

# A novel arsenic removal process for water using cupric oxide nanoparticles

K.J. Reddy\*, K.J. McDonald, H. King

Department of Ecosystem Science and Management, University of Wyoming, Laramie, WY, USA

## ARTICLE INFO

### Article history:

Received 5 December 2012

Accepted 20 January 2013

Available online 8 February 2013

### Keywords:

Adsorption

Desorption

Arsenic

Kinetics

CuO nanoparticles

Flow-through reactor

## ABSTRACT

Recent studies suggest that the cupric oxide (CuO) nanoparticles effectively adsorb aqueous arsenic species under a wide range of water chemistries. However, to develop CuO nanotechnology to a field application level, further studies are necessary. Batch adsorption kinetic experiments were conducted to determine the time course of uptake of arsenic by CuO nanoparticles. A reactor with CuO nanoparticles was developed to conduct continuous flow-through experiments to filter arsenic from groundwater samples. Groundwater samples spiked with 100 µg/L of arsenic were passed through (1 L/h) the flow-through reactor. Samples from the flow-through reactor were collected at a regular interval and analyzed for arsenic and other chemical components (e.g., pH, major and trace elements). The CuO nanoparticles adsorbed with arsenic were regenerated with a sodium hydroxide (NaOH) solution and tested again in the flow-through reactor. Three natural groundwater samples with above 10 µg/L of arsenic were also tested with the flow-through reactor. The arsenic adsorption process by CuO nanoparticles was kinetically rapid and followed the pseudo-second-order rate. The continuous flow-through reactor with CuO nanoparticles was effective in filtering arsenic from spiked or natural groundwater. The regenerated CuO nanoparticles were also effective in filtering arsenic from groundwater. Arsenic mass balance data from regeneration studies suggested that 99% of input arsenic concentration was recovered. The CuO nanoparticle treatment did not show any discernible effects on the chemical quality of groundwater samples. Results of this study suggest that CuO nanoparticles show potential for developing a simple process for field applications to remove arsenic from water.

© 2013 Elsevier Inc. Open access under CC BY-NC-ND license.

## 1. Introduction

Arsenic in water is derived from natural and anthropogenic sources. The natural sources include weathering and dissolution of arsenic minerals. The anthropogenic sources include disposal of solid by-products from combustion processes (e.g., coal plants, solid waste incinerators, cement plants, and paper mills), discharge of produced water from in situ extraction processes (e.g., uranium, oil, and natural gas), and application of arsenic based pesticides [1,2]. The most common inorganic arsenic species found in natural water under anoxic and oxic environments include arsenite(III) and arsenate(V), respectively. Dissolved inorganic arsenic in water is toxic to humans. Studies suggest that arsenite is more toxic than arsenate to humans; long-term exposure to drinking water containing arsenic in excess of 50 µg/L causes increased occurrences of skin, lung, bladder, and kidney cancer resulting in premature death [3]. Widespread occurrence of natural arsenic (As) in groundwater has been reported from many parts of the world. The health of millions of people is at risk due to exposure to unsafe

levels of arsenic in groundwater. The World Health Organization (WHO) and US EPA recommend 10 µg/L of arsenic as the limit for human drinking water.

Global awareness of arsenic contamination of drinking water supplies has skyrocketed during the 1990s when more than 35 million people in Bangladesh and West Bengal, India were inadvertently poisoned by drinking arsenic contaminated water [4,5]. Further studies illustrate that elevated levels of naturally occurring arsenic in groundwater are a prevalent problem affecting many regions of the world [6].

Widespread efforts are being made globally to develop effective and affordable technologies for the removal of arsenic from water. Conventional adsorbents such as aluminum, iron, manganese, titanium, and ferric phosphate were studied extensively to remove arsenic from water [7–11]. In addition to these, zeolites and coal combustion by-products (e.g., fly ash) were also used as sorbents to remove arsenic from water. However, it is difficult to remove both oxidation states simultaneously from water under a wide range of pHs and concentrations of competing anions including phosphate, silicate, and sulfate [12]. In addition, disposal of waste by-products (sludge or spent media) produced from conventional adsorbents is a problem. Due to these reasons, the conventional adsorbents are not sustainable [12–16].

\* Corresponding author.

E-mail address: katta@uwyo.edu (K.J. Reddy).

Reddy and Viswatej [17] were the first to observe that cupric oxide (CuO) can remove both arsenite and arsenate from water without adjusting sample pH or redox potential. Martinson and Reddy [18] expanded these studies and reported that CuO was effective arsenic adsorbent because it did not require pH or redox potential adjustments, and it worked well in the presence of competing anions. These studies attributed the effective removal of arsenic to CuO high zero point of charge (ZPC) ( $9.4 \pm 0.4$ ) and the oxidation of arsenite to arsenate by the CuO surface. Martinson and Reddy [18] also modeled the arsenic adsorption equilibrium process using Langmuir and Freundlich isotherms and reported that adsorption of arsenic by CuO nanoparticles was best modeled with the Langmuir isotherm. These studies also reported that CuO nanoparticles were effective in removal of arsenic across a wide range of groundwater chemistries. Since Martinson and Reddy [18] studies were published, and other researchers also tested arsenic removal from water using CuO nanoparticles and reported similar results [19–23].

