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(54) Title: REMOVAL OF MICROORGANISMS AND DISINFECTION BYPRODUCT PRECURSORS USING ELEMENTAL IRON OR ALUMINUM

(57) Abstract: A process for removing microbes and/or DBPs from a media sought to be treated comprising treating said media with one or more elements capable of forming an oxide and/or an oxyhydroxide through corrosion is disclosed. Products are also contemplated.



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REMOVAL OF MICROORGANISMS AND DISINFECTION BYPRODUCT PRECURSORS USING ELEMENTAL IRON OR ALUMINUM

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from US Provisional Application Serial No. 60/503,266, filed September 15, 2003, the content of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to water and wastewater treatment processes and more specifically, to processes used to remove pathogens from water or other media.

Description of Related Art

Microorganisms pathogenic to humans are ubiquitous in the water cycle and have been found in drinking water and wells (Goyal et al., 1984; Gerba and Rose, 1990; Kramer et al., 1996). Major groups of microbial pathogens include viruses, bacteria, protozoa, and fungi. Significant sources of these pathogens may include septic tanks, wastewater discharge and reuse, landfills, and sewage sludge application on land (Yates et al., 1985), as well as runoff and infiltration from animal waste-amended fields (McMurry et al., 1998). The USEPA Science Advisory Board cited drinking water contamination as one of the highest-ranking environmental risks and reported that microbial contaminants (e.g., bacteria, protozoa, and viruses) are likely to be the greatest remaining health risk management challenge for drinking-water suppliers (USEPA, 1990). Types of illness that can result from exposure to microbial pathogens range from mild or moderate cases lasting a few days to more severe infections that last several weeks and may result in death in the more sensitive subpopulations (e.g., young children, elderly, and people with compromised immune systems). A major study of the occurrence of pathogens in U.S. ground waters tested

samples collected from 448 sites in 35 states for various indicators of fecal contamination (total coliform, *E. coli*, somatic and male-specific coliphages, and human viruses) (Abbaszadegan et al, 2003). It was found that 31.5% of the samples were positive for one or multiple pathogenic viruses using polymerase chain reaction (PCR), and human viruses were detected in 4.8% of the samples by cell culture.

Concerns over the number of waterborne disease outbreaks that continue to occur in the U.S. despite improvements in drinking water treatment practices, have resulted in the development of regulations to reduce such risks. The Surface Water Treatment Rule (SWTR) (USEPA, 1989a) and Interim Enhanced SWTR (USEPA, 1989b) were established in an effort to control microbial contaminants in drinking water systems using surface water or groundwater under direct influence of surface water. In addition, the EPA recently proposed a Ground Water Rule (GWR). The GWR is aimed at addressing microbial contamination of ground water-supplied drinking water systems in accordance with the Safe Drinking Water Act (SDWA) of 1974, as amended in 1986 and again in 1996 (USEPA, 2000). The 1986 SDWA amendments directed the EPA to establish national primary drinking water regulations requiring disinfection as treatment for the inactivation of microbiological contaminants for all public water systems, including systems supplied by ground water sources.

There are several requirements in the GWR that states may need to comply with currently or in the future. These include, for example, conducting system sanitary surveys and identification of significant deficiencies, undertaking hydrogeologic sensitivity assessments for non-disinfected systems, engaging in source water microbial monitoring, taking corrective actions (disinfection) on any system with significant deficiencies and/or positive microbial samples indicating fecal contamination, and compliance monitoring for systems which are used to disinfect to ensure that they reliably achieve 4-log (99.99%) inactivation or removal of viruses.

Although viruses are only one type of microbial pathogen known to contaminate groundwater, they are much smaller than bacteria and protozoan cysts, and thus are filtered out to a much smaller extent in porous media than bacterial due to their size. Therefore viruses can travel much longer distances in the subsurface (Jin

and Flury, 2002). Viruses are identified as the target organisms in the GWR because they are responsible for approximately 80% of disease outbreaks for which infectious agents were identifiable (Ryan et al., 2002).

Disinfection is an important water treatment process for preventing the spread of infectious diseases. While mostly effective for removing many bacteria, classical disinfectants such as chlorine have been shown as not always being sufficiently effective against viruses and protozoa (Payment and Armon, 1989, Bull et al., 1990). Data collected by the Centers for Disease Control and Prevention (CDC) and the EPA indicate that almost as many waterborne disease outbreaks were reported between 1971 and 1996 in systems with disinfection treatment that was inadequate or interrupted (134 outbreaks) as were reported in the same period among systems that did not disinfect (163 outbreaks) (USEPA, 2000). High doses of chlorine also often produce excessive amounts of disinfection by-products (DBPs) including total trihalomethanes (TTHM: chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and haloacetic acids (HAA5: monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic acids). Many of these DBPs are known or suspected human carcinogens and have been linked to bladder, rectal, and colon cancers (U.S. EPA, 2003a and b). Many studies on human epidemiology and animal toxicology have also demonstrated links between chlorination of drinking water and reproductive and developmental effects, such as fetal losses and neural tube and heart defects (U.S. EPA 2003b). It has been estimated that about 254 million Americans are exposed to DBPs, and the U.S. EPA is proposing the Stage 2 Disinfection Byproduct Rule (U.S. EPA, 2003c), which is aimed at protecting public health from DBPs in water.

