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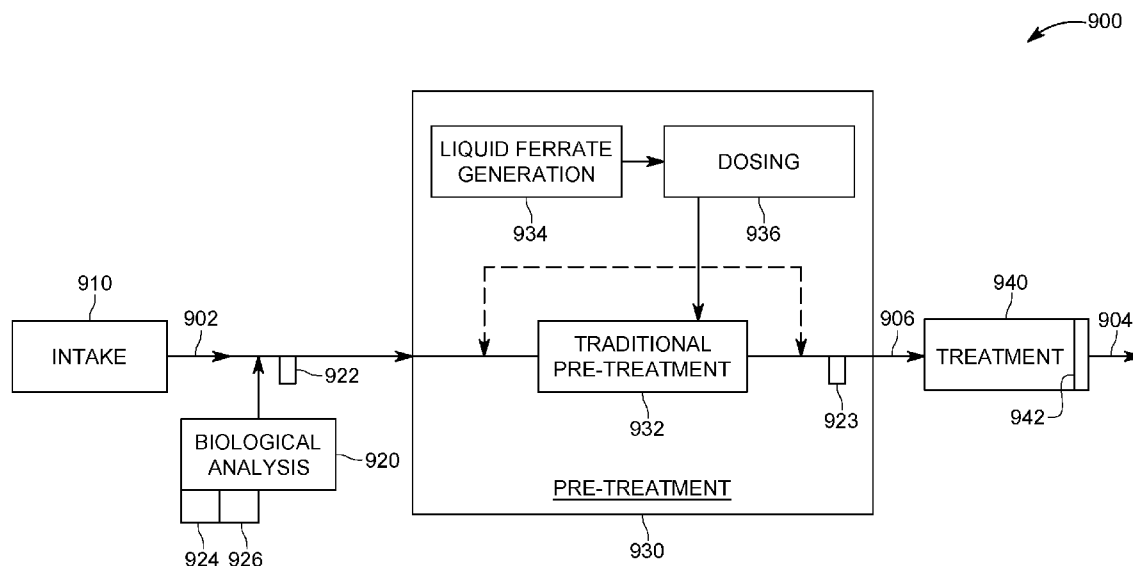


FIG. 9

(57) Abstract: A pretreatment module (930) for a water treatment plant (900) includes a pretreatment unit (932) configured to screen out solids from an incoming water feed (902); a liquid ferrate generation unit (934) configured to generate, in situ, a liquid ferrate (122); and a dosage unit (936) configured to release the liquid ferrate (122) with a given dose into the incoming water feed (902).

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**SEAWATER PRETREATMENT
METHOD AND SYSTEM BASED ON LIQUID FERRATE**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/828,011, filed on April 2, 2019, entitled "SYSTEM AND DEVICE FOR ENHANCED AND ADVANCED WATER TREATMENT USING IN-SITU GENERATED FERRATE (Fe VI) IN CONVENTIONAL PROCESSES COMMONLY USED IN PRETREATMENT TRAINS (e.g. COAGULATION - SEDIMENTATION - FILTRATION)," the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND

TECHNICAL FIELD

[0002] Embodiments of the subject matter disclosed herein generally relate to a system and method for coagulating algal blooms prior to delivering a water feed to a water treatment plant, and more particularly, to using a liquid ferrate to remove organic carbon material from the water feed.

DISCUSSION OF THE BACKGROUND

[0003] In arid regions with limited fresh water resources, the water supply through seawater desalination is often the only viable solution to meet the increasing water demand due to the population growth, economic growth, and urbanization. In

recent years, seawater desalination by reverse osmosis (SWRO) has become the dominant technology for desalination as it provides a high quality product, at lower cost, and with less environmental impact compared to conventional thermal desalination processes. Increasingly large SWRO desalination plants have been constructed over the past years to meet the growing demand of fresh water.

[0004] Although the number and capacity of SWRO plants is increasing, a major challenge to this technology is the membrane fouling, which affects the osmosis process by increasing the cost of the produced water. Fouling mitigation and control is a major activity in all desalination plants. Fouling occurs as a function of the feedwater quality and operating conditions used, and depending on the dominant type of fouling, leads to an increase in operating costs due to more frequent chemical cleaning needed, an increase in the pressure required to compensate the flux reduction from fouling, and an increase in the energy consumption.

[0005] Biofouling in particular is considered a major challenge and occurs when a biofilm forms on the RO membranes, eventually resulting in an increase in membrane resistance and reduction in its permeability and solute rejection. Biofilm development and growth is related to the feed water quality and depends on the concentration of bioavailable organic compounds and the presence of biofilm-forming bacteria in the feed. Effective pretreatment of the feed is often considered as the only strategy able to reduce the fouling potential by decreasing the amount of organic matter and inactivating the microorganisms in the feed. Conventional SWRO

pretreatment consists of coagulation/flocculation with sedimentation followed by conventional rapid dual media filtration and cartridge filters.

[0006] Algal blooms are a major threat to SWRO desalination plant operations, and can occur unexpectedly without any early detection warnings. The algae can invade the SWRO desalination plants and cause temporary shutdown of the plant. Algal blooms can be non-toxic or toxic (defined as harmful algal blooms, HABs), and independent of toxicity, they represent a severe challenge to the SWRO plants and their pretreatment systems. Several case studies of such events are reported in the literature. The tendency of algal bloom events, for example, along the coast of Oman has increased from 1976 to 2018, where reports show that the Gulf of Oman turns green twice a year during such events, with the blooms being the size of Mexico and spreading across the Arabian Sea all the way to India. A recent event reported in the Arabian Sea began in November 2017, lasting for almost five months, and during its peak in January, it covered an area three times the size of Texas. In another recent event along the coast of Florida (USA), an algal bloom caused the death of thousands of marine animals and later on caused health problems for humans. Red tides (caused by algal blooms) along the Florida coast typically last around 3-5 months. However, the most recent red tide in 2018 in Florida extended for more than 9 months, and it is considered to be the longest on record since 2006.

[0007] Many efforts have been made to improve and enhance pretreatment options for SWRO processes to reduce fouling potentials and optimize the overall production of fresh water. Particularly, during algal blooms, these efforts become a major challenge. Some of these processes include coagulation and flocculation.

Although coagulation and flocculation reduce the colloidal particles and the dissolved organics in the seawater, the fouling still occurs. Among traditional coagulants used in the desalination industry, there are ferric salts, which include iron (II) sulfate heptahydrate $FeSO_4 \cdot 7H_2O$, iron (III) nitrate $Fe(NO_3)_3$, iron (III) chloride $FeCl_3$, and iron (III) sulfate hydrate $Fe_2(SO_4)_3 \cdot 5H_2O$.

[0008] However, the conventional pretreatment options commonly used in the industry have been demonstrated to not be fully effective in mitigating the biological fouling. Thus, there is a need for a new system and method that is capable of removing or reducing the biofouling from the feed, during a pretreatment process, for diminishing membrane biofouling and improving the efficiency of the SWRO plants.

BRIEF SUMMARY OF THE INVENTION

[0009] According to an embodiment, there is a pretreatment module for a water treatment plant, and the pretreatment module includes a pretreatment unit configured to screen out solids from an incoming water feed, a liquid ferrate generation unit configured to generate, *in situ*, a liquid ferrate, and a dosage unit configured to release the liquid ferrate with a given dose into the incoming water feed.

[0010] According to another embodiment, there is a water treatment plant that includes a water intake configured to receive a salt water feed, a feed analysis unit configured to sample the salt water feed and generate a measurement associated with a parameter of the salt water feed, a pretreatment module configured to inject a given dose of liquid ferrate into the salt water feed to generate a pre-treated water feed, and a water treatment module configured to receive the pre-treated water feed and remove salt.

