Arsenic Removal from Natural Groundwater Using Cupric Oxide

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Abstract

Groundwater is a main source of drinking water for some rural areas. People in these rural areas are potentially at risk from elevated levels of arsenic (As) due to a lack of water treatment facilities. The objectives of this study were to (1) measure As concentrations in approximately 50 groundwater samples from rural domestic wells in the western United States, (2) explore the potential of cupric oxide (CuO) particles in removal of As from groundwater samples under natural conditions (i.e., without adding competing anions and adjusting the pH or oxidation state), and (3) determine the effects of As removal on the chemistry of groundwater samples. Forty-six groundwater well samples from rural domestic areas were tested in this study. More than 50% of these samples exceeded the U.S. Environmental Protection Agency Maximum Contaminant Limit (US EPA MCL) of 10 µg/L for As. CuO particles effectively removed As from groundwater samples across a wide range of pH (7.11 and 8.95) and concentrations of competing anions including phosphate (<0.05 to 3.06 mg/L), silica (<1 to 54.5 mg/L), and sulfate (1.3 to 735 mg/L). Removal of As showed minor effects on the chemistry of groundwater samples, therefore most of the water quality parameters remained within the US EPA MCLs. Overall, results of this study could help develop a simple one-step process to remove As from groundwater.

Introduction

Global health awareness of arsenic (As) contamination of drinking water supplies has increased enormously in recent years in response to unintentional human exposure to As poisoning through groundwater supplies in India and Bangladesh (Bagla and Kaiser 1996; Smith et al. 2000). Subsequently, several studies have reported that groundwater in many parts of the world contains elevated levels of As (Matschullat 2000; Welch et al. 2000; Nordstrom 2002; Chakraborti et al. 2003; Smith et al. 2003; Xia and Liu 2004; Martinson and Reddy 2009; Mukherjee et al. 2009; Trang et al. 2009). Studies have shown that long-term human exposure to drinking water containing

As in excess of 50 µg/L causes increased risk of skin, lung, bladder, and kidney cancer and increased risk of premature death (Bates et al. 1992). Both the World Health Organization and the US EPA recommend 10 µg/L of As as the limit for human drinking water.

Arsenic in groundwater can be mobilized by natural processes and anthropogenic activities. The natural processes include weathering of aquifer minerals. Anthropogenic activities include but are not limited to in situ extraction of coal bed natural gas and uranium (Jackson and Reddy 2007; Sowder et al. 2010). Groundwater is an important drinking water resource for many people. In the western United States, millions of people in rural areas depend on groundwater for drinking water. To our knowledge limited data is available in documenting As levels in groundwater of rural areas of the western United States. These rural areas may be at high risk for potential As-related health problems due to a lack of water treatment facilities.

Widespread efforts are being made globally to develop effective and affordable technologies for removal of As from water. Arsenic in water exists in two oxidation

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states, arsenite (III) and arsenate (V), and it is difficult to remove both oxidation states simultaneously under a wide range of pHs and different concentrations of competing anions (Oremland and Stolz 2003; Mohan and Pittman 2007). Conventional adsorbents such as aluminum, iron, titanium, zirconium, and manganese were studied extensively to remove As from water (Pierce and Moore 1982; Kartinen and Martin 1995; Bajpai and Chaudhuri 1999; Zeng 2003; Bang et al. 2005; Lenoble et al. 2005; Mohan and Pittman 2007). However, these conventional As adsorbents have various limitations. Some of these limitations include requirement of pH adjustments, oxidation of As (III) to As (V), preferential adsorption of As (V) over As (III), and competition of anions (e.g., phosphate, silicate, and sulfate) with As for adsorption sites (Jain and Loeppert 2000; Meng et al. 2000). Because of these problems, field application of conventional adsorbents to filter As is limited (Chiw et al. 2009; Pillewan et al. 2011).

Reddy and Viswatej (2005) studies found that cupric oxide (CuO) was an effective As adsorbent because it did not require pH or redox potential adjustments and it performed well in the presence of competing anions. In addition, these studies reported that CuO can be regenerated, by leaching with sodium hydroxide (NaOH) solution, and the regenerated CuO can be reused to remove As from water. Subsequently, Reddy (2007, 2011) received two U.S. patents (US 7,235,179 B2 and US 7,897,052 B2) for these discoveries. These studies attributed the effective removal of As by CuO to its high zero point of charge (ZPC) of 9.4 $\pm$ 0.4 (Yoon et al. 1979). Martinson and Reddy (2009) examined the effects of competing anions, particularly silica, sulfate, and phosphate, and the mechanism of the adsorption of As (III) and As (V) by the CuO surface. These studies attributed the effective adsorption of As species to the oxidation of As (III) to As (V) by the surface of CuO. Recently, Pillewan et al. (2011) conducted in-depth studies of As removal from water using CuO incorporated mesoporous alumina. These studies also reported similar results.