Although disinfectants other than chlorine, such as chloramines, ozone, and chlorine dioxide, are being used in the U.S. and Europe, and alternative disinfection methods such as ultraviolet (UV) irradiation are available, those options are often more expensive in terms of capital investment and operation cost and/or complex and thus difficult to implement. In addition, some of these disinfection alternatives also generate DBPs, including bromate.

In addition to drinking water treatment, wastewater discharge and reuse (e.g., through groundwater recharge) and land-application of sewage sludge have attracted increasing public attention and growing concern because of the presence of human and animal pathogens in treated wastewater and sludge. Because wastewater treatment generally include primary and secondary treatment, which may only remove a fraction of the pathogenic microorganisms, discharge of treated wastewater and sludge represent a potential source of microbial contamination. In addition, chlorination and dechlorination (often with sulfur dioxide or sulfite salts) of treated wastewater prior to its discharge not only adds to the treatment cost but also generates undesirable DBPs including THMs, HAAs, and *N*-nitrosamines that are highly toxic to aquatic organisms (Jensen and Helz, 1998; MacCrehan et al., 1998).

Recently, the Department of Homeland Security has reported that water treatment facilities that use chlorine are more attractive targets for terrorist attack. A major failure of chlorine storage tanks could produce a chlorine gas plume that affects residents within a ten-mile radius. Currently about 600 facilities could threaten between 10,000 and 100,000 people (U.S. DHS, 2003). If a safer, non-oxidant-based disinfection method is used in a treatment facility to provide additional removal of pathogens, the usage and on-site storage of chlorine may be reduced, thus minimizing the risk associated with such system failure or attack.

One of the most complex problems facing the water industry today is how to provide adequate protection against infectious diseases without the risk from disinfectants and DBPs. It is difficult to manage both microbial and DBP risks, and even more challenging to do so at an acceptable cost. With increasing population and growing demand for potable water, increasingly stringent environmental regulations, and heightened security concerns, developing innovative, inexpensive, and robust technologies that can simultaneously reduce the risks of pathogens, DBPs, and residual disinfectants in drinking water is of utmost urgency.

In the last decade, elemental iron (a.k.a. zero-valent iron, metallic iron, Fe(0), and iron metal) has been increasingly used as a reactive material in permeable reactive barriers (PRBs) to remediate groundwater contaminated with solvents and other organic, metallic, and radioactive chemicals (Vidic, 2001; EPA 2002a). PRBs

are subsurface treatment zones that contain reactive materials, such as elemental iron, placed in the flow path of contaminated groundwater. PRBs have higher permeability than adjacent aquifer materials and, as groundwater flows through, dissolved contaminants are removed from water through physical and chemical processes such as adsorption, reduction reactions, and precipitation. Since 1994, about fifty full- and pilot-scale PRBs have been installed in North America and abroad (RTDF, 2003). Approximately 80% of the PRBs contain elemental iron, typically in the form of inexpensive commercial iron filings (EPA, 2002a). Unlike the conventional pump-and-treat method, PRBs are *in situ* and passive and involve minimal maintenance and operation costs. Iron PRBs also have long service lives and have been shown to remove and/or degrade pollutants effectively and continuously for multiple years (EPA, 2002a,b).

In addition to its use in PRBs for groundwater remediation, iron was evaluated for water and wastewater treatment in recent years. It has been shown that elemental iron could be used to treat wastewaters containing refractory compounds such as azo dyes, nitroaromatic compounds, and explosives (Perey et al., 2002; Oh et al, 2003). It has also been demonstrated that reductive treatment with iron rapidly converts certain refractory compounds into products that are much more degradable in the subsequent chemical or biological oxidation processes (Perey et al., 2002; Oh et al, 2003). Furthermore, elemental iron has also be shown to remove arsenic and other chemical pollutants from water (Ferrell et al., 2001; Melitas et al., 2002). These authors reported that corrosion of iron continuously generates iron oxides to adsorb and remove arsenic from water. In December 2003, Sengupta of Lehigh University reported that the use of polymeric ion exchange beads impregnated with ferric hydroxide could be used to remove arsenic from well water in India.

To date, however, elemental iron, nor any other zero-valent metal, has not been shown to remove biological contaminants from water or other media.

SUMMARY OF THE INVENTION

In accordance with the present invention, elemental iron and/or aluminum is employed to remove and/or inactivate waterborne and/or airborne biological agents,

including, but not limited to, viruses, bacteria, protozoa, algae, fungi, and prions. The invention is also directed to methods for the removal of precursors of disinfection by-products (DBPs). This invention may be used to treat any material, and is particularly suitable for treating liquids such as water, including drinking water, wastewater, surface water, groundwater, backwash water, leachate, and other aqueous wastes such as medical wastes. This invention is also suitable for treating air and other gases. Other uses with non-liquid and non-gas materials are also envisioned.