For example, Pillewan et al. [20] examined arsenic removal from water using CuO incorporated mesoporous alumina. These studies reported that incorporation of CuO into alumina improved the removal of arsenic from water. Goswami et al. [21] reported that CuO found to be a potential nano-adsorbent to remove arsenic from water. In another study, Schilz et al. [23] treated in situ uranium produced water with CuO nanoparticles to remove arsenic. These studies reported CuO nanoparticles effectively removes arsenic and render in situ uranium produced water less toxic to cells. Overall, above studies demonstrate the effectiveness of CuO nanoparticles in removal of arsenic from water under a wide range of water chemistries and geo-hydrological conditions. However, in addition to batch equilibrium studies, a better understanding of adsorption kinetics and continuous flow-through experiments are required to develop CuO nanotechnology for field applications.

The objectives of this research were to (1) examine arsenic adsorption kinetics by CuO nanoparticles and (2) design and develop a reactor to conduct continuous flow-through experiments. Batch and continuous flow-through reactor experiments were conducted to determine the effectiveness of CuO nanoparticles in the removal of arsenic from groundwater samples. Cupric oxide nanoparticles adsorbed with arsenic were regenerated and tested again with the continuous flow-through system to test their effectiveness in the removal of arsenic from groundwater samples. Data from these experiments could help develop a practical one-step

process for field applications to filter arsenic from natural groundwater.

## 2. Materials and methods

### 2.1. Materials

The groundwater used in this study was collected from the Casper aquifer at a residential site in eastern Laramie, WY, USA following the procedures of Wyoming Department of Environmental Quality [24]. The water was collected in high-density polyethylene (HDPE) bottle. Before collection of the sample, the well was purged until a water quality indicator (e.g., pH) was stable. The groundwater was spiked with equal volumes of 1000  $\mu\text{g/L}$  As(III) and 1000  $\mu\text{g/L}$  As(V) standard solutions to obtain 100  $\mu\text{g/L}$  arsenic-spiked water. The standard solutions were prepared by dissolving sodium arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , Sigma) and sodium arsenite ( $\text{NaAsO}_2$ , Sigma) in distilled water. The CuO nanoparticles used in this study were synthesized following the procedures as described in Martinson and Reddy [18]. The synthesized CuO nanoparticles were subjected to shape and surface area experiments.

### 2.2. Batch experiments

All experiments were conducted in 50 mL polypropylene centrifuge tubes (Corning 430829). 200 mg and 10 mg of the nanoparticles were placed in the tubes, and then, the arsenic-spiked groundwater sample was added to set the concentration of nanoparticles to 4 g/L and 0.2 g/L, respectively. The tubes were sealed and placed on a bench top orbital shaker table (Labline Orbit Shaker) set at 250 rpm. The samples were allowed to react with nanoparticles for a period of time between 2 min and 12 h. After the set reaction time, the samples were centrifuged for 4 min to allow the nanoparticles to settle at the bottom of the tubes. The supernatant was then filtered using a syringe filter (Millipore 0.45  $\mu\text{m}$ ) and then collected in a beaker for arsenic analysis. Samples were acidified with nitric acid and analyzed for arsenic concentrations.

### 2.3. Flow-through experiments

#### 2.3.1. Design of flow-through reactor

An acrylic flow-through reactor was designed and developed to test arsenic removal with CuO nanoparticles (Fig. 1). The flow-

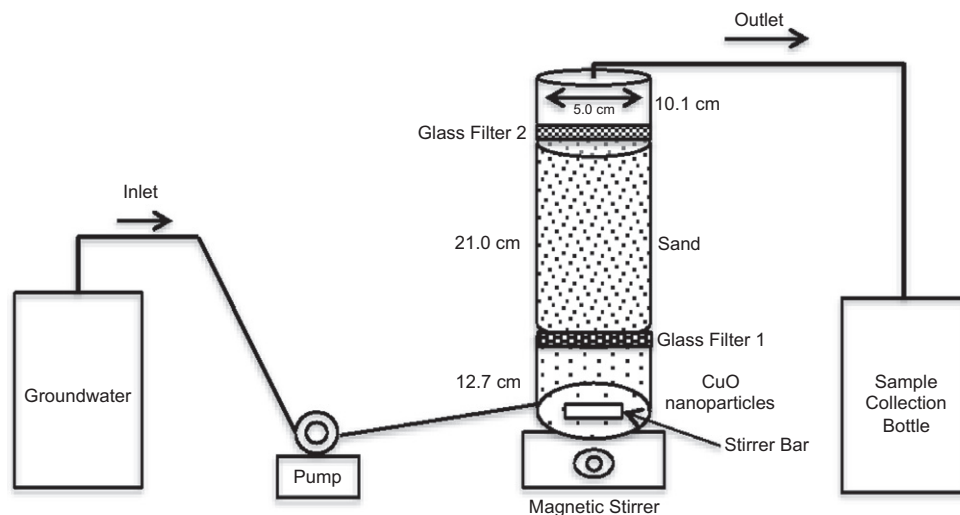


Fig. 1. Continuous flow-through reactor to remove arsenic from groundwater samples.

