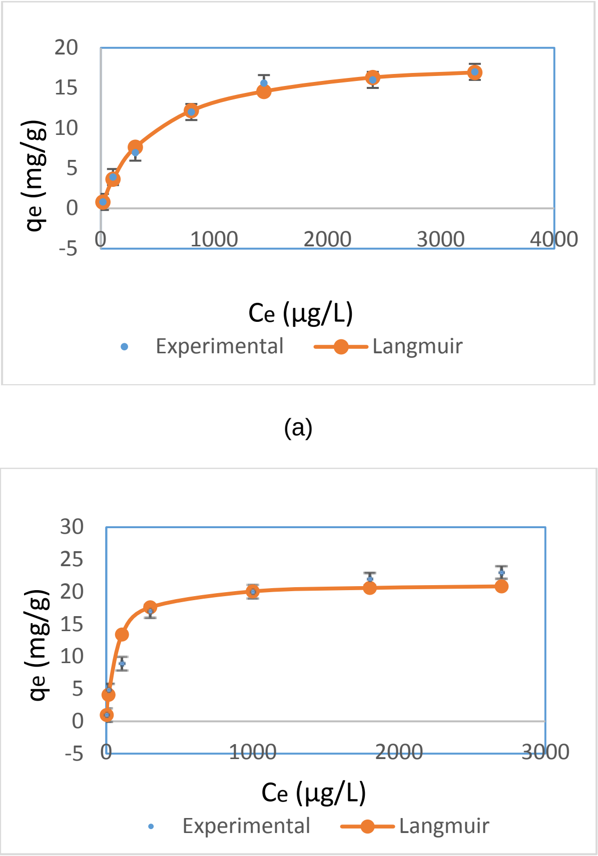
$\ln(q_e - q_t) = \ln q_e - k_a d_t$ [7]

If the rate of adsorption is a second-order mechanism, the chemisorption kinetic rate equation is expressed as:

$d_q/d_t = ka (q_e - q_t)^2$

The linear equation for which can be written as (Lagergren, 1898):

$t/q_t= 1/h +t/q_e \quad h=kq_e^2$



(a)

(b)

Figure 1: Equilibrium isotherm model for arsenic adsorption: (a) As(III), (b) As(V)

where q_t is the amount of arsenic adsorbed at time t (mg g^{-1}), q_e is the amount of arsenic adsorbed at equilibrium (mg g^{-1}), and h is the initial sorption rate (mg g^{-1} min^{-1}). The values of q_e (1/slope), k (slope^2/intercept) and h (1/intercept) can be calculated from the plots of t/q_t versus t.

Adsorption kinetic results are presented in Fig. 2. There was a rapid uptake of As(V) in the first 15 minutes, and then it reached equilibrium. For As(III), all adsorption occurs in the first 30 minutes and after that it reaches equilibrium.

The experimental data were fitted to pseudo-first-order and pseudo-second-order equations. The kinetic model parameters are shown in Tables 2 and 3. The correlation coefficient (R^2) values represent that the pseudo-second-order model is more suitable than the pseudo-first- order model for arsenic adsorption on Fe/Cu nanoparticles.

Table 1. Langmuir and Freundlich isotherm constants for arsenic adsorption.

Form of As	Langmuir			Freundlich		
	q_0 (mg/g)	b(L/mg)	R^2	KF((mg/g)/((mg/L)1/n))	n	R^2
As(III)	19.68	0.0021	0.9996	0.191	1.696	0.9488
As(V)	21.32	0.0158	0.9964	1.0025	2.31	0.9144

Table 2. Kinetic model parameters (As (III))

C_0 (mg/L)	Pseudo First			Pseudo Second		
	q_e (mg/g)	K (1/min)	R^2	q_e (mg/g)	K (g/mg min)	R^2
0.5	0.34	0.0601	0.9488	3.937	0.724	0.9999
1	0.8906	0.1351	0.8884	6.983	0.471	0.9999
2	3.6128	0.1493	0.975	12.165	0.1198	0.9999
4	7.2921	0.0792	0.9919	16.694	0.0256	0.9981

Table 3. Kinetic model parameters (As (V))

