US 20080308499A1

(19) **United States**
(12) **Patent Application Publication**
Vance et al.
(10) **Pub. No.: US 2008/0308499 A1**
(43) **Pub. Date: Dec. 18, 2008**

(54) METHOD AND SORBANT FOR REMOVING CONTAMINATES FROM WATER

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(21) Appl. No.: **12/177,302**

(22) Filed: **Jul. 22, 2008**

Related U.S. Application Data

(63) Continuation-in-part of application No. 12/097,281, filed on Jun. 13, 2008, filed as application No. PCT/US2006/004028 on Feb. 2, 2006.

Publication Classification

(51) **Int. Cl.**
C02F 1/28 (2006.01)
B01J 20/06 (2006.01)

(52) **U.S. Cl.** **210/681**; 210/660; 502/400

(57) ABSTRACT

A method and corresponding sorbant for removing dissolved contaminants, such as arsenate, from water. The sorbant comprises an oxide of titanium and a sulfate salt, such as calcium sulfate.

METHOD AND SORBANT FOR REMOVING CONTAMINATES FROM WATER

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part application and claims the benefit of co-pending U.S. application Ser. No. 12/097,281 filed 13 Jun. 2008, which is the National Stage of International Application No. PCT/US2006/004028 filed 2 Feb. 2006, both of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The instant invention is in the field of methods and sorbants for removing dissolved contaminates from water and more specifically by the use of a sorbant comprising an oxide of titanium and a sulfate salt or a base.

[0003] U.S. Pat. No. 6,919,029, herein fully incorporated by reference, describes a method and sorbant for removing dissolved contaminates from water, such as arsenic compounds, using among other things a sorbant comprising an oxide of titanium.

SUMMARY OF THE INVENTION

[0004] The instant invention provides a method and sorbant for removing dissolved contaminants from water, wherein the sorbant comprises an oxide of titanium and a sulfate salt or a base. More specifically, the instant invention in one embodiment is a method for removing dissolved contaminants from water, comprising the step of contacting a sorbant with the water, the sorbant comprising more than ten weight percent (wt. %) of an oxide of titanium and more than one tenth weight percent of a sulfate salt having a solubility in water at room temperature of less than 0.5 grams per liter of water, wherein the oxide of titanium is primarily titanium dioxide.

[0005] In another embodiment, the instant invention is a method for removing dissolved contaminants from water, comprising the step of contacting a sorbant with the water, the sorbant comprising more than ten weight percent of an oxide of titanium and more than one tenth weight percent of a base, the base having a solubility in water at room temperature of less than 0.5 grams per liter of water, wherein the oxide of titanium oxide is primarily titanium dioxide.

[0006] In another embodiment, the instant invention is a sorbant for removing dissolved contaminants from water, the sorbant comprising more than ten weight percent of an oxide of titanium and more than one tenth weight percent of a sulfate salt having a solubility in water at room temperature of less than 0.5 grams per liter of water, wherein the oxide of titanium is primarily titanium dioxide.

DETAILED DESCRIPTION

[0007] The instant invention is a method and sorbant for removing dissolved contaminants from water. The dissolved contaminates comprise the same contaminates as listed in the '029 patent and can further include, without limitation thereto, dissolved lead, vanadium, selenium, copper, nickel, mercury and chromium. The method and sorbant of the instant invention are especially effective for removing dissolved arsenic compounds from water.

[0008] The sorbant of the instant invention in one embodiment comprises more than ten weight percent of an oxide of titanium and more than one tenth weight percent of a sulfate salt having a solubility in water at room temperature of less than 0.5 grams per liter of water, wherein the oxide of titanium is primarily titanium dioxide.

[0009] In another aspect of the invention the sorbant comprises at least about 50 wt. %, preferably at least about 80 wt. % and in some embodiments at least about 85 wt. % of an oxide of titanium. The sorbant preferably comprises less than or equal to about 97 wt. %, more preferably less than or equal to about 95 wt. % and in some embodiments less than or equal to about 93 wt % of an oxide of titanium. In most embodiments the sorbant comprises a range of an oxide of titanium from about 50 to about 95 wt. %, more preferably about 85 to about 95 wt. % and in other embodiments from about 87 to about 93 wt. %. Titanium dioxide is preferably the dominant species of titanium present and in preferred embodiments comprises at least about 50 wt. % of the total titanium present, more preferably at least about 80 wt. % and even more preferably at least about 90 wt. %.

