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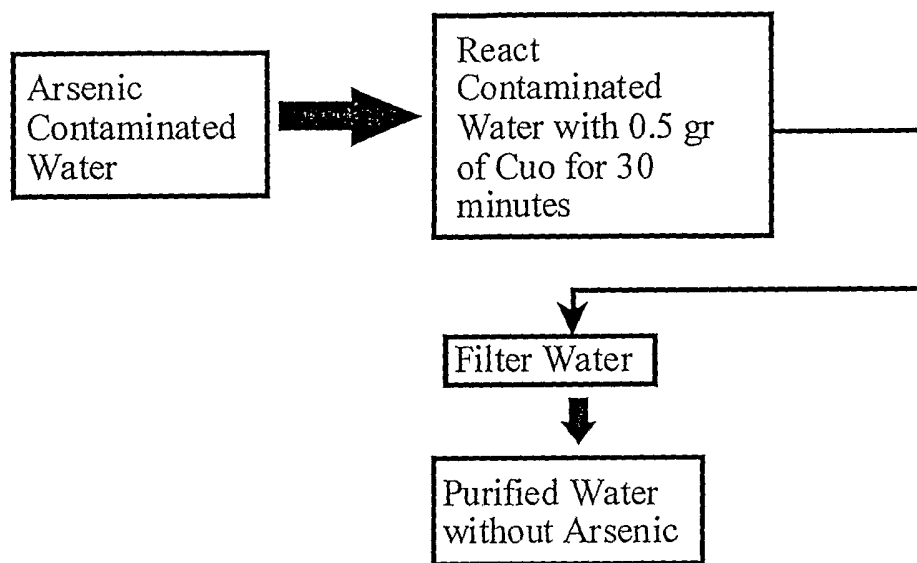
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(54) Title: SYSTEM AND METHOD FOR REMOVING ARSENITE AND ARSENATE FROM WATER



(57) Abstract: A method for removing arsenite and arsenate from water is provided. The method comprises reacting the water with cupric oxide (CuO) particles for a predetermined time and filtering the reacted water. A system for removing arsenite and arsenate from liquids is also provided.

WO 2005/028376 A1

SYSTEM AND METHOD FOR REMOVING ARSENITE AND ARSENATE, FROM WATER

The present application is a continuation of pending provisional patent application Serial No. 60/504,329, filed on September 19, 2003, entitled "System and Method for Removing Arsenite and Arsenate From Water".

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to a system and method for removing arsenite and arsenate from water and, more particularly, the invention relates to a system and method for removing arsenite and arsenate from water which reacts arsenic contaminated water with cupric oxide (CuO) particles for a predetermined time.

2. Description of the Prior Art

Arsenic is a naturally occurring substance found in a variety of combined forms in the earth. Arsenic contamination of drinking water has been reported from many parts of the world. The United States Environmental Protection Agency (EPA) has stated that arsenic in drinking water causes cancer in humans and that the amount of arsenic in water at the current allowed concentration may equal that caused by smoking cigarettes.

Arsenic is a Group 5A nonmetal with the more common valences of -3, 0, +3 and +5. Arsenite (As^{+3}) and arsenate (As^{+5}) are the most common forms found in drinking water and wastewater streams. In some arsenic affected areas, substitution of drinking water source by a safe and easily available one can be very expensive. In order to meet the maximum contaminant level (MCL) for human drinking water, irrigation water, livestock and wildlife watering, and aquatic life, the arsenic must be removed to meet the safe level. In fact, arsenic removal may be a more appropriate water supply option in these situations.

Therefore, water providers have a need for an economical safe method to remove arsenic from drinking water. Further, residential homes obtaining water from wells have a need for a low cost, safe, and efficient point of entry or point of use arsenic removal system.

In the past, there have been methods for removal of arsenic including the following: (1) adsorption onto activated alumina within a fixed bed contactor; (2) complexing arsenic with hydrous metallic floc, previously aluminum and iron hydroxides or oxyhydroxides, in conventional water treatment plants; (3) sieving the metal from water by membrane technologies such as reverse osmosis; and (4) electrodynamic processes such as electrodialysis.

Unfortunately, most conventional methods for arsenic removal have difficulties of removing arsenite (As^{+3}). Even though certain techniques are fairly successful on large municipal supplies, they are not practical for residential application because of space requirements, the use of dangerous chemicals, frequent monitoring, and expense. In fact, each of these methods require highly skilled personnel for operation and maintenance on an ongoing basis rendering them unsuitable for residential use at point of entry.

