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(54) Title: ARSENIC REMEDIATION METHODS AND COATED ADSORBENT COMPOSITIONS THEREFOR

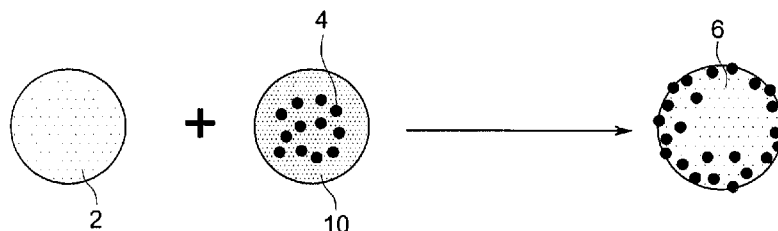


FIG. 1

(57) Abstract: Methods for making nano-sized iron oxide or iron oxyhydroxide particle dispersions wherein the particles are coated onto a carrier substrate. Additionally, coated adsorbent compositions are provided and include the nano-sized iron oxide or iron oxyhydroxide particles adsorbed onto the surface of the substrate. Additionally, methods of using the coated adsorbent compositions to reduce arsenic levels in aqueous mediums are disclosed. Water purification units are also provided and include an adsorbent layer.

ARSENIC REMEDIATION METHODS AND COATED ADSORBENT COMPOSITIONS THEREFOR

FIELD OF INVENTION

5 The application pertains to methods for making nano-sized iron oxide or iron oxyhydroxide particle coated onto a carrier microparticle substrate; coated adsorbent compositions including the nano-sized iron oxide or iron oxyhydroxide particles adsorbed onto the surface of the substrates; and to methods of using the coated adsorbent compositions to reduce As levels in aqueous media.

10 BACKGROUND OF THE INVENTION

 Arsenic is a naturally occurring element in the earth's crust and can be found in many natural ecosystems. Groundwater from intermediate aquifers of various parts of India and Bangladesh was found to contain arsenic above the permissible limit of 50 ppb. Under conditions of prolonged exposure to arsenic, many organs may be
15 damaged, skin pigmentation may occur, hair may fall out, and nail growth may stop. Arsenic related health effects are usually not acute, but mostly encompass cancer, mainly skin cancer. Arsenic may cause low birth weight and spontaneous abortion. The WHO recommended limit for As is 10 ppb. Thus, the water from many tube wells and hand pumps may not be fit for human consumption. Arsenic contamination
20 of ground water therefore assumes a serious public health issue as groundwater serves more than 80% of the drinking water needs primarily in the public sector in India. There is no indication of presence of arsenic, because arsenic does not have smell, color, and taste.

 Several methods for reducing arsenic concentrations to acceptable levels have
25 been studied and are being used currently. These methods include coagulation and precipitation using ferric chloride and sulfate, ion exchange, reverse osmosis, and adsorption using activated carbon and alumina. These methods are effective to a limited extent. Moreover, these methods are considerably more expensive and generally narrower in application than is desired for the treatment of large volumes of
30 water. These methods produce sludge that requires dewatering or solidification and eventually landfill storage as hazardous waste. And these are more particularly dependent on the pH for attaining the specific oxidation state of arsenic. Some of the arsenic remediation processes require additional oxidation step to convert the arsenite

to arsenate. The instant remediation process does not require additional oxidation processes and is not pH dependent.

SUMMARY OF THE INVENTION

In one exemplary embodiment, a method of reducing arsenic content in an aqueous medium is provided wherein the arsenic in the medium is contacted by a coated adsorbent substrate which is a microparticle substrate coated by iron oxide/oxyhydroxide particles. In one embodiment, the substrate is chosen from celite, raw diatomite, and rice husk ash.

Advantageously, in one embodiment, after contact of the arsenic containing aqueous medium with the coated adsorbent substrate, arsenic concentration in the medium is reduced to less than 10 ppb arsenic.

In another aspect of the invention, the iron oxide/oxyhydroxide nanoparticles that are coated onto the substrate are nanoparticles having particle sizes of from about 20 to 100 nanometers. After contact is made with the coated adsorbent substrate, the aqueous medium may then be contacted with a polishing unit that is adapted to reduce microbiological content, odor and/or color of the aqueous medium.

In certain embodiments of the invention, the substrate will have a particle size distribution ranging about 10 to 200 microns.