through column is 43.8 cm long and 5.0 cm diameter with two compartments. The first compartment consists of CuO nanoparticles (8 g) to remove arsenic. The second compartment consists 300 g of sand layer (Fisher Scientific, S25-10, SiO<sub>2</sub> powder) to filter CuO nanoparticles. A micro-glass filter (Ace Glass Incorporated), as shown in Fig. 1, separates each compartment. The pore size of the first filter is between 10 and 20 μm (part no. 7176-145), and the pore size of the second filter is between 4 μm and 8 μm (part no. 7176-146). The smaller pore size filter was used to capture any CuO nanoparticles escaping from the sand. A peristaltic pump was used to pump groundwater through the reactor at a flow rate of 1 L/h. The outlet from the reactor was connected to a sample collection bottle.

### 2.3.2. Sand layer

Twenty liters of arsenic-spiked groundwater sample (100 μg/L) was pumped through the reactor without CuO nanoparticles to determine the effect of the sand layer in the removal of arsenic (first experiment). A 50 mL of water samples was collected at time intervals of 0, 5, 10, 15, and 30 min and subsequently for 1, 2, 3, 4, 5, 10, 15, and 20 h. After passing 20 L of groundwater sample through the column, a composite sample was collected from the sample collection bottle to determine the final concentration of arsenic. A portion of each sample was analyzed for pH, and the remaining sample was acidified with nitric acid. Acidified samples were analyzed for arsenic and other major and trace elements. Unacidified samples were analyzed for anions.

### 2.3.3. CuO nanoparticles with sand layer

Twenty liters of arsenic-spiked groundwater sample (100 μg/L) was pumped through the column with CuO nanoparticles (8 g) followed by the sand layer as shown in Fig. 1 (second experiment). A 50 mL of water samples was collected at time intervals of 0, 5, 10, 15, 30 min and subsequently for every hour. A composite sample from the collection bottle was collected. Samples were analyzed for pH, arsenic, and major and trace elements. This experiment was repeated (third experiment) with 20 L of arsenic-spiked groundwater sample (100 μg/L).

### 2.3.4. Regeneration of CuO nanoparticles

After the completion of the third experiment, CuO nanoparticles, adsorbed with arsenic, from the column were removed and regenerated by washing with 182 mL of 0.3 M NaOH (sodium hydroxide) and 300 mL of distilled deionized water. The total volume of wash fluids was 482 mL. These wash fluids were analyzed for arsenic to calculate the mass balance. A fourth experiment was conducted with regenerated CuO nanoparticles with 20 L of arsenic-spiked groundwater sample (100 μg/L) to determine their effectiveness in the removal of arsenic.

### 2.3.5. Natural groundwater well samples

In addition to the above experiments, three natural groundwater well samples from Torrington, Wyoming, were tested using the flow-through reactor. These groundwater well samples were selected for testing because arsenic concentrations in these wells were consistently above 10 μg/L over the last 3 years. These groundwater samples were collected following the sample collection protocols of Wyoming Department of Environmental Quality [24]. Five liters of each groundwater well sample (without pH or redox potential adjustment) was passed through the continuous flow-through reactor with 1.2 g of CuO nanoparticles followed by the sand layer (Fig. 1). A 50 mL of water samples was collected at time intervals of 0, 5, 10, 15, 30 min and subsequently for every hour. A composite sample from the collection bottle was collected. These samples were analyzed for the pH, arsenic, and major and trace elements.

## 3. Analytical methods

The water samples were analyzed for arsenic and major and trace element concentrations by inductively coupled plasma–mass spectroscopy (ICP–MS). The detection limit for arsenic by ICP–MS was 0.001 mg/L. Anion concentrations were measured with ion chromatography (IC). More details about model number and detection limits of these two instruments are given in [Supplemental information \(Table S1\)](#). The Transmission Electron Microscopy (TEM) images of CuO nanoparticles were obtained using a Hitachi H-7000 equipped with a Gatan UltraScan 4000 digital camera. The samples were dispersed in ethanol, exposed to ultrasonic vibration for 30 min, and then placed on a carbon coated copper grid for TEM analysis. The surface area of CuO was analyzed with BET method. In this method, nanoparticles were dried under inert atmosphere at 110 °C prior to the measurement. Nitrogen adsorbed on the surface of the particles was analyzed using TriStar 3000 analyzer. The pH was measured with Orion FiveStar pH probe.