The two most common techniques for residential water correction have been reverse osmosis (RO) and activated alumina. Activated alumina requires the use of caustic chemicals and a very large volume for the high flow rates available with this invention. RO is no longer certified as an arsenic removal technique because of its inability to reduce arsenite (As^{+3}) significantly.

SUMMARY

The present invention is a method for removing arsenite and arsenate from water. The method comprises reacting the water with cupric oxide (CuO) particles for a predetermined time and filtering the reacted water.

The present invention also includes a system for removing arsenite and arsenate from water. The system comprises water contaminated with arsenic, cupric oxide (CuO) particles added to the contaminated water, a filter for filtering the CuO /water.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view illustrating arsenic removal from contaminated water, in accordance with the present invention;

FIG. 2 is a schematic view illustrating a filter plant design, constructed in accordance with the present invention; and

FIG. 3 is a schematic view illustrating a filter design, constructed in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preparation of Cupric Oxide:

Proposed method uses inexpensive solid particles and removes arsenite and arsenate from water. Removal kinetics are rapid, method is simple, and process does not produce harmful by products. Reduces arsenic species from water to lower than the EPA's required ten (10) $\mu\text{g/L}$ for human drinking water. We conducted experiments with (pH of 6.0) and without (pH between 7.5 - 8.5) adjusting the pH of the system.

When sodium hydroxide reacts with copper chloride, copper hydroxide is formed. When copper hydroxide is left in the room temperature for a day, it precipitates as cupric oxide.

CuO is filtered, dried, and then grounded to fine powder. This lab prepared CuO is used to remove arsenic from water.

Preparation of Standards:

Arsenite standards were prepared using sodium arsenite salt (NaAsO_2).

Arsenite standards of 1 ppm, 500 ppb, 250 ppb, 100 ppb, and 10 ppb were prepared using 1000 ppm of arsenite standard.

Arsenate standards were prepared using sodium arsenate salt (Na_2AsO_4).

Arsenate standards of 1 ppm, 500 ppb, 250 ppb, 100 ppb, and 10 ppb were prepared using 1000 ppm of arsenate standard.

Sodium sulfate salt (Na_2SO_4) was used to prepare 1,250 ppm, 1,000 ppm, 250 ppm, and 50 ppm of sulfate standards.

Experiments:

Arsenic standard solutions were prepared and 50ml of each standard solution was reacted with 0.5 grams of CuO in a conical flask. Conical flasks were kept on a mechanical shaker and reacted for a predetermined time. After the reaction, solutions were filtered and analyzed for arsenic using ICP Mass Spectrometry.

Results:

1. Arsenite reacted with 0.50 grams of CuO particles.

As standards (in ppb)	Total arsenic conc. before reaction	Total arsenic conc. after reaction	% Removed
10	8	-0.3	100
100	87	-0.1	100
250	217	-0.3	100
500	426	-0.1	100
1000	868	-0.1	100

2. Arsenate reacted with 0.25 grams of CuO particles.

As standards (ppb)	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	% Removed
10	8	0	100
100	87	0.3	99.65
250	217	24.8	88.57
500	426	85.1	80.02
1000	868	210.7	75.80

3. Five hundred (500) ppb of arsenite and different concentration of sulfate reacted with 0.5 grams of CuO particles.

Sulfate conc. before reaction (ppm)	Sulfate conc. after reaction (ppm)	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	% Removed
1070	1055	540.9	1.2	99.77
1303	1293	555.8	4.1	99.26
269	260	544.9	2.7	99.50
64.2	57.9	610.4	0.1	99.98

4. Arsenate reaction with 0.5 grams of CuO particles.

Arsenate standards (ppb)	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	% Removed	Cu ²⁺ conc. after reaction (ppb)
10	14	0	100	3426
100	82	1	98.78	779
250	257	0	100	325

500	428	0	100	340
1000	837	0	100	124

5. Five hundred (500) ppb of arsenate and different concentration of sulfate reacted with 0.5 grams of CuO particles.

Sulfate conc. before reaction (ppm)	Sulfate conc. after reaction (ppm)	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	% Removed	Cu ²⁺ conc. after reaction (ppb)
1277.3	1268.6	430	1	99.76	206
263.6	244.6	430	0	100	10
50.3	42.7	352	0	100	10

6. Arsenate (125 ppb) spiked from the water collected from four different streams and reacted with 0.5 grams of CuO particles.