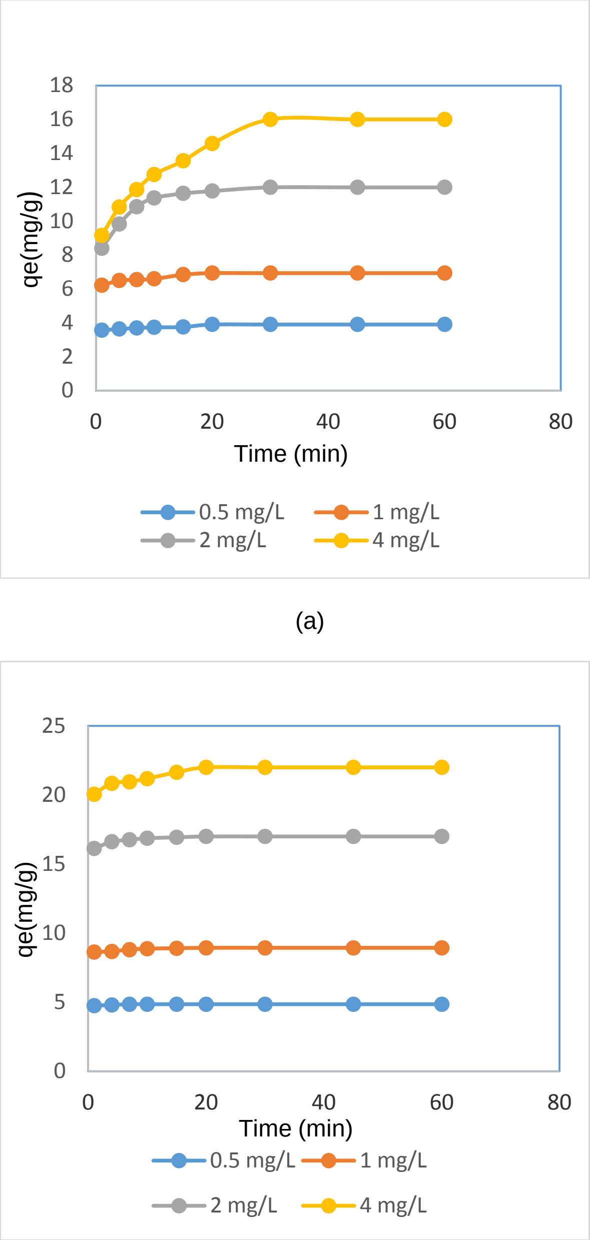
C_0 (mg/L)	Pseudo First			Pseudo Second		
	q_e (mg/g)	K (1/min)	R^2	q_e (mg/g)	K (g/mg min)	R^2
0.5	0.12599	0.231	1	4.852	14.159	1
1	0.42109	0.178	0.9705	8.944	1.43669	1
2	0.9115	0.1872	0.9881	17.035	0.7657	1
4	2.1271	0.1116	0.955	22.123	0.1746	1

3.3 Arsenic immobilization: batch tests

The effectiveness of stabilized Fe/Cu nanoparticles for immobilizing arsenic in the soil was tested in batch desorption experiments. Fig. 3 compares arsenic desorption kinetics from the arsenic contaminated soil in the absence and presence of the nanoparticles at a SLR of 0.1. When the soil was mixed with the DI water without the nanoparticles, the equilibrium concentration of As in the aqueous phase reached 90 µg/L at SLR=0.1. In contrast, in the presence of the nanoparticles, the water-soluble As concentration was reduced by 30 to 50%. This result indicates that adding a small fraction of the nanoparticles to the soil enhances immobilization of As by transferring water leachable As from the soil onto the nanoparticles. According to prior spectroscopic studies the enhanced As immobilization by the nanoparticles is related to the formation of the strong complexes (Fe–O–As) between arsenic and the nanoparticles (An et al, 2011).

4. Conclusions

Arsenic can be adsorbed very quickly onto the Fe/Cu nanoparticles even at higher initial arsenic concentrations. The results demonstrate that this nanoparticle has a good capacity to uptake arsenic from the contaminated water. The results also suggest that starch stabilized nanoparticles can be used to immobilize arsenic in polluted soil environments.



(a)

(b)

Fig. 2: Adsorption kinetic data of arsenic at different initial concentrations: (a) As(III), (b) As(V)

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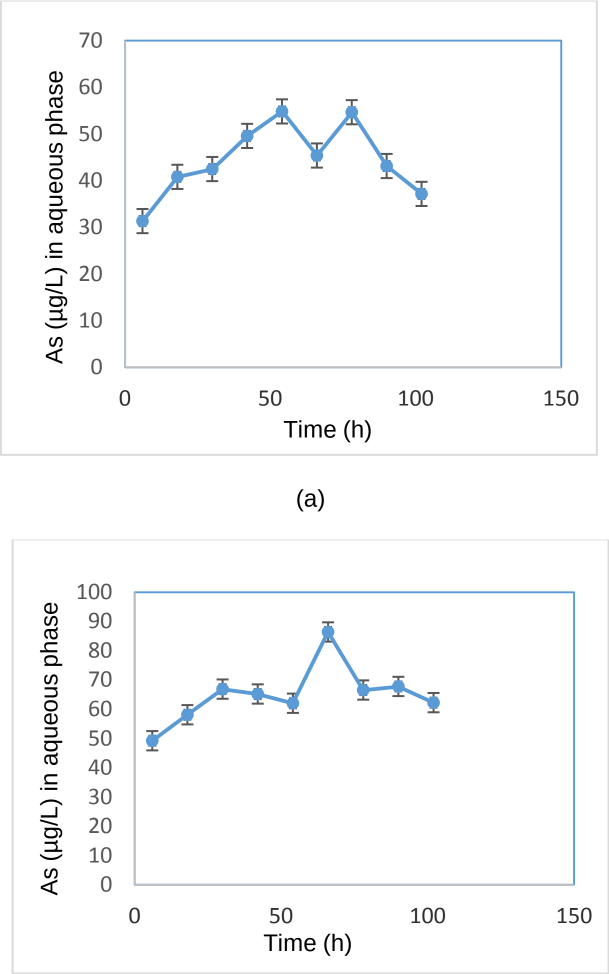

(a)

(b)

Fig. 3. Desorption kinetics of arsenic from soil: (a) In presence of nanoparticles, (b) In absence of nanoparticles

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