In another aspect of the invention, a water purifier is provided and comprises an inlet for entry of an arsenic containing feedwater therein and located downstream from the inlet; an outlet is provided for the exit of reduced arsenic content water. The water purifier may comprise a plurality of replaceable cartridge-type units and, in certain embodiments, a prefilter is disposed downstream from the inlet to reduce suspended solids in the feedwater. An adsorption bed may be provided downstream from the prefilter and is in fluid communication with the prefilter. The adsorption bed comprises a multiplicity of coated adsorbent microparticles therein that are adapted to reduce arsenic content of the feedwater when contacted with the feedwater. The coated adsorbent particles include a substrate composed of celite, raw diatomite, rice husk ash, or a combination of these, and an adsorbent coating layer on the substrate. The adsorbent coating layer comprises iron oxide/oxyhydroxide nanoparticles having particle sizes on the order of from about 20 to about 100 nanometers. In other embodiments, the water purification device comprises a polishing section located downstream from the adsorption bed and upstream from the outlet. The polishing

section is adapted to reduce microorganism content, color, and/or odor of the feedwater. In certain embodiments, the polishing section comprises a bacteria growth inhibitor such as silver metal. The adsorption bed, in some embodiments, may comprise a packed column of coated adsorbent particles, and the prefilter may
5 comprise an ultrafiltration (UF) or microfiltration (MF) membrane.

Other aspects of the invention are directed toward a method of making coated adsorbent substrates comprising providing substrate microparticles from the group consisting of celite, raw diatomite, and rice husk ash and mixtures thereof. The substrate particles have particle sizes of from about 10 to 200 microns. The substrate
10 particles are added to an aqueous medium to which ferric chloride and HCl are also added. The medium is heated to about 98-100 °C with stirring. The reactants are retained in suspension for about 24 hours, and then the solids are separated from the medium.

Depending on whether the reactants, namely ferric chloride and hydrochloric
15 acid, along with the aqueous medium are heated slowly (slow nucleation) or heated fast (fast nucleation) to attain the desired temperature of 100 °C, different iron species are formed. In the case of the fast nucleation method, the resultant product is spherical ferric oxide (Fe_2O_3) nanoparticles of about 100 nm in size. In the case of the slow nucleation method, the product is iron oxyhydroxide (FeOOH). These iron
20 oxyhydroxide particles are rod shaped and have a particle size distribution of about 20-40 nm (width) and about 200 nm (length). It is noted that the iron oxide (Fe_2O_3) nanoparticles form under distinct conditions. For example, in the "fast" nucleation embodiment, water is heated to about 100 °C and then ferric chloride and the catalyst (i.e., HCl) are added to the heated water. Instantaneously, Fe_2O_3 nanoparticles are
25 formed: this is a single phase product characterized by XRD. In another aspect referred to as the "slow" nucleation method, water, ferric chloride, and HCl are placed together in the reaction vessel, and the mixture is slowly heated. In this "slow" nucleation method, when the temperature of the mixture reaches about 70°C, hydrolysis begins, and FeOOH nanoparticles start to form. Formation of the FeOOH
30 nanoparticles then continues until the temperature of the reaction mixture reaches about 100 °C. Again, this is a single phase product characterized by XRD.

The separated solids are characterized as a multiplicity of coated adsorbent substrate microparticles having iron oxide/oxyhydroxide particles adsorbently coated

on the substrate. The iron oxide/oxyhydroxide particles have particle sizes of from about 20 to 100 nanometers. After solid/liquid separation, the separated solid materials may be washed, and the washing step may be monitored for one or more parameters selected from the group consisting of iron content, chloride content, conductivity, and pH. In another exemplary embodiment, the aqueous medium is maintained at a pH of about 1-2 during the reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram illustrating a method for producing a coated adsorbent in accordance with the invention;

Fig. 2 is a schematic diagram showing a container or sieve containing the coated adsorbent particles;

Fig. 3 is a schematic illustration of a water purification device including a replaceable cartridge or layer of coated adsorbent particles; and

Fig. 4 is a graph showing As remediation levels in accordance with Example 2 of the specification.

DETAILED DESCRIPTION

Exemplary embodiments of this invention are related to a composition, process for making the composition, and water purification device for reducing arsenic levels in water systems including potable water systems. In one embodiment, a composition is provided that comprises a substrate chosen from celite (calcined diatomaceous earth), raw diatomite, and rice husk ash or a mixture of these wherein the substrate is coated with iron oxide/oxyhydroxide nanoparticles.