Additional objects, features, and advantages of the invention will be set forth in the description which follows, and in part, will be obvious from the description, or may be learned by practice of the invention. Objects, features and advantages of the invention may be realized and obtained by means of the instrumentalities and combination particularly pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a schematic of a suitable experimental column setup for use in connection with the present invention.

Figure 2(a) and (b) shows the breakthrough curves of two viruses, ϕ X174 (a) and MS2 (b), from columns packed with only oxide-removed (cleaned) sand vs. oxide-removed sand plus three millimeters of embedded elemental iron particles (in the form of PeerlessTM iron granules), over 37 pore volumes (i.e., the volume of virus-laded solution treated in this demonstration was 37 times that of the total void space in the column).

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Elemental iron (or other elements such as aluminum or combinations thereof) can be used to remove microorganisms and/or other biological agents from water because elemental iron and other metallic elements can continuously generate and renew the surface oxides and oxyhydroxides through corrosion in water, and metal oxides and oxyhydroxides can remove and/or inactivate biological agents such as viruses. In accordance with the present invention, the term "microorganism-removing agent" means any element or combination of elements in any form that are capable of

forming metal oxides and/or oxyhydroxides through corrosion. The terms "microbe," "microorganism," "microbial agent," "microbiological agent," and "biological agent" are interchangeably used throughout the instant disclosure and connote a living organism or non-living biological agent typically too small to be seen with the naked eye; including bacteria, fungi, protozoa, and microscopic algae; also includes viruses and prions. In accordance with the present invention, it was found that even a very thin layer (e.g. about 3 mm) of elemental iron particles (used as the microorganism-removing agent) in the flow path of virus-(or other) contaminated water (8.8 min residence time) resulted in approximately 2-log (99%) removal of two viruses over 40 pore volumes, and 90% of the removal was due to inactivation rather than reversible sorption. Result of the study using iron and two viruses supports the invention that elements such as iron are capable of removing and/or inactivating microorganisms such as viruses.

As mentioned *supra*, dealing with microbiological contamination of drinking water continues to be a great challenge to public health risk management in the 21st century. To protect humans from microbial contamination, US EPA proposed Ground Water Rule (GWR) and other regulations to address microbial contamination and DBP formation in drinking water systems, in order to reduce public health risks resulting from pathogenic contamination and DBP toxicity. In the last decade, zero-valent iron has been increasingly used as a reactive material in permeable reactive barriers (PRBs) to remediate groundwater contaminated with solvents and other organic, metallic, and radioactive chemicals. However, iron has never been shown to remove biological agents. In accordance with the present invention, saturated column studies were conducted to test zero-valent iron to remove the viruses MS2 and ϕ x 174 from contaminated water. As shown *infra* results indicate that both MS2 and ϕ x 174 were significantly removed from solution after pumping the water through the zero-valent iron column. The more zero-valent iron that was used, the more viruses that were removed. Removal efficiencies for viruses can be 3-log₁₀ (99.9%) or even higher. In addition to iron amount, flow velocity may also affect the removal efficiency in some cases. Namely, a slower flow velocity can result in a higher removal efficiency. Mass balance results suggest that the removal of viruses is primarily due to inactivation or irreversible sorption. In accordance with the present

invention, zero-valent iron can be employed for the treatment of microbially contaminated aqueous media, including drinking water, wastewater, groundwater, backwash water, leachate, and other aqueous wastes such as medical wastes, and gaseous media including pathogen-laden air streams and process off-gases. In addition, processes of the present invention are also potentially useful for removal of prions, which may cause, for example, mad cow disease. Prions are nanometer-size protein particles that are biological in nature. Since elemental iron (through corrosion and oxide/oxyhydroxide formation) can remove viruses, which consist of a protein sheath, iron is expected to also be effective in removing prions. In addition, processes of the present invention are also useful for the removal of DBP precursors such as natural organic matter including humic acid and fulvic acid, as these DBP precursors are known to adsorb to metal oxides (Stumm and Morgan, 1996) and thus can be removed with elemental iron or other metals.

Elemental iron corrodes in water; that is, it is oxidized by dissolved oxygen, other oxidants in water, and water itself. Any element or combination of elements that corrodes in water may be useful in some embodiments of the present invention. Iron corrosion generates minerals such as iron (Fe^{++} and Fe^{+++}) oxides and oxyhydroxides (e.g., goethite and magnetite) on the surface, and iron oxides and oxyhydroxides are capable of removing microorganisms from water. The mechanisms of removal may involve adsorption of microbial particles (e.g., viruses and bacteria) in water to iron surfaces through electrostatic attraction and/or other interactions. Aluminum functions in the same way by forming an aluminum oxide and hydroxides on the surface, and these aluminum corrosion products remove microorganisms from water. Iron and aluminum oxides and oxyhydroxides contain abundant positively charged surface sites because these minerals typically have a zero point of charge (pH_{ZPC}) at circum-neutral or alkaline pH, whereas most bacteria and viruses are negatively charged at neutral pH and therefore are attracted to the metal surface. Since iron corrodes to form new surface sites continuously in water and other aqueous media, iron can be used to remove viruses for as long as the corrosion continues. This can be multiple years, as has been demonstrated in many field-scale iron PRBs. However, aluminum may function slightly differently than iron in this regard in some cases. That is, aluminum oxides are more protective (less permeable)

and can slow down aluminum corrosion, so new oxides are not generated as quickly. Thus, iron may be preferable in some cases although use of aluminum and other corrodible metals is also possible. When water containing microbes (such as viruses and bacteria) and DBP precursors (such as humic acid) comes into contact with elemental iron or aluminum particles (for example, in a treatment column or filter media), corrosion products of iron or aluminum will be generated constantly and microbes and DBP precursors can be removed from water in a continuous fashion. As used herein, iron and/or aluminum are referred to specifically and such reference also includes other materials that will corrode to remove microbes and/or DBP precursors or other materials.