[0011] According to still another embodiment, there is a method for treating salt water in a water treatment plant and the method includes receiving a salt water feed, performing a feed analysis on the salt water feed and generating a measurement associated with a parameter of the salt water feed, generating *in situ* liquid ferrate, selecting a given dose of the liquid ferrate based on the measurement of the parameter, and releasing the given dose of the liquid ferrate into the salt water feed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0013] Figure 1 illustrates various parameters of water feed samples used to test the liquid ferrate and traditional coagulants;

[0014] Figure 2 illustrates the process used to test the water feed samples with the liquid ferrate and the traditional coagulants;

[0015] Figure 3A illustrates the total organic carbon removal with the various water feed samples illustrated in Figure 1, for the same pH;

[0016] Figure 3B illustrates the total organic carbon removal with the liquid ferrate for various pH contents;

[0017] Figure 4 illustrates the turbidity removal for the various water feed samples;

[0018] Figure 5A illustrates the dissolved organic matter removal for the various water feed samples for the same pH;

[0019] Figure 5B illustrates the dissolved organic matter removal with the liquid ferrate for various pH contents;

[0020] Figures 6A and 6B illustrate the effectiveness of a low dose of liquid ferrate with regard to the turbidity and ATP;

[0021] Figure 7A illustrates the algae cells removal for the ferric chloride and liquid ferrate for a given water feed sample, for a same pH;

[0022] Figure 7B illustrates the algae cells removal with the liquid ferrate for a given water feed sample, for various pH values;

[0023] Figure 8 illustrates the adenosine triphosphate removal for various coagulants and various water feed samples;

[0024] Figure 9 illustrates a water treatment plant that uses liquid ferrate as a coagulant;

[0025] Figure 10 illustrates the configuration of a pretreatment module of the water treatment plant, which is configured to generate *in situ* the liquid ferrate;

[0026] Figure 11 illustrates a process used to run the water treatment plant for injecting the liquid ferrate into an incoming water feed; and

[0027] Figure 12 is a flowchart of a method for generating liquid ferrate and injecting it into a water feed prior to treating the water feed.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The following description of the embodiments refers to the accompanying drawings. The same reference numbers in different drawings identify the same or similar elements. The following detailed description does not limit the invention. Instead, the scope of the invention is defined by the appended claims. The following embodiments are discussed, for simplicity, with regard to an *in-situ* generation of a liquid ferrate and treating by coagulation the feed of a SWRO plant with the liquid ferrate. However, the embodiments to be discussed next are not limited to a SWRO plant, but they may be applied to other water treatment plants or to other processes that need a feed with reduced organic material and biological activity.

[0029] Reference throughout the specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with an embodiment is included in at least one embodiment of the subject matter disclosed. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” in various places throughout the specification is not necessarily referring to the same embodiment. Further, the particular features, structures or characteristics may be combined in any suitable manner in one or more embodiments.

[0030] According to an embodiment, a pretreatment module at a water treatment plant uses liquid ferrate, which is generated *in-situ* by wet oxidation of ferric iron using hypochlorite in a caustic medium, to reduce the amount of organic

material, colloids, suspended solids, and/or biological activity in a feed that is used by the plant for generating fresh water.

[0031] The use of a ferrate as an alternative coagulant has been tested in both drinking water and wastewater treatment, where beneficial effects such as advanced oxidation and disinfection compared to traditional coagulants has been highlighted [1]. Ferrate is a powerful oxidant and also considered an environmentally friendly or green disinfectant. However, the disinfection and advanced oxidation processes in marine waters (e.g., salty water that may include ballast water treatment, marine aquaculture) have mainly focused on ozone and UV based technologies and not on the use of the liquid ferrate. Most studies on the ferrate reported in the literature focus on ferrate's oxidation efficiency in surface water and wastewater treatment, and only a few studies investigated the potential disinfectant capabilities of the ferrate [2-4]. In addition, the ferrate used in the past is unstable and expensive to generate. For these reasons, the ferrate was not adopted in the industry.

[0032] The inventors have noted that the liquid ferrate (the liquid ferrate is different from the pure ferrate in the sense that the liquid ferrate includes, in addition to the ferrate, part of the reagents that were used for generating the ferrate, as discussed later) is unexpectedly efficient in the treatment of the saltwater. In addition, the inventors have designed a process that determines when the addition of the liquid ferrate is necessary, makes the generation of the liquid ferrate cheaper, and the ferrate itself stable, and dose the liquid ferrate appropriately, as also discussed later. Thus, the inventors have designed a process for using the liquid

ferrate as an advanced coagulant in a water treatment plant, for example, during a pretreatment phase, especially during algal blooms. However, this process can also be used for removing various undesired elements from the feed, e.g., bio-elements.

[0033] The efficiency of the liquid ferrate as a coagulant is now discussed. In this embodiment, the liquid ferrate is generated *in-situ*. The liquid ferrate is defined as being a liquid that includes an iron-based anion having two negative charges, i.e., $[FeO_4]^{2-}$, which is also called Fe(VI). For comparison, the liquid ferrate's performance was studied versus the standard ferric chloride $FeCl_3$ (Fe(III)), which is commonly used for seawater pretreatment for coagulation and flocculation. The biocidal effect of the liquid ferrate on algae was also assessed. The efficiency of these two coagulants was tested on raw seawater and two seawater samples artificially generated, which reproduce feed conditions observed during severe algal blooms in water treatment plants.

[0034] The effect of the liquid ferrate on these three different water feed samples having various qualities was investigated. The first water feed sample is the raw Red Sea seawater, which was collected from the intake line of the full-scale reverse osmosis (SWRO) desalination plant at KAUST (Thuwal, Saudi Arabia). The total organic carbon (TOC) is one of the parameters used to assess the seawater quality. From this point of view, the Red Sea water is generally considered to be of high quality with low TOC concentrations. Hence, to assess the impact of changing the feed water qualities during harmful algal blooms, two saltwater feed samples having similar conditions were prepared in the lab. One was prepared by enriching the raw seawater with sodium alginate (SA), and the other by cultivating

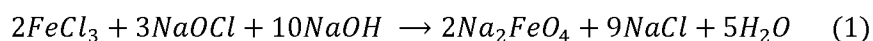
Chaetoceros Affinis (CA) algae, which is a bloom forming algae, and adding it to the raw sea water sample. Characteristics of the natural raw seawater and the two analog feeds are summarized in Table 1, as shown in Figure 1.

[0035] The first water feed sample is based on the *Sodium alginate model* (SA). The sodium alginate is commonly used as a surrogate to mimic algal blooms in seawater. Sodium alginate was used to make the first feed water sample by mixing 1 g of sodium alginate in 1 L of Milli-Q water. The stock solution was designed to have a desired TOC concentration of 10 mg/L. A TOC analyzer was used to determine the concentration of the sodium alginate solution.

[0036] The second water feed sample is based on the *Algal organic matter* (AOM) model. The bloom-forming algae species *Chaetoceros Affinis* (CA) was cultivated to produce natural biopolymers found during algal blooms. The marine diatom species (*Chaetoceros Affinis*, CCAP 1010/27, imported from Culture Collection of Algae and Protozoa (CCAP) company, Oban, Scotland) was cultivated in Red Sea water spiked with Guillard's medium (CCAP, 2010) under controlled laboratory conditions. The cultures were aerated with filter-sterilized air to ensure nutrient distribution and to avoid settling of cells. The cultures were exposed to 12h dark / 12h light cycles using mercury fluorescent lamps (average photon flux density $40 \mu\text{mol m}^{-2} \text{s}^{-1}$) at a constant growth temperature of 20 °C. The culturing protocol starts with a 2 ml inoculum of new strain in a 50 ml sterile culture tube enriched with marine nutrients based on Guillard F/2 medium, and incubating it in an environmental chamber. Strain cultures were renewed every week by taking an inoculum of 0.1-0.2 ml (from test tubes) or 0.5 to 1 ml (from Erlenmeyer flasks),

using the best old culture which is free of contamination, to inoculate three to four new vessels of the same size to start a new strain. The total algal concentration and cell viability was measured using a flow cytometer based on a standard protocol proposed for drinking water analysis.

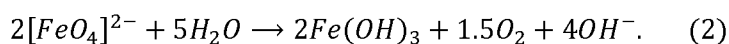
[0037] The liquid ferrate was generated as now discussed. A cost-efficient way of generating ferrate is by aqueous chemical oxidation (wet oxidation) of ferric iron using chlorine in a caustic medium [5]. More specifically, ferric chloride (FeCl_3) is oxidized to ferrate (FeO_4^{2-}) by sodium hypochlorite (NaOCl) in the presence of sodium hydroxide (NaOH), as exemplified by equation (1):



[0038] Note that the wet oxidation process above results in the generation of the liquid ferrate, which is different from pure ferrate. The pure ferrate is what the industry has tried to use in the past, but it is expensive to generate (as it requires a large amount of heat and/or electricity; in this regard, pure ferrate can only be obtained through a separation process where it is isolated from other reaction byproducts, which adds to the cost of obtaining the ferrate) and even worse, it is not stable, i.e., the pure ferrate changes its properties in time. To the contrary, the liquid ferrate used by the inventors is inexpensive and stable in time. The liquid ferrate does not need a separation process, and thus, the ferrate is present in a solution mixed with unreacted ferric chloride. Thus, the term “liquid ferrate” refers to a solution that includes the ferrate and at least one other component, usually the ferric chloride. The ratio of the ferrate to ferric chloride can vary from 1:9 to 6:4, up to 8:2. The liquid ferrate used in these tests is environmentally friendly and inexpensive in

terms of operation and maintenance. In fact, by producing the liquid ferrate by wet oxidation, the pure reagents are the only contributors to the cost of the solution.