In another exemplary embodiment, a method is provided to synthesize iron oxide/oxyhydroxide nanoparticles by a fast nucleation method and a coating of the nanoparticles on the above-mentioned substrates in situ to form a coated adsorbent composition. As to the aforementioned substrate, celite may be mentioned as exemplary and (also known as diatomite or kieselgur) is a naturally occurring soft, siliceous, porous material typically having particle sizes between 10 and 200 microns. Celite contains -80-90% silica, 2-4% alumina and 0.5 to 2% iron oxide. Raw diatomite may also be mentioned as exemplary and is similar to celite in composition. Another naturally occurring raw material, namely rice husk, is also exemplary and, when burnt, produces rice husk ash. It is also a highly siliceous (-80-90% silica and 5-10% activated carbon), porous material and has particle sizes typically between 50

to 100 microns. RHA may also be used as a substrate onto which the nano-sized iron oxide/oxyhydroxide particles are coated.

In another embodiment, arsenic levels in drinking water are reduced when the drinking water is contacted with the coated adsorbent compositions comprising iron oxide/oxyhydroxide nanoparticles adsorbed onto the aforementioned substrates. Preferably, this interaction removes $\text{As}^{(\text{III})}$ levels in the water to <10 ppb. It is thought that the coated nanoparticles provide an increased surface area and thus, increased active sites, on which the contact occurs, and when the coated adsorbent compositions are packed in columns or the like, they provide a tortuous path for the drinking water to traverse during such contact.

It is thought that the coated nanoparticles interact with As species in the drinking water to form an arsenic-iron complex which may be characterized as a non-leachable bidentate binuclear complex, $\text{—Fe—O—As—O(OH)—Fe—}$, which is adsorbed on the coated substrate. Thus, the treated water shows greatly reduced As levels. A bed including such coated nanoparticles will function optimally until there are not enough active iron oxide/oxyhydroxide sites available for interaction with the arsenic species. Slowly, the concentration of these active sites will decrease, leading to inefficiency. Once the saturation of these sites is achieved, the bed will no longer effectively remove arsenic, and both the input and output concentrations will be the same.

Turning now to Fig. 1 of the drawings, there is schematically shown a celite, raw diatomite, or rice husk ash substrate particle 2 and suspension of Fe-oxide/oxyhydroxide nanoparticles 4 in an aqueous medium 10. The iron oxide/oxyhydroxide nanoparticles are adsorbed onto the surface of the substrate to form a coated adsorbent particle 6. The iron oxide/oxyhydroxide particles are formed via an acid hydrolysis reaction using HCl as a catalyst to promote the hydrolysis of FeCl_3 in aqueous media. The iron oxide/oxyhydroxide particles are nano-sized, on the order of from about 20-100 nm.

As shown in Fig. 2, a multiplicity of the coated adsorbent particles 6 may then be provided in layers on other dispositions which may be structured to form a filter cartridge 8. The desired As containing aqueous medium is brought into contact with the filter cartridge to effect As reduction in the medium.

Turning now to Fig. 3, there is shown an integrated water purifier in accord with one exemplary embodiment of the invention. As shown, influent water is fed from inlet 20 via gravity feed from an upstream to downstream direction through a coarse filter or pre-filter section 22, then to adsorption bed 28 including the coated adsorbent particles and then through a polishing section 30 to exit the device as shown at 32 wherein the thus treated aqueous medium exhibits reduced As content. All or some of the components 22, 28, 30 may be in the form of modular, replaceable disk cartridges or replaceable filter units. The coarse granular sand filter section 22 can comprise a coarse filter also known as a pre-filter to remove suspended solids. Further, the pre-filter may comprise layers of fibers or membranes designed to capture suspended particles. The following filter media may be mentioned as exemplary: nylon 66, polytetrafluoroethylene, polypropylene, resin-bonded glass fibers, and cellulosic materials.

Additionally, the coarse filter or prefilter 22 can comprise conventional ultrafiltration (UF) and/or microfiltration (MF) membranes. As is known in the art, UF membranes are adapted to remove colloidal particles on the order of 0.01-1.0 micron, while MF membranes are adapted to remove particulate matter greater than 1.0 micron. The UF or MF membranes may be made of a polymeric material such as polyvinylidene fluoride (PDF) or a ceramic material such as titanium oxide, zirconium oxide, or aluminum oxide. The physical configuration of the UF or MF membranes may be hollow fiber, tubular, flat sheet, or spiral wound. The direction of water flow through the hollow fiber UF or MF membranes may be outside-in or inside-out. Preferred UF membranes are part of the "Zeeweed"TM membrane technology products sold by GE.