[0010] The sorbant of the instant invention preferably comprises more than about 0.5 percent by weight of the sulfate salt but more preferably at least about: 2, 3, 5, and 7 wt. % and in some embodiments at least about 10 wt. %. The sorbant preferably comprises less than or equal to about 50 wt. %, more preferably less than or equal to about 20 wt. % and in some embodiments less than or equal to about 15 wt. % of sulfate salt. Preferred ranges of sulfate salt include from about 5 to about 50 wt. %, preferably about 5 to about 15 wt. %, and more preferably about 7 to about 13 wt. %. In some embodiments, the preferred range of sulfate salt is from about 12 to 13 wt. %. Preferably, the sulfate salt is a calcium sulfate salt; however, other relatively insoluble salts may also be used such as magnesium sulfate and barium sulfate. Moreover, combinations of such sulfate salts may be used. However, when the sulfate salt is a calcium sulfate salt, the sorbant preferably comprises less than about 6 wt %, but more preferably less than about 5 wt. %, and in some embodiments less than about 4 wt. % calcium on an elemental analysis basis. The preferred chemical analysis method used to determine the sulfate salt and the titanium oxide form (for example, calcium sulfate can be present in the gypsum and/or the bassenite form while titanium dioxide can be present in the anatase or rutile form) of the sorbant of the instant invention is X-ray diffraction spectroscopy. The titanium, calcium (and/or magnesium, barium, etc.) and sulfur concentrations of the sorbant of the instant invention can be determined by X-ray fluorescence analysis. The present sorbant has at least about 0.5 wt. % sulfur on an elemental analysis basis, but preferably at least about 1, 1.5, or even at least about 2 wt. %; and preferably less than or equal to about 12, 10, 8, 6 or 5 wt. %. In some embodiments, the sorbant has a range of sulfur from about 1 to about 5 wt. % but more preferably from about 1.5 to about 4 wt. % on an elemental analysis basis.

[0011] Analysis of the sorbant of the instant invention in terms of elemental titanium can be performed by neutron activation analysis or X-ray fluorescence. Preferably, the oxide of titanium of the sorbant of the instant invention is produced by the well known sulfate process. Preferably, the sorbant of the instant invention comprises more than about twenty weight percent titanium, but preferably at least about 25, 30, 40, 45 or even 50 wt. %, on an elemental analysis basis. In some embodiments, the range of titanium is from about 35 to about 55 wt. % but more preferably from about 45 to about 55 wt. % on an elemental analysis basis. Alternatively, the sorbant for use in the instant invention can comprise more than ten weight percent of an oxide of titanium and more than one tenth weight percent of a base, the base having a solubility in water at room temperature of less than 0.5 grams per liter of water, wherein the oxide of titanium oxide is primarily titanium dioxide. Any base can be used which meets the above mentioned solubility limit, including hydroxide ion form ion-exchange resin.

[0012] The method of the instant invention comprises the step of contacting a sorbant of the instant invention with the water. Preferably, the water is flowed through a bed of the sorbant.

[0013] Preferably, more than 80% by weight of the sorbant has a particle size in the range of from 10 to 60 US mesh. More preferably, more than 80% by weight of the sorbant has a particle size in the range of from 16 to 60 US mesh. Even more preferably, more than 80% by weight of the sorbant has a particle size in the range of from 25 to 45 US mesh. However, it should be understood that for some applications smaller sized sorbant can be used such as a sorbant wherein more than 80% by weight of the sorbant has a particle size in the range of from 100 to 400 US mesh or from 200 to 325 US mesh.

[0014] The sorbant of the instant invention is preferably made by adding lime and water to uncalcined sulfate process titanium dioxide to form a paste which is then extruded through a die to form rod-like granules which are dried and then ground (and optionally sieved) to produce a particle size distribution appropriate for a specific application. The use of such lime in the instant invention has the additional benefit of producing a sorbant having higher mechanical strength (less attrition) and a lower bulk density than the sorbants of the '029 patent.

[0015] One surprising aspect of the present invention is the unexpected improvement of adsorption capacity of the sorbant when the oxide of titanium is combined with sulfate. In order for the effect to be sustainable, the sulfate form must be relatively insoluble. That is, soluble salts of sulfate such as ammonium or sodium sulfate are washed away during use and the beneficial effect is significantly diminished; however, relatively insoluble sulfate salts such as calcium sulfate are sufficient insoluble to maintain the improved performance. The phrase "relatively insoluble" means a solubility in water of less than 0.5 grams per liter at ambient temperature (e.g. about 22° C.).