Previous As removal studies have shown that phosphate, silica, and sulfate, which are common anions of water, compete with As for adsorbent surface sites. Among these competing anions, phosphate has shown a major effect on As removal (Meng et al. 2000, 2002; Roberts et al. 2004). Martinson and Reddy (2009) conducted a detailed study to determine the effect of competing ions in removal of As by CuO particles. In these studies, 0.9 mg/L of As (III) and As (V) solutions were spiked with 20, 100, and 500 mg/L of phosphate, silica, and sulfate. The high concentrations of competing anions were used in these experiments to force the competition. Results suggested that even in the presence of 20 mg/L of phosphate, CuO particles were able to remove 83% of As (III) and almost 100% As (V) from water. Other competing anions in solutions showed little or no effect in removal of As by CuO particles. Martinson and Reddy (2009) also treated over 30 groundwater samples using CuO particles and reported an excellent As removal rate

(>90%). Even though groundwater samples in these studies had significant concentrations of silica and sulfate, the phosphate concentrations were below the detection limit of 0.05 mg/L.

The As removal studies often examine the effects of competing anions by spiking an individual anion or multiple anions, because it is difficult to study simultaneous competition effects of competing anions under natural conditions. However, it is important to study the effectiveness of As removal by adsorbents under natural conditions in the presence of multiple competing anions (e.g., sulfate, silicate, and phosphate), because such information could help develop a practical As filtration method for field applications. The objectives of this study were to (1) measure As concentrations in approximately 50 groundwater samples from rural domestic wells in the western United States, (2) study the effectiveness of CuO particles in removal of As from groundwater under natural conditions, that is, without adjusting the pH, oxidation state, or spiking with competing anions (e.g., phosphate, silica, and sulfate), and (3) determine the effects of CuO treatment on the chemistry of groundwater samples.

Materials and Methods

All chemicals used in this research including copper (II) chloride (CuCl$_2$·2H$_2$O) and NaOH were ACS (analytical standard) grade.

Preparation of CuO Particles

CuO particles were precipitated by reacting 2 M of NaOH (98.6%, Sigma-Aldrich, St. Louis, Missouri) with 1 M of copper (II) chloride (CuCl$_2$·2H$_2$O, 99.99%, Sigma-Aldrich) at room temperature. The CuO particles were separated from the solution by filtering through the Whatman grade 1 medium fast qualitative filter paper and washed several times with distilled water until the filtrate pH was around 7. The CuO particles were dried approximately at 250 to 300 °C, ground with mortar and pestle, and were subjected to powdered X-ray diffraction analyses (XRD), particle size, and Brunauer-Emmett-Teller (BET) surface analysis. The XRD analysis was conducted with SCINTAG XDS 2000. The particle size was estimated from the scanning electron microscope (SEM) analysis using SEM instrument (JOEL JSM-5800LV). The BET surface area was determined by dinitrogen (N$_2$) adsorption using a Tristar 3000. Samples were dried under N$_2$ at 110 °C for 15 h prior to BET analysis.

Collection of Groundwater Samples

We identified approximately 50 rural domestic wells without water treatment facilities in the western United States for groundwater sampling. These domestic wells were from Colorado, Montana, Nevada, South Dakota, Utah, and Wyoming. The Cooperative State Research, Education, and Extension Service (CSREES) water quality coordinators in these states helped us to identify these landowners. Forty-six groundwater samples were collected from these private wells (Table 1). All

Table 1
Well ID, State, pH, ORP, and EC of Groundwater Samples Collected from Rural Domestic Wells in the Western United States

Well ID	State	pH	ORP (mV)	EC (μS/cm)
1	CO	7.94	−76	222
2	CO	8.12	−80	228
3	CO	8.14	−73	242
4	CO	8.12	−53	753
5	CO	8.46	−64	722
6	CO	7.84	−29	302
7	CO	7.56	−53	318
8	CO	7.28	−35	565
9	CO	8.32	−90	183
10	CO	8.22	−83	230
11	CO	8.36	−98	167
12	MT	8.15	−28	473
13	MT	8.35	−20	612
14	MT	8.16	−25	753
15	MT	7.71	−43	265
16	MT	8.23	−34	560
17	MT	7.97	−27	426
18	MT	7.27	−29	565
19	SD	7.81	−32	1524
20	SD	8.31	−86	351
21	SD	8.04	−25	1530
22	SD	7.57	−41	452
23	SD	7.53	−41	413
24	SD	7.11	−15	473
25	SD	7.59	−35	124
26	SD	8.18	−44	294
27	UT	8.65	−25	414
28	UT	8.38	−33	429
29	UT	8.00	−20	695
30	UT	7.41	−80	211
31	UT	7.99	−15	477
32	UT	8.25	−27	560
33	UT	8.62	−45	228
34	WY	8.00	−58	598
35	WY	7.41	−9	834
36	WY	7.36	−17	381
37	WY	7.56	−17	1036
38	WY	7.64	−22	723
39	WY	7.91	−35	1114
40	WY	7.92	−37	1064
41	WY	8.39	−81	1018
42	WY	8.06	−48	638
43	NV	8.10	−24	380
44	NV	8.53	44	346
45	NV	8.95	−15	576
46	NV	8.91	29	645