The present invention is useful, for example, for use in water treatment plants producing drinking water. Water can be treated in a treatment column, cartridge, or filter containing elemental iron (in the form of filings or granules of pure, cast, or scrap iron, for example) as an active component to remove microorganisms and/or DBP precursors in the water. Alternatively, iron or aluminum particles (and/or other corrodible metals) may be applied to treat water in a reactor, such as a mixed tank reactor or a batch reactor, to remove microbes, DBP precursors, and other undesirable materials from the water. Similar applications for the removal of microorganisms and/or DBP precursors from other aqueous (such as wastewater and groundwater) and gaseous media (such as air and off gases) are also envisioned. The present invention provides substantial benefits over other standard treatment options as it provides an effective, inexpensive, simple, and flexible method for removing virtually any type of microorganisms. In addition, through oxide and hydroxide formation, iron and aluminum can remove natural organic matter such as humic and fulvic acids from water and thus minimize the formation of toxic DBPs in drinking water. Incorporation of zero-valent iron (and/or aluminum or other similar material) into new or existing filtration media and/or tank reactors can be used, for example, as follows:

- a) as a pre-disinfection process before chlorination or other disinfection treatment, to eliminate the need for storing liquid chlorine in water and wastewater treatment plants and other facilities, which can raise

- risks of accidental or deliberate release of chlorine (e.g., due to terrorist attack);
- b) to reduce the dosage and/or contact time of disinfectant(s) required to achieve desired removal of microorganisms and prevent re-growth during distribution, thus minimizing pathogens, DBP formation, and residual disinfectant levels in water simultaneously;
 - c) to circumvent and/or prevent potential terrorist activities as zero-valent iron and other similar materials may be effective against many toxic chemicals and biological agents released to air or water by terrorists;
 - d) to help to reduce or possibly completely eliminate chlorine use in water which would be useful to government agencies and utility companies seeking to meet drinking water standards.

Elemental iron can be found in anything containing iron metal, such as but not limited to steel (or its derivatives, like nuggets, shots, grit, etc.), scrap iron, cast iron, iron sponge, powder, filings, and slugs. Aluminum containing material of any type, shape and form can also be used if desired for any reason. Elemental iron is in some cases preferred over Fe^{++} and Fe^{+++} compounds because its capacity to remove microbes and DBP precursors is renewed continuously through corrosion and thus it will last much longer without having to be replaced or rejuvenated as often. For example, elemental iron can remain active for as long as ten years in the field and more than one year in a laboratory column study, whereas Fe^{++} and Fe^{+++} oxides may cease to work quickly as surface sites are occupied, covered, or inactivated over time.

Similarly, for wastewater treatment, an active or passive treatment system involving elemental iron or aluminum may be used to remove viruses, bacteria, protozoa, other microbes, and/or DBP precursors from wastewater to meet the treatment or discharge requirement and to minimize the negative impact of wastewater discharge to the ecosystem. For groundwater applications, passive underground iron PRBs or active injection of iron particles or suspensions into the subsurface, for example, are two possible approaches to remove microorganisms such as viruses from groundwater and/or to prevent their migration in the subsurface. In

these examples, such treatment (or pre-treatment) with elemental iron or aluminum may save the cost of disinfection (e.g., through use of less disinfectants and other chemicals) and at the same time reduce the formation of harmful DBPs associated with use of chlorine, ozone, or other disinfectants.

The present invention has several significant benefits, including better protection of public health from diseases related to water-borne and other pathogens and/or DBPs, cost savings due to lower overall disinfection cost, lower residual disinfectant level and reduced production of undesirable DBPs during water or wastewater treatment. In addition, the proposed iron/aluminum process has the following advantages:

- (1) Cast or scarp iron is an industrial waste material and may be a readily available and inexpensive form of elemental iron (typically $\geq 90\%$ iron content).
- (2) Elemental iron and aluminum particles can have many years of service life without regeneration and can be used (among other processes) in a passive process, such as a gravity-fed treatment column or filter, to minimize maintenance and operational cost.
- (3) Corrosion of iron and aluminum does not create any toxic by-products and therefore poses little threat to the environment and human health. In fact, when used for drinking water treatment, iron and aluminum corrosion products, such as Fe^{++} , Fe^{+++} , and Al^{+++} ions, can serve as coagulants to improve the efficiency of water treatment (i.e., better removal of suspended solids from water) and reduce the chemical cost for coagulants, such as ferric sulfate, ferric chloride, and aluminum sulfate.
- (4) Depending on the amount of iron/aluminum used and the contact time, the treatment alone may achieve sufficient disinfection. Or, the proposed process may be combined with a subsequent and/or prior disinfection method such as UV, chlorination, or chloramination to meet the desired treatment goal. In the latter case, the iron/aluminum (pre)treatment can lower the material and operational costs for disinfection and can also minimize the safety concerns associated with using chemical disinfectants.