[0016] Oxides of titanium produced via the well known sulfuric acid processes often have residual sulfates present, albeit in soluble forms that are washed away during use. Such sorbant materials may be converted within the scope of the present invention by the addition of a cation capable of forming a relatively insoluble salt with sulfate, such as calcium, barium and magnesium. The addition of lime has the combined advantage of offering a relatively inexpensive source of calcium along with pH control. In applications were sulfates have been washed out of the titanium or where the titanium oxide is prepared by an alternative method involving no residual sources of sulfate, a relatively insoluble sulfate salt may be combined with the titanium oxide.

COMPARATIVE EXAMPLE 1

[0017] 1.06 kilograms of uncalcined titanium oxide powder (having an anatase titanium dioxide concentration of about 80% by weight) is mixed with 3 kilograms of water and then let stand overnight. The mixture was then dried at 80 degrees Celcius for at least 4 hours or until the % moisture was less than 10% as measured by a laboratory moisture balance. 0.97 kilograms of the resulting solid is then ground to a fine powder and mixed with 89 grams of Ludox brand binding agent (30 wt % colloidal SiO_2 in water) and 430 grams of water and mulled to produce a pug extruded through a 3 hole (1/16 inch diameter) extruder. The extrudates from the extruder are dried at 80 degrees Celsius overnight and then ground and sieved to produce Sorbant #1 having a particle size of from 16 to 60 US mesh. The packed bed density of the material (Sorbant #1) is 0.91 grams per milliliter (ASTM test method B-527). The wet attrition was measured by placing 20 g each of a 20×30 and 30×40 mesh sample in a wide mouth glass jar with 80 ml of water. The jar is placed on a roller and rolled at 85 rpm for a period of 30 minutes. The contents of the jar are poured through a 60 mesh screen and the screen is dried in air at 80° C. for 6 to 16 hours. After accounting for moisture lost or gained in the procedure, the % attrition is calculated from the amount retained on the screen relative to that originally placed in the jar. The wet attrition of Sorbant #1 is 17%.

[0018] Tap water having a pH of about 7.8 is flowed through a one half liter filter cartridge packed with Sorbant #1. The initial pH of the treated water is about 2.3. The pH of the treated water after 50 liters of water have been treated is about 3.2. The pH of the treated water after 100 liters of water have been treated is about 3.6. The pH of the treated water after 150 liters of water have been treated is about 5.0.

EXAMPLE 1

[0019] 1.08 kilograms of uncalcined titanium oxide powder (having an anatase titanium dioxide concentration of about 80% by weight) is mixed with 36 grams of $Ca(OH)_2$, 3 kilograms of water and then let stand overnight. The mixture was then dried at 80 degrees Celcius for at least 4 hours or until the % moisture was less than 10% as measured by a laboratory moisture balance. 1.04 kilograms of the resulting solid was then ground to a fine powder and mixed with 94 grams of Ludox brand binding agent (30 wt % colloidal SiO_2 in water) and 490 grams of water and mulled to produce a pug extruded through a 3 hole (1/16 inch diameter) extruder. The extrudates from the extruder are dried at 80 degrees Celsius overnight and then ground and sieved to produce Sorbant #2 having a particle size of from 16 to 60 US mesh. The packed bed density of Sorbant #2 is 0.84 grams per milliliter. The wet attrition (described in COMPARATIVE EXAMPLE 1) of the material is 6%.

[0020] Tap water having a pH of about 7.8 is flowed through a one half liter filter cartridge packed with Sorbant #2. The initial pH of the treated water is about 6.7. The pH of the treated water after 50 liters of water have been treated is about 6.2. The pH of the treated water after 100 liters of water have been treated is about 6.3. The pH of the treated water after 150 liters of water have been treated is about 6.5.

COMPARATIVE EXAMPLE 2

[0021] 1.0 kilograms of uncalcined titanium oxide powder (predominately anatase titanium dioxide, having an elemental titanium analysis of about 53% by weight, an elemental sulfur analysis of about 2.2% by weight, and an elemental calcium analysis of about 0.01% by weight, available commercially as Grade G-3 uncalcined ultra fine TiO_2 from Millennium Chemicals, Hunt Valley, Md.) is mixed with 100 grams of Ludox brand binding agent (30 wt % colloidal SiO_2

in water) and water and mulled to produce a pug extruded through a 3 hole (1/16 inch diameter) extruder. The extrudates from the extruder are dried at 80 degrees Celsius overnight and then ground and sieved to produce Sorbant #3 having a particle size of from 16 to 60 US mesh.