groundwater sample were measured on site with Thermo Orion 5 Star portable meter. Samples were filtered with 0.45 μm filters within 24 h of collection, and subsamples were preserved by lowering the pH to approximately 2.0 with concentrated nitric acid following the WDEQ standards. Samples were kept in HDPE bottles with zero headspace at 2 °C after being collected. Acidified samples were analyzed for major and trace elements (calcium [Ca], sodium [Na], magnesium [Mg], potassium [K], arsenic [As], chromium [Cr], silica [Si], copper [Cu], iron [Fe], manganese [Mn], lead [Pb], and selenium [Se]) with inductively coupled plasma—mass spectrometry (ICP-MS, AGILENT 7500e, Santa Clara, California). The ICP-MS is a simple procedure and offers a better sensitivity for As and other elements when compared with other techniques, like graphite furnace atomic absorption. In an ICP-MS analytical procedure, a acidified sample solution is sprayed into high-temperature plasma, which will atomize and ionize the water sample. From the mass spectrum of the plasma, the data can be obtained for almost the entire periodic table.

The unacidified samples were analyzed for sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), and phosphate (PO_4^{3-}) with ion chromatography (IC, DIONEX DX 500, Sunnyvale, California). In this procedure, a small volume of sample is injected into IonPac AS14 column with autosampler (As50). The anions adsorbed on the column are separated with eluent solution consisting of 3.4 mM sodium carbonate and 1.0 mM sodium bicarbonate. The concentration of separated anion is measured with a conductivity detector.

CuO Treatment Studies

Most groundwater samples with As concentrations greater than 11 μg/L were subjected to CuO treatment studies (Table 2). The As removal studies were conducted by reacting 50 mL of each groundwater sample with 0.5 g of CuO particles in centrifuge tubes for 30 min on a mechanical shaker at 150 rpm. Suspensions were centrifuged for 2 to 3 min; solutions were filtered through 0.45 μm filters. Each clear filtrate was divided into two subsamples. One subsample was acidified with nitric acid, and the other subsample was left unacidified. Acidified samples were analyzed for major and trace elements, such as Ca, Na, Mg, K, As, Cr, Si, Cu, Fe, Mn, Pb, and Se with ICP-MS (AGILENT 7500e). Unacidified samples were analyzed for pH as well as anions (SO_4^{2-}, Cl^-, NO_3^-, and PO_4^{3-}). The pH was measured with Thermo Orion 5 Star model and anions were analyzed with IC (DIONEX DX 500).

Results

The XRD confirmed that CuO prepared in the laboratory was clean without any other phases present in detectable amounts. This was confirmed by comparing a sample X-ray pattern to the reference pattern 41-254 in the Joint Committee for Powder Diffraction Studies reference file (Geyer and Eysel 1989). The particle size of the CuO was ≤5 μm and surface area was 21.656 m^2/g.

groundwater samples were collected following the guidelines of the Wyoming Department of Environmental Quality (WDEQ) in the manual of standard operating procedures for sample collection and analysis.

High-density polyethylene (HDPE) 1000 mL bottles were used for sample collection. Before collection of samples, wells were purged until water quality indicator (e.g., pH) was stable. The pH, oxidation and reduction potential (ORP), and electrical conductivity (EC) of each

Table 2
Chemistry of Groundwater Samples Collected from Rural Domestic Wells in the Western United States