## 4. Results and discussion

### 4.1. Nanoparticle and groundwater characterization

The CuO prepared in this study formed cylindrical shape nanoparticles (Fig. 2). The BET analysis of the CuO nanoparticles yielded a specific surface area of 86.51 m<sup>2</sup>/g. The groundwater sample pH was 7.62. Concentrations of major elements in mg/L were 76.2 (Ca), 17.0 (Mg), 3.25 (Na), 1.1 (K), 5.0 (Si), 17.6 (SO<sub>4</sub><sup>2-</sup>), 5.7 (Cl<sup>-</sup>), and 4.66 (NO<sub>3</sub><sup>-</sup>) (Table S2). The spiked arsenic concentration was found to be 0.109 mg/L. Trace element concentrations in mg/L were 0.069 (Cu), 0.001 (Pb), and 0.03 (Zn). Iron, Cr, Mn, Se, Cd, and PO<sub>4</sub><sup>3-</sup> were non-detectable (Table S2).

### 4.2. Kinetic models

The adsorption kinetics of arsenic on the nanoparticle is of great importance for designing appropriate adsorption technologies. To study the reaction kinetics, pseudo-first-order and pseudo-second-order models were used. A pseudo-first-order kinetic model, the Lagergren equation, which is represented as:

$$dq/dt = k_{s1}(q_{eq} - q_t) \quad (1)$$

where  $q_{eq}$  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  $k_{s1}$  is the rate constant of pseudo-first order sorption

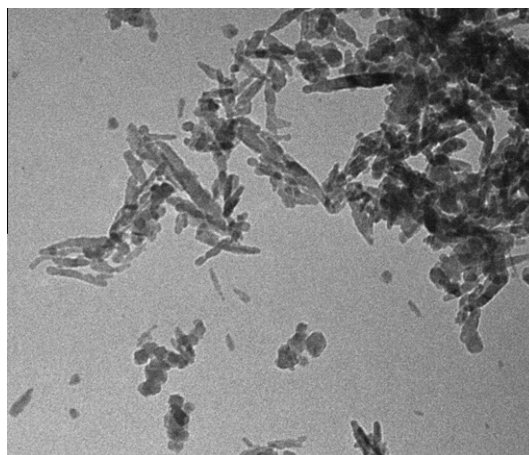


Fig. 2. TEM photographs of CuO nanoparticles at 30× magnification (50 nm).

(1/min). After integration and applying boundary conditions, for  $t = 0, q = 0$ , the integrated form of Eq. (1) becomes

$$\log(q_{\text{eq}} - q_t) = \log(q_{\text{eq}}) - (k_{s1}/2.303) * t \quad (2)$$

If the rate of adsorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation [25] is expressed as:

$$dq/dt = k(q_{\text{eq}} - q_t)^2 \quad (3)$$

where  $k$  is the rate constant of pseudo-second-order sorption (g/(mg min)). Integrating this equation for the boundary conditions for  $t = 0, q = 0$  gives

$$t/q = (1/kq_{\text{eq}}^2) + (1/q_{\text{eq}}) * t \quad (4)$$

The intercept of the linearized pseudo-second-order rate equation gives the second-order rate constant,  $k$ . The experimental data were fitted to pseudo-first-order and pseudo-second-order equations. The kinetic model parameters are shown in Table 1. The correlation coefficient ( $R^2$ ) values show that the pseudo-second-order model (Fig. 3) is more suitable than the pseudo-first-order model (Fig. S1) for arsenic adsorption.

These results suggest that the adsorption of arsenic onto CuO nanoparticles follows pseudo-second-order kinetics, as shown in Fig. 3. At higher CuO nanoparticle concentrations, the rate constant of the pseudo-second-order equation was 36.18 g/mg min. However, at lower concentrations, the pseudo-second-order equation was 0.26 g/mg min (Fig. 4).