[0039] When the liquid ferrate is added to an aqueous system, for example, the water feed, the liquid ferrate is a powerful oxidant that readily decomposes to ferric iron $Fe(OH)_3$ and oxygen [6], as follows:



[0040] The ferrate concentration in the liquid ferrate solution was measured for the tests performed by the inventors using the spectroscopy method, where the absorbance of a ferrate solution at 510 nm can be converted to the ferrate concentration using a coefficient, which is defined as the ratio of the ferrate absorbance at 510 nm (cm^{-1}) to the ferrate concentration. Concentrations were determined for a given amount of ferrate diluted in a given volume of phosphate buffer (5mM phosphate/ 1mM borate, at pH 9.1) and the absorbance was measured at the 510 nm wavelength, based on equation (3)

$$\varepsilon = \frac{A}{BC}, \quad (3)$$

where “A” is the UV/V absorbance by sample, “B” represents the Fe (VI) concentration (M) in the examined sample, and “C” is light path (cm) of the quartz cell used in the study. The molar absorption coefficient ε at 510 nm was determined to be equal to $1150 \text{ M}^{-1}\text{cm}^{-1}$. Note that these measurements were performed for showing the efficiency of the liquid ferrate in the pretreatment of the water feed, and when the process discussed herein is implemented in an actual pretreatment module at a water treatment plant, as discussed later, these measurements are not required.

[0041] The following method was employed to study the liquid ferrate performance for water feed pretreatment. pH measurements were conducted by using a pH meter (e.g., pH6000, Eutech instruments). The turbidity analysis, performed without filtering the samples, was carried out with a HACH-Lange turbidity meter (Germany). TOC analysis was carried out with a Shimadzu TOC analyzer (TOC-V CPH, Shimadzu, Japan). Dissolved organic matter (DOC) analysis was conducted using liquid chromatography with an organic carbon detection (LC-OCD), from (LC-OCD-OND Model 8, DOC-Labor, Germany), after filtering the samples (0.45 μm filter pore size). Samples having a volume of 3000 μL were injected for analysis with 180 min of retention time and a flow rate of 1.1 mL/min. The organic matter expected to be found in the various samples can be divided into five fractions defined as: biopolymers, humic substances, building blocks, low molecular weight (LMW) neutrals, and LMW acids. The active biomass in the samples was determined through adenosine triphosphate (ATP) analysis (a test that measures actively growing microorganisms through detection of adenosine triphosphate) using a Celsis ATP-Analyzer and analysis reagent kit (Celsis, USA), based on firefly luciferin-luciferase bioluminescence reaction. Interference by salts was minimized by diluting the sample 50 times with milli-Q water (100 μL of each sample was added to 1500 μL of milli-Q water) with a final volume of the measured sample of 50 μL . Algae concentrations were measured using a BD Accuri® C6 flow cytometer, based on laser excitation of unstained auto-fluorescent algal cells. The samples were analyzed at a medium flow setting (35 $\mu\text{L}/\text{min}$) with an injection volume of 50 μL . All samples were measured in triplicate to ensure accuracy.

[0042] Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (98% pure, anhydrous, Sigma-Aldrich) was used to prepare 1 M of stock solution. The liquid ferrate was produced in the laboratory by wet oxidation (as described above) by mixing components according to the following procedure: 21.4 g NaOH were added into 103 mL of NaOCl to obtain a pH value >10 , and intensive mixing with a stirrer (1,200 rpm) was applied to achieve a homogeneous solution. Then, 2.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the solution and it was mixed for 60 minutes to obtain the final ferrate solution.

[0043] In one application, the concentration of the reagents can be adjusted as follows: for the FeCl_3 , its concentration can be adjusted between 8 and 35 g/L, for the NaOCl, its concentration can be adjusted between 0.5 and 2 M, and for NaOH, its concentration can be adjusted between 2 and 14 M.

[0044] Tests were conducted on the three water feed samples under various conditions to simulate various mixing, flocculation and settling conditions in order to obtain an optimum dose of the liquid ferrate and the pH of such dose. In this regard, it was noted that the liquid ferrate starts to be effective from a dose of 0.01 mg/L, which achieves a 99% or higher removal of bacteria. In one application, a low dose has been found to be around 1 mg/L, a medium dose is around 2 mg/L, and a high dose is about 3 mg/L, where the term “around” is used to mean within a $\pm$ range of 10%. These numbers may be modified based on the actual conditions in the water treatment plant. In one application, these doses are much smaller, e.g., up to 100 times smaller than the conventional coagulants, thus reducing the amount of Fe used in the process. The liquid ferrate may also be dosed together with some

additives, e.g., other coagulant aids, flocculant, clays, etc., to enhance the removal. During the test, 2 L beakers with the same treatment programs using different feed water samples and different coagulant dosages were run. Jar tests were conducted by adding 10 mg C/L of sodium alginate stock or AOM into the two liters of seawater. After that, an appropriate volume of ferric chloride or liquid ferrate stock solutions (according to the desired dose) were added. After mixing the coagulant and the water feed sample for one minute, the mixing rate was reduced to 35 rpm (regular mixing, 35 s^{-1}) to maintain completely stirred conditions for 20 min. The solution was then left to settle for 1 hour before samples of the supernatant were taken to measure the water quality parameters. Figure 2 schematically illustrates the three water feed samples 110 (seawater SW), 112 (SW and Alginate), and 114 (SW and CA Algae) having the desired amount of organic material (TOC). Figure 2 also shows the two coagulants 120 (Fe(III)) and 122 (liquid ferrate or Fe(VI)), the jars 130 used to mix (with corresponding mixers 132) the water feed samples and the coagulants, and the testing equipment 140 (for example, microscope, spectrometer, turbidity nephelometric turbidity unit, total suspended solid device, etc.) for performing various water quality calculations. The mixer 132 was used to have a first velocity for the coagulation process (for example, 200 rpm for 1 min) and a second velocity for the flocculation process (for example, 35 rpm for 20 min).

[0045] A TOC concentration of 10 mg C/L for the two water feed samples 112 and 114 was chosen as this represents severe fouling conditions. Jar test experiments were conducted for pH values varying between 5–9 and liquid ferrate dosages range between 1–3 mg L⁻¹ for the Fe. The pH range represents the region

of best performance for iron-based coagulants, and also allows assessing liquid ferrate performance at pH ranges of natural seawaters (8–9). The pH was adjusted by adding predetermined quantities of 0.5 N NaOH or HCl.

[0046] For the experiments illustrated in Figure 2, the liquid ferrate was obtained by wet chemical oxidation of the ferric chloride by sodium hypochlorite in alkaline conditions, as discussed above with regard to equation (1). A 12% yield was obtained for this experiment. However, as discussed above, by changing the reagents' concentration, the maximum achievable yield can be adjusted between 10% to 70%. Therefore, the liquid ferrate solution employed for the experiments illustrated in Figure 2 contained a Fe(III) to Fe(VI) ratio of almost 9:1. For a practical implementation, other yields may be used depending on the degree of the organic material detected in the water feed, the characteristics of the membrane used in the water treatment plant, the speed of the water feed, its pH, etc.

[0047] The efficiency of the SWRO pretreatment is commonly assessed by measuring the turbidity and TOC removals in the feedwater. TOC is considered a collective parameter used to quantify the concentration of organic matter in the seawater. The performance of RO membranes has been correlated to TOC content in the feedwater, where concentrations greater than 2 mg/L have been shown to impact membrane fouling and likely lead to biofouling. During algal blooms, TOC in the raw seawater can reach up to 12 mg/L, thus causing major operational challenges. Performance of the pretreatment process under these conditions is critical to prevent biofouling of the RO membranes. The performance of the liquid ferrate as an advanced coagulant was compared to the performance of the

conventional ferric chloride for pretreatment of seawater, applied to raw seawater and the two water feed samples simulating the algal bloom conditions (e.g. 10 mg C/L SA, and 10 mg C/L AOM).

[0048] The results for TOC removal are summarized in Figures 3A and 3B. For the case of the raw seawater 110, having a TOC of 1.0 ± 0.2 mg/L, a 65–69% TOC removal was observed (see bar 302 in Figure 3A) when using liquid ferrate compared to around 43% for the case of using ferric chloride (see bar 300 in Figure 3A). An increase in the TOC removal was not observed with increasing the liquid ferrate solution dosages (the dosage of the ferrate is indicated by the X axis in Figure 3A) in the raw seawater. For the first and second water feed samples 112 and 114, having a TOC of 10.0 ± 0.4 mg/L, a removal of 56-71% was observed for the liquid ferrate. More specifically, for the first SA sample 112, a 22-49% (Fe(VI), see bar 306) vs. 15-40% (Fe(III), see bar 304) removal was observed while a 56-71% (Fe(VI), see bar 310) vs. 17-42% (Fe(III), see bar 308) removal was observed for the second AOM sample 114. For the tested first and second water feed samples, a general trend of increasing the removal of the organic material was observed with increasing the coagulant dose for both the liquid ferrate and ferric chloride coagulants.