(5) By removing natural organic matter, well-known precursors of DBPs, and lowering the dosage of disinfectants used, the proposed iron/aluminum treatment also has an added advantage of reducing the potential of DBP formation and the toxicity of residual disinfectants. DBPs are toxic and/or carcinogenic compounds formed through reactions of DBP precursors (e.g., natural organic matter) and chemical disinfectants used in water and wastewater treatment processes (such as chlorine).

In accordance with the present invention, elemental iron and/or other elements alone or in combination are employed to remove and/or inactivate microorganisms from water or other media. The two viruses and a cast iron employed are merely exemplary. Similar results would also be achieved with other types of elemental iron and aluminum. In addition, a combination of iron and aluminum and/or other elements could be used. It is desirable in many embodiments if the amount of elemental iron or other microorganism-removing agent is from 0.1 to 99.9% by weight based on the total weight of material used for treatment of the media, such as based on the weight of sand, rock, gravel, and/or other filtration component particularly preferably from 1 to 99% by weight. In some embodiments, the present invention relates to a conduit such as a column filled with standard water filtration media (e.g. anthracite, sand and/or gravel). Alternatively, the present invention could take any other desired form such as a continuous-flow, batch, or semi-batch mixed-tank reactor containing water to be treated, to which iron or aluminum is added to remove microorganisms and/or DBP precursors.

This invention preferably employs a device which utilizes a medium that contains elemental iron or aluminum as an active component in a batch, semi-batch, or flow-through column or tank system for the treatment of drinking water, wastewater, surface water, groundwater, backwash water, leachate, or any other liquid or gaseous streams containing microbial agents and/or DBP precursors. The device may comprise a column, cartridge, filter, barrier, tank, or another device or process (termed "device" hereafter) which utilizes a microorganism-removing agent. The device contains any microorganism-removing agent such as elemental iron or aluminum as an active treatment component and may also contain other constituents, such as sand or gravel, for functional, economic, or any other desired purposes (e.g.,

to minimize head loss, to prevent clogging, or to control pH). Water or air (or other material sought to be treated) is introduced into the device containing the microorganism-removing agent such as elemental iron or aluminum. After a sufficient contact time, which depends on factors such as system configuration, amount of microorganism-removing agent, mixing, and flow rate, microorganisms and/or DBP precursors are removed from the influent water or air by iron and/or aluminum particles. The treated water or air exiting the device (i.e., the effluent) will have a lower content of microorganisms and/or DBP precursors than the influent water. In our study, the viral content in water can be reduced using iron by 97% to 99% and even 99.9% in some cases. In the present invention, any flow velocity can be employed. The flow velocity when a column is employed is preferably from 0.1 cm/h to 10 m/min, particularly preferably at least 1.0 cm/h. Any desired residence time can be employed. In some embodiments a residence time in the corrodible material is preferably at least 0.1 minute, particularly preferably from 1 minute to 500 minutes, and even more preferably from 5 minutes to 60 minutes.

Column experiments have been conducted using two viruses, to prove the concept and to demonstrate the effectiveness of elemental iron to remove microorganisms from water. The experimental setup and procedure had been developed and used previously by the inventors to study the transport of viruses in porous media (Jin, 1997, 2000; Chu et al., 2000; Chu et al., 2001). A schematic diagram of the experimental setup is shown in Figure 1. Fritted stainless steel plates were placed at both ends of the columns to obtain a uniform flow distribution. A fraction collector was used to collect samples. All columns were packed wet to avoid trapping of gas bubbles. The solution was deoxygenated by nitrogen and degassed under vacuum to remove dissolved oxygen and other gases. Column performance and hydrodynamic properties were determined with bromide as a conservative tracer, which was quantified by a Dionex ion chromatograph. The column experiments were conducted in a cold room with temperature controlled at 4–6 °C to avoid virus inactivation by high temperatures. A detailed description is set forth *infra* in the examples section.

Elemental iron or aluminum can remove and/or inactivate water-borne microorganisms such as viruses. When influent water containing microbes such as viruses and bacteria comes into contact with elemental iron particles (e.g., placed in a treatment column or filter medium), microorganisms can be removed from water continuously.