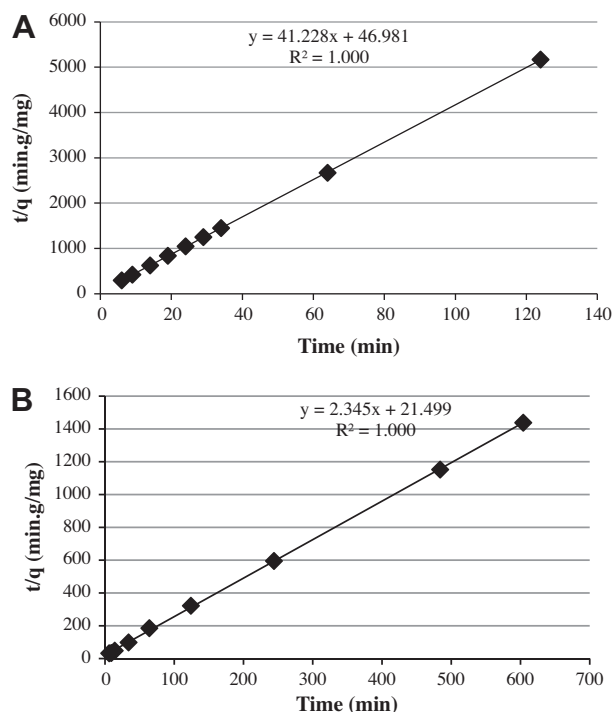
The rate values indicated that the removal of arsenic by CuO nanoparticles was faster at higher concentrations than in lower concentrations. These results agree with previous studies, which also predicted that arsenic adsorption by CuO followed pseudo-second-order kinetics [21].

#### 4.3. Adsorption of arsenic by CuO nanoparticles

The arsenic adsorption onto nanoparticles was studied by batch experiments with varying reaction times. The arsenic adsorbed per unit weight of nanoparticle as a function of time is shown in Fig. S2. The experimentally predicted  $q_{\text{eq}}$  values for 4.0 and 0.2 mg/L of CuO nanoparticles were very close to  $q_{\text{eq}}$  values estimated from pseudo-second-order kinetic model (Fig. S2 and Table 1). Initial adsorption of arsenic at both concentrations (4 and 0.2 mg/L) was very rapid. Within 30 min, most of the arsenic was adsorbed by CuO nanoparticles. At the lower concentration, CuO nanoparticle showed the highest capacity to adsorb arsenic. Moreover, arsenic adsorption per unit of nanoparticle was decreased with increasing concentrations of nanoparticle in solution. Therefore, it can be concluded that the removal of arsenic by CuO nanoparticles should be more favorable at a lower concentration than a higher one. These results are similar to recent CuO adsorbent dose effect studies reported by Goswami et al. [21]. In addition, Pena et al. [26] and Basu and Ghosh [27] also suggested similar results using titanium oxide and iron oxide, respectively.

**Table 1**  
Kinetic model parameters.

CuO (mg/L)	$R^2$	Rate constant, $k$ (g/mg min)	Model estimate, $q_{\text{eq}}$ (mg/g)	Experimental, $q_{\text{eq}}$ (mg/g)
<i>Pseudo-1st-order kinetic model</i>				
4.0	0.831	0.093	0.009	0.024
0.2	0.890	0.013	0.199	0.420
<i>Pseudo-2st-order kinetic model</i>				
4.0	1.000	36.18	0.0243	0.0240
0.2	1.000	0.26	0.4263	0.420



**Fig. 3.** Pseudo-second-order adsorption kinetics of arsenic (initial arsenic concentration = 100  $\mu\text{g/L}$ , CuO nanoparticle concentration, A = 4.0 g/L, and B = 0.2 g/L).

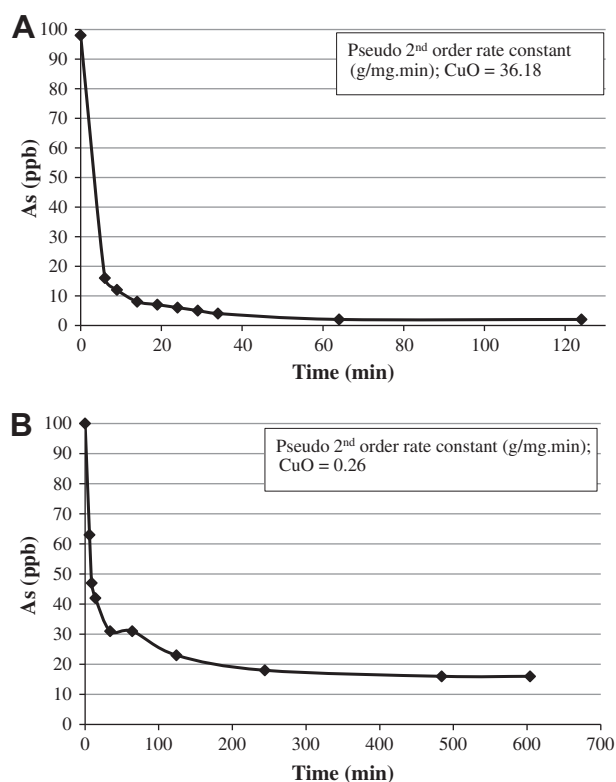
#### 4.4. Evaluation of flow-through reactor for arsenic removal

##### 4.4.1. Sand layer

Arsenic concentrations from the continuous flow-through reactor experiment with the sand layer only are shown in Table 2. Initially, arsenic concentration in groundwater decreased from 96 to 29  $\mu\text{g/L}$  after passing 1 L of spiked groundwater through the reactor. The initial variations in inlet versus outlet arsenic concentrations in groundwater are thought to be due to the capillary retention of water molecules by the sand particles in the pore spaces. This effect is diminished as more inlet water was passed through the reactor. After 20 L of inlet water passed through the reactor, arsenic concentration in groundwater was 83  $\mu\text{g/L}$ . The concentration of arsenic in the composite sample was 68  $\mu\text{g/L}$ . The pH and concentration of major and trace elements in groundwater with sand layer treatment did not change significantly (Table S3). The results shown in Table 2 suggest that the sand layer used in this study alone is not an effective media to remove arsenic from water.