Arsenic removal layer or absorption bed 28 may, for example, be a packed column of glass or charcoal impregnated with the coated adsorbent compositions, namely, the nanoparticle iron oxide/oxyhydroxide particles adsorbed onto the desired substrates. This layer 28 is in fluid contact with layer 22. The flowing water exiting from layer 22 is brought into contact with the coated adsorbent particles in the adsorption bed 28 to reduce As^(III) levels in the water to 10 ppb or less.

Located downstream from adsorption bed 28 and in fluid contact therewith is polishing section 30. The polishing unit 30 may be employed to reduce microorganism content, color, odor, etc., if needed. In one embodiment, the polishing

unit may be composed of replaceable cartridge types and, in one embodiment, include a bacterial growth inhibitor. In preferred embodiments, the bacterial growth inhibitor is an oligo-dynamic metal such as silver. Other materials such as activated carbon can also be mentioned. The polishing unit 30 may comprise a host of materials such as microporous carbon filtration blocks, silvered microporous carbon filtration blocks, granular activated carbon, silvered granular activated carbon, microporous ceramic filtration blocks, ultrafiltration membranes, nanofiltration membranes, chelating cation exchange resin, strong acid cation exchange resin, weak acid cation exchange resin, strong base anion exchange resin, weak base anion exchange resin, macroporous anion exchange resin, granular absorbents, iodinated ion-exchange resin and specialized lead removal media. Reduced As content potable water exits the filter unit as shown at 32.

EXAMPLES

The invention is illustrated by the following examples which are intended merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it may be practiced.

Example 1 - Coating of Particles - - General Procedure.

Ferric chloride and HCl are added to water, and the water is heated to about 100 °C. Thereafter, celite particles, raw diatomite, and/or rice husk ash particles are added to the heated water, and the reactants are maintained in suspension for 24 hours under slight agitation. Solids are separated from the liquid, and the thus coated particles are dried in an oven at 100 °C for 10-12 hours followed by removal of unreacted ferric chloride, HCl, and unadsorbed iron oxide/oxyhydroxide nanoparticles by washing with water. The completion of washing is monitored by measurement of pH, ionic conductivity, and iron content. The product is further dried in the oven at 100 °C for an additional 10-12 hours.

HCl is used as a catalyst to promote the hydrolysis of FeCl_3 . Trials have been conducted with different quantities of HCl (0.1 ml, 0.2 ml, 0.5 ml, 0.75 ml, 1 ml, 3 ml, and 5 ml of HCl for 12 g (0.073 mole) of FeCl_3 in 665 mL H_2O). The thus synthesized iron oxide/oxyhydroxide nanoparticles were found to be on the order of -50-100 nm. The reaction is carried out at an acidic pH of 1-2. The pH, conductivity, and iron content of the washed water are measured. The first step in the measurement protocol involves the identification of chloride in the eluted water.

(This is done using silver nitrate). The washing process is typically carried out until the pH is about 5. Other parameters that signal completion of the washing step include conductivity measurement to obtain wash water conductivity of about 0.1 mS/cm, and iron content of the washed water of about 10-20 ppb (from Inductivity
5 Coupled Plasma analysis).

Example 2 - (As removal by the coated particles)

As^(III) species from an arsenic solution was passed from an overhead container through a 40 mm diameter packed bed glass column containing the iron oxide/oxyhydroxide coated substrates namely celite, raw diatomite, or rice husk ash
10 having a particle size distribution of between about 20 and 200 microns supported by glasswool and sand. Starting from an input concentration of 500 ppb, the arsenic concentration in the output water was reduced to <10 ppb. Arsenite remediation results as a function of volume passed (in liters) are shown in Fig. 4.

While this invention has been described with respect to particular
15 embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications.

We Claim:

1. A method of reducing arsenic concentration in an aqueous medium containing arsenic, comprising:

5 contacting the aqueous medium with a coated adsorbent substrate; and
 adsorbing the arsenic on the coated adsorbent substrate, wherein the
 coated adsorbent substrate comprises a microparticle substrate coated
 with iron oxide or iron oxyhydroxide nanoparticles.