This invention can potentially be used to treat any liquid or gaseous media, and in particular, is adapted for use with drinking water, wastewater, surface water, backwash water, leachate, groundwater, other aqueous wastes, contaminated air, and off gases. For example, for water treatment plants producing drinking water, a treatment column, cartridge, or filter containing elemental iron (in the form of filings or granules of cast or scrap iron, for example) as an active component may be used to remove microorganisms and/or DBP precursors in the water. Similar, for wastewater treatment, an active or passive treatment system involving elemental iron may be used to remove microbes and/or DBP precursors from wastewater prior to disinfection and/or effluent discharge. For groundwater applications, passive underground iron PRBs or active injection of iron particles or suspensions into the subsurface, for example, are two possible approaches to remove microorganisms in groundwater and/or reduce their migration in the subsurface. In these examples, such treatment (or pre-treatment) with elemental iron may save the cost of disinfection (e.g., through use of less disinfectants and other chemicals) and at the same time reduce the residual disinfectant level and the formation of harmful DBPs associated with use of chlorine, ozone, or other disinfectants.

Existing water disinfection methods involve use of strong oxidizing chemicals, such as chlorine (or hypochlorite), bromine, iodine, chloramines, chlorine dioxide, and ozone to kill microorganisms in water. Chlorine is the most commonly used disinfectant in the U.S. and many other countries, but it has been shown to be less effective for viruses and protozoa than for bacteria. These disinfectants, all of which are toxic chemicals and have many safety concerns, need to be stored or generated on-site and applied on a continuous basis. In addition, the process requires active control and laborious maintenance. Furthermore, other chemicals (e.g., hydrochloric acid, sodium hydroxide, sulfur dioxide, etc.) are needed to control the pH and/or neutralize

excess disinfectants. Some disinfection methods, such as ozone and UV disinfection, are less flexible, more complex and difficult to operate, and require large initial capital investment. Finally, many of these chemical disinfectants can react with constituents, such as natural organic matter, in water and wastewater to produce significant levels of toxic or carcinogenic DBPs including trihalomethanes, haloacetic acids, and bromate.

In contrast, the invention differs from existing water and wastewater disinfection processes in that (1) it can be passive and long-lasting and requires little maintenance, (2) it does not involve use of hazardous chemicals, (3) it does not generate harmful (by)products, (4) it is less expensive than the existing chemical (oxidative) methods to disinfect water, and (5) it is flexible and involves low capital investment, and can be used as a stand-alone unit or added/retrofitted to existing treatment facilities.

EXAMPLES

In one of the experiments that we have conducted to demonstrate the utility of the invention, a thin layer (~3 mm) of PeerlessTM iron was sandwiched into a column (3.5 cm i.d. x 8 cm length) packed with 8-cm Accusand sand, which had been treated to remove any trace metal oxides. An input solution containing ~10⁸ plaque-forming units per liter ("pfu/L," a measure of the concentration of viable or infective viruses in solution) of MS2 and ϕ X174, respectively, was pumped into the column at a flow velocity of 2.05 cm/h. This gives a residence time of 8.8 min in the iron layer. Effluent samples were collected with a fraction collector and analyzed for both viruses. In the control experiment, only treated (oxide-free) sand was used to pack the column and the experiment was run as described above. A 3% beef extract solution (pH 9.5) was used to elute the columns at the end of experiments to recover viable viruses and determine if the viruses retained were due to reversible sorption or inactivation. The column was packed wet by filling it partially with artificial ground water (AGW, pH 7.5, ionic strength 2.0 mM) to avoid trapping of air bubbles and ensure packing uniformity. The AGW contained 0.075 mM CaCl₂, 0.082 mM MgCl₂, 0.051 mM KCl, and 1.5 mM NaHCO₃. In this example a solution containing approximately 10⁸ pfu/L of both MS2 and ϕ X174 was introduced into the column as a

step input, using a peristaltic pump at a flow velocity of 2.05 cm/h. This gave a residence time of 8.8 min in the iron section based on the porosity of the PeerlessTM iron. Effluent samples were collected with a fraction collector and analyzed for both viruses using the standard procedures according to Adams, 1959, detailed *infra*. In another experiment, only treated (iron oxide-free) sand was used to pack the column and the virus removal experiment was repeated as described above. A 3% beef extract solution (pH 9.5) was used to elute the columns at the end of each experiment to obtain a mass balance for the viruses and to determine whether the viruses were removed due to reversible sorption or irreversible sorption/inactivation.

Breakthrough curves of ϕ X174 and MS2 from the clean (oxide-free) sand column and the sand column containing 3 mm of PeerlessTM iron are shown in Figure 2. As the data show, in the cleaned (oxide-free) sand column without elemental iron, the viruses broke through completely and little removal was observed. In contrast, with only 3 mm of PeerlessTM iron, greater than 99% and 97% removal from the AGW was achieved for MS2 and ϕ X174, respectively. These removal efficiencies were sustained over about 40 pore volumes, indicating that elemental iron can continuously remove viruses from the incoming water. Based on the mass recovery results from beef extract elution, the observed (97-99%) removal of both viruses by elemental iron was predominantly (approximately 90%) due to inactivation or irreversible sorption, and only about 10% was due to reversible sorption.

These results clearly demonstrate that even a very thin layer (3 mm) of commercial cast iron was able to remove a large fraction of viruses from contaminated water continuously. For large-scale treatment systems, the removal efficiency can be increased as desired by increasing the contact time of viruses with iron particles. This may be achieved by increasing the contact time through one of the following or their combinations: increasing the amount of iron used, decreasing the iron particle size, or reducing the water flow rate (e.g., by increasing the column's cross-section area).