Well ID	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Fe (mg/L)	Cu (mg/L)	Mn (µg/L)	Pb (µg/L)	As (µg/L)	Se (µg/L)	Cr (µg/L)	Si (mg/L)	Cl⁻ (mg/L)	PO₄³⁻ (mg/L)	SO₄²⁻ (mg/L)
1*	42.5	6.7	0.3	11	<0.1	0.05	1.6	<0.1	53.1*	3.5	2.2	50.4	6.8	0.3	11.5
2*	45.1	5.0	0.1	8.1	<0.1	0.02	2.6	<0.1	81.5*	4.3	1.4	51.1	2.7	<0.05	10.7
3*	46.1	6.7	0.3	12.0	<0.1	0.03	3.9	<0.1	50.9*	1.7	1.7	54.5	5.5	0.3	15.1
4*	122	28.1	8.3	16.0	<0.1	0.05	0.6	0.7	29.0*	9.6	6.7	16.1	33.4	0.7	97.4
5*	143	15.6	4.6	13.0	<0.1	0.02	0.2	<0.1	33.3*	16.1	7.5	12.9	22.6	<0.05	91.9
6*	11.4	28.8	8.6	11.9	0.1	0.02	0.4	0.6	11.3*	1.4	6.2	25.6	7.9	0.1	8.4
7	10.2	37.0	10.6	8.2	0.2	<0.01	<0.1	<0.1	8.3	<0.1	<0.1	26.9	1.81	0.22	6.79
8	30.0	64.2	13.5	10.3	0.2	<0.01	<0.1	2.8	8.0	5.1	<0.1	24.6	38.8	<0.05	33.81
9*	33.0	4.3	0.2	8.8	<0.1	0.01	0.1	0.5	20.5*	0.9	3.7	47.3	6.8	0.1	7.4
10*	43.9	5.3	0.2	4.7	<0.1	0.01	4.1	0.2	17.2*	0.4	4.1	39.9	2.8	<0.05	7.4
11	35.1	3.8	<0.1	3.6	<0.1	<0.01	<0.1	<0.1	8.8	<0.1	<0.1	47.3	0.7	<0.05	5.92
12*	28.3	45.5	15.3	2.1	0.1	0.01	1860	<0.1	15.3*	3.3	6.5	10.6	2.9	<0.05	1.3
13*	64.1	41.4	12.0	16.8	0.1	0.05	1.0	<0.1	102*	3.3	6.9	31.8	18.9	<0.05	29.9
14*	82.8	55.0	13.1	6.2	0.1	<0.01	427	<0.1	71.3*	3.3	7.2	21.3	33.0	2.6	49.8
15*	17.7	23.5	7.1	3.5	<0.1	0.045	4.0	<0.1	15.9*	1.1	1.6	10.9	9.9	<0.05	32.5
16*	52.4	49.0	11.5	10.0	0.1	0.01	0.9	<0.1	14.4*	3.5	2.3	24.3	13.1	<0.05	59.7
17*	10.7	60.0	10.1	4.1	0.1	0.03	3.6	<0.1	20.9*	1.8	<0.1	10.2	2.9	<0.05	113.1
18	102	29.0	5.8	3.7	0.1	<0.01	<0.1	<0.1	8.9	<0.1	<0.1	25.7	5.39	<0.05	12.95
19*	55.5	138	74.1	4.6	0.4	0.01	7.3	<0.1	30.8*	1.7	8.3	14.0	2.8	<0.05	458
20	816	7.5	2.3	7.0	0.1	0.01	16.3	<0.1	2.2	5.8	1.7	4.1	303	<0.05	735
21*	328	28.6	13.4	9.7	0.1	<0.01	4.9	<0.1	34.1*	0.6	8.5	14.9	24.6	<0.05	241
22	70.3	24.1	3.2	10.8	0.1	<0.01	43.4	<0.1	10.4	<0.1	0.8	32.8	1.1	<0.05	20.6
23	7.1	44.0	22.0	3.4	0.1	<0.01	0.4	<0.1	10.2	19.2	1.0	5.3	2.5	<0.05	16.1
24	1.7	58.7	26.6	1.5	0.6	0.051	20.3	9.8	4.0	0.5	1.3	5.0	1.1	<0.05	5.2
25*	9.2	11.2	2.7	2.1	<0.1	0.01	0.3	<0.1	13.4*	1.4	0.2	13.5	3.9	0.2	7.5
26*	2.2	47.7	8.1	1.0	0.1	<0.01	0.7	<0.1	19.0*	1.3	0.8	7.4	1.6	<0.05	11.0
27	54.8	5.0	2.4	1.2	<0.1	0.01	1.9	<0.1	10.9	<0.1	0.5	10.0	27.1	<0.05	17.1
28	53.9	16.3	9.4	3.4	0.1	<0.01	1.6	<0.1	10.0	<0.1	2.0	18.1	41.0	<0.05	28.1
29	59.0	27.3	14.0	4.2	0.1	0.012	0.7	<0.1	9.0	<0.1	4.9	17.5	68.3	<0.05	113
30	3.8	15.2	5.2	1.0	0.1	0.013	0.2	2.0	10.8	<0.1	1.3	4.1	8.77	<0.05	12.5
31*	13.8	55.2	13.7	6.3	0.2	0.014	0.4	0.6	19.8*	1.2	4.1	8.0	16.3	<0.05	35.1
32*	126	2.8	0.7	8.4	<0.1	0.02	5.6	0.7	21.1*	0.8	7.8	4.3	11.6	0.2	44.0
33	9.1	17.5	4.5	2.0	<0.1	<0.01	<0.1	<0.1	8.1	<0.1	<0.1	15.5	3.73	<0.05	2.4
34	13.7	76.4	20.3	2.6	0.3	0.065	0.5	0.4	1.7	5.5	1.1	5.9	2.9	<0.05	138
35	29.1	94.6	34.4	1.7	1.2	<0.01	25.7	0.2	1.1	1.6	1.3	8.3	6.2	<0.05	174
36	11.9	43.2	12.9	1.7	0.6	0.08	5.2	0.8	0.4	0.8	1.6	5.7	2.2	<0.05	35.0
37	44.1	140	19.1	2.3	0.5	<0.01	195	0.2	<0.1	<0.1	0.7	9.2	7.5	<0.05	389
38	82.1	60.7	5.9	1.3	0.3	<0.01	69	<0.1	<0.1	<0.1	0.3	7.4	5.1	<0.05	189
39	62.2	100	41.4	1.9	0.5	<0.01	145	<0.1	0.4	<0.1	0.2	10	5.7	<0.05	313
40	193	30.0	7.9	1.8	0.3	<0.01	20.2	0.8	<0.1	<0.1	1.5	4.8	5.5	<0.05	241
41	208	5.3	<0.1	0.4	0.1	<0.01	1.7	0.4	5.5	<0.1	0.4	5.0	24.6	<0.05	260
42*	56.1	18.5	9.0	14.8	<0.1	0.023	1.3	0.3	12.4*	2.0	6.2	29.2	14.9	0.3	38.7
43*	97.4	3.3	0.8	7.2	<0.1	0.013	2.4	<0.1	56.8*	<0.1	<0.1	<1	18.1	0.1	61.5
44*	89.7	<1	<0.1	3.3	0.2	0.036	23.6	<0.1	142*	7.2	<0.1	<1	6.72	1.1	42.2
45*	189	<1	<0.1	3.2	0.3	0.018	22.0	2.4	302*	<0.1	<0.1	19.0	7.4	3.06	32.8
46*	216	<1	<0.1	4.0	0.2	0.023	33.1	1.8	398*	<0.1	<0.1	20.0	11.1	2.7	35.4
Min.	1.7	<1	<0.1	1.0	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<1	0.7	<0.05	1.3
Max.	816	140	74.1	16.8	1.2	0.08	1860	9.8	398	19.2	8.5	54.5	303	3.06	735

*Samples tested for As removal studies.