[0049] The impact of the feed water sample's pH on the liquid ferrate coagulation was tested for the AOM seawater sample at pH of 5, 7 and 9, as show in Figure 3B. A low removal was observed at pH = 5 (4–13%), with a slight increase (25%) of the removal at pH = 7 for dosage of 1 mg/L Fe, while at a pH = 9, higher

removals were observed (56-71%). The higher removal efficiencies at pH = 9 are due to the higher stability of the Fe(VI) in the alkaline conditions.

[0050] In general, the TOC removal was higher for the liquid ferrate when compared to the traditional ferric chloride. Previous studies on oxidation and coagulation of wastewater with no salt, using pure ferrate, reported approximately 35% removal of TOC in secondary wastewater treatment. However, the experiments performed by the inventors show unexpectedly improved results when using a liquid ferrate instead of a ferrate, applied to a seawater feed instead of a non-seawater feed, as the use of the liquid ferrate enabled a removal of the TOC of about 65% in raw seawater and around 70% on the first and second seawaters feed samples, which are representative of algal bloom events. This doubling in the TOC removal when using the liquid ferrate on a seawater feed was not expected based on the existing literature.

[0051] Another factor that was investigated by the inventors with regard to the efficiency of the liquid ferrate when applied to a seawater based feed is the turbidity. The turbidity removal results are summarized in Figure 4. For the raw seawater 110, the turbidity removal varied between 1-24% for Fe(III), see bar 400, and 44-60% for the Fe(VI), see bar 402. For the AOM seawater sample 114, the turbidity removal was around 27% for Fe(III), see bar 404, compared to 63% for Fe(VI), see bar 406. It is worth to notice that no improvement was observed with increasing the Fe dose in the liquid ferrate, which is illustrated along the X axis, while the Y axis indicates the turbidity removal percentage.

[0052] These results show that the 12% yield of the liquid ferrate used in these experiments was more effective in turbidity removal when compared to the ferric chloride, for all tested cases. Other studies have reported that low doses of sodium ferrate helped in removing the turbidity in wastewater samples, removing suspended particles and color from the feed water during the coagulation process. Thus, in one embodiment, sodium ferrate may be used in addition or instead of the liquid ferrate.

[0053] Next, the inventors have tested the removal of the dissolved organic matter (DOC) in a seawater based feed, by using the ferric chloride and the liquid ferrate as the coagulants. The results of these tests are summarized in Figures 5A and 5B. Using the traditional Fe (III) 120, see bar 500 in Figure 5A, a lower DOC removal (~40 %) was obtained when compared to the liquid Fe (VI) 122, see bar 502 in Figure 5A (~60%) for a sample 110 of raw seawater. For the SA based seawater sample 112, the two coagulants showed similar performances on DOC removal, with around ~60% for the liquid Fe(VI), see bar 506 in Figure 5A, and 50% for the traditional Fe(III), see bar 504 in Figure 5A. For the seawater sample 114, which mimicks the algal bloom conditions, the liquid Fe (VI) 122 led to a DOC removal of 88-93%, see bar 510, while the traditional Fe (III) coagulant achieved a lower removal of around 58-87%, see bar 508 in Figure 5A, depending on the Fe dosage.

[0054] The effect of the pH was tested for the AOM sample 114 at pH of 5, 7, and 9, as shown in Figure 5B, for various doses of the ferrate in the solution (the doses are represented on the X axis in the figure, while the Y axis show the DOC

removal in percentage). The DOC removal was generally less than 30% under acidic and neutral pH while the DOC removal was around 93% under alkaline conditions, i.e., pH about 9. The higher DOC removal achieved at pH 9 is due to the liquid Fe (VI) being more stable in alkaline conditions, thus facilitating the oxidation reactions before decomposition to the ferric species takes place. Note that the liquid ferrate is unstable in acidic conditions, and thus its effect quickly disappears in acidic water feeds.

[0055] The results presented in these figures confirm the positive effect of the liquid ferrate in removing the organic matter from the seawater feed, due to the oxidation ability of the liquid ferrate. This is so because the liquid ferrate enables the oxidation of the organic compounds through a radical reaction with the formation of hydrogen bonds and facilitates removal by coagulation/precipitation [7].

[0056] The inventors further performed tests regarding the performance of a low dose of liquid Fe (VI) for turbidity and ATP removal. Figure 6A shows the ATP 600 for the seawater feed with no liquid ferrate, the ATP 602 for a low dose of 0.01 mg/L ferrate, and the ATP 604 for the same low dose of 0.01 mg/L ferrate together with an aid. Figure 6B illustrates the turbidity reduction for pure seawater (610), the low dose of 0.01 mg/L ferrate 612, and the low dose of ferrate and an aid 614. In both graphs, it is noted that unexpected result of high ATP and turbidity reduction as a result of the low dose of liquid ferrate. The inventors further performed test regarding the performance of the liquid ferrate for natural organic matter (NOM) removal. The NOM is defined as being mater composed of organic compounds that have come from the remains of organisms such as plants and animals and their

waste products in the environment. The organic matter in seawater consists of a mixture of different organic compounds including aquatic humic and fulvic acids and products generated from bacterial and algal activity (*i.e.* microbial and algal organic matter). A similar DOC removal for the two coagulants was observed in raw seawater. Around 95% removal was observed for the bio-polymers and building blocks. The removal of these compounds is mainly due to the coagulation effect of both coagulants. As reported in literature, the fluvic and humic acids are highly removed by using the ferrate. In fact, by using the liquid ferrate, the ferrate decomposition from Fe (VI) to Fe (III) leads to the formation of $\text{Fe}(\text{OH})_3$, which enables the removal of fluvic acid through adsorption and coprecipitation. While the LMW acids showed a similar removal 98-100%, a higher removal was observed for LMW neutrals, 14-29% for traditional Fe (III) vs. 38-65% for liquid Fe (VI). While the two coagulants showed similar performances in the treatment of the SA seawater sample, a significant difference was observed for the AOM seawater samples. For the AOM seawater sample, biopolymer removal by traditional Fe (III) was ~74% while the removal was higher, 97-100%, for the liquid Fe (VI) coagulant.

[0057] In seawater, the biopolymer fraction is composed of acids, proteins, simple sugars, anionic polymers, negatively charged and neutral polysaccharides, which are a major concern for biofouling of RO membranes and other membranes. All these compounds are also present in the algal organic matter (AOM). The liquid ferrate completely removes the biopolymers through adsorption and enmeshment in ferric hydroxide, forming large Fe-biopolymer aggregates [8]. The removal in concentration of the building blocks was similar to the biopolymers, with 86% for the

liquid Fe(VI) and 81% for the traditional Fe(III). Due to ferrate's oxidation ability, a significantly higher removal of LMW acids (73%) was observed compared to the ferric chloride, which showed an adverse effect of increasing the LMW acids concentration with increasing the ferric chloride dose.

[0058] Indeed, the high oxidation potential of the liquid ferrate enables the oxidation of small molecules like LMW acid and neutrals. The results suggest that the liquid Fe (VI) has a lower removal of LMW neutrals compared to traditional Fe (III), i.e., 4% vs. 52%. However, in the case of the liquid ferrate, the LMW neutrals are formed during the oxidation of the bio-polymers. Applying the liquid ferrate on the AOM seawater sample showed a higher concentration of LMW neutrals compared to the feedwater tested.

[0059] Based on the same Fe dose, the liquid ferrate option showed a better performance compared to a conventional ferric chloride coagulant. The enhanced performance of the liquid ferrate is explained by the liquid ferrate having a combined oxidation and coagulation effect from the two different oxidation states. In this regard, the liquid ferrate acts as a strong oxidant, and combined with the formation of ferric hydroxide as the ferrate decomposes, it improved the conditions for coagulation and removal of metals, non-metals and humic acids.

[0060] The inventors also studied the biocidal effect and algae removal due to the liquid ferrate when compared to the ferric chloride. As discussed above, algal blooms are responsible for producing large amounts of organic matter in the seas and oceans. From the perspective of seawater desalination, AOM produced by the algal cells can cause significant operational problems and membrane fouling in RO

plants and other water treatment plants that use a membrane. The biocidal effect of the liquid ferrate and potentially enhanced algae removal is now discussed.

[0061] Higher algae removal was observed for the liquid ferrate for all the tested concentrations. Equivalent dosages of 1, 2 and 3 mg Fe/L were applied (see X axis in Figure 7A), at a pH of 9. With the liquid ferrate, 94-100% removal (see bar 700 in the figure) in the algae concentration was observed, compared to 48-72% removal (see bar 702 in the figure) with ferric chloride, for the various applied doses. The effect of the pH on the liquid ferrate efficiency was tested at various pH, e.g., 5, 7, and 9, as illustrated in Figure 7B, resulting in an increased algae cells removal with increasing the pH for all applied doses. The highest algae removal was achieved at a pH of 9 and it is due to the stability of liquid ferrate under the alkaline conditions.