Using one type of elemental iron and two different viruses as examples, the above study provides supporting evidence for this invention. While studies have not been conducted for all types of microorganisms and/or DBP precursors, the outcomes

of these studies are expected to support this invention. Also, while studies with aluminum was not carried out, we expect the results to be comparable and supportive of the invention as well. The reasons for these expected results are as follows. First, the main mechanism for the removal of viruses with elemental iron is adsorption of negatively charged virus particles to the surface iron oxides and oxyhydroxides, which contain abundant positively charged surface sites at circum-neutral pH (Stumm and Morgan, 1996; Schwarzenbach et al., 2002). Since many microorganisms, including bacteria and protozoa, are negatively charged at near-neutral pH, these microbes can be removed by iron oxides and oxyhydroxides via electrostatic interactions. For example, *Cryptosporidium* (a disease-causing protozoan) has a pH_{zpc} of 2.5 and is negatively charged in most natural waters (Drozd and Schwartzbrod, 1996). Second, it has been demonstrated that iron oxides can adsorb and remove natural organic matter such as humic and fulvic acids (Stumm and Morgan, 1996), which are well-known precursors of many DBPs in water and wastewater treatment. By removing natural organic matter from the influent solution using elemental iron, the formation of toxic DBPs in water and wastewater treatment is expected to be lowered. Finally, because aluminum oxides have similar or higher pH_{zpc} than iron oxides (Stumm and Morgan, 1996; Schwarzenbach et al., 2002), corrosion products of aluminum in water are also expected to contain abundant positively charged surface sites, which can remove and/or inactivate biological agents and/or DBP precursors in a similar manner. In summary, if column studies similar to that described above are carried out, with elemental iron replaced by elemental aluminum and/or the two viruses replaced by other microorganisms or DBP precursors, the results are expected to be similar; that is, the concentrations of microorganisms and/or DBP precursors in the effluent are expected to be lower than that in the influent solution, due to removal by iron or aluminum.

All the references described above are incorporated by reference in its entirety for all useful purposes. These references include the following:

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While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope

of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

As used herein and in the following claims, terms such as “a”, “the” and so on can connote the singular or plural of terms that follow.

What is claimed is:

1. A process for removing microorganisms and/or disinfection by-product precursors from a media sought to be treated comprising treating said media with one or more elements capable of forming an oxide and/or an oxyhydroxide through corrosion.
2. A process as claimed in claim 1, wherein the media comprises at least one of surface water, drinking water, wastewater, backwash water, groundwater, leachate, other aqueous waste or medical waste.
3. A process according to claim 1, wherein said element comprises at least one of aluminum or iron.
4. A process according to claim 1, wherein said element comprises iron.
5. A process for reducing the use of a chemical disinfectant used to disinfect water comprising treating said water sought to be disinfected with a microorganism-removing agent such that said chemical disinfectant can be decreased and/or eliminated without a negative change in efficacy of said disinfection of said water.
6. A process according to claim 5, wherein said microorganism-removing agent comprises one or more elements capable of forming an oxide and/or an oxyhydroxide through corrosion.
7. A process according to claim 5, wherein said microorganism-removing agent is added to said water prior to application of a chemical disinfectant, irradiation, or filtration.
8. A process to improve the quality of water by decreasing the formation of disinfection by-products during disinfection which comprises treating water

with one or more elements capable of forming an oxide and/or an oxyhydroxide through corrosion.

9. A disinfection system capable of being used to reduce microbiological agents in water comprising either a conduit packed with filtration media and at least one microorganism-removing agent, or a container comprising at least one microorganism-removing agent and water.
10. A system according to claim 9 wherein said filtration media comprise at least one of anthracite, sand or gravel.
11. A system according to claim 9, wherein said at least one microorganism-removing agent is selected from the group consisting of elements capable of forming an oxide and/or an oxyhydroxide through corrosion in water.
12. A system according to claim 11, wherein said microorganism-removing agent is in contact with media to be treated for a time of 0.1 minute or more.
13. A disinfection product comprising a conduit, and within said conduit, filtration media and a microorganism-removing agent packed in said conduit wherein said microorganism-removing agent is present in an amount of from 0.1 to 99.9% based on the weight of the filtration media.
14. A product according to claim 13, wherein said filtration media comprises at least one of anthracite, sand or gravel.
15. A product according to claim 13, wherein said microorganism-removing agent comprises one or more agents capable of forming an oxide and/or an oxyhydroxide through corrosion in water.
16. A product according to claim 13, wherein said microorganism-removing agent comprises iron and/or aluminum.