Chemistry of Groundwater Samples

The pH ranged between 7.11 and 8.95 and ORP was between −98 and 44 mV. These results suggest that groundwater samples were neutral to slightly alkaline and moderately reduced (Table 1). The salt concentration, as measured by EC, for most of the wells was reasonable except for a few wells in SD and WY, which were high. For example, EC for well 21 (SD) was 1530 µS/cm.

Concentrations of major elements in mg/L were between 1.7 to 816 (Na), <1 to 140 (Ca), <0.1 to 74.1 (Mg), and 1.0 to 16.8 (K) (Table 2). Concentrations of major anions in mg/L were between <1 to 54.5 (Si),
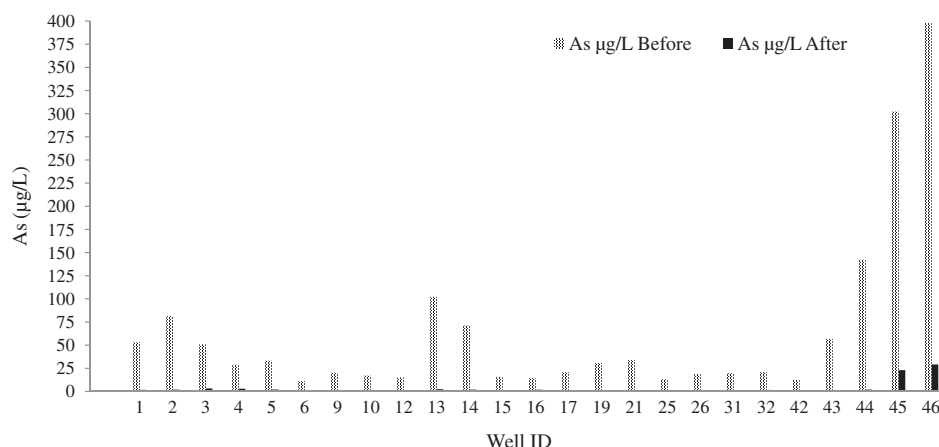

Figure 1. Effect of CuO treatment on As concentrations in groundwater samples. US EPA MCL for As is 10 µg/L.

0.70 to 303 (Cl^-), <0.05 to 3.06 (PO_4^{3-}), and 1.3 to 735 (SO_4^{2-}). The Fe concentrations were low and ranged between nondetectable and 1.2 mg/L, and Cu concentrations were between <0.01 and 0.08 mg/L. The Mn concentrations were generally low, except for one sample, which showed an unusually high concentration of 1.86 mg/L (1860 µg/L). Trace element concentrations in µg/L across all samples were very low and ranged between <0.1 to 9.8 (Pb), <0.1 to 19.2 (Se), and <0.1 to

8.5 (Cr). The As concentrations in groundwater samples ranged from nondetectable to as high as 398 µg/L. Out of 46 groundwater samples tested, 29 samples exceeded the US EPA MCL of 10 µg/L for As (Table 2). However, As concentrations in samples 13, 44, 45, and 46 were almost 10 to 40 times higher than the US EPA MCL 10 µg/L. These results show that groundwater samples tested in this research cover a wide range of water chemistries.

Table 3
Trace Element Concentrations Before and After Removal of As from Groundwater Samples