[0062] In general, the liquid ferrate enhances the removal efficiency of algae in the seawater as demonstrated by the AOM seawater sample tested above. The positive effect is due to the multiple capabilities of liquid ferrate that include not only oxidation and coagulation, but also biocidal properties.

[0063] Reports in the literature have documented the strong oxidation capacity of the ferrate and its potential as an alternative disinfectant to inactivate micro-organisms (viruses, bacteria, algae). Studies have shown that the ferrate is effective in treating bacteria such as *Staphylococcus aureus*, *Streptococci faecalis*, *Escherichia coli*, and *Salmonella typhimurium* and can inactivate the microorganisms over a wide range of pH and salinities at relatively low dosages and short contact times. Liquid ferrate is considered an environmentally friendly biocide compared to

other disinfectants such as chlorine, chlorine dioxide, ozone and chloramines as it is reduced to ferric iron in the process without the formation of any toxic byproducts. The ferrate action as disinfectant is mainly due to the loss in activities of both polymerase and nuclease.

[0064] Conventional coagulation with ferric chloride can only remove a small amount of microorganisms through adsorption on precipitates and does not have a biocidal effect. Microorganisms will therefore remain in the feedwater using the conventional ferric coagulants and can enter the RO membrane pressure vessels and contribute to biofouling development. The biocidal capabilities of the liquid ferrate represent an additional benefit of using the liquid ferrate as an alternative coagulant in the pretreatment stage.

[0065] The biocidal efficiency of the liquid ferrate was assessed by measuring the ATP to evaluate the microbial activity in the seawater. ATP measurements have been reported to correlate with biomass and bacterial growth potential in SWRO membrane processes. Tests conducted on the raw seawater showed that ATP removal was between 87-99.99% for the liquid ferrate (see bar 802 in Figure 8) compared to 16-41% for the ferric chloride (see bar 800 in Figure 8). In the AOM seawater sample using cultivated CA algae, a 98–99.99% removal (see bar 806 in Figure 8) was achieved with the liquid ferrate compared to 38–57 % removal (see bar 804) with the ferric chloride. These findings confirm the potential efficiency of the liquid ferrate as an advanced pretreatment option in water treatment plants that use membranes or similar device, to also control bacterial activity during algal blooms, thereby further reducing biofouling potential during algal blooms

[0066] Based on the above tests, the inventors have noted that the liquid ferrate has a more efficient and beneficial interaction with the seawater and sodium alginate (SA) and algal organic matter (AOM) based seawater samples, which is suitable for pretreatment processes for a water treatment plant. The two seawater samples contained 10 mg C/L derived from sodium alginate (SA) and algal organic matter (AOM) by cultivating the bloom-forming algae species *Chaetoceros Affinis* (CA). Results from these experiments showed that the liquid ferrate achieved better removals in terms of organic carbon and microorganism content compared to the conventional ferric chloride using equivalent dose range of iron (Fe).

[0067] Based on these findings, the inventors have discovered that a pretreatment module that could be added to a water treatment plant could achieve the following advantages:

[0068] Relatively high yields of liquid ferrate can be generated *in-situ* through wet oxidation of ferric chloride by hypochlorite in caustic media;

[0069] Higher removals of TOC, DOC, and NOM can be achieved by using liquid ferrate compared to conventional ferric chloride;

[0070] Removal efficiencies by liquid ferrate increased with increasing pH due to an increase in ferrate stability at alkaline conditions (e.g., for pH = 9);

[0071] The liquid ferrate is more effective in removing AOM compared to ferric chloride, particularly with a higher removal biopolymers; and

[0072] The liquid ferrate is able to fully inactivate microorganisms in the feed waters and enhance the removal of algal cells.

[0073] Thus, such a pretreatment module would be very beneficial for any water treatment plant because the liquid ferrate coagulant provides better pretreatment than the conventional ferric chloride for seawater with high organic content, which is typically found during algal blooms, and also provides high yields for generating the liquid ferrate through an *in-situ* wet oxidation process, more effective coagulation and flocculation pretreatment, which results in a more effective organic carbon removal process (*i.e.* TOC, DOC, AOM, and NOM fractions) in seawater under algal bloom conditions, and an added biocidal effect through efficient inactivation of microorganisms in the feedwater.

[0074] Therefore, a pretreatment module that uses the liquid ferrate is now discussed with regard to Figure 9. A water treatment plant 900 is schematically shown in this figure and includes an intake 910 at which the feed 902 is received. The feed 902 may be seawater that includes various amounts of organic matter. A feed analysis unit 920 samples the feed 902 before any treatment is applied to the feed. For example, the feed analysis unit 920 may include one or more sensors 922 that measure the turbidity, and/or the silt density index (SDI), and/or the total suspended solid (TSS), and/or modified fouling index (MFI), and/or the biological activity (e.g., using ATP luminometer, Flowcytomer FCM, fluorogenic substrate), and/or the temperature, pressure, pH, etc. The information detected by the sensor 922 is shared with a processor 924 and may be stored in a memory 926. Various rules may be stored in the memory 926, that are used by the processor 924 for instructing the other modules of the plant how to act, which is discussed later. In one application, an additional sensor 923, similar to sensor 922, may be placed

downstream, after the liquid ferrate has been injected into the feed, to estimate the efficiency of the injected liquid ferrate, and to adjust the dose based on this feedback.

[0075] The water feed 902 is then entering a pretreatment module 930 where various processes are applied before being allowed to enter the actual treatment module 940. The output of the water treatment module 940 is the treated water 904, which at a minimum includes less salt. In some implementation, the treated water 904 includes fresh water. The treatment module 940 includes at least one membrane 942 that is configured to remove the organic material and other inorganic material from the water feed 902, to generate the treated water 904. In one application, the membrane 942 is a SWRO membrane. Other types of membrane may be used.

[0076] The pretreatment module 930 includes a traditional pretreatment unit 932 that is responsible for at least one of screening of solids, prefiltration pH adjustment, cartridge filtration, and oxidizing dosing, such as chlorine and also coagulants. In one implementation, there could be also membrane pretreatment, dissolved air flotation (DAF), and dual media filter (DMF). When chlorine is used, it is desired to reduce it with sodium bisulfite (SBS) before the RO membrane. In addition, it is possible to dose one or more lines with acid, anti-scalants and sodium bisulfite. The SBS is necessary in case there are residual oxidants. The RO membrane can be damaged by chlorine. The dose is linked to an Oxidation-Reduction Potential (ORP) sensor. The pretreatment module 930 further includes a liquid ferrate generation unit 934 for generating *in-situ* the liquid ferrate 122

discussed above, and a dosing unit 936 for releasing a desired amount of the liquid ferrate into the incoming water feed 902.

[0077] The liquid ferrate generation unit 934 is shown in Figure 10 in more detail, and it includes three tanks T1 to T3 for storing ferric chloride, sodium hypochloride, and sodium hydroxide, respectively. These three different compounds are measured and pumped by corresponding pumps P1 to P3 (or equivalent devices) into a fourth tank T4, where a mixer 1010 mixes the three compounds for a given time T. A computing device 1020 having a processor 1022 determines, based on input from the feed analysis module 920, shown in Figure 9, the amount of each of the compounds to be pumped into the mixing tank T4, so that a desired dose of the ferrate in the liquid ferrate is obtained. The computing device 1020 also includes an interface 1024 for communicating (in a wired or wireless manner) with the mixer 1010, the processor 924 of the feed analysis module, and the dosing unit 936. Further, the computing device 1020 includes a memory 1026 that may store various thresholds and rules related to the readings from the feed analysis unit 920. Based on these rules and thresholds, the processor 1022 decides how much of each of the three chemical components the pumps P1 to P3 allow into the mixing tank T4 so that a given dose D is obtained.

[0078] For example, in one embodiment, the memory 1026 stores instructions for preparing three different dosages, called herein a low dosage DL, a medium dosage DM, and a high dosage DH. In one application, the low dosage DL includes 0.1 mg/L Fe or less, the medium dosage DM includes between 0.1 and 1 mg/L Fe, and the high dosage DH includes between 1 and 3 mg/L Fe. Based on the readings

received from the feed analysis unit 920, the processor 1022 verifies the existing rules and thresholds and decides to implement one of the three dosages discussed above, or no dosage at all if no fouling is inferred from the measurements from the feed analysis unit 920. Those skilled in the art would understand that other values for these dosages may be used and a larger or smaller number of such dosages may be implemented.

[0079] After the processor 1022 decides which dose to implement, it instructs the pumps P1 to P3 accordingly and generates *in situ* the liquid ferrate having the desired dosage. After mixing the three chemical components with the mixer 1010, for a given time T, which is also stored in the memory 1026 and may be dependent of the selected dosage, the processor 1022 instructs the dosing unit 936, which may include a pump P4 or similar device, to pump out a desired amount of the liquid ferrate solution 122, into the incoming water feed 902. The liquid ferrate solution 122 may be injected into the incoming water feed 902 either before applying the traditional pretreatment processes or after, as illustrated by the dashed arrows in Figure 9. After this, a pre-treated water feed 906 is obtained and this feed is supplied to the membrane 942 of the treatment module 940.

