



- (51) International Patent Classification:
C02F 1/28 (2006.01) *C02F 9/00* (2006.01)
- (21) International Application Number:
PCT/US2014/020662
- (22) International Filing Date:
5 March 2014 (05.03.2014)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/777,010 12 March 2013 (12.03.2013) US
61/875,998 10 September 2013 (10.09.2013) US
- (71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).
- (72) Inventors: **DOYLE, Meredith, M.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **PEMBERTON, Eric, C.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **SIEDLE, Allen, R.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-

3427 (US). **STOUFFER, Mark, R.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **LAPOS-KUCHAR, Julie, A.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

[Continued on next page]

(54) Title: REMOVAL OF CHLORINE AND/OR CHLORAMINE FROM AQUEOUS SOLUTIONS

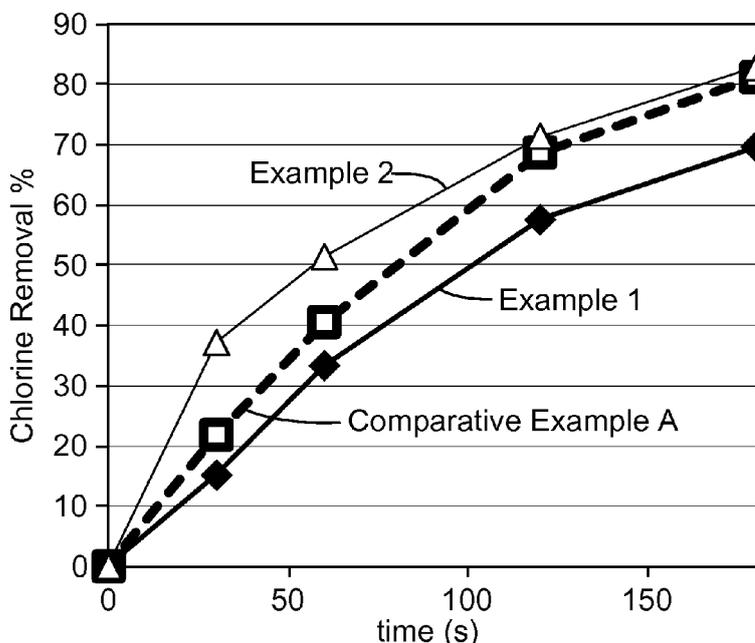


FIG. 3

(57) Abstract: Described is a method of removing chlorine from an aqueous solution by: providing an aqueous solution having chloramine and/or chlorine; and contacting the aqueous solution with a medium having a porous carbon substrate having at least 1.5 % by mass of sulfur.

WO 2014/164120 A1

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

REMOVAL OF CHLORINE AND/OR CHLORAMINE FROM AQUEOUS SOLUTIONS**TECHNICAL FIELD**

5 [0001] A filtration medium comprising material with the ability to remove chloramine and/or chlorine from aqueous solutions is described along with methods of removal.

SUMMARY

10 [0002] There is a desire to provide a filtration medium, which is less expensive, more efficient, and/or has a higher capacity for the removal of chloramine and/or chlorine than currently available filtration media. In some instances, it is desirable to identify filtration media that is able to be used effectively in applications requiring high throughput and short contact time between the aqueous stream and the filtration bed.

15 [0003] In one aspect, a method of removing chloramine and chlorine from an aqueous solution is provided comprising: providing an aqueous solution comprising chloramine and chlorine; and contacting the aqueous solution with a medium comprising a porous carbon substrate, wherein the porous carbon substrate comprises at least 1.5 % by mass of sulfur.

20 [0004] In one aspect, a method of removing chlorine from an aqueous solution is provided comprising: providing an aqueous solution comprising chloramine and chlorine; and contacting the aqueous solution with a medium comprising a porous carbon substrate, wherein the porous carbon substrate comprises at least 1.5 % by mass of sulfur.

25 [0005] In another aspect, a method of removing chlorine from an aqueous solution is provided comprising: contacting an aqueous solution comprising at least 0.5 ppm of chloramine and chlorine with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and collecting the eluate, wherein the eluate comprises less than 0.1 ppm of chloramine.

[0006] In another aspect, a method of removing chlorine from an aqueous solution is provided comprising: contacting an aqueous solution comprising about 2 ppm chlorine with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and collecting the eluate, wherein the eluate comprises less than 1 ppm, 0.5 ppm, or even 0.1 ppm of chlorine.

30 [0007] In still another embodiment, a method is provided comprising: providing a medium prepared by thermal treatment of (i) the surface of a carbonaceous solid and (ii) a sulfur-containing reactant compound; and contacting the medium with an aqueous solution comprising chloramine and chlorine, wherein after contact with the medium, the aqueous solution has a decreased amount of chloramine and a decreased amount of the chlorine.

35 [0008] In another embodiment, a method is provided comprising: providing a medium prepared by thermal treatment of (i) the surface of a carbonaceous solid and (ii) a sulfur-containing reactant

compound; and contacting the medium with an aqueous solution comprising chlorine, wherein after contact with the medium, the aqueous solution has a decreased amount of chlorine.

[0009] In another embodiment, a liquid filtration device is provided comprising: a vessel for treating a chlorine-containing liquid, wherein the vessel contains an active chlorine removal material and wherein the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

[0010] In another embodiment, a liquid filtration device is provided comprising a fluid conduit for liquids, fluidly connecting a fluid inlet to a fluid outlet; and a filtration medium disposed in the fluid conduit; wherein the filtration medium contains an active chlorine removal material and wherein the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

[0011] In another embodiment, the liquid filtration device of paragraphs [0009] or paragraph [0010] is provided wherein the liquid filtration device is used in conjunction with at least one of an electrodeionization water treatment system, an electrodialysis water treatment system or a household water treatment system.

[0012] The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages will be apparent from the description and from the claims.

DESCRIPTION OF THE FIGURES

[0013] Fig. 1 is a chart of the percent chloramine removed versus time for Comparative Example A and Examples 1 and 2;

[0014] Fig. 2 is a chart of the percent chloramine removed versus time for Comparative Example B and Example 3;

[0015] Fig. 3 is a chart of the percent chlorine removed versus time for Comparative Example A and Examples 1 and 2;

[0016] Fig. 4 is a chart of the percent chlorine removed versus time for Comparative Example B and Example 3;

[0017] Fig. 5 is a chart of the chlorine concentration in the effluent versus gallons treated for Comparative Example C run in duplicate and Example 4 run in duplicate;

[0018] Fig. 6 is a chart of the percent free chlorine removed versus gallons treated for Comparative Example F and Example 5, measured using Chlorine Testing Protocol II (Flow-Through Test) at an Empty Bed Contact Time of 2.4 sec; and

[0019] Fig. 7 is a chart of percent free chlorine removed versus throughput gallons for Comparative Example F and Example 5, using a carbon block half the length of the carbon block of Fig. 6 at an Empty Bed Contact Time of 1.1 sec.

5

DETAILED DESCRIPTION

[0020] As used herein, the term

“a”, “an”, and “the” are used interchangeably and mean one or more; and

“and/or” is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B).

10

[0021] Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

[0022] Also herein, recitation of “at least one” includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least 100, etc.).

15

[0023] The replacement of chlorine by chloramine as a disinfectant by US municipal water districts is increasing mainly due to government regulations that limit the amount of carcinogenic disinfectant byproducts present in water such as haloacetic acids and trihalomethanes (of which chlorine is a main contributor). Chloramine is more stable than chlorine in water and the majority of water filters optimized for chlorine reduction are ineffective at reduction of chloramines. It is desirable to remove chloramine because it has taste and odor concerns and chloramine is toxic to kidney dialysis patients and aquatic organisms.

20

[0024] A number of activated carbon particles having catalytic activity have been used to remove chloramine from aqueous streams. For example, U.S. Pat. No. 5,338,458 (Carrubba et al.) discloses an improved process for the removal of chloramine from gas or liquid media by contacting the media with a catalytically-active carbonaceous char. U.S. Pat. No. 6,699,393 (Baker et al.) shows improved chloramine removal from fluid streams, when the fluid stream is contacted with an activated carbon, which has been pyrolyzed in the presence of nitrogen-containing molecules, versus a catalytically-active carbonaceous char. WO Publ. No. 2011/125504 (Hitomi et al.) discloses an activated carbon having high catalytic activity containing 1.40-4.30 mass % oxygen, 0.90-2.30 mass % nitrogen, 0.05-1.20 mass % sulfur, and 0.40-0.65 mass % hydrogen, which is said to effectively break down chloramines. Hitomi et al. discloses that if the amounts of these elements are too high, the catalytic activity of the activated carbon will be diminished.

25

30

[0025] Recently, Applicants have discovered carbon-based filtration media that is less expensive, and/or more efficient at the removal of chloramine than currently available filtration media.

35

Furthermore, this filtration media can be used effectively in high throughput applications to remove chloramine, which have short contact time in the filtration bed. It has now been

discovered that these treated carbon substrates, optimized for chloramine reduction through treatments with sulfur, retain the carbon substrate's ability to reduce chlorine prior to modification, despite the modification employed. Further, it has been discovered that in some embodiments, the carbon substrate's capacity for removal of chlorine is improved through thermal treatments with sulfur as disclosed herein.

[0026] It has now been discovered that in addition to the removal of chloramine, this reaction product as disclosed herein can be tuned to remove other contaminants in the aqueous streams, such as chlorine, enabling a single filtration medium to remove multiple impurities, for example chloramine and chlorine.

[0027] Chlorine may be added to water in a gaseous form or as sodium or calcium hypochlorite as a disinfectant in drinking water supplies. Because of the odor and/or taste it imparts on potable water, it is desirably removed. In one embodiment, it would be desirable to have a media that is efficient at removing both chloramine and chlorine. As used herein chlorine refers to free chlorine. When chlorine (i.e., Cl_2) is added to water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) form, which are traditionally referred to as "free chlorine". Although chlorine is being replaced by chloramine, municipalities may switch between the disinfectant systems, and therefore, it would be advantageous to not have to change the filtration media when the disinfectant system is changed. Further, water streams can be combined, changes in the pH of the water or the ratio of ammonia to chlorine can impact the amount of free chlorine present, and/or end-use customers may not know what disinfectant system was used; therefore, it would be helpful to have a media that able to remove both chloramine and chlorine from aqueous streams.

[0028] Chlorine, when used as a disinfectant, would be present in part per million quantities (e.g., 0.1 to 2.5 ppm). There is, therefore, a desire to have a media that can remove both chloramine and chlorine. The objective of the present disclosure is to provide such a medium, and preferably provide a medium having high capacity for removal of both chloramine and chlorine.

[0029] In the present disclosure, a reactant compound comprising sulfur and a carbon substrate are contacted and exposed to thermal treatment to form the medium of the present disclosure.

[0030] Reactant Compound

[0031] The reactant compound used to prepare the filtration medium of the present disclosure comprises sulfur. In one embodiment, the reactant compound is a sulfur-containing reactant compound, or a sulfur and nitrogen-containing reactant compound. As used herein, a sulfur-containing reactant compound refers to any reactant containing sulfur, which can include elemental sulfur. In one embodiment, additional compounds may be added, such as for example, nitrogen-containing reactant compounds or oxygen. In one embodiment, the reactant compound

may be a metal salt. In another embodiment, the reactant compound does not comprise a metal salt.

[0032] In one embodiment, the reactant compound has a molecular weight of no more than 800, 600, 500, 400, or even 200 grams/mole. In one embodiment, the reactant compound has a molecular weight of at least 32, 50, or even 100 grams/mole. The molecular weight of the compound needs to be appropriate for the nature of the carbon substrate used.

[0033] Sulfur-containing Reactant Compound

[0034] WO Appl. No. US2012/052502, herein incorporated by reference in its entirety, discloses the use of sulfur-containing compounds such as elemental sulfur, SO_2 , SOCl_2 , SO_2Cl_2 , CS_2 , COS , H_2S , and ethylene sulfide and sulfur analogs of epoxides, which are thermally treated with a carbon substrate.

[0035] WO Appl. No. US2012/070300, herein incorporated by reference in its entirety, discloses the use of metal sulfides, which are thermally treated with a carbon substrate. A metal sulfide comprises a metal chemically combined with sulfur and further can optionally include other elements such as oxygen or carbon. The metals of the metal sulfide refer to chemical elements that are located in columns 3-12 and rows 4-6 in the periodic table of the elements; and also elements 57-71, known as the lanthanides. Exemplary metals of the metal sulfide include: copper, iron, manganese, silver, zirconium, niobium, molybdenum, tungsten, and combinations thereof.