2. Method as recited in claim 1 wherein the arsenic is reduced to a concentration of less than 10 ppb.

10 3. Method as recited in claim 1 wherein the iron oxide/oxyhydroxide
nanoparticles have a particle size of about 20 to 100 nanometers.

4. Method as recited in claim 1 wherein after said contacting said aqueous medium is brought into contact with a polishing unit adapted to reduce microbiological content of said aqueous medium.

15 5. Method as recited in claim 1 wherein the microparticle substrate has a
particle size of about 10 to 200 microns.

6. Method as recited in claim 5 wherein the microparticle substrate is celite.

20 7. Method as recited in claim 5 wherein the microparticle substrate is rice
husk ash.

8. Method as recited in claim 5 wherein the microparticle substrate is raw diatomite.

25 9. A water purifier comprising:
 an inlet for entry of an arsenic containing feedwater;
 a prefilter disposed downstream from said inlet to minimize suspended solids
 in the feedwater;

 an adsorption bed downstream of the prefilter; and

 an outlet for exit of a lowered arsenic content water, wherein the adsorption
bed comprises a coated adsorbent substrate comprising a microparticle substrate
30 coated with iron oxide or iron oxyhydroxide nanoparticles, and wherein the
microparticle substrate is selected from the groups consisting of celite, raw diatomite,
rice husk ash, or combinations thereof.

10. The water purifier as recited in claim 9, further comprising a polishing unit downstream of the inlet and upstream of the outlet to lower microorganism content, color, or odor of the feedwater.

11. The water purifier as recited in claim 10, wherein said polishing unit
5 comprises a bacterial growth inhibitor.

12. The water purifier as recited in claim 10 wherein said bacterial growth inhibitor comprises silver.

13. The water purifier as recited in claim 10 wherein the polishing unit is a replaceable cartridge.

10 14. The water purifier as recited in claim 9, wherein said adsorption bed comprises a packed column of said coated adsorbent substrate.

15. The water purifier as recited in claim 9, wherein the prefilter comprises an ultrafiltration (UF) membrane or microfiltration (MF) membrane.

16. A method of making coated adsorbent substrates comprising:
15 providing an aqueous medium and a microparticle substrate;
adding the microparticle substrate, ferric chloride solution, and hydrochloric acid solution to the aqueous medium;

heating the aqueous medium to about 98-100 °C to form the coated adsorbent substrate;

20 separating the coated adsorbent substrate from the heated medium, wherein the microparticles substrate having particle sizes of about 10 to 200 microns selected from celite, raw diatomite, and rice husk ash or mixtures thereof and wherein the coated adsorbent substrate particles coated with iron oxide or iron oxyhydroxide nanoparticles having particle sizes of about 20 to 100 nanometers.

25 17. The method as recited in claim 16 further comprising washing the separated coated adsorbent substrate and monitoring wash water from said washing step for one or more parameters chosen from iron content, chloride content, conductivity, and pH or combinations thereof.

18. The method as recited in claim 16, wherein aqueous medium is
30 maintained at a pH of about 1-2.

19. The method as recited in claim 16 further comprising drying said washed separated solids in an oven at about 100 °C.

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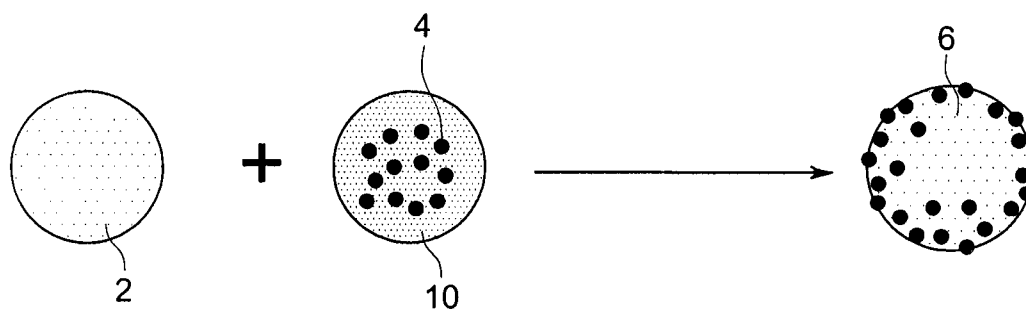