[0080] Figure 11 illustrates how the water treatment plant 900 is configured to handle the liquid ferrate and its distribution into the incoming water feed. The method starts in step 1100, in which the sensor 922 of the feed analysis unit 920 collects a water sample from the incoming water feed 902. The incoming water feed 902 includes seawater. Depending on the ocean conditions (or sea or gulf from which the seawater is received), e.g., the presence of algae, it is possible that a substantial

amount of organic material is present in the water feed 902. If the sensor 922 is a turbidity sensor, then a turbidity threshold is stored in the memory 926 and/or 1026 that indicates when the feed water 902 is considered to be contaminated enough that pretreatment with liquid ferrate is necessary. If the sensor 922 is associated with a silt density index, then a SID threshold is stored in one or both of these memories. If the sensor 922 is associated with a biological activity, then a corresponding threshold is stored. No matter what sensor or sensors are used to characterize the water feed 902, corresponding threshold(s) are stored at the computing device 1020.

[0081] A data analysis step 1102 is then performed. In one implementation, the processor 924 at the feed analysis unit 920 processes the signal read by the sensor 922 and transforms it into an associated parameter (e.g., turbidity, or SDI, or biological activity, or ATP, or pH, etc.), which is then checked against a corresponding threshold that is stored in the memory 926. If the associated parameter is larger than the threshold (in some cases the opposite is true, i.e., if it is smaller than the threshold, depending on the parameter), then the processor 924 informs the processor 1022 about this violation. In one application, it is possible to insert a turbidimeter after the dosage of the liquid ferrate to assess the quality of the water after the treatment. In this way, the processor 1022 could be programmed to correct the dosage and be sure that the use of chemicals is minimized. In other words, a logical loop may be implemented to continuously evaluate and adjust the liquid ferrate dose. The processor 1022 may be configured to rely on this comparison, between the measured parameter and the associated threshold, or it may perform the analysis by itself. Once it is determined that the measured

parameter is larger than the threshold, the processor 1022 selects in step 1104, based on the rules stored in the memory 1026, which dose of the ferrate to prepare. The rules may be entered manually by the operator of the plant or may be calculated by the processor and then stored into the memory.

[0082] If the processor 1022 has determined in step 1104 that the water feed is clean, i.e., the measured parameter is below its corresponding threshold, then the process advances to step 1106, where the instructions for preparing the corresponding dose (no dose is required in this case, thus, no instructions are retrieved for this specific case) are retrieved from the memory 1026, and then, in step 1108, the processor 1022 instructs the pumps P1 to P3 to generate, *in situ*, the corresponding dose of liquid ferrate. However, for this specific case, because the water feed 902 is considered to be clean, no dose is prepared. The process then returns to step 1110.

[0083] However, if the treatment selection in step 1104 is a light dose DL, i.e., the measured parameter is slightly (for example, 10% or less) above the corresponding threshold, then the process advances to step 1110, where the instructions for preparing the corresponding dose (dose DL) are retrieved from the memory 1026, and then, in step 1112, the processor 1022 instructs the pumps P1 to P3 to generate, *in situ*, the corresponding dose DL. After the dose DL is prepared, the processor instructs the pump P4 to inject the dose DL into the water feed 902. The process then returns to step 1110.

[0084] If the treatment selection in step 1104 is a medium dose DM, i.e., the measured parameter is above (for example, between 10% and 20%, but note that

these numbers are just an example and other ranges may be used) the corresponding threshold, then the process advances to step 1114, where the instructions for preparing the corresponding dose (dose DM) are retrieved from the memory 1026, and then, in step 1116, the processor 1022 instructs the pumps P1 to P3 to generate, *in situ*, the corresponding dose DM. After the dose DM is prepared, the processor instructs the pump P4 to inject the dose DM into the water feed 902. The process then returns to step 1110.

[0085] If the treatment selection in step 1104 is a high dose DH, i.e., the measured parameter is substantially above (for example, more than 20%) the corresponding threshold, then the process advances to step 1118, where the instructions for preparing the corresponding dose (dose DH) are retrieved from the memory 1026, and then, in step 1120, the processor 1022 instructs the pumps P1 to P3 to generate, *in situ*, the corresponding dose DH. After the dose DH is prepared, the processor instructs the pump P4 to inject the dose DH into the water feed 902. The process then returns to step 1110.

[0086] In one embodiment, a timer may be introduced so that the seawater sensing in step 1100 is only repeated after the elapse of a given time, which is counted by the timer. In one application, the given time may be an hour, a day, a couple of days or even a week. Those skilled in the art would know how to select the given time based on the local conditions of the water treatment plant 900.

[0087] A method for treating salt water in a water treatment plant 900 is now discussed with regard to Figure 12. The method includes a step 1200 of receiving a salt water feed, a step 1202 of performing a feed analysis on the salt water feed

(e.g., check turbidity or any other parameter discussed herein) and generating a measurement associated with a parameter of the salt water feed, a step 1204 of generating *in situ* liquid ferrate, a step 1206 of selecting a given dose of the liquid ferrate based on the measurement of the parameter, a step 1208 of injecting the given dose of the liquid ferrate into the salt water feed, a step 1210 of performing another feed analysis on the treated salt water feed to determine the impact of the given dose of the liquid ferrate, and a step 1212 of evaluating the impact of the given dose of the liquid ferrate. If the result of the step 1212 is negative, the method returns to step 1202, to essentially adjust the given dose of the liquid ferrate. However, if the result of the step 1212 is positive, the system stops the liquid ferrate production and becomes idle for a given period of time. After this time, the method restarts from step 1200. The given period of time can be in the order of seconds, minutes, hours or days.

[0088] The method may further include a step of treating the salt water feed with the liquid ferrate to remove the salt, and/or a step of screening out solids from the salt feed water in a pretreatment module, a step of injecting the given dose of the liquid ferrate in the pretreatment module, and a step of filtering the salt out of the salt water feed in a treatment module, which is placed downstream from the pretreatment module.

[0089] The disclosed embodiments provide a pretreatment regimen for a water treatment plant so that liquid ferrate is generated *in situ* and used to coagulate various impurities found in an incoming water feed for a water treatment plant. It should be understood that this description is not intended to limit the invention. On

the contrary, the embodiments are intended to cover alternatives, modifications and equivalents, which are included in the spirit and scope of the invention as defined by the appended claims. Further, in the detailed description of the embodiments, numerous specific details are set forth in order to provide a comprehensive understanding of the claimed invention. However, one skilled in the art would understand that various embodiments may be practiced without such specific details.

[0090] Although the features and elements of the present embodiments are described in the embodiments in particular combinations, each feature or element can be used alone without the other features and elements of the embodiments or in various combinations with or without other features and elements disclosed herein.

[0091] This written description uses examples of the subject matter disclosed to enable any person skilled in the art to practice the same, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the subject matter is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims.

References

- [1] T.D. Waite, K.A. Gray, Oxidation and Coagulation of Wastewater Effluent, *Stud. Environ. Sci.* 24 (1984) 407–420.
- [2] E.R. Bandala, J. Miranda, M. Beltran, M. Vaca, L.G. Torres, Wastewater disinfection and organic matter removal using ferrate (VI) oxidation, (2018) 507–513.
doi:10.2166/wh.2009.003.
- [3] M. Gilbert, T.D. Waite, C. Hare, Applications of ferrate ion to disinfection, *J. Am. Water Work. Assoc.* 56 (1976) 466–474.
- [4] F. Kazama, Viral inactivation by potassium ferrate, *Water Sci. Technol.* 31 (1995) 165–168.
- [5] G.W. Thompson, L.T. Ockerman, J.M. Schreyer, Preparation and Purification of Potassium Ferrate. VI, *J. Am. Chem. Soc.* 73 (1951) 1379–1381.
doi:10.1021/ja01147a536.
- [6] H. Goff, R.K. Murmann, Mechanism of isotopic oxygen exchange and reduction of ferrate (VI) ion (FeO_4^{2-}), *J. Am. Chem. Soc.* 93 (1971) 6058–6065.
- [7] H. Huang, D. Sommerfeld, B.C. Dunn, E.M. Eyring, C.R. Lloyd, Ferrate(VI) Oxidation of Aqueous Phenol: Kinetics and Mechanism, *J. Phys. Chem. A.* 105 (2001) 3536–3541. doi:10.1021/jp0039621.
- [8] S.A.A. Tabatabai, J.C. Schippers, M.D. Kennedy, Effect of coagulation on fouling potential and removal of algal organic matter in ultrafiltration pretreatment to seawater reverse osmosis, *Water Res.* 59 (2014) 283–294.