[0036] Exemplary metal sulfides include: copper sulfide, iron sulfide, manganese sulfide, zirconium sulfide, zinc sulfide, niobium sulfide, molybdenum sulfide, and tungsten sulfide and oxysulfides of these metals, such as molybdenum oxysulfide.

[0037] WO Appl. No. US2012/069414, herein incorporated by reference in its entirety, discloses the use of metal salts (including metal salts or metal complexes) comprising a sulfur-containing anion. The sulfur-containing anions may comprise an anion selected from at least one of a sulfate, sulfamate, sulfite, bisulfate, bisulfite, and/or thiosulfate ion. The metal portion of the metal salt may include any metal, however, metals that are acceptable for presence in drinking water are preferred. Exemplary metals include: copper, iron, silver, and manganese. Exemplary metal salts include: manganous sulfate, copper sulfate, chromium sulfate, and combinations thereof.

[0038] In one embodiment, the sulfur-containing reactant compound is a thiometallate or an oxythiometallate, wherein a thiometallate includes at least one of: a salt of MS_4^{2-} , $\text{MO}_2\text{S}_2^{2-}$, and MOS_3^{2-} , wherein the metal, M, is molybdenum or tungsten. Exemplary salts include: $(\text{NH}_4)_2\text{MS}_4$, $(\text{NH}_4)_2\text{MO}_2\text{S}_2$, and $(\text{NH}_4)_2\text{MOS}_3$, where M is Mo or W, which are water soluble.

[0039] Sulfur and Nitrogen-containing Reactant Compound

[0040] US Prov. Pat. Appl. No. 61/699324, filed 11 Sep 2012, herein incorporated by reference in its entirety, discloses the use of sulfur and nitrogen-containing salts. In one embodiment, the

reactant compound is a salt represented by the formula $[C]^{+y}[A]^{-x}$, wherein $[C]$ is a cation; $[A]$ is an anion; and x and y are independently at least 1. These salts include at least one sulfur atom and at least one nitrogen atom.

5 [0041] In one embodiment, the cation $[C]$ is a conjugate acid of a nitrogen-containing base and contains at least one nitrogen atom. Exemplary cations include: ammonium and alkylated or arylated derivatives thereof (e.g., $(NH_4)^+$, $(NH_3CH_3)^+$, etc.), guanidinium, imidazolium, morpholinium, anilinium, thiomorpholinium, pyridinium, and combinations thereof. In another embodiment, the cation $[C]$ contains at least one sulfur atom. Exemplary cations include: trimethylsulfonium, trimethylsulfoxonium, and combinations thereof. In yet another embodiment,
10 the cation $[C]$ contains at least one sulfur atom and at least one nitrogen atom. An exemplary cation includes phenothazinium.

[0042] In one embodiment, the anion $[A]$ contains at least one sulfur atom. Exemplary anions include: sulfate, bisulfate, sulfite, bisulfate, polysulfide, sulfamate, polythionates [i.e. $S_n(SO_3)_2^{2-}$], and combinations thereof. In another embodiment, the anion $[A]$ contains at least one nitrogen
15 atom. Exemplary anions include: cyanate, guanidine, imidazole, pyridine, triazole, and combinations thereof. In yet another embodiment, the anion $[A]$ contains at least one sulfur atom and at least one nitrogen atom. Exemplary anions include: thiosulfate, thiocyanate, and combinations thereof.

[0043] In one embodiment, the salt, $[C]^{+y}[A]^{-x}$, may be a metal containing salt, e.g., potassium
20 thiocyanate or sodium thiocyanate.

[0044] In another embodiment, the reactant compound containing both sulfur and nitrogen is not a salt. Exemplary reactant compounds include: thiomorpholine, phenothiazine, 2-mercaptopyridine, thiourea, and combinations thereof.

[0045] Additional Compounds

25 [0046] In addition to the sulfur-containing reactant compound and/or the sulfur- and nitrogen-containing reactant compound used in the thermal treatment with the carbon substrate, additional compounds such as a nitrogen-containing reactant compound and/or an oxygen-containing reactant compound may also be used to achieve the medium of the present disclosure.

[0047] WO Appl. No. US2012/069414, herein incorporated by reference in its entirety, discloses
30 the use of metal salts (including metal salts or metal complexes) to incorporate a metal into the reaction product. Metals that are acceptable for presence in drinking water are preferred.

[0048] In one embodiment, oxygen may also be included in addition to the sulfur- and/or sulfur- and nitrogen-containing reactant compound.

[0049] In one embodiment, the oxygen may be part of the sulfur- and/or the sulfur- and nitrogen-
35 containing reactant compound.

[0050] In one embodiment, the surface of the carbon substrate comprises oxygen. The carbon substrate, as received, may contain chemically significant amounts of oxygen attached to surface carbon atoms. For example, according to X-ray photoelectron spectroscopic (XPS) analysis, granular activated carbon available under the trade designation "RGC" by Mead Westvaco Corp, Richmond, VA contains about 2.9 atomic percent of oxygen. This amount of oxygen may be sufficient for the present disclosure but, when higher amounts of surface oxygen are desired, additional oxygen may be incorporated into the carbon substrate.

[0051] In one embodiment, oxygen may be added to the carbon substrate before exposure to the sulfur- and/or nitrogen-containing reactant compound. For example, the carbon substrate can be heated in air or treated with aqueous nitric acid, ammonium persulfate, ozone, hydrogen peroxide, potassium permanganate, Fenton's Reagent, or other well known oxidizing agents.

[0052] In another embodiment, additional oxygen can be incorporated into the medium of the present disclosure by carrying out the thermal treatment between the carbon substrate and the sulfur- and/or sulfur- and nitrogen-containing reactant compound in the presence of air or water. The amount of air used must be limited to prevent combustion of the carbon. Additional oxygen may also be supplied by addition of water or steam, which can be added during the heating reaction or may be present on the surface of the carbon substrates, such as in the case of high surface area carbonaceous materials, particularly hydrophilic oxidized carbons, which chemisorb water. Oxygen may be added during the heating reaction in the form of dioxygen, sulfur dioxide, carbon dioxide, or combinations thereof.

[0053] In addition to adding an oxygen source during thermal treatment of the carbon substrate and the sulfur- and/or sulfur-and nitrogen-containing reactant compound, in an alternative embodiment, the thermal treatment is conducted in the absence of added oxygen.

[0054] Carbon Substrate

[0055] The carbon substrate may be a granular material, a powder material, a fiber, a tube, a web or a foam.

[0056] The morphology of the carbon substrate is not particularly limited and may include a non-particulate, a particulate, or an aggregate. A non-particulate carbon substrate is a support that is not composed of discernible, distinct particles. A particulate carbon substrate is a support that has discernible particles, wherein the particle may be spherical or irregular in shape (including e.g., non-spherical, cubic, faceted particles, and/or other geometric shapes) and has an average diameter of at least 0.1, 1, 5, 10, 20, or even 40 micrometers (μm) to at most 75 μm , 100 μm , 500 μm , 1 millimeter (mm), 2 mm, 4mm, 6.5 mm, or even 7 mm. An aggregate (or a composite) is formed by the joining or conglomeration of smaller particles with one another or with larger carrier particles or surfaces. The aggregates may be free standing (self-supporting against gravity).

[0057] Typically, the morphology of the carbon substrate will be selected based on the application. For example, particulate with a large particle size is desirable when the medium of the present disclosure is used in applications requiring low pressure drops such as in beds through which gases or liquids are passed. In another example, particle sizes of about 20 to 200 μm may be preferable when used in a carbon block monolith.

[0058] The size of the pores of the carbon substrate can be selected based on the application. The carbon substrate may be microporous carbon (having pore widths smaller than 2 nanometers), macroporous carbon (having pore widths between 2 and 50 nanometers), mesoporous carbon (having pore widths larger than 50 nm), or a mixture thereof.

[0059] In one embodiment, the carbon substrate is comprised of activated carbon, in other words carbon that has been processed to make it highly porous (i.e., having a large number of pores per unit volume), which thus, imparts a high surface area.

[0060] In one embodiment, it is preferable for the carbon substrate is porous. Preferably the carbon substrate has a high surface area (e.g., at least 100, 500, 600 or even 700 m^2/g ; and at most 1000, 1200, 1400, 1500, or even 1800 m^2/g based on BET (Brunauer Emmet Teller method) nitrogen adsorption). High surface areas may be made available using a highly porous carbon substrate such as an activated carbon substrate.

[0061] Activated carbons may be generated from a variety of materials, however most commercially available activated carbons are made from peat, coal, lignite, wood, and coconut shells. Based on the source, the carbon can have different pore sizes, ash content, surface order, and/or impurity profiles. For example, coconut shell-based carbon has predominantly a microporous pore size, whereas a wood-based activated carbon has a predominately mesoporous or macroporous pore size. For example, coconut shell- and wood-based carbon typically have ash contents less than about 3% by weight, whereas coal-based carbons typically have ash contents of 4-10% by weight or even higher.

[0062] In one embodiment, the porous carbon substrate used in the present disclosure is predominately microporous, meaning that 65, 75, 80, 85, 90, 95, or even 99% of the pores of the carbon substrate are microporous, however some of the pores may be larger than microporous.

[0063] Commercially available carbon substrates include: activated wood-based carbon available under the trade designation "NUCHAR RGC", by Mead Westvaco Corp, Richmond, VA; wood-based carbon available under the trade designation "AQUAGUARD" by Mead Westvaco Corp; activated coconut shell-based carbon available under the trade designation "KURARAY PGW" by Kuraray Chemical Co., LTD, Okayama, Japan; and coal-based carbon available under the trade designations "CARBSORB" and "FILTRASORB" by Calgon Carbon Corp., Pittsburgh, PA.

[0064] Thermal Treatment

[0065] Reactions of elemental carbon typically exhibit large activation energies and so are conducted at high temperature. Reactions used to introduce the reactant compounds into the carbon substrate surface may be conducted at a temperature sufficient to thermally decompose the sulfur chemical species (and additional reactant species, if present) as well as enable their reaction with the carbon substrate. Exemplary temperatures include at least 200, 250, 300, 400, or even 500°C; and at most 650, 700, 800, 900, 1000, 1200, or even 1400°C. The resulting product herein is referred to as the reaction product or medium.

[0066] Generally the temperature at which to conduct the thermal treatment may be determined, by first analyzing the reactant compound by differential thermal analysis/thermal gravimetric analysis (DTA/TGA) performed under controlled conditions (atmosphere and heating rate) to determine its thermal decomposition behavior. Then trials may then be performed by heat treating the carbon substrate and the reactant compound at various temperatures beginning with the onset temperature of decomposition to determine at what point and under what conditions (temperature, time, and atmosphere) the most active material is formed.

[0067] The thermal treatment may occur in an air environment. However, to control combustion, sources of oxygen, such as air or water, may be excluded (e.g., by pulling a vacuum) or replaced by an inert gas such argon or nitrogen in which the oxygen concentration is less than 2000 ppm (parts per million), 200 ppm, or even less than 50 ppm.

[0068] The reactant compound may be used in the solid, liquid, or gas form. A single reactant compound may be used or more than one reactant compound may be used (for example, a sulfur-containing reactant compound and a nitrogen-containing reactant compound). Reaction temperatures, which are above the boiling point of the reactant compound(s) may be used.

[0069] In one embodiment, the reactant compound(s) may be combined with the carbon substrate by dry mixing and then exposed to the thermal treatment (heated). The amount of reactant compound added to the carbon support is determined through experimentation to yield sufficient sulfur (and optionally nitrogen and/or oxygen) present in the end product to produce an active removal material.

[0070] In another embodiment, the reactant compound(s) may be melted or dissolved or dispersed in a solvent (e.g., water or methanol or mixtures of solvents) and the liquid is used to wet the carbon substrate, impregnating the carbon substrate with the reactant compound. Such impregnation can be accomplished using simple techniques, such as spraying the reactant compound-containing solution onto the carbon substrate or melting the reactant compound and contacting it with the carbon substrate. When forming a solution using a solvent, the reactant compound is dissolved in the solvent to its solubility limit to maximize the amount of sulfur and/or

nitrogen present, although lesser amounts may be used so long as there is sufficient sulfur and/or nitrogen present in the end product to produce an active removal material.