##### 4.4.2. CuO nanoparticles with sand layer

Arsenic concentrations from the continuous flow-through reactor experiments with CuO nanoparticles followed by the sand layer are shown in Table 3. Two runs, before regeneration of CuO



**Fig. 4.** Pseudo-second-order rate constant of arsenic adsorption (initial arsenic concentration = 100  $\mu\text{g/L}$ , A = CuO nanoparticle concentration = 4.0 g/L, and B = CuO nanoparticle concentration = 0.2 g/L).

**Table 2**

Arsenic concentrations from continuous flow-through reactor experiment with sand layer.

Reaction time (min)	Volume (L)	pH	As ( $\mu\text{g/L}$ )
Control sample			
0	0.05	7.89	96.0
5	0.1	6.54	5.4
10	0.15	6.77	7.1
15	0.25	7.08	10
30	0.5	7.33	13.0
60	1.0	7.58	20.0
120	2.0	7.72	29.0
180	3.0	7.80	49.0
240	4.0	7.82	63.0
300	5.0	7.84	68.0
600	10.0	7.85	73.0
900	15.0	7.86	77.0
1200	20.0	7.83	82.0
Composite sample			
		8.02	68.0

nanoparticles, with 20 L of arsenic-spiked groundwater samples gave very similar results. The arsenic concentration decreased from 109 to 12.5  $\mu\text{g/L}$ . The pH ranged between 7.55 and 7.92. Initially, arsenic concentrations in groundwater sample remained below 10  $\mu\text{g/L}$ , up to 6 L of groundwater sample passing through the reactor. The CuO nanoparticle treatment did not show any discernible effects on major or trace element concentration (Table S4). Copper concentration in outlet sample increased from 0.051 to 0.210 mg/L. However, Cu concentrations in both inlet and outlet samples were below the US EPA MCL (maximum contaminant limit) of 1.3 mg/L. Other studies with CuO nanoparticles also reported that Cu concentration in treated water remains below the US EPA MCL [17–23,28]. For example, Martinson and Reddy [18] and Reddy

and Roth [19] studies have treated over fifty groundwater samples, collected from different western United States, with CuO and found similar results. The dissolved Cu concentration in all above studies remained well below the US EPA MCL limit. These results suggest that CuO nanoparticles are an effective material to remove arsenic from groundwater under a wide range of water chemistries.

#### 4.5. Regeneration of CuO nanoparticles

Regenerated CuO nanoparticles were found to be more effective than initial CuO nanoparticles in removal of arsenic from spiked groundwater sample (Table 3). This is probably due to renewed reactive surface area of regenerated CuO nanoparticles. The pH of outlet groundwater sample increased slightly from 7.56 to 7.83, whereas arsenic concentrations decreased effectively from 110 to 6.0  $\mu\text{g/L}$ . Initially, arsenic concentrations remained below 10  $\mu\text{g/L}$ , up to 14 L of groundwater sample passing through the reactor. The regenerated CuO nanoparticle treatment did not significantly affect the concentrations of major and trace elements in groundwater sample. In fact, Cu concentration decreased from 0.058 to 0.011 mg/L (Table S5) in treated groundwater sample. These results suggest that regenerated CuO nanoparticles can be used to remove arsenic from water. Arsenic mass balance data from regeneration of CuO nanoparticles are shown in Table 4. These results suggest that 99.4% of input arsenic concentration was recovered through the regeneration process.

#### 4.6. Arsenic removal from natural groundwater samples

The data for three natural groundwater samples treated with the continuous flow-through reactor are shown in Table 5. These results suggest that the CuO nanoparticle flow-through reactor effectively removed arsenic from groundwater samples without pH or redox potential adjustments or removing competing ions. Arsenic concentration in three samples remained well below the detection limit of 1  $\mu\text{g/L}$  after the treatment. These results are consistent with data from the 20 L arsenic-spiked groundwater experiments. The CuO nanoparticle treatment did not show any significant changes in pH or major and trace element concentrations (Table S6).