WHAT IS CLAIMED IS:

1. A pretreatment module (930) for a water treatment plant (900), the pretreatment module (930) comprising:
 - a pretreatment unit (932) configured to screen out solids from an incoming water feed (902);
 - a liquid ferrate generation unit (934) configured to generate, *in situ*, a liquid ferrate (122); and
 - a dosage unit (936) configured to release the liquid ferrate (122) with a given dose into the incoming water feed (902).
2. The pretreatment module of Claim 1, further comprising:
 - a processor configured to select the given dose based on input from a feed analysis unit.
3. The pretreatment module of Claim 2, wherein the input is a measurement of a parameter of the incoming water feed or a parameter of a pre-treated water feed.
4. The pretreatment module of Claim 3, wherein the parameter is one of a turbidity, total suspended solids, silt density index, modified fouling index, or biological activity.

5. The pretreatment module of Claim 3, wherein the processor is configured to compare a measured value of the parameter with a given threshold, and based on the comparison, to select the given dose.

6. The pretreatment module of Claim 5, wherein the given dose is a no dose, or a low dose or a medium dose, or a high dose.

7. The pretreatment module of Claim 6, wherein the low dose has 0.1 mg/L of ferrate or less, the medium dose has between 0.1 and 1 mg/L of the ferrate, and the high dose has between 1 and 3 mg/L of the ferrate.

8. The pretreatment module of Claim 1, wherein the liquid ferrate includes ferrate (FeO_4^{2-}), ferric chloride (FeCl_3), sodium hypochlorite (NaOCl), and sodium hydroxide (NaOH).

9. The pretreatment module of Claim 8, wherein the incoming water feed includes seawater.

10. The pretreatment module of Claim 1, wherein the liquid ferrate generation unit (934) includes a first tank storing ferric chloride (FeCl_3), a second tank storing sodium hypochlorite (NaOCl), and a third tank storing sodium hydroxide (NaOH).

11. The pretreatment module of Claim 10, further including a fourth tank that receives the ferric chloride (FeCl_3), the sodium hypochlorite (NaOCl), and the sodium hydroxide (NaOH), and a mixer that mixes the ferric chloride (FeCl_3), the sodium hypochlorite (NaOCl), and the sodium hydroxide (NaOH).

12. The pretreatment module of Claim 11, wherein the dosage unit is in fluid communication with the fourth tank and includes a pump that doses out the given dose.

13. A water treatment plant (900), comprising:
a water intake (910) configured to receive a salt water feed (902);
a feed analysis unit (920) configured to sample the salt water feed (902) and generate a measurement associated with a parameter of the salt water feed (902);
a pretreatment module (930) configured to inject a given dose of liquid ferrate (122) into the salt water feed (902) to generate a pre-treated water feed (906); and
a water treatment module (940) configured to receive the pre-treated water feed (906) and remove salt.

14. The water treatment plant of Claim 13, wherein the pretreatment module comprises:

a pretreatment unit (932) configured to screen out solids from the incoming water feed (902);

a liquid ferrate generation unit (934) configured to generate, *in situ*, the liquid ferrate (122); and

a dosage unit (936) configured to generate the liquid ferrate (122) to have the given dose.

15. The water treatment plant of Claim 13, further comprising:

a processor configured to select the given dose based on the measurement from the feed analysis unit, and

a sensor associated with the feed analysis unit and configured to obtain the measurement, wherein the sensor is configured to measure one of a turbidity, total suspended solids, silt density index, modified fouling index, or biological activity.

16. The water treatment plant of Claim 15, wherein the processor is configured to compare the measurement of the parameter with a given threshold, and based on the comparison, to select the given dose, wherein the given dose is a no dose, or a low dose or a medium dose, or a high dose, and wherein the low dose has 0.1 mg/L of ferrate or less, the medium dose has between 0.1 and 1 mg/L of the ferrate, and the high dose has between 1 and 3 mg/L of the ferrate.

17. The treatment plant of Claim 13, wherein the liquid ferrate includes ferrate (FeO_4^{2-}), ferric chloride (FeCl_3), sodium hypochlorite (NaOCl), and sodium hydroxide (NaOH).

18. A method for treating salt water in a water treatment plant (900), the method comprising:

- receiving (1200) a salt water feed (902);
- performing (1202) a feed analysis on the salt water feed (902) and generating a measurement associated with a parameter of the salt water feed (902);
- generating (1204) *in situ* liquid ferrate (122);
- selecting (1206) a given dose of the liquid ferrate (122) based on the measurement of the parameter; and
- releasing (1208) the given dose of the liquid ferrate (122) into the salt water feed (902).

19. The method of Claim 18, further comprising:

- treating the salt water feed with the liquid ferrate to remove the salt.

20. The method of Claim 19, further comprising:

- screening out solids from the salt feed water in a pretreatment module;
- injecting the given dose of the liquid ferrate in the pretreatment module; and
- filtering the salt out of the salt water feed in a treatment module, which is placed downstream from the pretreatment module.

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Table 1 Characteristics of water feeds

Parameters	Raw Red Sea water	Analog seawater	
		Sodium alginate	Cultivated Algae
Temperature	23.5 ± 0.5 C	23.5 ± 0.5 C	23.5 ± 0.5 C
pH	8.00 ± 0.20	8.00 ± 0.20	8.00 ± 0.20
TDS	40000 ± 2100 mg/L	40000 ± 2100 mg/L	40000 ± 2100 mg/L
Conductivity	59 ± 1 mS/cm	59 ± 1 mS/cm	59 ± 1 mS/cm
Turbidity	1.27 ± 0.52 NTU	2.50 ± 0.50 NTU	12.00 ± 1.00 NTU
TOC	1.0 ± 0.2 mg/L	10.0 ± 0.2 mg/L	10.0 ± 0.4 mg/L
DOC	0.8 ± 0.1 mg/L	9.0 ± 0.1 mg/L	8.5 ± 0.8 mg/L
Total alkalinity	118 ± 2 mg/L	118 ± 2 mg/L	118 ± 2 mg/L