5 [0071] Then, the impregnated carbon substrate is heated to generate the media of the present disclosure. The decomposition of the reactant compound on the surface of the carbon substrate is thought to produce a reactive sulfur and optionally a reactive nitrogen species. It is thought that the impregnation of the carbon substrate with the reactant compound would enable a more evenly dispersed reactive surface on the carbon substrate, yielding a more uniform and better performing medium.

10 [0072] In thermal treatment with a metal salt a thermolysis process can be used, which involves heating a metal salt at or above the temperature at which the metal salt begins to lose metal-bound water, if present, and at which the salt portion of the compound begins to decompose. As used herein a “thermolysis product” refers to a product that results from the dissociation or decomposition of a compound by heat. This thermolysis process is believed to change the nature of the metal salt to a material having a different stoichiometry and composition and different chemical properties, wherein at least a portion of the salt is thermally decomposed and is removed by volatilization as a gas.

15 [0073] Described below are specific embodiments of thermal treatment to generate the reaction product disclosed herein.

20 [0074] In one embodiment, a carbon substrate is impregnated with a reactant compound comprising both sulfur and nitrogen (e.g., ammonium sulfate, ammonium hydrogen sulfite and ammonium thiosulfate) and then thermally treating impregnated carbon under a nitrogen atmosphere to a temperature above the decomposition point of the reactant compound and preferably higher than about 445°C, 500°C, 550°C, or even 800°C, followed by cooling under nitrogen.

25 [0075] In one embodiment, a carbon substrate is treated with a sulfur-containing reactant compound (e.g., elemental sulfur, H₂S, SO₂, and ammonium sulfur-containing compounds) at temperatures of 550 °C or higher. Elemental sulfur may be preferable, as a sulfur source because it may be used in the absence of solvent and without need for high pressures of gas.

30 [0076] In one embodiment, a reaction product comprising a metal sulfide may be prepared by treating a metal oxide supported on a carbon substrate with a sulfur source.

[0077] In another embodiment, a carbon substrate with a metal carbonyl is heated in the presence of a sulfur-containing reactant compound.

[0078] In another embodiment, a carbon substrate comprising a thiometallate or oxythiometallate is thermally decomposed to form a reaction product of the present disclosure.

[0079] Reaction Product

[0080] The reaction product of the carbon substrate and the reactant compound comprising sulfur is referred to herein interchangeably as the reaction product or medium.

5 [0081] The reaction product of the present disclosure may be obtained via solid-gas (or solid-vapor) chemistry. In certain reactions of this class only the outer portions of the carbon substrate are exposed to the reactive gas because diffusion of the reactant compound into the inner pores of the carbon substrate can be slow relative to the treatment time. Additionally, in some cases, reactions can become self-limiting in that an overlayer of product inhibits inward diffusion of the gas. In such cases, the new compounds that form may be confined to regions near the surface and
10 comprise a surface compound (e.g., 10 nanometers (nm) or less on the carbon substrate).

[0082] By using a solid-vapor thermal treatment process several advantages may be realized. Because the reaction may be solventless or at least free of organic solvent, no drying operation is needed to isolate the product. Further, there are generally no non-volatile by-products that remain to clog small pores in the solid. If no solvent is used, the process as described herein can be
15 envisioned to run as a continuous process, which can reduce cost and/or increase throughput. The solid-vapor process of this disclosure permits penetration of small molecule reactants into micropores and niches formed by highly irregular surfaces. This results in an advantageous, even distribution of sulfur and/or nitrogen species.

[0083] In another embodiment, the reactive compound is melted, dissolved in a liquid, or
20 suspended in solution and the resulting liquid is used to impregnate the carbon substrate. In this embodiment, the reactive species is dispersed throughout the carbon substrate and is thus able to react with the carbon substrate in the thermal treatment yielding a uniformly treated substrate. Advantageously, reactive species that are not easily vaporized or are fine powders can be used. Further, because the reactive compound is impregnated into the carbon substrate as a liquid
25 without the concern of gas diffusion, larger carbon substrates can be uniformly treated.

[0084] When the carbon substrate is a large particle, a core-shell structure results, where the core is the carbon substrate, which is covered by a shell or second layer comprising the reaction product resulting from the thermal treatment of the reactant compound with the carbon substrate.

30 [0085] Because the reaction disclosed herein is a surface reaction, when the carbon substrate is in the form of small particles with high surface area (e.g., RGC powder nominally -325 mesh, having a nominal surface area of 1400-1800 m²/g), then the surface and interior of the particle may become coextensive. In one instance there may be no apparent chemical distinction between the outer surface and the interior of the particle. In another instance, the sulfur and/or nitrogen content on the bulk can approach or even exceed that on the surface.

[0086] In one embodiment of the present disclosure, the carbon of the carbon substrate, and the sulfur, and optionally the nitrogen, and/or oxygen (if present), chemically interact with one another, meaning, that these elements may be combined chemically (i.e., covalent chemical bonding between contiguous elements) or there may be weaker interactions between non-contiguous elements, such as hydrogen bonding.

[0087] In one embodiment, when the reaction product comprises sulfur, at least 15%, 20%, 25%, 30%, or even 50% of the sulfur in the reaction product is in an oxidation state higher than 0. For example in a +1, +2, +4, or even +6 oxidation state. Because the reaction product of the present disclosure comprises at least 1.5% by mass of sulfur, in one embodiment, at least 0.2%, 0.5%, or even 1% by mass of the medium comprises sulfur in an oxidation state higher than 0 based on XPS surface analysis.

[0088] By using a thermal treatment (solid-vapor process), several advantages may be realized. Because the reaction may be solventless or at least free of organic solvent, no drying operation is needed to isolate the product. Further, there are generally no non-volatile by-products that remain to clog small pores in the solid. If no solvent is used, the process as described herein can be envisioned to run as a continuous process, which can reduce cost and/or increase throughput. The solid-vapor process of this disclosure permits penetration of small molecule reactants into micropores and niches formed by highly irregular surfaces. This results in an advantageous, even distribution of sulfur and/or nitrogen species.

[0089] Because not all of the sulfur (and/or nitrogen, if present) from the reactant compound is incorporated into the carbon substrate surface (e.g., some may be converted to COS or H₂S), it may be important to analyze the resulting composition to determine the atom fraction of carbon, oxygen, sulfur, and nitrogen on the carbon substrate surface of the medium.

[0090] If the carbon substrate is highly porous, the reaction product of the reactant compound and the carbon substrate can be analyzed by combustion analysis to determine how much carbon, hydrogen, nitrogen, and sulfur, are present.

[0091] In one embodiment, the medium of the present disclosure comprises carbon, and sulfur wherein the sulfur content of the medium is at least 1.5, 2.0, 3.0, 4.0, 6.0, 8.0, or even 10.0 mass % based on the total mass of the reaction product.

[0092] In one embodiment, the medium of the present disclosure comprises carbon and nitrogen wherein the nitrogen content is greater than 0.5, 1.0, 1.5, 2.0, 2.4, 2.5, 2.7, 3.0, 4.0, 5.0, 7.0, or even 10.0 mass % nitrogen based on the total mass of the reaction product.

[0093] In one embodiment, the medium of the present disclosure comprises more than 4.0, 4.5, 5.0, 7.0, 9.0, 10.0, 12.0, 15.0, or even 22.0 mass % of the sum of nitrogen and sulfur based on the total mass of the of the reaction product.

[0094] In one embodiment, the medium of the present disclosure is substantially free of hydrogen, comprising less than 0.40, 0.30, 0.20, 0.10, 0.05, or even 0.01 mass % hydrogen based on the total mass of the active chloramine removal material.

5 [0095] In one embodiment, the medium of the present disclosure is substantially free of metals, in other words, comprising less than 1, 0.5, 0.1, or even 0.05 mass % of metal based on the total mass of the of the reaction product.

[0096] In one embodiment, metals (such as calcium, magnesium, iron, etc.) may be present in low levels in the media of the present disclosure due to low levels of metals intrinsic to plant-derived materials such as carbons made from nut shells or coal.

10 [0097] In one embodiment, the medium of the present disclosure comprises CN_pS_r , wherein p and r are independently greater than 0. In one embodiment, p can be greater than 0.004, 0.008, 0.013, 0.020, 0.025, 0.035, 0.045, 0.065, or even 0.10, and r can be greater than 0.004, 0.006, 0.008, 0.015, 0.025, 0.035, or even 0.42.

15 [0098] In one embodiment, the medium of the present disclosure comprises CO_xS_y , where in one embodiment, x is 0 or is at least 0.005, 0.01, 0.02, 0.03, 0.04, or even 0.05; and at most 0.07, 0.08, 0.09, 0.1, 0.12, 0.15, or even 0.2; and y is at least 0.001, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, or even 0.06; and is at most 0.12, 0.14, 0.15, 0.16, 0.18, 0.2, 0.22, 0.25, 0.3, 0.35, or even 0.4. In one embodiment, the carbon substrate has a surface consisting essentially of CO_xS_y , meaning that the surface necessarily includes carbon, oxygen, and sulfur and may also include other atoms so long
20 as the other atoms do not materially affect the basic and novel properties of the invention. In other words, besides carbon, oxygen, and sulfur, the surface of the substrate comprises less than 10% or even less than 5 % total of other atoms. These other atoms may originate in the starting materials and/or the atmosphere used during the thermal treatment. Impurities are typically less than 5%, 2%, 1%, 0.1%, 0.05%, or even 0.01% of a particular impurity atom based on the weight of the
25 composition.

[0099] In one embodiment, the carbon, oxygen, and sulfur of the reaction product chemically interact with one another, meaning, that these elements may be combined chemically (i.e., covalent chemical bonding between contiguous elements) or there may be weaker interactions between non-contiguous elements, such as hydrogen bonding.

30 [00100] In one embodiment, the compositions of the present disclosure have high thermal stability. For example, with the carbon substrate comprising CO_xS_y , significant weight loss under nitrogen has not been observed at temperature up to 800° C, well above the boiling point of sulfur, indicating that these compositions are not mere physical mixtures of starting materials.

[00101] Based on the analysis of compositions of the present disclosure, in at least one embodiment, the sulfur and oxygen are combined chemically on the surface of the carbon substrate. The oxygen and carbon are an integral part of the surface of the carbon substrate and are not easily removed by heating to 400°C. The nature of the structure and bonding is complex.

5 Carefully deconvoluted XPS (X-ray photoelectron spectroscopy) spectra of the carbon substrate comprising CO_xS_y reveal that sulfur is in four different chemical environments with $\text{S}2p_{3/2}$ binding energies of about 162.0, 164.3, 165.8 and 168.9 eV [$\text{C}(1s) \equiv 285.0$ eV]. They therefore contain chemically combined sulfur in three formal valence states [S(VI), S(IV) and S(II)] and four different chemical environments. These chemical environments are: (1) S(VI) as in SO_4^{2-} or
10 organic sulfones, C-SO₂-C (2) S(IV) as in organic sulfoxides, C-SO-C, (3) S(II) as in thiophene and (4) S(II) as in organic sulfides, C-S-C or disulfides, C-S-S-C.

[00102] In one embodiment, the reaction product has a bulk density of greater than 0.50, 0.57, 0.60, or even greater than 0.65 g/cc.

[00103] In one embodiment, the reaction product has an ash content of less than 4% or less
15 than 3%, or even less than 2%.

[00104] Because sulfur is associated with a rotten egg smell, and the present disclosure is directed toward use in treatment of aqueous solutions (e.g., drinking water), one may be dissuaded from using sulfur-containing materials for treatment of drinking water. However, advantageously, although the reaction products disclosed herein comprise sulfur, and in some
20 instances large amounts of sulfur (e.g., 10% by wt), the reaction products do not have a noticeable smell.

[00105] Carbon block

[00106] In one embodiment, the reaction product is disposed in a matrix to form a filter. The matrix may be a web, a polymer-containing composite block, on the surface of a tube, or in
25 another structure that enables aqueous solutions to pass there through. In one embodiment, the reaction product may be blended and compressed with a binder material, such as a polyethylene, e.g., an ultra high molecular weight polyethylene, or a high-density polyethylene (HDPE). In another embodiment, the reaction product may be loaded into web, such as a blown microfiber, which may or may not be compacted such as described in U.S. Publ. No. 2009/0039028 (Eaton et al.), herein incorporated in its entirety.
30

[00107] In one embodiment, the matrix, including the reaction product of the present disclosure, further comprises particles of titanium, in the form of oxides or silicates. These particles may be added to the matrix to improve removal of undesirable metals such as lead. Typically, these particles have a sizing of 20 to 50 microns.