17. A system according to claim 12, wherein said microorganism-removing agent comprises iron and/or aluminum.

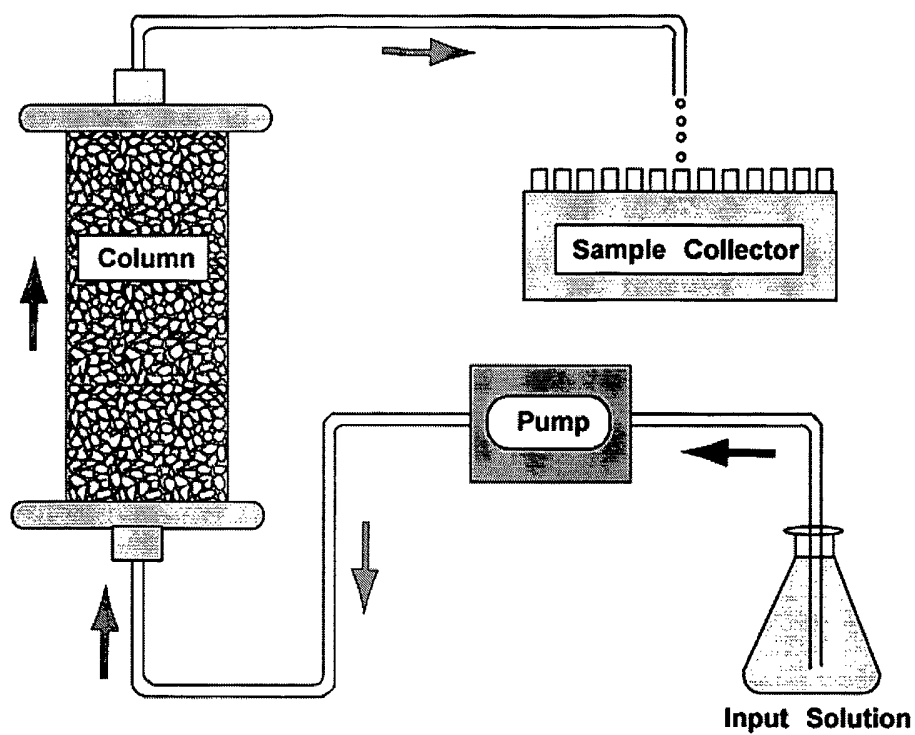


Figure 1. Schematic diagram of the experimental setup to demonstrate virus removal from water.

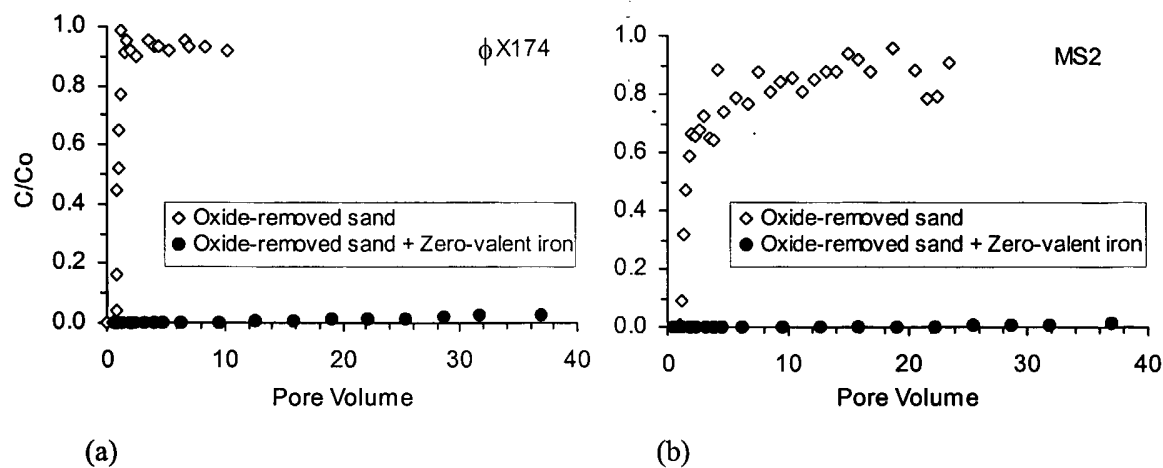
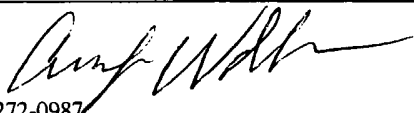


Figure 2. Breakthrough curves of two viruses, ϕ X174 (a) and MS2 (b), from columns packed with only oxide-removed (clean) sand vs. oxide-removed sand plus 3 mm of embedded PeerlessTM iron granules.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/30025

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : C02F 1/50 US CL : 210/764 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. : 210/764,668, 669, 691,694,719,757,192,198.1,203,205,266,282,290; 422/28,29 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	US 5,198,118 A (HESKETT) 30 March 1993, col. 5 line 8 through col. 8 line 68	9
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Y		1-17
Y	US 5,795,471 A (NAITO) 18 August 1998, col. 3 line 41 through col. 5 line 35	10, 14
A	US 4,178,249 A (COUNCILL) 11 December 1979	
A	US 5,928,720 A (KUHN et al.) 27 July 1999	
A	US 6,221,262 B1 (MACDONALD et al.) 24 April 2001	
A	US 5,935,609 A (DENKEWICZ JR, et al.) 10 August 1999	
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* 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 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 20 December 2004 (20.12.2004)		Date of mailing of the international search report 04 JAN 2005
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. (703) 305-3230		Authorized officer Peter A. Hruskoci  Telephone No. 571-272-0987