Streams	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	% Removed	Cu ²⁺ conc. before reaction (ppb)	Cu ²⁺ conc. after reaction (ppb)	Sulfate conc. after reaction (ppm)
Oregon	146.3	2.9	98.00	9.1	17.5	628.0
Six Mile Drain	125.2	0	100	0.0	36.3	740.0
Casper	119.0	0	100	0.0	33.1	1439.0
Bait's	117.8	0	100	0.0	15.3	573.0

7. Arsenite (150 ppb) spiked from the water collected from four different streams and reacted with 0.5grams of CuO particles.

Streams	Total arsenic conc. before reaction (ppb)	Total arsenic conc. after reaction (ppb)	%Removed	Cu ²⁺ conc. before reaction (ppb)	Cu ²⁺ conc. after reaction (ppb)	Sulfate conc. after reaction (ppm)
Oregon	156.5	25.7	83.57	4.0	15.4	628.0
Six Mile	149.6	0	100	2.9	11.9	740.0

Drain						
Casper	143.6	0	100	4.4	50.2	1439.0
Bait's	142.5	0	100	0.6	14.6	573.0

The following arsenic removal data from natural waters without adjusting the pH show that arsenic can be removed from water with the invention of the present application.

Sample	Arsenate Before Reaction ($\mu\text{g/L}$)	Arsenate After Reaction ($\mu\text{g/L}$)	% Removed
B-1	133.6	0.7	99.4
B-3	141.5	0.7	99.5
B-5	136.7	1.0	99.2
B-7	139.7	0.9	99.3

Sample	Arsenite Before Reaction ($\mu\text{g/L}$)	Arsenite After Reaction ($\mu\text{g/L}$)	% Removed
B-2	121.9	1.6	98.6
B-4	117.0	1.3	98.8
B-6	119.0	5.4	95.4
B-8	121.0	0.3	99.7

In the present invention, three possible mechanisms have been found for effective removal of arsenic species by the CuO particles under natural conditions; 1) the pH at which ZPC for CuO particles in water is at higher pH than any other sorbents therefore, these particles may have higher affinity of arsenic species; 2) arsenite and arsenate have appropriate atomic size so that these atoms move into the structure of CuO particle; and/or 3) Cu^{2+} dissolved from CuO particles probably complexes with arsenite in the pH range of 7 – 9, which is in turn adsorbed by the CuO particles. The data suggests that CuO particles can lower both arsenite and arsenate in water, under different conditions, to well below the required contaminant limit of 10 $\mu\text{g/L}$ for human drinking water.

The method of the present invention is rapid and does not require pH adjustments. Other common ions of water do not affect the removal of arsenic species. In addition, the method is simple, effective, and inexpensive. Also, the method produces no harmful by-products. The method of the present invention has potential to address serious health and environmental problems facing both under developed and developed nations by improving the quality of drinking water they depend upon.

Conclusions:

1. Arsenate and arsenite showed a strong affinity to CuO in water.
2. Arsenate and arsenite can be removed from water in the presence of high sulfate concentrations when 0.5 grams of CuO is used.
3. CuO has efficiently removed spiked arsenate and arsenite from the natural waters.
4. CuO can be used efficiently to remove arsenic species from drinking water and/or contaminated water without adjusting the natural pH.

A system for removing arsenite and/or arsenate from tap water, as illustrated in FIG. 2, comprises an oxidation stage for converting arsenic in the liquid to As^3 and/or As^5 . A cupric oxide contact chamber is disposed downstream from the oxidation stage for receiving cupric oxide and for mixing cupric oxide with the liquid containing As^3 and/or As^5 . A filter is disposed downstream from the contact chamber for removing arsenic complex or complexes from the liquid. The system can further comprise an activated carbon chamber for receiving the filtered liquid and a mix bed ion exchange medium for receiving the carbon filtered liquid.