[00108] The loading, expressed as weight of the reaction product by the total weight of the filter (comprising the reaction product, the matrix and additional additives), can vary depending on the matrix used. In one embodiment, the amount of reaction product comprises at least 10, 25, 40, 50, 60, 75, or even 80 %; at most 90, 92, 95, 97, or 99%, or even 100% mass of the filter. For example, when carbon blocks are used, the filter may comprise about 50-85% mass of the reaction product, while for a carbon loaded web, the filter may comprise about 80-95% mass of the reaction product.

[00109] In one embodiment, the reaction product is disposed in a fluid conduit (e.g., a housing or a vessel comprising an inlet and an outlet), wherein the fluid conduit is fluidly connected to a fluid inlet and a fluid outlet. Such systems may include packed beds.

[00110] Removal

[00111] The medium of the present disclosure may be used to remove chloramines and chlorine from a fluid stream, particularly a liquid fluid stream, more specifically, an aqueous fluid stream.

[00112] Chloramines are formed from the aqueous reaction between ammonia and chlorine (hypochlorite). Thus, adding ammonia (NH_3) to a chlorination system converts chlorine to chloramines. Specifically, monochloramine, hereafter referred to as "chloramine," in low concentrations arise from the disinfection of potable water sources. In one embodiment, after contacting the aqueous solution with the medium of the present disclosure, as disclosed herein, the resulting aqueous solution comprises a reduced amount of chloramines. As mentioned above, if the pH or ammonium levels change in the water, the equilibrium can shift to favor chlorine in the water as opposed to chloramine. Thus, it may be advantageous to have a composition that would remove both chloramine and chlorine.

[00113] In the Applicants' previous filings, referenced above, it was found that thermally treating a carbon substrate in the presence of various reactants, such as sulfur containing compounds and/or sulfur- and nitrogen-containing compounds, resulted in materials that were active for chloramine removal. These materials were found to have similar or even higher activity for removal of chloramine from aqueous solutions than untreated activated carbon, including those commercially marketed for chloramine removal. Previously, wood-based carbon substrates were primarily investigated because (a) the best available chloramine removal carbon to date was a wood-based carbon and (b) it was thought that chloramine reduction was limited by pore diffusion (i.e., diffusion of chloramine into the carbon pores and counter diffusion of reaction products from the pores). Thus, wood-based carbon, having a larger pore size, was thought to be desirable.

[00114] However, in Applicants' studies, reaction products comprising carbon sulfides (C_xS_z) made from coconut shell-based carbon substrates showed chloramine removal kinetics and

chloramine capacity as high as reaction products comprising carbon sulfides (C_xS_z) made from wood-based carbon substrates. Thus, the use of carbon substrates being predominately microporous did not appear to appreciably slow diffusion rates of the chloramine.

5 [00115] In one embodiment, it has been discovered that reaction product made from thermal treatment of carbon substrates and a reactant compound comprising sulfur provide improved capacity and/or reaction rates for both the removal of chloramine and chlorine than current commercially available filtration media marketed specifically for chloramine removal.

10 [00116] The medium of the present disclosure reduces the amount of chloramine and chlorine in an aqueous solution, when the solution is contacted with the medium. In one embodiment, the aqueous solution comprises from 3 ppm to less than 0.5 ppm chloramine. Upon contact with the medium, the aqueous solution has a reduced chloramine content to 0.1 ppm or less. For example, in one embodiment, the amount of chloramine is decreased by at least 70%, 75%, 80%, 85%, 90%, 95%, 99%, or even 100% when challenged with a solution comprising 3 ppm chloramine. In one embodiment, the aqueous solution comprises from 2.5 ppm to 0.5 ppm of chlorine. Upon contact with the medium, the aqueous solution has a reduced chlorine content of less than 0.5 ppm. For example, in one embodiment, the amount of chlorine is decreased by at least 40%, 45%, 50%, 55%, 60%, 70%, 80%, 85%, 90%, 95%, 99%, or even 100% when challenged with a solution comprising 2 ppm chloramine.

15 [00117] In one embodiment, the thermal treatments disclosed herein improve the capacity of the carbon substrate to remove chloramine and/or chlorine. In one embodiment, the medium of the present disclosure has a high capacity for removing chloramine (e.g., at least 0.1 g/cc, or even 0.2 g/cc based on the amount of chloramine removed per volume of reaction product). In one embodiment, the filter media made using the medium of the present disclosure has a high capacity for removing chlorine (e.g., at least 0.2 g/cc, 0.5 g/cc, 0.8 g/cc, or even 1 g/cc based on the amount of chlorine removed per volume of reaction product). The capacity, and thus throughput of water, is a key for designing a filter with an acceptably long service life.

20 [00118] Capacity (or service life) of the carbon block sample comprising the reaction product disclosed herein is reported as the throughput attained before the concentration of chloramines in the effluent rises above 0.5 mg/L. In one embodiment, the medium when challenged with 3 ppm chloramine, will have a capacity of at least 0.05, 0.1 or even 0.19 g chloramine per gram of the medium at 3 ppm for chloramine at an empty bed contact time of 9.5 sec.

25 [00119] In designing filtration media, it is also advantageous to have media that is able to quickly react with the contaminant of interest. It has been found that filtration media made using the reaction product disclosed herein can provide a fast reaction rate, and thus yields good

30

35

performance for the removal of chloramines and/or chlorine with empty bed contact times as low as 3 to 5 seconds. Empty bed contact time is defined as the volume of the filter in gallons divided by the water flow rate in gallons per second. The ability to quickly and effectively remove chloramines and/or chlorine is a key to reducing the required size of filters. In many applications space is limited, so “miniaturizing” filter volume is a key for customer acceptance. Applications where space is limited include refrigerator filters, end of faucet filters, countertop filters, filters for portable and home dialysis systems, gravity flow devices (pitchers) and point-of-entry house filters. Therefore, the media disclosed herein can extend the range of applications where chloramine and chlorine removal from water is feasible and desirable for the customer. Currently, such filters for the above mentioned applications would be too large or too low in capacity to be practical for a broad range of users.

[00120] The reaction product as disclosed herein may be useful for the following applications: point-of-use or point-of-entry filters for home or commercial use, and filters for dialysis water for the removal of contaminants (such as chloramine, chlorine, etc.) in aqueous streams.

[00121] The reaction product as disclosed herein may be used to not only remove chloramine and/or organic compounds, it may also be used to remove other contaminants as well. As shown in U.S. Provisional Appl. No. 61/777,013, filed March 12, 2013 and U.S. Provisional Appl. No. 61/777,017, filed March 12, 2013, both of which are herein incorporated by reference in their entirety, the reaction product can be used to remove mercury and/or organic compounds, such as trihalomethanes like chloroform. In some instances, the end-user may not know what contaminants are in their aqueous stream due to changes in the water supply, exposure of the aqueous solution to contaminants from a treatment source to the point of use. Thus, multiple filters, specific to each contaminant, may be needed. Having a filtration media that is able to remove a variety of contaminants may save on foot-print size and/or cost. In some instances, the treatment of the water supply may change, known or unknown to the end-user, and thus it would be advantageous to have a filtration media that does not need to be changed with changes that occurred upstream.

[00122] In one embodiment of the present disclosure, a method of removing various contaminants from an aqueous solution is provided comprising: providing an aqueous solution comprising at least two contaminants selected from: chloramine, chlorine, an organic compound (such as trihalomethanes, e.g., chloroform), and mercury; and contacting the aqueous solution with a medium comprising a porous carbon substrate, wherein the porous carbon substrate comprises at least 1.5 % by mass of sulfur, whereby the medium reduces the amount of the at least two contaminants.

[00123] In another embodiment, a medium is disclosed comprising carbon and sulfur, wherein the medium has the capability to remove at least one of: chloramine, free chlorine, mercury, and trihalomethane (exemplified by chloroform), wherein a composite carbon block filter comprising the medium and a binder has a filtration capacity of at least 5000 liters of water per liter of carbon block volume and wherein the filtration capacity is measured at about 2.4 sec (\pm 5%) empty bed contact time when tested according to the National Sanitation Foundation Standard 53 (for mercury and chloroform) and 42 (for chloramine and chlorine) protocols. For disclosure of the testing methods, refer to the Example Section below and the methods disclosed in U.S. Provisional Appl. No. 61/777,013, filed March 12, 2013 and U.S. Provisional Appl. No. 61/777,017, filed March 12, 2013, both of which are herein incorporated by reference in their entirety.

[00124] In another embodiment of the present disclosure, a medium for filtration of aqueous solutions is provided, wherein when tested at about 2.4 sec (\pm 5%) the empty bed contact time according to the National Sanitation Foundation Standard 53 and 42 protocols the medium comprises the following capacity: at least 0.05, 0.06, 0.07, 0.08, or even 0.1 g chloramine per gram of the medium when challenged with 3ppm chloramine, at least 0.5, 0.7, 0.8, or even 1g chlorine per gram of the medium when challenged with 2 ppm chlorine; at least 0.002, 0.003, 0.004, or even 0.0050 g organic compound per gram of the medium when challenged with 150 ppb organic compound (as measured by chloroform); and at least 0.002, 0.003, 0.004, 0.005 or even 0.007 g mercury per gram of the medium when challenged with mercury. For disclosure of the testing methods, refer to the Example Section below and the methods disclosed in U.S. Provisional Appl. No. 61/777,013, filed March 12, 2013 and U.S. Provisional Appl. No. 61/777,017, filed March 12, 2013, both of which are herein incorporated by reference in their entirety.

[00125] An important embodiment is a point-of-entry residential filter with the capability for high-efficiency chlorine reduction at high flow rates (greater than about 10 gpm) and with high capacity. This will be especially attractive for protecting electrodeionization water treatment systems without the necessity of frequent filter change outs. It will also be attractive for applications where it is desired to have all household water below chlorine odor thresholds without requiring frequent change outs. Data suggest that a single, compact, point-of entry, filter cartridge (for example, the size of a replacement cartridge available under the trade designation "AQUA-PURE" AP917HD, from 3M Co., St. Paul, MN) comprising the reaction product disclosed herein, could provide greater than 90% chloramine reduction efficiency at 10 gpm with more than one year service life ($>$ 100,000 gal). By comparison, a state-of-the-art filter of this same size using conventional activated carbon would require change out every 2-3 months to maintain this same high efficiency at high flow. Another embodiment is for small, high-flow, high-efficiency gravity

flow filters for point-of-use application. The subject filters are enabled by media comprising activated carbon reacted with sulfur compounds at high temperature yielding an active surface comprising sulfur (C_xS_z).

5 [00126] Exemplary embodiments of the present disclosure include, but are not limited to the following:

[00127] Embodiment 1. A method of removing chloramine and chlorine from an aqueous solution comprising:

providing an aqueous solution comprising chloramine and chlorine; and

contacting the aqueous solution with a medium comprising a porous carbon substrate,

10 wherein the porous carbon substrate comprises at least 1.5 % by mass of sulfur.

[00128] Embodiment 2. The method of embodiment 1, wherein the surface of the porous carbon substrate comprises a species of CO_xS_y , wherein x is no more than 0.1, and y is 0.005 to 0.3.

15 [00129] Embodiment 3. The method of any one of the previous embodiments, wherein the porous carbon substrate further comprises nitrogen and the sum of the sulfur and nitrogen is at least 4.0% by mass.

[00130] Embodiment 4. The method of any of the previous embodiments, wherein the porous carbon substrate is an activated carbon.

20 [00131] Embodiment 5. The method of any of the previous embodiments, wherein at least 0.2% by mass of the medium comprises sulfur in an oxidation state higher than 0 based on XPS surface analysis.

[00132] Embodiment 6. The method of any of the previous embodiments, wherein the medium has a bulk density of greater than 0.6 g/cc.

25 [00133] Embodiment 7. The method of any of the previous embodiments, wherein the medium has an ash content less than 3%.

[00134] Embodiment 8. The method of any of the previous embodiments, wherein the medium is disposed within a matrix, wherein the matrix is a polymer matrix.

[00135] Embodiment 9. The method of embodiment 8, wherein the medium further comprises particles comprising titanium.

30 [00136] Embodiment 10. A method of removing chlorine from an aqueous solution comprising:

contacting an aqueous solution comprising at least 0.5 ppm of chloramine and chlorine with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and collecting the eluate, wherein the eluate comprises less than 0.1 ppm of chloramine.

[00137] Embodiment 11. A method comprising:

providing a medium prepared by thermal treatment of (i) the surface of a carbon support and (ii) a reactant compound comprising sulfur; and

contacting the medium with an aqueous solution comprising chloramine and chlorine,

5 wherein after contact with the medium, the aqueous solution has a decreased amount of chloramine and a decreased amount of the chlorine.