[0022] Water containing 300 parts per billion of arsenate (prepared according to NSF/ANSI standard 53) having a pH of about 7.5 is flowed through a 0.45 inch inside diameter, 4 inch long column packed with Sorbant #3 at a flow rate controlled to give an empty bed contact time (EBCT) of 120 seconds. The treated water is sampled periodically and analyzed for arsenic. The initial arsenic concentration of the treated water is below the detection limit of about 1 part per billion. The initial pH of the treated water is 2.5 (and reaches a pH of 7 after 830 bed volumes of water have been treated). The arsenic concentration of the effluent water is about 1 part per billion after 4,000 bed volumes of water have been treated. The arsenic concentration of the effluent water is about 10 part per billion after 6,000 bed volumes of water have been treated.

EXAMPLE 2

[0023] 1.0 kilograms of uncalcined titanium oxide powder treated with lime (predominately anatase titanium dioxide, having an elemental titanium analysis of about 52% by weight, an elemental sulfur analysis of about 1.9% by weight, and an elemental calcium analysis of about 2.1% by weight, available commercially as Grade G-2 uncalcined ultra fine TiO_2 from Millennium Chemicals, Hunt Valley, Md.) is mixed with 100 grams of Ludox brand binding agent (30 wt % colloidal SiO_2 in water) and water and mulled to produce a pug extruded through a 3 hole (1/16 inch diameter) extruder. The extrudates from the extruder are dried at 80 degrees Celsius overnight and then ground and sieved to produce Sorbant #4 having a particle size of from 16 to 60 US mesh.

[0024] Water containing 300 parts per billion of arsenate (prepared according to NSF/ANSI standard 53) having a pH of about 7.5 is flowed through a 0.45 inch inside diameter, 4 inch long column packed with Sorbant #4 at a flow rate controlled to give an empty bed contact time (EBCT) of 120 seconds. The treated water is sampled periodically and analyzed for arsenic. The initial arsenic concentration of the treated water is below the detection limit of about 1 part per billion. The initial pH of the treated water is 5 (and reaches a pH of 7 after 120 bed volumes of water have been treated). The arsenic concentration of the effluent water is about 1 part per billion after 4,000 bed volumes of water have been treated. The arsenic concentration of the effluent water is about 10 part per billion after 7,500 bed volumes of water have been treated.

[0025] While the instant invention has been described above according to its preferred embodiments, it can be modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the instant invention using the general principles disclosed herein. Further, the instant application is intended to cover such departures from the present disclosure as come within the known or customary practice in the art to which this invention pertains and which fall within the limits of the following claims.

1. A method for removing dissolved contaminants from water comprising the step of contacting a sorbant with the water, the sorbant comprising at least about 50 wt. % of an oxide of titanium and at least about 3 wt. % of a sulfate salt having a solubility in water of less than 0.5 grams per liter of water; and on an elemental analysis basis at least about 20 wt. % titanium and at least about 1 wt. % sulfur.

2. The method of claim **2** wherein the sorbant comprises at least about 80 wt. % of an oxide of titanium and at least about 5 wt. % of a sulfate salt.

3. The method of claim **2** wherein the sorbant comprises about 85 to about 95 wt. % of an oxide of titanium and about 5 to about 15 wt. % of a sulfate salt.

4. The method of claim **2** wherein the sorbant comprises about 87 to about 93 wt. % of an oxide of titanium and about 7 to about 13 wt. % of a sulfate salt.

5. The method of claim **4** wherein the sulfate salt comprises calcium sulfate.

6. The method of claim **2** wherein the sorbant comprises less than about 6 wt. % calcium on an elemental analysis basis.

7. The method of claim **5** wherein the sorbant comprises less than about 5 wt. % calcium on an elemental analysis basis.

8. The method of claim **2** wherein the sorbant comprises from about 1 to about 5 wt.

9. The method of claim **2** wherein the sorbant comprises from about 1.5 to about 4 wt. % sulfur and about 45 to about 55 wt. % titanium on an elemental analysis basis.

10. A sorbant comprising about 85 to about 95 wt. % of an oxide of titanium and about 5 to about 15 wt. % of a sulfate salt having a solubility in water of less than 0.5 grams per liter of water, wherein the sorbant comprises from about 1 to about 5 wt. % sulfur and about 35 to about 55 wt. % titanium on an elemental analysis basis, and wherein the oxide of titanium is primarily titanium dioxide.

11. The sorbant of claim **10** wherein the sulfate salt comprises calcium sulfate and wherein the sorbant comprises less than about 6 wt. % calcium on an elemental analysis basis.

12. The sorbant of claim **11** wherein the sorbant comprises about 87 to about 93 wt. % of an oxide of titanium and about 7 to about 13 wt. % of calcium sulfate.

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