Well ID	As (µg/L) Before	As (µg/L) After	Cu (µg/L) Before	Cu (µg/L) After	Mn (µg/L) Before	Mn (µg/L) After	Pb (µg/L) Before	Pb (µg/L) After	Cr (µg/L) Before	Cr (µg/L) After	Se (µg/L) Before	Se (µg/L) After
1	53.1	1.8	50.0	40.0	1.6	0.1	<0.1	1.8	2.2	3.0	3.5	2.1
2	81.5	2.0	20.0	40.0	2.6	<0.1	<0.1	1.4	1.4	3.2	4.3	1.6
3	50.9	3.3	30.0	70.0	3.9	<0.1	<0.1	1.6	1.7	10	1.7	17.7
4	29	2.9	50.0	50.0	0.6	<0.1	0.7	0.9	6.7	8.8	9.6	8.2
5	33.3	2.1	20.0	60.0	0.2	<0.1	<0.1	0.3	7.5	9.4	16.1	15.2
6	11.3	0.1	20.0	30.0	0.4	0.1	0.6	0.3	6.2	4.8	1.4	1.0
9	20.5	0.6	20.0	10.0	0.1	0.2	0.5	0.3	3.7	4.6	0.9	0.7
10	17.2	0.4	10.0	10.0	4.1	0.2	0.2	0.2	4.1	5.2	0.4	0.3
12	15.3	1.1	10.0	980	1860	361	<0.1	3.2	6.5	9.5	3.3	0.8
13	102	2.4	50.0	580	1.0	0.2	<0.1	4.6	6.9	9.5	3.3	1.7
14	71.3	2.0	<10.0	40.0	427	81.7	<0.1	<0.1	7.2	10.8	3.3	1.7
15	15.9	0.8	50.0	30.0	4.0	0.1	<0.1	<0.1	1.6	2.9	1.1	<0.1
16	14.4	1.9	<10.0	80.0	0.9	0.1	<0.1	0.2	2.3	7.9	3.5	5.6
17	20.9	0.1	30.0	30.0	3.6	0.1	<0.1	<0.1	<0.1	2.4	1.8	<0.1
19	30.8	0.2	<10.0	10.0	7.3	45	<0.1	<0.1	8.3	9.8	1.7	<0.1
21	34.1	0.7	<10.0	220	4.9	3.1	<0.1	<0.1	8.5	18.0	0.6	1.0
25	13.4	1.5	10.0	30.0	0.3	<0.1	<0.1	<0.1	0.2	<0.1	1.4	2.8
26	19	0.7	<10.0	20.0	0.7	<0.1	<0.1	<0.1	0.8	2.2	1.3	1.8
31	19.8	0.4	14.0	30.0	0.4	0.1	0.6	0.6	4.1	8.7	1.2	0.4
32	21.1	1.7	20.0	30.0	5.6	0.1	0.7	0.5	7.8	10.8	0.8	0.2
42	12.4	0.4	23.0	30.0	1.3	0.2	0.3	0.3	6.2	8.1	2.0	2.0
43	56.8	1.2	13.0	30.0	2.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
44	142	2.0	46.0	80.0	23.6	3.5	<0.1	<0.1	<0.1	<0.1	7.2	2.5
45	302	23.0	20.0	420	22.0	7.0	2.4	0.4	<0.1	<0.1	<0.1	<0.1
46	398	29.1	30.0	250	33.1	5.5	1.8	0.2	<0.1	<0.1	<0.1	<0.1
US EPA MCLs	10		1300		50		15		100		50	

Treatment Effect on As, Cu, Mn, Pb, Cr, and Se

The CuO particles effectively lowered As concentrations across all samples, and removal rates were between 86 and 100% (Figure 1 and Table 3). In all treated samples As concentrations were well below the US EPA MCL of 10 µg/L, except for samples 45 and 46. The CuO treatment lowered As concentrations (µg/L) in these two samples from 302 to 23 (sample 45) and 398 to 29.1 (sample 46).

The CuO treatment did not show any discernible effects on trace element concentrations (Cu, Mn, Pb, Cr, and Se) in groundwater (Table 3). The US EPA MCLs for these trace elements were also included into Table 3 for comparison. The Fe concentrations did not change in most of the samples after the removal of As and were very low; therefore, Fe concentrations were not included in Table 3. Copper concentrations in groundwater samples increased slightly after the removal of As, except for a few samples. For example, in sample 12 the Cu concentration increased from 10 to 980 µg/L. However, Cu concentrations in both treated and untreated samples were below the US EPA MCL of 1300 µg/L. In most of the samples CuO treatment lowered the Mn concentrations. Before the CuO treatment, the Mn concentrations in samples 12 and 14 were 1860 and 427 µg/L, respectively. These levels of Mn concentrations in groundwater are not common. However, CuO treatment lowered Mn concentrations by 80% in these two groundwater samples. Except

for these two samples, the Mn concentrations in the rest of the samples, before or after the treatment, were well below the US EPA MCL of 50 µg/L (Table 3). Other trace element concentrations (Pb, Cr, and Se) in groundwater samples were similarly low before and after the treatment (below US EPA MCLs, Table 3).

Treatment Effect on pH, Na, Ca, Mg, K, Cl^-, SO_4^{2-}, Si, and PO_4^{3-}

The addition of CuO to the groundwater samples could affect the pH, and consequently could affect the concentration of major cations (Na, Ca, Mg, and K). Therefore, it is important to examine the effect of CuO treatment on the concentration of major cations in groundwater samples. The CuO treatment showed very little effect on the pH of the samples (Table 4). Most of the sample pHs were slightly lower in treated samples. The pHs of both treated and untreated samples were within the range of US EPA MCL of 6.5 to 8.5, except for samples 45 and 46, which were slightly above the limit. However, CuO treatment was able to lower the pH of these samples from approximately 8.9 to 8.7. The CuO treatment and As removal showed very little or no change in concentrations of Na, Ca, Mg, and K, except for a few samples (Table 4). Concentrations of these elements in groundwater samples were almost identical before and after the removal of As.