[00138] Embodiment 12. The method of embodiment 11, wherein the thermal reaction product further comprises (iii) a reactant compound comprising nitrogen.

[00139] Embodiment 13. The method of any one of embodiments 11-12, wherein the
10 reactant compound comprising sulfur is selected from at least one of: elemental sulfur, sulfur oxides, hydrogen sulfide, salts containing oxyanions of sulfur, and combinations thereof.

[00140] Embodiment 14. The method of any one of embodiments 11-13, wherein the thermal treatment is conducted at a temperature greater than 445°C in an inert atmosphere.

[00141] Embodiment 15. The method of any one of embodiments 11-14, wherein the
15 amount of chloramine is decreased by at least 80% when challenged with a solution comprising 3 ppm chloramine.

[00142] Embodiment 16. The method of any one of embodiments 11-15, wherein the amount of chlorine is decreased by at least 50% when challenged with a solution comprising 2 ppm chlorine.

20 [00143] Embodiment 17. A method of removing chlorine from an aqueous solution comprising:

providing an aqueous solution comprising chlorine; and

contacting the aqueous solution with a medium comprising a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

25 [00144] Embodiment 18. The method of embodiment 17, wherein the surface of the carbon substrate comprises a species of CO_xS_y , wherein x is no more than 0.1, and y is 0.005 to 0.3.

[00145] Embodiment 19. The method of any one of embodiments 17-18, wherein the carbon substrate further comprises nitrogen and the sum of the sulfur and nitrogen is at least 4.0% by mass.

30 [00146] Embodiment 20. The method of any of embodiments 17-19, wherein the carbon substrate is an activated carbon.

[00147] Embodiment 21. The method of any of embodiments 17-20, wherein at least 0.2% by mass of the medium comprises sulfur in an oxidation state higher than 0 based on XPS surface analysis.

[00148] Embodiment 22. The method of any of embodiments 17-21, wherein the medium is disposed within a matrix, wherein the matrix is a polymer matrix.

[00149] Embodiment 23. A method of removing chlorine from an aqueous solution comprising:

5 contacting an aqueous solution comprising at least 0.5 ppm of chlorine with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and collecting the eluate, wherein the eluate comprises less than 0.1 ppm of chlorine.

[00150] Embodiment 24. A liquid filtration device comprising: a vessel for treating a chlorine-containing liquid, wherein the vessel contains an active chlorine removal material and
10 wherein the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

[00151] Embodiment 25. A liquid filtration device comprising a fluid conduit for liquids, fluidly connecting a fluid inlet to a fluid outlet; and a filtration medium disposed in the fluid conduit; wherein the filtration medium contains an active chlorine removal material and wherein
15 the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

[00152] Embodiment 26. The liquid filtration device of embodiment 24 or 25, wherein the device is used in conjunction with at least one of an electrodeionization water treatment system, an electro dialysis water treatment system or a household water treatment system.

20

EXAMPLES

[00153] Advantages and embodiments of this disclosure are further illustrated by the
25 following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[00154] All materials are commercially available, for example from Sigma-Aldrich Chemical Company; Milwaukee, WI, or known to those skilled in the art unless otherwise stated
30 or apparent.

[00155] These abbreviations are used in the following examples: g = gram, hr = hour, in = inch, min = minutes, mol = mole; M = molar, cc = cm³, cm = centimeter, mm = millimeter, mL = milliliter, L = liter, N = normal, psi = pressure per square inch, MPa = megaPascals, rmp = revolutions per minute, and wt = weight.

[00156] Methods**[00157] Chloramine Testing Protocol (Beaker Test)**

[00158] A chlorine stock solution was prepared by diluting commercial bleach (6.0% NaOCl) with deionized (DI) water (1 part bleach to 19 parts water.) An appropriate amount of this stock solution was added to a jug of deionized water to reach the desired concentration of NaOCl in water. While stirring, 1.5 equivalents of a stock solution of ammonium chloride in water was added to the bleach solution and stirred for 1 h. The pH was adjusted to 7.6 by the addition of NaOH or HCl and tested by an Orion 3-Star pH meter (Thermo Fisher Scientific, Waltham, MA). Free chlorine (Cl_2) and total chlorine (Cl_2 plus chloramines) were tested by the standard Hach method, using powdered reagents and the Pocket Colorimeter II in the high range detection mode, purchased from the Hach Company (Loveland, CO). Acceptable initial readings were ≤ 0.2 ppm free chlorine and 2.9 – 3.2 ppm total chlorine (as Cl_2). Further adjustments to chloramine concentrations were made by adding additional quantities of NaOCl and/or NH_4Cl stock solutions.

[00159] In all cases, RGC powder carbon (MeadWestvaco, Richmond, VA) was run as a standard in order to compare samples measured on different days. RGC carbon standards matched up very closely between different days in all examples described herein. For analysis, a test material was added to 1 liter of 3 ppm chloramine solution at 27 °C while stirring at 400 rpm in a 2-liter beaker. All carbon-based samples were weighed to 0.46 grams and added to the beaker containing chloramine solution. Time equal to zero was recorded immediately after material was added, and samples of 6 mL aliquots were taken at 30 sec, 1 min, 2 min, and 3 min. After withdrawing an aliquot, it was filtered with a syringe filter (0.45 μL polypropylene, Radnor, Pennsylvania) into a test vial and analyzed for total chlorine concentration within 30 seconds. The percentage of chloramine reduction is taken as the amount removed at the indicated time compared with the starting concentration (at $t = 0$). Desirably, chloramine should be reduced to at least 0.5 ppm or less.

[00160] Chlorine Testing Protocol (Beaker Test)

[00161] The National Sanitation Foundation requirements for chlorine reduction are to start with 2.0 ppm (+/-10%) Cl_2 concentration, and remove equal to or greater than 50%. However, in order to better compare the rates of removal for chlorine to chloramine, a similar test to the chloramine protocol was employed. The starting free chlorine concentration was adjusted to 3.0 (+/- 0.2) ppm by the addition of stock NaOCl solution (see above) to deionized water, and the pH was adjusted to 7.65 with NaOH or HCl. A test material was added to 1 liter of 3.0 (+/- 0.2) ppm chlorine solution at 20 °C (room temperature) while stirring at 400 rpm in a 2-liter beaker. All carbon-based samples were weighed to 0.46 grams and added to the beaker containing chlorine solution. Time equal to zero was recorded immediately after material was added, and samples of 6

mL aliquots were taken at 30 sec, 1 min, 2 min, and 3 min. After withdrawing an aliquot, it was filtered with a syringe filter (0.45 μ L polypropylene, VWR, Radnor, Pennsylvania) into a test vial and analyzed for free chlorine concentration within 30 seconds. The percentage of chlorine reduction is taken as the concentration in the aliquot removed at the indicated time compared with the starting concentration ($t = 0$).

[00162] Chlorine Testing Protocol II (Flow-Through Test)

[00163] The free chlorine (OCl^-) concentration was measured by the DPD Free Chloramine Analysis, Hach Method 8021. All reagents and the instruments were those described in the standard Hach Method and can be obtained from Hach Company, Loveland, CO.

[00164] Chlorine reduction performance was evaluated by a flow through test method. A 2 +/- 0.1 mg/L aqueous chlorine test solution was prepared by the addition of a sodium hypochlorite solution to water.

[00165] An end-capped carbon block sample (prepared as described below) was placed into a standard filtration vessel that allowed radial flow from the outside to the inside of the filter media. The vessel was equipped with an inlet and outlet. The aqueous chlorine test solution was run through the filtration system at a flow rate of 0.5 gallons/minute. In this test, the water flow rate followed a duty cycle of 15 min on / 15 min off for 16 hours/day.

[00166] The aqueous chlorine test solution was flowed through the filtration system for 5 minutes to wet out the carbon block sample. After this, samples of the effluent (outflow from the carbon block sample) were taken periodically and the throughput in gallons was recorded. Effluent samples were analyzed for chlorine by the DPD Free Chloramine Analysis, Hach Method 8021 described above. The chlorine effluent concentration was then plotted as a function of the aqueous chlorine test solution throughput. The maximum chlorine concentration is 1 ppm per the National Sanitation Foundation 42 protocol.

[00167] Combustion Analysis of Carbon, Hydrogen, Nitrogen and Sulfur

[00168] The weight percent of carbon, hydrogen, nitrogen and sulfur in a sample was measured by combustion using a LECO TruSpec Micro CHNS elemental analyzer, Laboratory Equipment Co. St. Joseph, MI. Briefly, the sample is placed in the instrument and purged of atmospheric gases. The sample is then heated to over 1000°C in the presence of oxygen to combust the sample. The sample is then passed through a second furnace for further oxidation, reduction, and particulate removal. The combustion gases are then passed through various detectors to determine the content of the carbon, hydrogen, nitrogen, and sulfur.

[00169] A sulfamethazine standard (>99%, from LECO) was diluted to make a calibration curve ranging from 1 mg to 2.6 mg sulfamethazine. The instrument is baselined with ambient air until the CHNS detectors stabilized. Then, 3-4 empty crucibles were measured and set as

instrument blanks. Next, the sulfamethazine standards were analyzed to form a calibration curve. The absolute standard deviation of the sulfamethazine standard (acceptable precision for a pure homogeneous material) for the elements were: < +/- 0.3 wt % for hydrogen, < +/- 0.3 wt % for nitrogen and < +/- 0.3 wt. % for sulfur with a limit of detection of 0.10 wt % for each of the elements.

[00170] Surface Analysis of Sample

[00171] Chemical states and elemental compositions of a sample were analyzed by X-ray photoelectron spectroscopy, using a Kratos Axis Ultra™ XPS system (Shimadzu Corp., Columbia, MD) at a base pressure bellow 10^{-9} Torr. The monochromatic AlK α (1486.6 eV) X-ray source was operated at 140 Watts (14 KV, 10 mA). Hemispherical electron energy analyzer operated at constant pass energy of 160 eV for survey and 20 eV for high resolution spectra. The binding energy (BE) scale was calibrated relative to the BE of C 1s peak. The spectra were acquired at 90 ° take-off angle with respect to the sample surface. The data processing was done with PHI MultiPak V8. 2B, 2006 and Casa XPS Version 2.3.16 Dev41 software. Surface compositions were calculated from measured photoelectron peak areas in survey spectra after correction for appropriate Scofield ionization cross sections. The reported overall atomic concentrations are mean values derived from the survey spectra collected at multiple randomly selected sample regions. The surface content of catalyst functional groups was determined by de-convolution/curve fitting analysis of C 1s, O 1s, N 1s and S 2p core level spectra. The curve fitting analysis was based on summed Gaussian/Lorentzian GL function and Shirley type background subtraction.

[00172] Carbon Substrate A

[00173] Carbon Substrate A was a wood-based activated carbon (nominal 80x325 mesh) obtained from MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation “RGC 80x325”.

[00174] Carbon Substrate B

[00175] Carbon Substrate B was a coconut shell activated carbon (nominal 80x325 mesh, obtained from Kuraray Chemical, Osaka, Japan, under the trade designation “PGW-100MP”). It had a nominal 100 micron median particle size.

[00176] Carbon Substrate C

[00177] Carbon Substrate C was a coconut shell activated carbon (nominal 80x325 mesh, obtained from Kuraray Chemical, Osaka, Japan, under the trade designation “PGW-120MP. It had a nominal 120 micron median particle size.

[00178] Carbon Substrate D

[00179] Carbon Substrate D was an activated carbon powder with an ash content of 2.9wt% (nominal -325 mesh, obtained from MeadWestvaco Specialty Chemicals, North Charleston, SC under the trade designation "RGC POWDER").

5 **[00180] Carbon Substrate 1**

[00181] Carbon Substrate A was heated to 180 °C in a crucible and then elemental sulfur (0.2 g sulfur per gram carbon, obtained from Alfa Aesar, Ward Hill, MA, -325 mesh, 99.5%) was added with stirring. The sulfur melted and was incorporated into the Carbon Substrate A.

10 **[00182]** A loose fitting lid was placed on the crucible containing the carbon substrate-sulfur mix. The crucible was then placed in a nitrogen purged muffle furnace, equilibrated to 550 °C and held at that temperature for 15 minutes. The crucible was removed from the furnace and transferred to a nitrogen-purged container for cooling to near room temperature. Carbon Substrate 1 was found to have 76.50 wt% carbon, 14.42 wt% sulfur, and the hydrogen and nitrogen were below the limit of detection (0.10 wt%) when tested following the "Combustion Analysis of
15 Carbon, Hydrogen, Nitrogen and Sulfur" procedure above.