## 5. Conclusions

The emergence of natural arsenic in groundwater supplies in many parts of the world, which adversely affects the health of millions of people, has raised awareness for the need to develop an effective arsenic removal system. Conventional adsorbents (e.g., oxides of aluminum, iron, titanium, zirconium, and manganese) have various limitations such as the requirement of pH adjustments, oxidation of water, and removal of competing ions (e.g., phosphate, silicate, and sulfate). Also, disposal of waste sludge or spent media produced from the conventional sorbents is a problem. Recent studies demonstrate that CuO nanoparticles remove arsenic under a wide range of water chemistries without adjusting the pH or redox potential or removing the competing anions (e.g., phosphate, silicate, and sulfate). The results of this study suggest that arsenic adsorption process by CuO nanoparticles was kinetically rapid and follow the pseudo-second-order rate. These nanoparticles are easy to regenerate and can be reused to remove arsenic from water. Arsenic collected from the regeneration process can be recycled or used in industrial processes because the volume of regeneration fluids will be minimal. The regeneration process of CuO nanoparticles could also help avoid difficulties in the disposal of spent CuO nanoparticles. In addition, the removal of arsenic with CuO nanoparticle showed only minor effects on

**Table 3**  
Arsenic concentrations from continuous flow-through reactor experiments with CuO nanoparticles plus sand layer. A = CuO nanoparticles. B = regenerated CuO nanoparticles.

Time (min)	Volume (L)	A* = CuO nanoparticles		B = Regenerated CuO nanoparticles	
		pH	As ( $\mu\text{g/L}$ )	pH	As ( $\mu\text{g/L}$ )
	Control sample	7.55	109	7.56	110
0	0.05	5.98	1.5	6.76	<1.0
5	0.1	6.60	2.5	7.08	<1.0
10	0.15	6.36	2.5	7.21	<1.0
15	0.25	6.51	3.0	7.46	<1.0
30	0.5	6.78	2.5	7.59	<1.0
60	1.0	7.25	2.0	7.63	<1.0
120	2.0	7.08	3.0	7.53	<1.0
180	3.0	7.17	3.0	7.46	<1.0
240	4.0	7.48	5.5	7.41	1.0
300	5.0	7.46	6.5	7.47	2.0
360	6.0	7.44	8.5	7.5	2.0
420	7.0	7.52	11.0	7.50	2.0
480	8.0	7.54	11.5	7.53	3.0
540	9.0	7.48	12.5	7.54	4.0
600	10.0	7.69	12.5	7.61	5.0
660	11.0	7.54	14.0	7.53	6.0
720	12.0	7.57	15.5	7.49	7.0
780	13.0	7.55	16.5	7.5	8.0
840	14.0	7.63	18.5	7.57	8.0
900	15.0	7.63	19.0	7.55	10.0
960	16.0	7.66	20.5	7.55	10.0
1020	17.0	7.79	21.0	7.53	11.0
1080	18.0	7.62	21.0	7.59	13.0
1140	19.0	7.62	23.0	7.63	13.0
1200	20.0	7.66	23.0	7.59	14.0
	Composite sample	7.92	12.5	7.83	6.0

\* Average of two runs.

**Table 4**  
Arsenic mass balance data from the regeneration of CuO nanoparticles. Arsenic mass balance data for regeneration of CuO nanoparticles was calculated based on the second run. Initial arsenic concentration was 110  $\mu\text{g/L}$  and arsenic concentration in composite sample was 13  $\mu\text{g/L}$ .

Total arsenic in spiked groundwater	2.2 mg	Total arsenic in 182 mL of NaOH	0.43 mg
Total As remained in composite sample	0.26 mg	Total arsenic in 300 mL of distilled deionized water	1.50 mg
Total As removed by the CuO	1.94 mg	Total arsenic recovered in regeneration wash fluids	1.93 mg
Total % of arsenic recovered			99.4

**Table 5**  
Arsenic concentrations from continuous flow-through reactor experiments with natural groundwater samples.

Time (min)	Volume (L)	Well 1		Well 2		Well 3	
		pH	As ( $\mu\text{g/L}$ )	pH	As ( $\mu\text{g/L}$ )	pH	As ( $\mu\text{g/L}$ )
0	Control sample	7.60	12.0	7.39	12.0	7.48	15.0
0	0.05	6.55	<1.0	6.57	<1.0	6.39	<1.0
5	0.100	6.79	1.0	6.82	<1.0	6.47	<1.0
10	0.150	6.95	1.0	6.99	<1.0	6.75	<1.0
15	0.200	7.03	1.0	7.01	<1.0	6.84	<1.0
30	0.250	7.17	1.0	7.03	<1.0	7.04	<1.0
60	1.0	7.30	1.0	7.23	<1.0	7.18	<1.0
120	2.0	7.46	1.0	7.32	<1.0	7.31	<1.0
180	3.0	7.45	1.0	7.40	<1.0	7.36	<1.0
240	4.0	7.54	<1.0	7.46	<1.0	7.47	<1.0
300	5.0	7.52	1.0	7.49	<1.0	7.46	<1.0
	Composite sample	7.80	<1.0	7.70	<1.0	7.74	<1.0

the water chemistry (e.g., pH, major elements, and trace elements) of treated groundwater samples. The arsenic adsorption and desorption phenomenon of CuO nanoparticles demonstrated in this study, through the flow-through reactor experiments, shows potential in developing a practical one-step process for field applications.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2013.01.041>.