The CuO ZPC occurs in water at pH 9.4 ± 0.4. Below this pH the net electrical charge on the CuO surface in

Table 4
Analytical Data for pH, Na, Ca, Mg, and K Before and After Removal of As from Groundwater Samples

Well ID	pH Before	pH After	Na (mg/L) Before	Na (mg/L) After	Ca (mg/L) Before	Ca (mg/L) After	Mg (mg/L) Before	Mg (mg/L) After	K (mg/L) Before	K (mg/L) After
1	7.94	7.74	42.5	42.4	6.7	6.2	0.3	0.5	11.0	6.7
2	8.12	7.89	45.1	45.1	5.0	4.6	0.1	0.3	8.1	7.4
3	8.14	7.9	46.1	45.0	6.7	13.7	0.3	4.6	12.0	10.4
4	8.12	8.14	122	119	28.1	25.4	8.3	8.1	16.0	13.8
5	8.46	8.32	143	138	15.6	13.8	4.6	4.5	13.0	10.0
6	7.84	7.81	11.4	10.6	28.8	28.9	8.6	9.0	11.9	7.4
9	8.32	7.96	33.0	34.4	4.3	4.2	0.2	0.5	8.8	6.7
10	8.22	7.91	43.9	44.3	5.3	4.9	0.2	0.5	4.7	4.4
12	8.15	8.23	28.3	29.4	45.5	44.1	15.3	15.4	2.1	3.0
13	8.35	8.2	64.1	64.9	41.4	36.1	12.0	11.6	16.8	17.2
14	8.16	8.15	82.8	81.6	55.0	52.7	13.1	12.7	6.2	6.4
15	7.71	7.67	17.7	18.5	23.5	22.5	7.1	7.2	3.5	4.3
16	8.23	8.15	52.4	51.6	49.0	45.5	11.5	11.2	10.0	11.9
17	7.97	7.89	10.7	11.7	60.0	58.2	10.1	10.2	4.1	5.3
19	7.81	7.86	55.5	56.9	138	166	74.1	74.5	4.6	5.5
21	8.04	8.05	329	319	28.6	47.3	13.4	13.0	9.7	10.0
25	7.59	7.47	9.2	9.6	11.2	11.2	2.7	2.9	2.1	2.7
26	8.18	7.98	2.2	2.4	47.7	46.4	8.1	8.5	1.0	1.3
31	7.99	8.01	13.8	13.4	55.2	54.0	13.7	13.9	6.3	2.8
32	8.25	8.26	126	127	2.8	2.4	0.7	0.9	8.4	3.8
42	8.06	8.03	56.1	56.2	18.5	17.9	9.0	9.2	14.8	8.0
43	8.1	7.87	97.4	95.0	3.3	3.0	0.8	0.9	7.2	7.1
44	8.53	8.23	89.7	85.0	<0.1	<0.1	<0.1	<0.1	3.3	4.0
45	8.95	8.77	189	185	<0.1	<0.1	<0.1	<0.1	3.2	3.0
46	8.91	8.75	216	218	0.1	0.4	0.1	0.2	4.0	3.8

water will be positive (+). Since the pH of groundwater samples were below 9.4, the CuO surface becomes positive (+) in samples. The positive surface of CuO could adsorb anions present in the samples. The CuO treatment and As removal showed very little or no change in concentrations of Cl^- and SO_4^{2-}, except for a few samples (Table 5). Concentrations of these elements in groundwater samples were almost similar before and after the removal of As. However, CuO treatment reduced Si and PO_4^{3-} concentrations in groundwater samples. The PO_4^{3-} concentrations after the treatment of CuO were nondetectable in all samples, except for sample 17 (Table 5).

Discussion

More than 50% of the groundwater samples from rural domestic wells, examined in this study, exceeded the US EPA MCL for As. Similarly, high concentrations of As (more than 50 µg/L) in groundwater of the western United States were reported by Welch et al. (2000). Results of this study confirm that CuO particles effectively remove As from groundwater samples under a wide range of water chemistries including pHs and competing anions. The effective removal of As by CuO is attributed to its high ZPC (Reddy and Viswatej 2005) as well as oxidation of As (III) to As (V) by the CuO surface (Martinson and Reddy 2009). A conceptual model of As adsorption process by CuO surface in water is published elsewhere

(Martinson and Reddy 2009). Earlier studies reported that CuO particles can be regenerated by leaching As from CuO particles using NaOH solution. The regenerated CuO particles were also effective in removing As from groundwater (Reddy 2007; Pillewan et al. 2011).

The CuO treatment did not significantly affect the pH and concentrations of major elements (Na, Ca, Mg, K, Cl^-, and SO_4^{2-}) in groundwater samples, except for Si, and PO_4^{3-}. The PO_4^{3-} concentrations in all CuO treated samples were below the detection limit of 0.05 mg/L. Analysis of trace elements (Fe, Cu, Mn, Pb, Cr, and Se) before and after removal of As with CuO particles confirmed no significant changes, and most of the trace elements were within the US EPA MCLs. These results are in agreement with the findings of Martinson and Reddy (2009) and Pillewan et al. (2011). These studies also reported no significant changes to water quality with the CuO treatment.