[00183] Carbon Substrate 2

[00184] Carbon Substrate 2 was prepared by first preparing a saturated solution of ammonium thiosulfate (at 180 °F) and adding this solution to Carbon Substrate A to the point of incipient wetness. The sample was dried prior to the heat treatment step and then placed in a
20 crucible. A loose fitting lid was placed on the crucible containing the carbon substrate-sulfur mix. The crucible was then placed in a nitrogen purged muffle furnace, equilibrated to 800 °C and held at that temperature for 20 minutes. The crucible was removed from the furnace and transferred to a nitrogen-purged container for cooling to near room temperature. Carbon Substrate 2 was found
25 to have 80.66 wt% carbon, 10.47 wt% sulfur, 1.29 wt% nitrogen, and 0.34 wt% hydrogen when tested following the "Combustion Analysis of Carbon, Hydrogen, Nitrogen and Sulfur" procedure above.

[00185] Carbon Substrate 3

[00186] Carbon Substrate 3 was prepared as in Carbon Substrate 1, above, except that Carbon Substrate B was used in place of Carbon Substrate A and the sample was heated at 550 °C
30 and held at that temperature for 30 minutes instead of 15 minutes.

[00187] Carbon Substrate 3 was found to have 83.42 wt% carbon, 9.36 wt% sulfur, 0.12 wt% nitrogen, and the hydrogen was below the limit of detection (0.10 wt%) when tested following the "Combustion Analysis of Carbon, Hydrogen, Nitrogen and Sulfur" procedure above.

[00188] Carbon Substrate 4

[00189] Carbon Substrate 4 was prepared as Carbon Substrate 3. Carbon Substrate 4 was found to have 8.44 wt% sulfur, 0.12 wt% nitrogen, and the hydrogen was below the limit of detection when tested following the “Combustion Analysis of Hydrogen, Nitrogen and Sulfur”.

5 **[00190] Carbon Substrate 5**

[00191] Carbon Substrate 5 was prepared as in Carbon Substrate 3, except Carbon Substrate C was used in place of Carbon Substrate B. Carbon Substrate 5 was found to have 14.79 wt% sulfur, and the hydrogen and nitrogen content was below the limit of detection (0.10 wt%) when tested following the “Combustion Analysis of Hydrogen, Nitrogen and Sulfur” procedure
10 above.

[00192] Carbon Substrate 6

[00193] Carbon Substrate 6 was prepared as in Carbon Substrate 3 and tested by the “Surface Analysis” method above. Carbon Substrate 6 was found to comprise 91.1 atomic % carbon, 0.6 atomic % nitrogen, 2.1 atomic % oxygen and 5.3 atomic % sulfur. Of the 5.3 atomic
15 percent sulfur on the surface of the sample: 7.4% was in the -2 oxidation state, 65.9% was in the 0 oxidation state, 13.4% was in the +2 oxidation state, 9.5% was in the +4 oxidation state and 3.8% was in the +6 oxidation state.

[00194] Carbon Substrate 7

[00195] Carbon Substrate 7 was prepared as in Carbon Substrate 5 and tested by the “Surface Analysis” method above. Carbon Substrate 7 was found to comprise 92.1 atomic %
20 carbon, 0.4 atomic % nitrogen, 2.3 atomic % oxygen and 5.1 atomic % sulfur. Of the 5.1 atomic percent sulfur on the surface of the sample: 7.5% was in the -2 oxidation state, 62.2% was in the 0 oxidation state, 14.1% was in the +2 oxidation state, 10.6% was in the +4 oxidation state and 5.6% was in the +6 oxidation state.

25 **[00196] Preparing Carbon Blocks Samples- Method 1**

[00197] 40 cm³ of the selected carbon substrate (80x325 mesh nominal particle size) was added into a blender. The volume of the carbon was determined at the maximum uncompressed density. 40 cm³ of Ticona GUR 2126 ultra high molecular weight polyethylene (UHMWPE) powder (from Ticona Engineering Polymers, Florence KY) at its maximum uncompressed density
30 was measured and placed into the blender. The carbon and UHMWPE were blended for 3 minutes. The mixture was then quantitatively transferred to a cylindrical shaped mold with a hollow cylindrical core having the dimensions of 1.35 in. (34.3 mm) outer diameter, 0.375 in. (9.5 mm) inner diameter, and 3.6 in. (91.4 mm) length. The mold was filled using an impulse filling as described in U.S. Pat. No. 8,206,627 (Stouffer et al.) to the maximum uncompressed density. The
35 mold was covered and then heated in a convection oven at 180 °C for 50 minutes. After heating,

the mold was immediately compressed with a piston to a fixed block length of 3.1 in. (78.7 mm.) The mold was cooled to room temperature and the resulting carbon block was removed from the mold. End caps were applied to the block using hot melt glue.

[00198] Example 1

5 **[00199]** Carbon Substrate 1 was made into a carbon block sample following the Preparing Carbon Blocks Samples- Method 1 procedure described above.

[00200] Example 2

[00201] Carbon Substrate 2 was made into a carbon block sample following the Preparing Carbon Blocks Samples- Method 1 procedure described above.

10 **[00202] Example 3**

[00203] Carbon Substrate 3 was made into a carbon block sample following the Preparing Carbon Blocks Samples- Method 1 procedure described above.

[00204] Comparative Example A

15 **[00205]** Carbon Substrate A was made into a carbon block sample following the Preparing Carbon Blocks Samples- Method 1 procedure described above.

[00206] Comparative Example B

[00207] Carbon Substrate B was made into a carbon block sample following the Preparing Carbon Blocks Samples- Method 1 procedure described above.

20 **[00208]** Examples 1-3 and Comparative Examples A and B were tested following the Chloramine Testing Protocol (Beaker Test) and the Chlorine Testing Protocol (Beaker Test). Shown in Figs. 1 and 2 is the percent chloramine removal over time, while Figs. 3 and 4 are the percent chlorine removal over time.

[00209] Example 4

25 **[00210]** A blender was filled with the following 35 wt% Carbon Substrate 4, 30 wt% Carbon Substrate 5, 7 wt % Ticona GUR 2126 ultra high molecular weight polyethylene (UHMWPE) powder (from Ticona Engineering Polymers, Florence KY), 18 wt % Ticona GUR 4150-3 ultra high molecular weight polyethylene (UHMWPE) powder (from Ticona Engineering Polymers, Florence KY) and ATS metals reduction media supplied by BASF Corp. The materials were blended for 3 minutes. The mixture was then quantitatively transferred to a cylindrical
30 shaped mold with a hollow cylindrical core having the dimensions of 1.35 in. (34.3 mm) outer diameter, 0.375 in. (9.5 mm) inner diameter, and 3.6 in. (91.4 mm) length. The mold was filled using an impulse filling to the maximum uncompressed density. The mold was covered and then heated in a convection oven at 180 °C for 50 minutes. After heating, the mold was immediately compressed with a piston to a fixed block length of 4.5 in. (11 cm) The mold was cooled to room

temperature and the resulting carbon block was removed from the mold. End caps were applied to the block using hot melt glue and the block was placed in a filter housing.

[00211] Comparative Example C

[00212] Carbon blocks were made in the same manner as Example 4 above, except that
5 Carbon Substrate 4 was replaced with Carbon Substrate B and Carbon Substrate 5 was replaced with Carbon Substrate C.

[00213] Example 4 and Comparative Example C were tested following the Chlorine Testing Protocol II (Flow-Through Test). Shown in Fig. 5 is the effluent chlorine concentration versus throughput for two trials of Example 4 and two trials of Comparative Example C. Capacity
10 for Comparative Example C is 0.4 gram of chlorine per gram of the carbon substrate and the capacity for Example 4 is greater than 0.81 gram of chlorine per gram of the reaction product.

[00214] Comparative Example D

[00215] An aqueous chloramine test solution was prepared comprising 3 ppm NH_2Cl at a pH 7.6 at 27°C. Immediately prior to chloramine analysis, the initial total chlorine content of the
15 aqueous chloramine test solution was measured. With continuous stirring, a 0.0105 g of sulfur powder (sublimed, -100 mesh, 99.5%, Alfa Aesar, Ward Hill, MA) was added to the aqueous chloramine test solution. Immediately after mixing, a timer was started ($t = 0$). After 30 sec, a 5 mL-aliquot of mixture was removed and within 5 sec of removal, the mixture was passed through a 0.45 μm syringe filter to remove suspended solids. The chloramine content of the filtered aliquot
20 was measured within 30 sec of taking the 5-mL aliquot. Aliquots from the mixture were taken periodically over the course of 5 minutes and analyzed for chloramine content. Note that the error of the analysis is ± 0.2 ppm.

[00216] Comparative Example E

[00217] The same testing as described in Comparative Example D was repeated using 0.46
25 g of Carbon Substrate D in place of the sulfur powder and was analyzed for chloramine removal. The results are shown in Table 1 below.

Table 1

Time (s)	Residual Chloramine in ppm	
	Comparative Example E	Comparative Example D
0	3.1	3.0
30	2.7	3.1
60	2.2	3.3
120	1.9	3.1
180	1.7	3.1
240	1.5	3.0
300	1.3	3.1

[00218] Example 5

[00219] A blender was filled with the following: 31 wt% Carbon Substrate 3, 26 wt% Carbon Substrate 5, 11 wt % Ticona GUR 2126 ultra high molecular weight polyethylene (UHMWPE) powder (from Ticona Engineering Polymers, Florence KY), 22 wt % Ticona GUR 4150-3 ultra high molecular weight polyethylene (UHMWPE) powder (from Ticona Engineering Polymers, Florence KY) and ATS metals reduction media supplied by BASF Corp. The materials were blended for 3 minutes. The mixture was then quantitatively transferred to a cylindrical shaped mold with a hollow cylindrical core having the dimensions of 1.2 inch (3 cm) outer diameter, 0.375 inch (9.5 mm) inner diameter, and a length of 4.6 inches (11.7 cm). The mold was filled using an impulse filling to the maximum uncompressed density. The mold was covered and then heated in a convection oven at 180 °C for 50 minutes. After heating, the mold was immediately compressed with a piston to a fixed block length of 4.5 inches (11.4 cm). The mold was cooled to room temperature and the resulting carbon block was removed from the mold. End caps were applied to the block using hot melt glue and the block was placed in a filter housing.

[00220] Comparative Example F

[00221] Carbon blocks were made in the same manner as described in Example 5 above, except that Carbon Substrate 3 was replaced with Carbon Substrate B, and Carbon Substrate 5 was replaced with Carbon Substrate C.

[00222] Example 5 and Comparative Example F carbon blocks were tested for free chlorine reduction using the Chlorine Testing Protocol II (Flow-Through Test) described above. Shown in Fig. 6 are the results for the carbon block with a length of 4.5 inches. Testing at 0.5 gpm (gallons per minute) gave an empty bed contact time (EBCT) of about 2.4 sec.

[00223] Example 5 and Comparative Example F carbon blocks were tested for free chlorine reduction as above except that the blocklength was reduced to 2.25 inches (5.7 cm). Shown in Fig. 7 are the results for the carbon block with a length of 2.25 inches. Testing at 0.5 gpm gave an empty EBCT of about 1.1 sec (seconds). Note that line for Comparative Example F goes off the chart at 250 gallons due to a data gathering error. The results in Fig. 6 and 7 show that the carbon substrate compositions of the present disclosure have dramatically higher capacity for removing free chlorine than standard activated carbons (by more than 5X), as well as significantly faster reaction rates.

[00224] Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes. To the extent that there is a conflict or discrepancy between this specification and the disclosure in any document incorporated by reference herein, this specification will control.