A treatment and filter system for removing arsenite and/or arsenate from water, as illustrated in FIG. 3, comprises a cupric oxide contact section for reacting cupric oxide with arsenic contained in a water stream to produce arsenite and/or arsenate. An activated carbon filter is disposed downstream of the cupric oxide contact section. A mixed bed ion exchange section is dispensed downstream of the activated carbon filter and wherein the cupric oxide contact section, activated carbon filter, and mixed bed ion exchange are housed within a housing that is adapted to connect to a water source. The housing of the treatment and filter system is

sufficiently compact to enable the system to be secured to the outlet of a household water faucet.

The foregoing exemplary descriptions and the illustrative preferred embodiments of the present invention have been explained in the drawings and described in detail, with varying modifications and alternative embodiments being taught. While the invention has been so shown, described and illustrated, it should be understood by those skilled in the art that equivalent changes in form and detail may be made therein without departing from the true spirit and scope of the invention, and that the scope of the present invention is to be limited only to the claims except as precluded by the prior art. Moreover, the invention as disclosed herein, may be suitably practiced in the absence of the specific elements which are disclosed herein.

CLAIMS

What is claimed is:

1. A method for removing arsenite and arsenate from liquids, the method comprising:
 - reacting the liquid with cupric oxide (CuO) particles for a predetermined time;
 - and
 - filtering the reacted liquid.
2. The method of claim 1 wherein the liquid has a pH of approximately 6.0.
3. The method of claim 1 wherein the liquid has a pH of between approximately 7.5 and approximately 8.5.
4. The method of claim 1 wherein the CuO particles is created by the method comprising:
 - reacting sodium hydroxide with copper chloride;
 - forming copper hydroxide;
 - placing the copper hydroxide in room temperature for a predetermined time;
 - precipitating into cupric oxide; and
 - filtering, drying, and grounding the CuO particles into fine powder.
5. The method of claim 1 wherein the filtered liquid has an arsenic concentration of less than approximately 10 µg/L.
6. The method of claim 1 wherein the amount of CuO particles is approximately 0.5 grams.
7. A system for removing arsenite and/or arsenate from liquids, the system comprising:
 - an oxidation stage for converting arsenic in the liquid to As³ and/or As⁵;

a cupric oxide contact chamber disposed downstream from the oxidation stage for receiving cupric oxide and for mixing cupric oxide with the liquid containing As^3 and/or As^5 ; and
a filter disposed downstream from the contact chamber for removing arsenic complex or complexes from the liquid.

8. The system of claim 7 wherein the liquid is tap water.
9. The system of claim 8 and further comprising:
an activated carbon chamber for receiving the filtered liquid.
10. The system of claim 9 and further comprising:
a mix bed ion exchange medium for receiving the carbon filtered liquid.
11. The system of claim 7 wherein the water has a pH of approximately 6.0.
12. The system of claim 7 wherein the water has a pH of between approximately 7.5 and approximately 8.5.
13. The system of claim 7 wherein the CuO particles are created by the method comprising:
reacting sodium hydroxide with copper chloride;
forming copper hydroxide;
placing the copper hydroxide in room temperature for approximately one day;
precipitating into cupric oxide; and
filtering, drying, and grounding the CuO into fine powder.
14. The system of claim 7 wherein the combined water is filtered to have an arsenic concentration of less than approximately 10 $\mu\text{g/L}$.
15. The system of claim 7 wherein the amount of CuO particles is approximately 0.5 grams.

16. A treatment and filter system for removing arsenite and/or arsenate from water comprising:

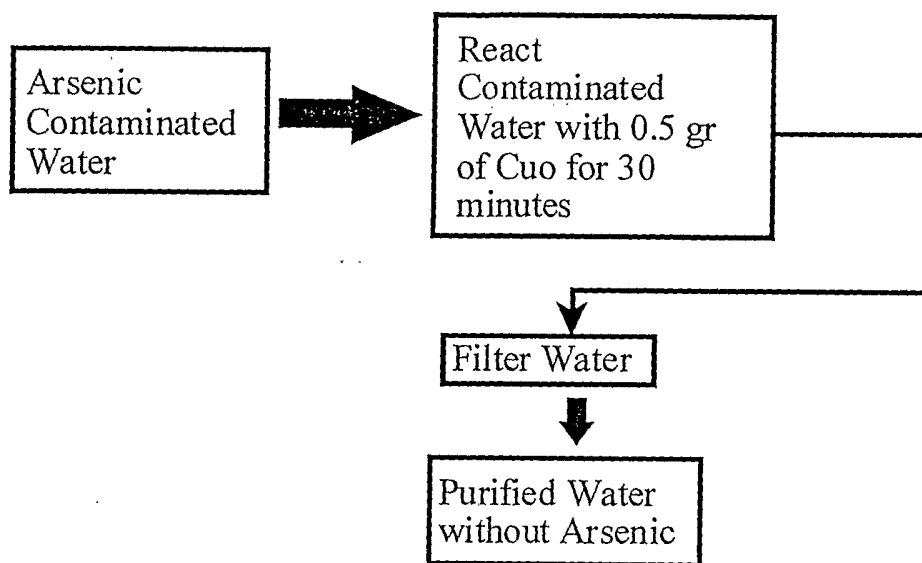
a cupric oxide contact section for reacting cupric oxide with arsenic contained in a water stream to produce arsenite and/or arsenate;