FIG. 1

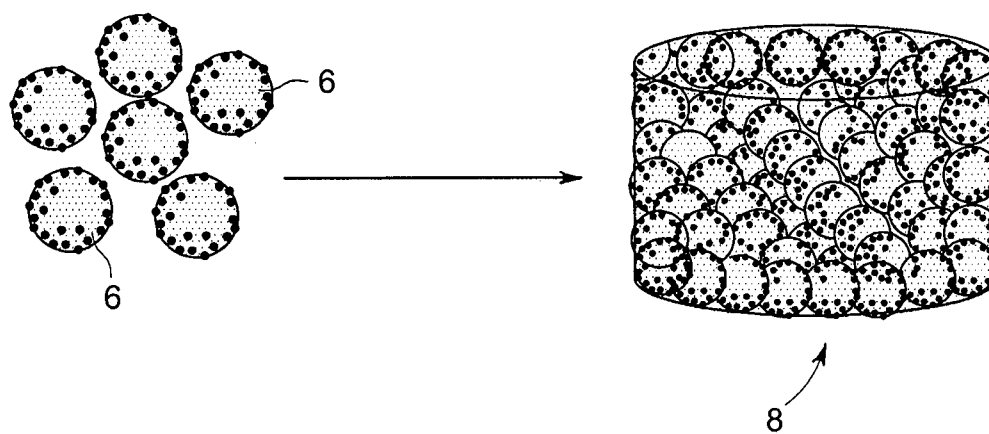


FIG. 2

2/2

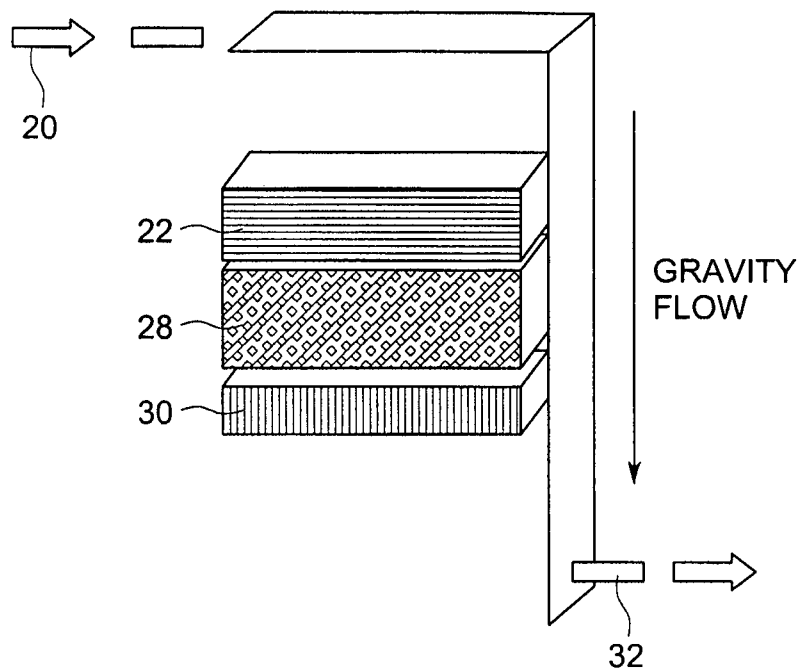


FIG. 3

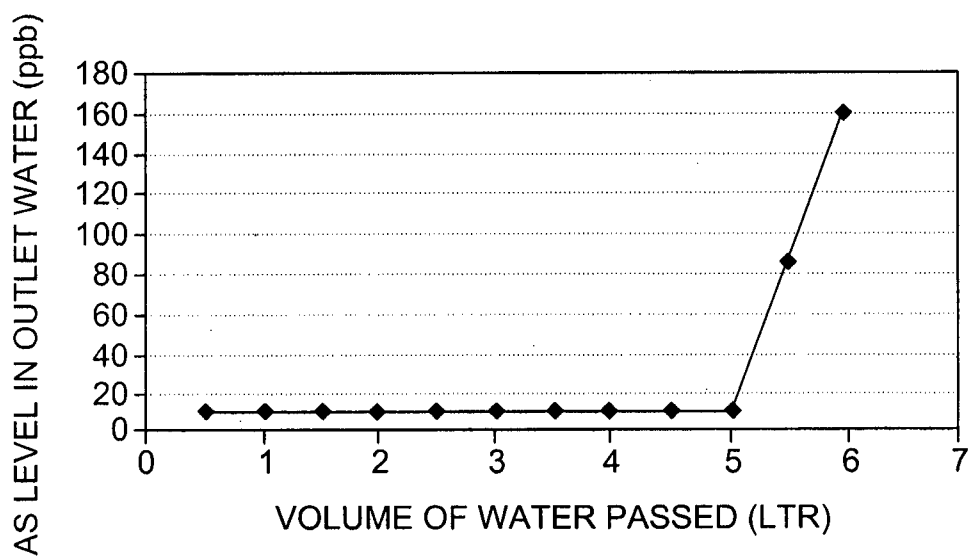


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 11/03051

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 20/24; C02F 1/44; C02F 1/42 (2012.01)**USPC - 210/681 ; 210/652; 210/651 ; 502/404**

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)

IPC(8): B01J 20/24; C02F 1/44; C02F 1/42 (2012.01); USPC: 210/681 ; 210/652; 210/651; 502/404

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 210/681; 210/652; 210/651; 502/404Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Google Scholar, Google Patents, PubWEST (PGPB,USPT,EPAB,JPAB) (Iron, oxide, oxyhydroxide, nanoparticle, coating, adsorbent, water, purify, arsenic, adsorbent, arsenate, arsenite, HCl, catalyst, membrane, celite, rice, husk, ash, diatomite)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0197081 A1 (Gadgil) 21 Aug 2008 (21.08.2008) paragraphs [0020]-[0024], [0038]-[0053], [0063]-[0065]	1-19
Y	US 2011/0124492 A1 (Loukine, et al.) 26 May 2011 (26.05.2011) paragraphs [0042]-[0045], [0063], [0105]-[0106], [0128]-[0130]	1-19
Y	US 2006/0186054 A1 (Webb, et al.) 24 Aug 2006 (24.08.2006) Figures 1, 2, paragraphs [0051]-[0057]	9-15



Further documents are listed in the continuation of Box C.



* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" 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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 Jun 2012 (23.06.2012)

Date of mailing of the international search report

06 JUL 2012

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

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PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 11/03051

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I: claims 1-8 directed to a method of reducing arsenic concentration in an aqueous medium containing arsenic, comprising:
contacting the aqueous medium with a coated adsorbent substrate;
adsorbing the arsenic on the coated adsorbent substrate, wherein the coated adsorbent substrate comprises a microparticle substrate coated with iron oxide or iron oxyhydroxide nanoparticles.

Group II: claims 9-15 directed to a water purifier comprising:
an inlet for entry of an arsenic containing feed water;
a prefilter disposed downstream from said inlet to minimize suspended solids in the feedwater;
an adsorption bed downstream of the prefilter; and
an outlet for exit of a lowered arsenic content water, wherein the adsorption bed comprises a coated adsorbent substrate comprising a microparticle substrate coated with iron oxide or iron oxyhydroxide nanoparticles, and wherein the microparticle substrate is selected from the groups consisting of celite, raw diatomite, rice husk ash, or combinations thereof.
—continued on Page 7—

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

Continuation of Box No. III Observations where unity of invention is lacking

Group III: claims 16-19 directed to a method of making coated adsorbent substrates comprising:
providing an aqueous medium and a microparticle substrate;
adding the microparticle substrate, ferric chloride solution, and hydrochloric acid solution to the aqueous medium;
heating the aqueous medium to about 98-100.degree.C to form the coated adsorbent substrate;
separating, the coated adsorbent substrate from the heated medium,
wherein the microparticles substrate having particle sizes of about 10 to 200 microns selected from celite, raw diatomite, and rice husk ash or mixtures thereof and wherein the coated adsorbent substrate particles coated with iron oxide or iron oxyhydroxide nanoparticles having particle sizes of about 20 to 100 nanometers.

Groups I and II do not include the method of making coated adsorbent substrates of group III.

Groups I and III do not include the water purifier with prefilter and adsorption bed of group II.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

US 201 1/0124492 A 1 to Loukine et al. (hereinafter 'Loukine') teaches the common feature of groups I, II and III of an adsorbent for the removal of arsenic from water (para [0013]; [0049]) that is a microparticle substrate (para [0063]; [0153]) coated with an iron oxide nanoparticle (para [0049]; [0153]). Loukine also teaches the common feature of groups II and III of rice husk ash (para [0153]); therefore, the common feature is not an improvement over the prior art.

Groups I through III therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.