#### References

- [1] R.S. Oremland, J.F. Stolz, *Science* 300 (2003) 939.
- [2] A.H. Welch, D.B. Westjohn, D.R. Helsel, R.B. Wanty, *Ground Water* 38 (2000) 589.
- [3] M.N. Bates, A.H. Smith, C. Hopenhaynrich, *Am. J. Epidemiol.* 135 (1992) 462.
- [4] P. Bagla, J. Kaiser, *Science* 274 (1996) 174.
- [5] A.H. Smith, E.O. Lingas, M. Rahman, *Bull. World Health Org.* 78 (2000) 1093.
- [6] D.K. Nordstrom, *Science* 296 (2002) 2143.
- [7] M.L. Pierce, C.B. Moore, *Water Res.* 16 (1982) 1247.
- [8] E.O. Kartinen, C.J. Martin, *Desalination* 103 (1995) 79.
- [9] S. Bajpai, M. Choudhari, *J. Environ. Eng.* 125 (1999) 782.
- [10] S. Bang, G.P. Korfiatis, X. Meng, *J. Hazard. Mater.* 121 (2005) 61.
- [11] V. Lenoble, C. Laclautre, B. Deluchat, B. Serpaud, J.C. Bollinger, *J. Hazard. Mater.* 123 (2005) 262.

- [12] D. Mohan, C.U. Pittman, J. Hazard. Mater. 142 (2007) 1.
- [13] H. Chiw, M.L. Sampson, S. Huch, S. Ken, B.C. Bostick, Environ. Sci. Technol. 43 (2009) 6295.
- [14] Md. Shafiquzzaman, Md. Shafiul Azam, I. Mishima, J. Nakajima, J. Health Popul. Nutr. 27 (2009) 674.
- [15] M. Husain, <[http://sos-arsenic.net/english/mitigation/update\\_miti.html#sec4.5](http://sos-arsenic.net/english/mitigation/update_miti.html#sec4.5)> (accessed 31.08.12).
- [16] R.B. Johnston, S. Hanchett, M.H. Khan, Nature Geosci. 3 (2010) 2.
- [17] K.J. Reddy, A. Viswatej, in: The 8th International Conference on Biogeochemistry of Trace Elements, Adelaide, Australia, 2005.
- [18] C.A. Martinson, K.J. Reddy, J. Colloid Interface Sci. 336 (2009) 406.
- [19] K.J. Reddy, T.R. Roth, Groundwater, DOI: <http://dx.doi.org/10.1111/j.1745-6584.2012.00926.x>, 2012.
- [20] P. Pillewan, S. Mukherjee, T. Roychowdhury, S. Das, A. Bansiwala, S. Rayalu, Hazard. Mater. 186 (2011) 367.
- [21] A. Goswami, P.K. Raul, M.K. Purkait, Chem. Eng. Res. Des. 90 (2012) 1387.
- [22] G. Zhang, Z. Ren, X. Zhang, J. Chen. Water Res., in press, (Special Issue: Nanotechnology).
- [23] J.R. Schilz, K.J. Reddy, S. Nair, T.E. Johnson, R.B. Tjalkens, K.P. Krueger, S. Clark, in: 12th International Conference on the Biogeochemistry of Trace Elements, 2013, Athens, Georgia.
- [24] Wyoming Department of Environmental Quality. SAP: Water Quality Rules and Regulations; Chapter 1; Department of Environmental Quality and Water Quality Division, Cheyenne, WY, 2001b; <[http://www.deq.state.wy.us/wqd/WQDrules/Chapter\\_01.pdf](http://www.deq.state.wy.us/wqd/WQDrules/Chapter_01.pdf)>, 2011.
- [25] G. Blanchard, M. Maunay, G. Martin, Water Res. 18 (1984) 1501.
- [26] M.E. Pena, G.P. Korfiatis, M. Patel, L. Lippincott, X. Meng, Water Res. (2005) 2327.
- [27] T. Basu, U.C. Ghosh, Desalination 266 (2011) 25.
- [28] T.R. Roth, K.J. Reddy, K.J. Arsenic in the environment and its remediation by a novel filtration method, in: J. Bundschuh, M.A. Armienta, P. Birkle, P. Bhattacharyya, J. Matschullat, A.B. Mukherjee (Eds.), Natural arsenic in groundwaters of Latin America: Arsenic in the Environment, vol. 1, CRC Press, London, UK, 2009, pp. 605–614.