What is claimed is:

1. A method of removing chloramine and chlorine from an aqueous solution comprising:
providing an aqueous solution comprising chloramine and chlorine; and
5 contacting the aqueous solution with a medium comprising a porous carbon substrate,
wherein the porous carbon substrate comprises at least 1.5 % by mass of sulfur.
2. The method of claim 1, wherein the surface of the porous carbon substrate comprises a species
of CO_xS_y , wherein x is no more than 0.1, and y is 0.005 to 0.3.
10
3. The method of any one of the previous claims, wherein the porous carbon substrate further
comprises nitrogen and the sum of the sulfur and nitrogen is at least 4.0% by mass.
4. The method of any of the previous claims, wherein at least 0.2% by mass of the medium
15 comprises sulfur in an oxidation state higher than 0 based on XPS surface analysis.
5. The method of any of the previous claims, wherein the medium has a bulk density of greater
than 0.6 g/cc.
- 20 6. The method of any of the previous claims, wherein the medium has an ash content less than 3%.
7. A method of removing chlorine from an aqueous solution comprising:
contacting an aqueous solution comprising at least 0.5 ppm of chloramine and chlorine
with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and
25 collecting the eluate, wherein the eluate comprises less than 0.1 ppm of chloramine.
8. A method comprising:
providing a medium prepared by thermal treatment of (i) the surface of a carbon support
and (ii) a reactant compound comprising sulfur; and
30 contacting the medium with an aqueous solution comprising chloramine and chlorine,
wherein after contact with the medium, the aqueous solution has a decreased amount of
chloramine and a decreased amount of the chlorine.
9. A method of removing chlorine from an aqueous solution comprising:
35 providing an aqueous solution comprising chlorine; and

contacting the aqueous solution with a medium comprising a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

10. A method of removing chlorine from an aqueous solution comprising:

5 contacting an aqueous solution comprising at least 0.5 ppm of chlorine with a medium comprising a porous carbon substrate having at least 1.5 % by mass of sulfur and collecting the eluate, wherein the eluate comprises less than 0.1 ppm of chlorine.

11. A liquid filtration device comprising: a vessel for treating a chlorine-containing liquid,
10 wherein the vessel contains an active chlorine removal material and wherein the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

12. A liquid filtration device comprising a fluid conduit for liquids, fluidly connecting a fluid inlet
15 to a fluid outlet; and a filtration medium disposed in the fluid conduit; wherein the filtration medium contains an active chlorine removal material and wherein the active chlorine removal material comprises a carbon substrate, wherein the carbon substrate comprises at least 1.5 % by mass of sulfur.

20 13. The liquid filtration device of claim 11 or 12, wherein the device is used in conjunction with at least one of an electrodeionization water treatment system, an electro dialysis water treatment system or a household water treatment system.