an activated carbon filter disposed downstream of the cupric oxide contact section; and

a mixed bed ion exchange section dispensed downstream of the activated carbon filter and wherein the cupric oxide contact section, activated carbon filter, and mixed bed ion exchange are housed within a housing that is adapted to connect to a water source.

17. The treatment and filter system of claim 16 wherein the housing is sufficiently compact to enable the system to be secured to the outlet of a household water faucet.

Fig. 1. Schematics of arsenic removal from contaminated water.



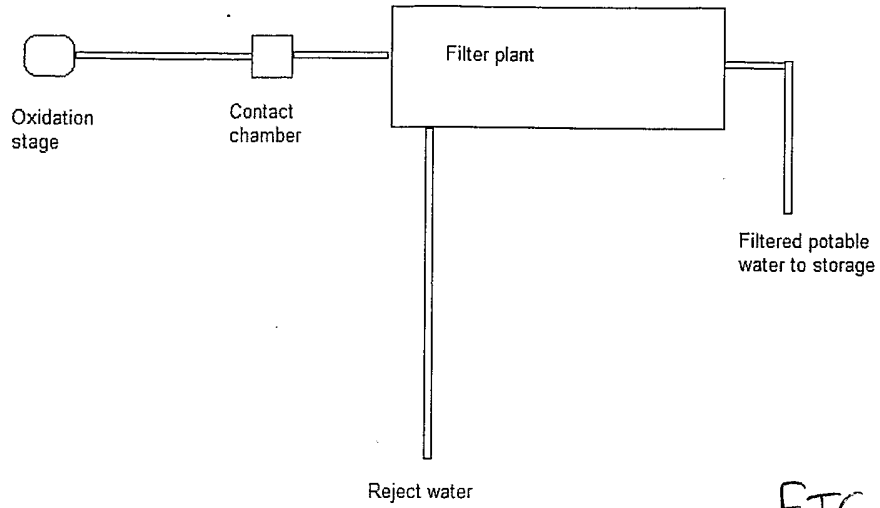


FIG. 2

Basic Filter Plant Design

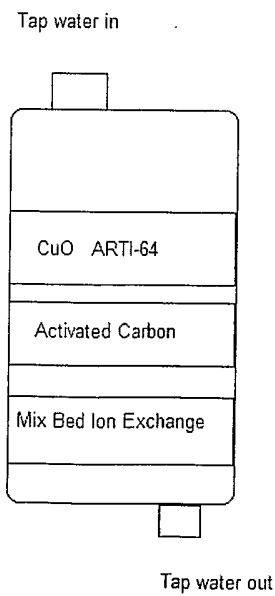


FIG. 3

Block Filter Design

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/30491

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(7) : C02F 1/42
 US CL : 210/665
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 210/665,668,669,681,683,686,688,694,716,717,724,192,202,203,205,209,282,284,290,911; 423/604

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,348,662 A (Yen et al.) 20 September 1994, col. 1 line 40 through col 5 line 47	1-3,7,8,11,12 ----- 1-17
Y	US 2001/0051103 A1 (SEO et al.) 13 December 2001, pages 1 and 2	4,13
Y	US 5,149,437 A (WILKINSON et al.) 22 September 1992, col. 2 line 19 through col. 4 line 61)	9,10,16,17
Y	US 4,913,808 A (HAQUE) 03 April 1990, col. 2 line 36 through col. 3 line 33	10,16,17
A	US 6,197,193 B1 (ARCHER) 06 March 2001	

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"
"A" document defining the general state of the art which is not considered to be of particular relevance	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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