The CuO particles effectively removed As in the presence of competing anions. Several studies have reported effects of competing anions in removal of As by different sorbents. For example, Meng et al. (2002) examined the combined effects of competing anions on As removal by iron hydroxides through spiking the test water with PO_4^{3-}, silicate (SiO_4^{4-}), and bicarbonate (HCO_3^-). These studies reported a significant reduction in As adsorption by iron hydroxides in the presence of SiO_4^{4-} and PO_4^{3-}. Su and Puls (2001) examined the effects of

Table 5
Analytical Data for Cl^-, SO_4^{2-}, Si, and PO_4^{3-} Before and After Removal of As from Groundwater Samples

Well ID	Cl^- (mg/L)		SO_4^{2-} (mg/L)		Si (mg/L)		PO_4^{3-} (mg/L)	
	Before	After	Before	After	Before	After	Before	After
1	6.8	3.2	11.5	10.8	50.4	31.3	0.3	<0.05
2	2.7	2.5	10.7	10.7	51.1	32.2	<0.05	<0.05
3	5.5	4.3	15.1	14.7	54.5	7.6	0.3	<0.05
4	33.4	31.8	97.4	96.1	16.1	10.4	0.7	<0.05
5	22.6	20.7	91.9	91.6	12.9	7.4	<0.05	<0.05
6	7.9	3.5	8.4	8.0	25.6	15.1	0.1	<0.05
9	6.8	5.3	7.4	7.4	47.3	28.1	0.1	<0.05
10	2.8	3.7	7.4	7.5	39.9	22.8	<0.05	<0.05
12	2.9	4.3	1.3	<0.1	10.6	6.7	<0.05	<0.05
13	18.9	19.9	29.9	29.7	31.8	16.5	<0.05	<0.05
14	33	34.9	49.8	50.2	21.3	12.5	2.6	<0.05
15	9.9	11.2	32.5	31.0	10.9	6.1	<0.05	<0.05
16	13.1	15.3	59.7	57.5	24.3	13.7	<0.05	<0.05
17	2.9	4.3	113	108	10.2	6.0	<0.05	0.20
19	2.8	3.9	459	447	14.0	10.0	<0.05	<0.05
21	24.6	25.2	241	229	14.9	9.8	<0.05	<0.05
25	3.9	4.7	7.5	6.4	13.5	7.5	0.2	<0.05
26	1.6	3.2	11.0	10.7	7.4	5.0	<0.05	<0.05
31	16.3	18.1	35.1	35.8	8.0	5.7	<0.05	<0.05
32	11.6	9.6	44.0	46.3	4.3	3.3	0.2	<0.05
42	14.9	9.3	38.7	37.3	29.2	17.7	0.3	<0.05
43	18.1	16.9	61.5	59.5	<0.1	<0.1	0.1	<0.05
44	6.72	3.5	42.2	45.0	<0.1	<0.1	1.1	<0.05
45	7.4	3.9	32.8	30.9	19.0	14.0	3.06	<0.05
46	11.1	10.0	35.4	34.0	20.0	13.0	2.7	<0.05

different competing anions (e.g., PO_4^{3-}, Si, and SO_4^{2-}) in removal of As (III) and As (V) by zerovalent iron. This study also suggested that among different competing anions, PO_4^{3-} caused the most significant decrease in As removal followed by Si. In addition, Roberts et al. (2004) emphasized the importance of testing simultaneous competition effects of competing anions (e.g., Si and PO_4^{3-}) under natural conditions in removal of As from groundwater. Recently, Chiw et al. (2009) demonstrated that under field conditions the Fe-amended BioSand filter failed in As removal due to naturally occurring PO_4^{3-} concentration (>0.5 mg/L) in groundwater. Overall, results of our study suggest that CuO particles are an effective material to remove As from groundwater in the presence of multiple competing anions under natural conditions. These results could help develop an effective As filtration system for field applications.

Conclusions

We explored the potential of CuO particles in removal of As from groundwater samples associated with rural domestic wells in the western United States. Results suggest that CuO particles effectively removed toxic As species from groundwater samples across a wide range of water chemistries. The common competing anions in water did not show any discernible effects in removal of As by CuO particles. The As adsorption and desorption phenomenon of CuO particles could help develop a simple and effective As removal process for groundwater. The groundwater data collected from this study was organized into extension pamphlets and mailed individually to the landowners. Whenever possible, we discussed with individual landowners the potential health problems from drinking groundwater with high levels of As (>10 μg/L), as well as resources for the removal of As from water. In addition, results were presented to the landowners through CSREES water quality workshops.

Acknowledgments

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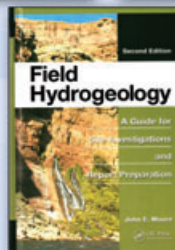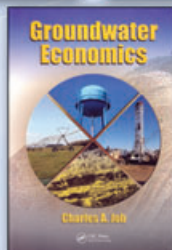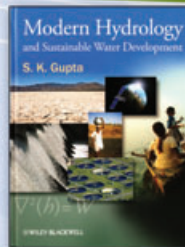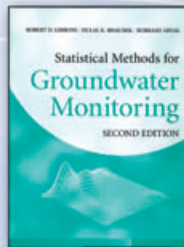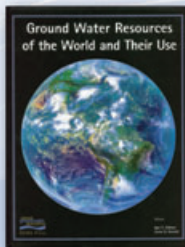
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