1/5

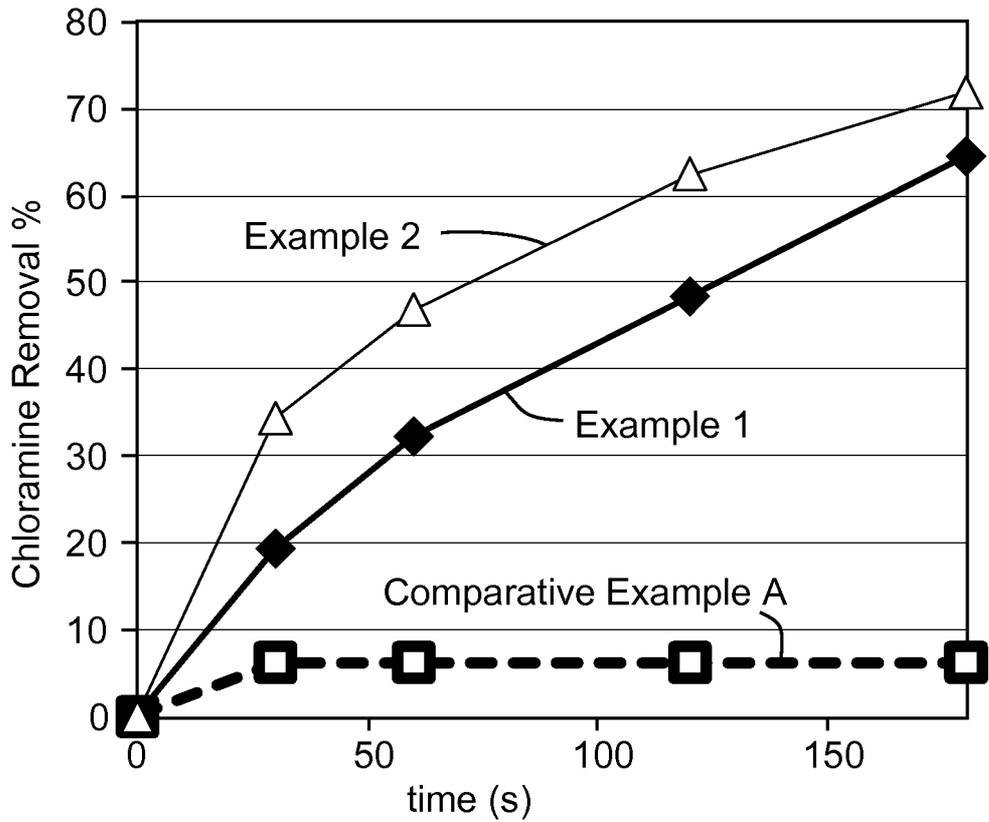


FIG. 1

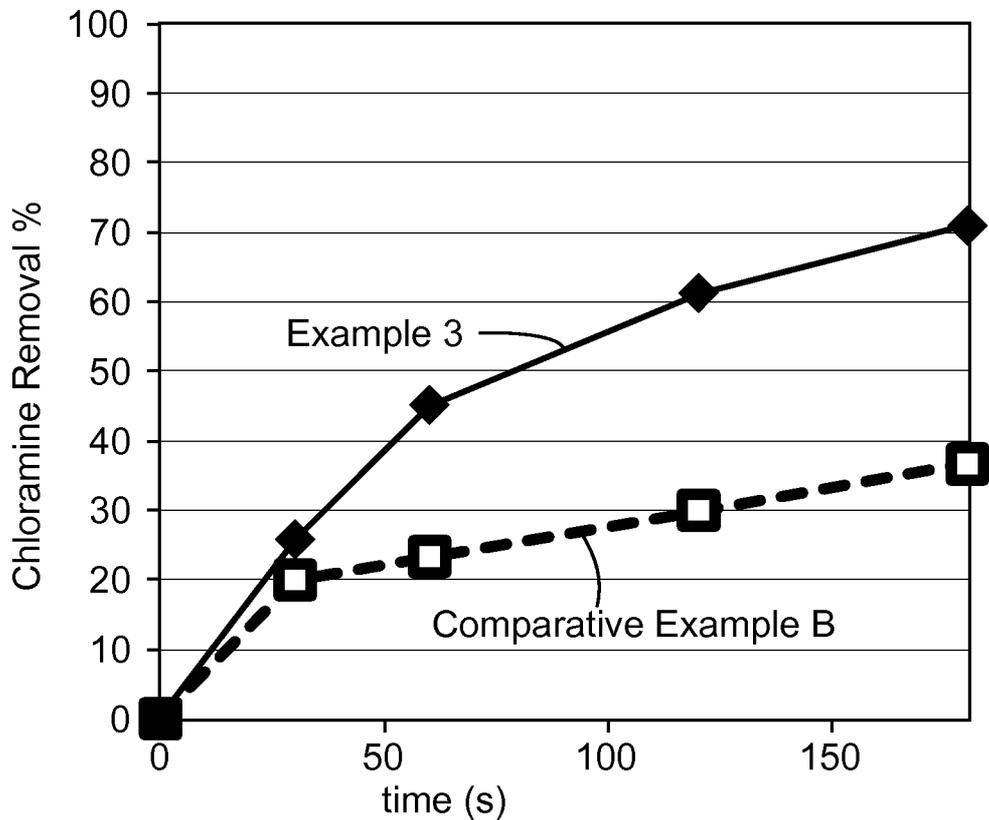


FIG. 2

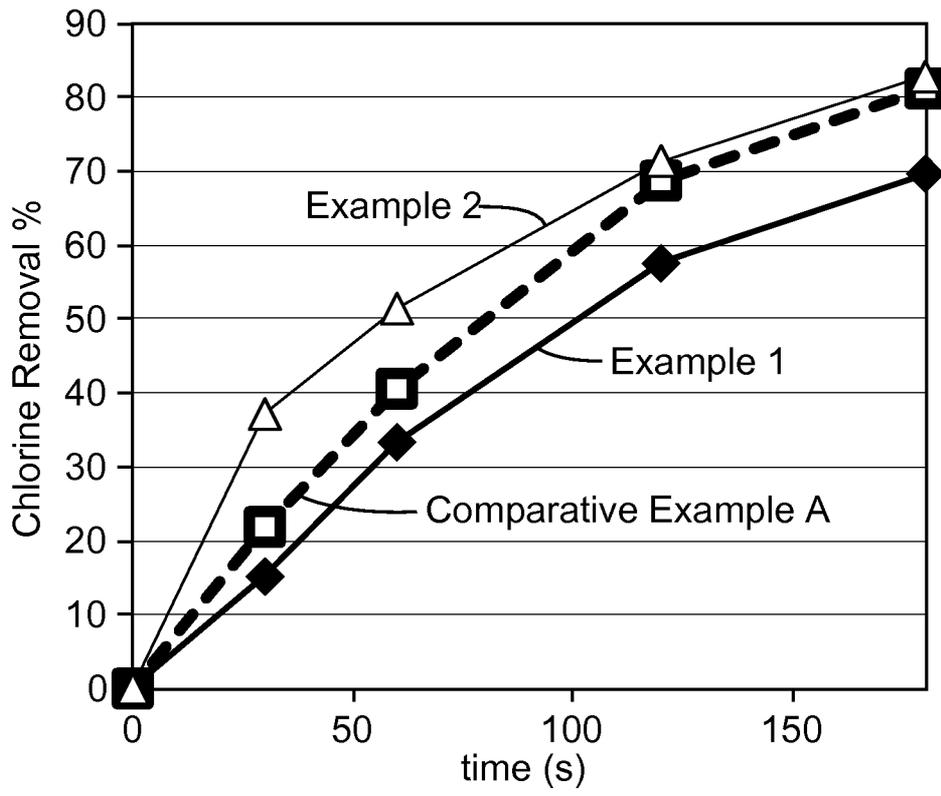


FIG. 3

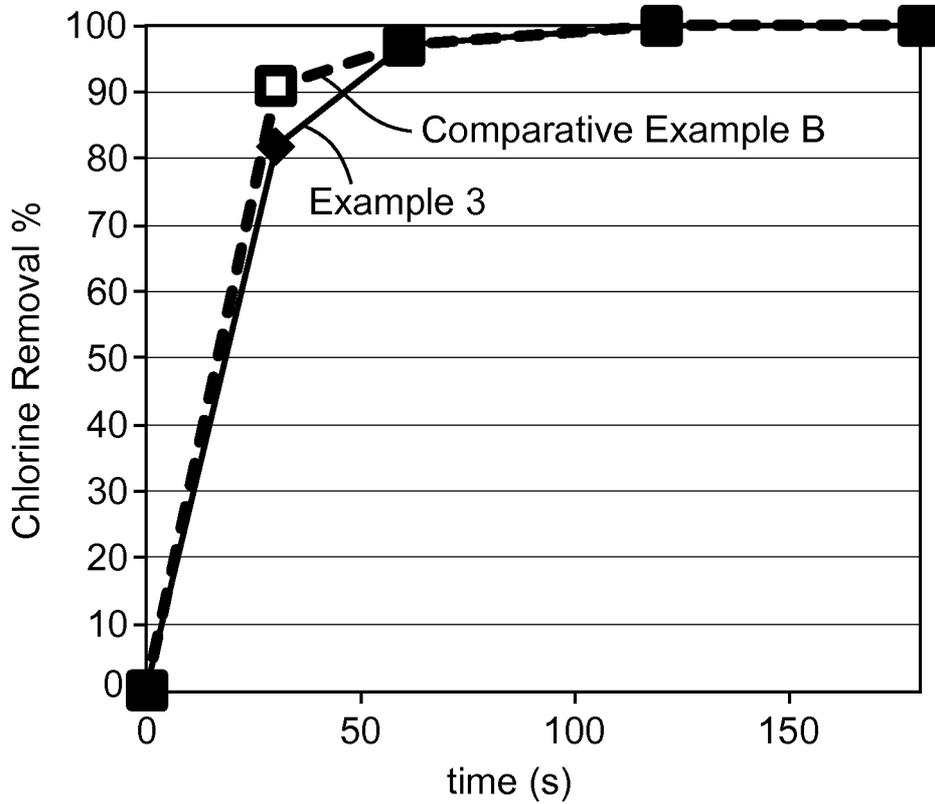


FIG. 4

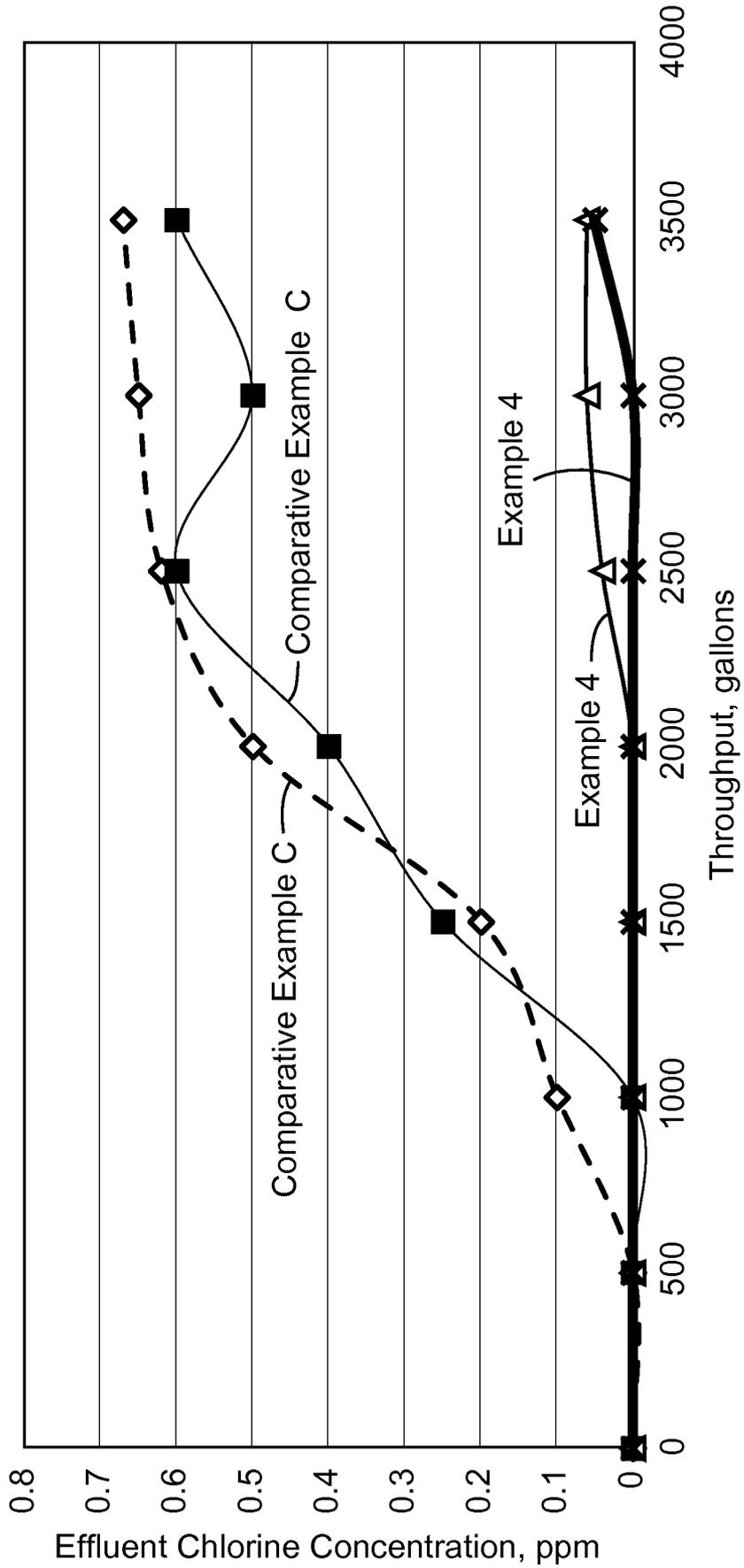


FIG. 5

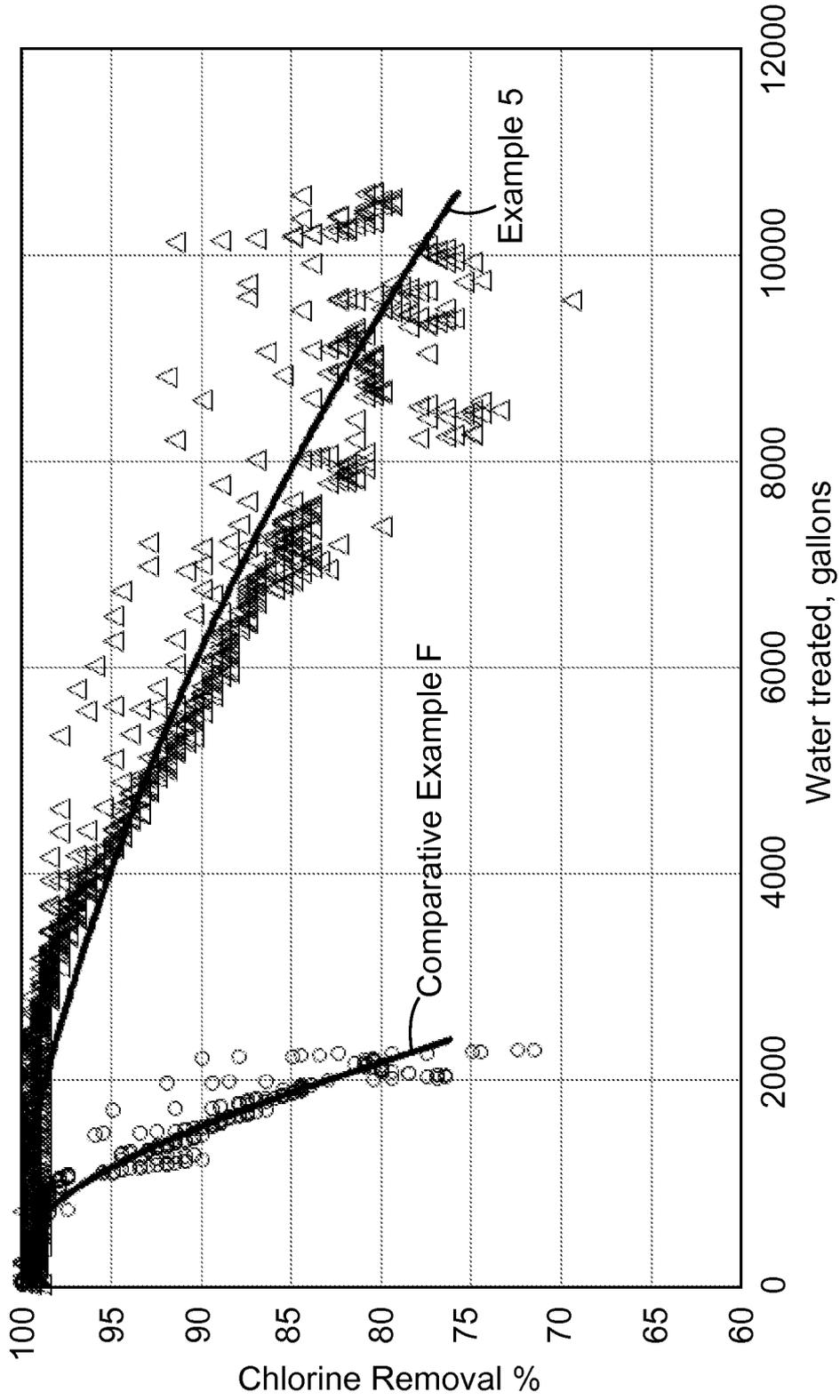
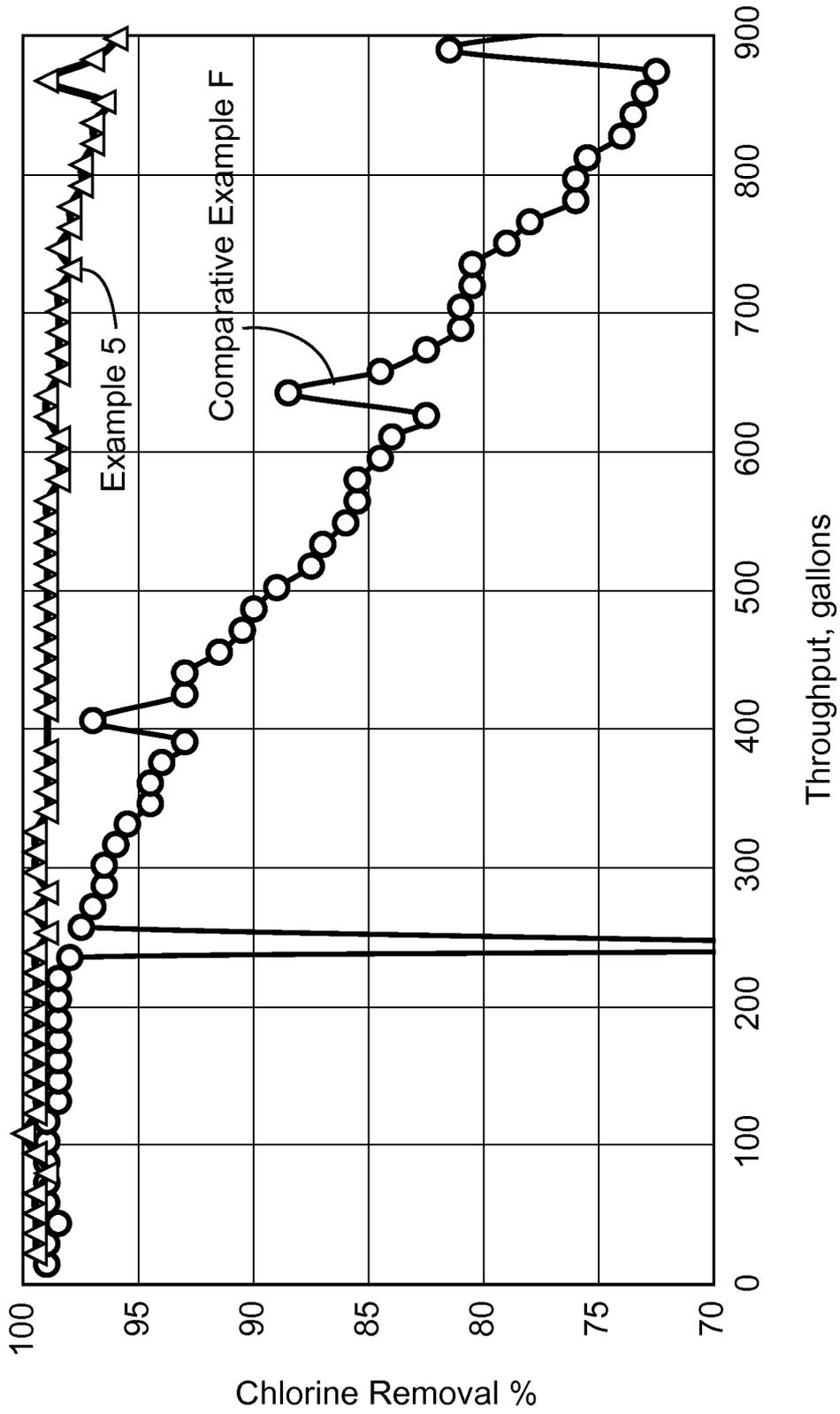


FIG. 6



Throughput, gallons

FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/020662

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/28 C02F9/00
ADD.
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)
C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 270 822 B1 (FRAZIER STEPHEN EARL [US]) 7 August 2001 (2001-08-07)	9-13
Y	claim 1; figure 3; example 8	1-8
Y	US 2013/023405 A1 (HITOMI MITSUNORI [JP] ET AL) 24 January 2013 (2013-01-24) paragraphs [0031], [0039]	1-8
X,P	WO 2013/096281 A1 (3M INNOVATIVE PROPERTIES CO [US]; MCMURDO MEREDITH J [US]; SIEDLE ALLE) 27 June 2013 (2013-06-27) paragraphs [0006], [0039] - [0057], [0067], [0091], [0102], [0128] - [0133]	1-13
E	WO 2014/042682 A1 (3M INNOVATIVE PROPERTIES CO [US]; STOUFFER MARK R [US]; MCLARTY STEVEN) 20 March 2014 (2014-03-20) the whole document	1-13

Further documents are listed in the continuation of Box C.

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 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
30 June 2014

Date of mailing of the international search report
08/07/2014

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Borello, Ettore

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/020662

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6270822	B1	07-08-2001	NONE

US 2013023405	A1	24-01-2013	CN 102822093 A 12-12-2012
			KR 20130049185 A 13-05-2013
			TW 201202136 A 16-01-2012
			US 2013023405 A1 24-01-2013
			WO 2011125504 A1 13-10-2011

WO 2013096281	A1	27-06-2013	NONE

WO 2014042682	A1	20-03-2014	NONE