FIG. 1

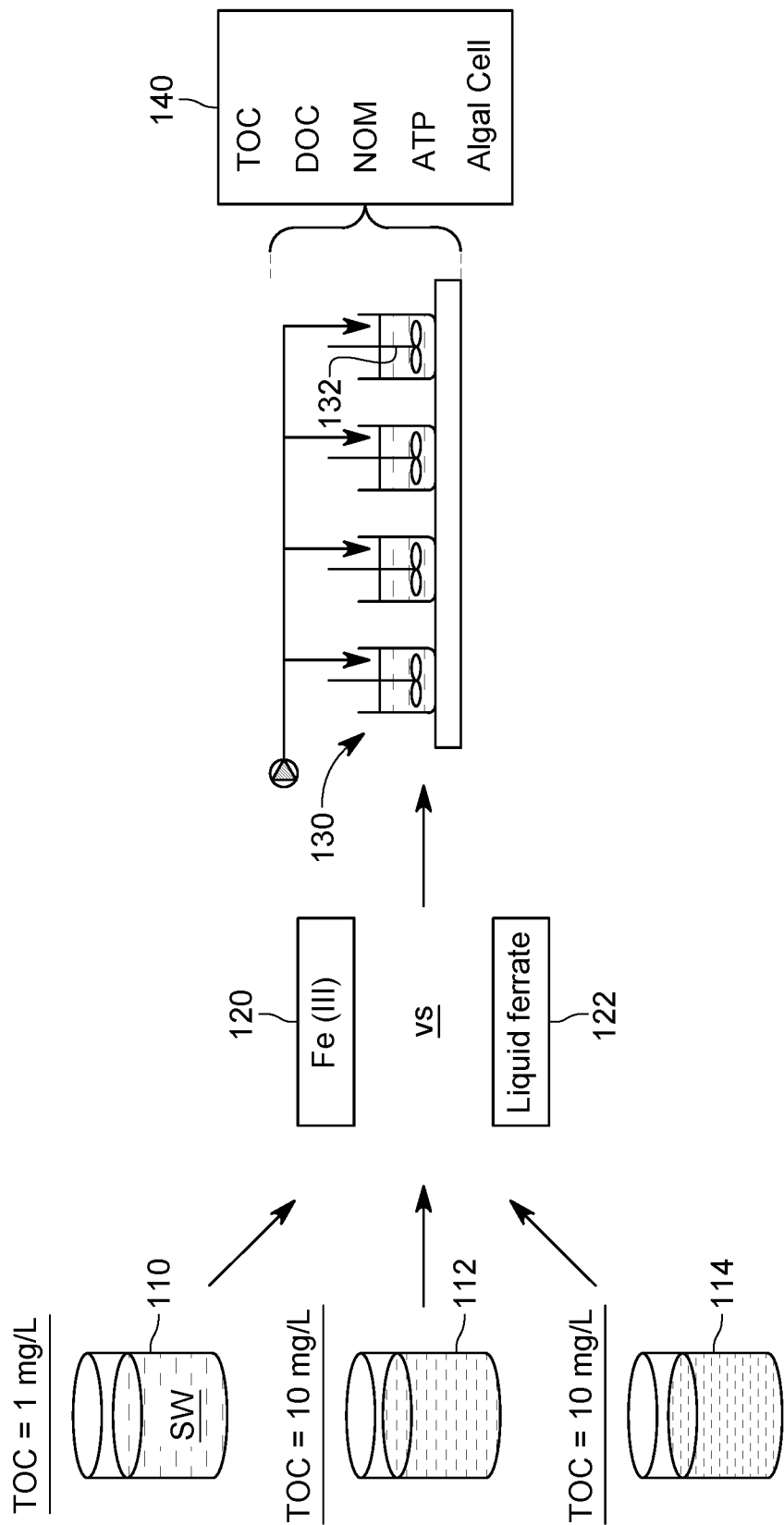


FIG. 2

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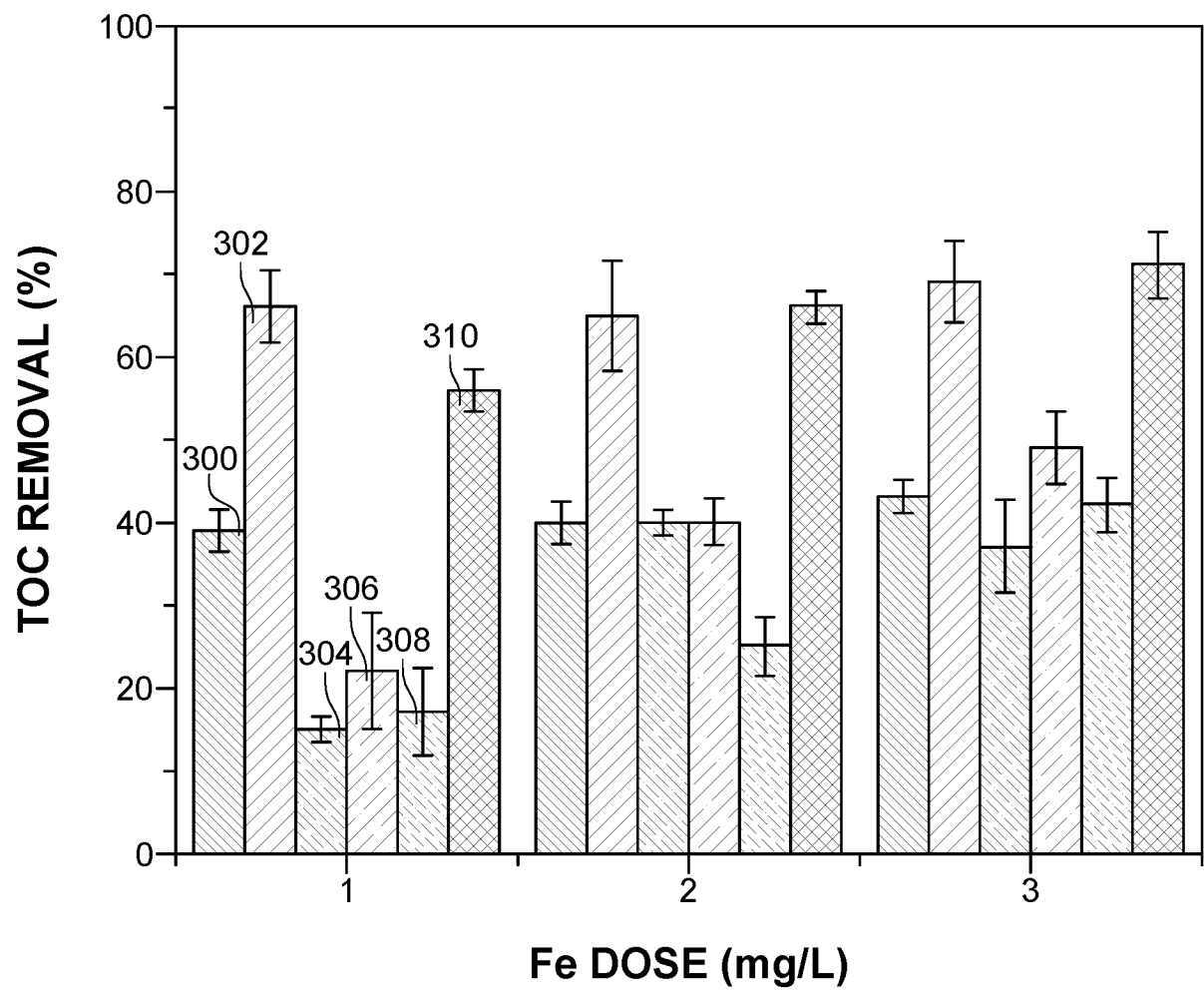


FIG. 3A

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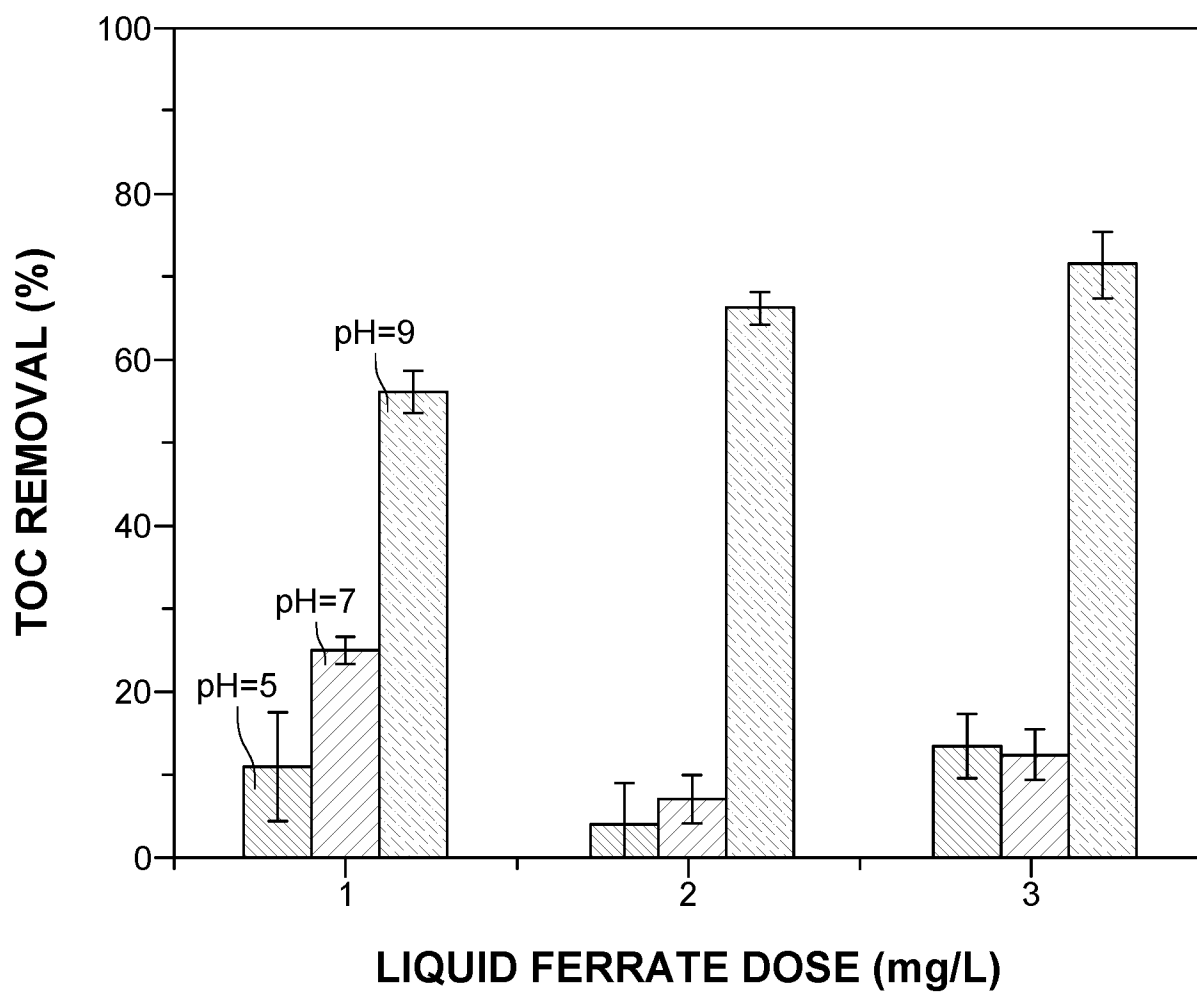


FIG. 3B

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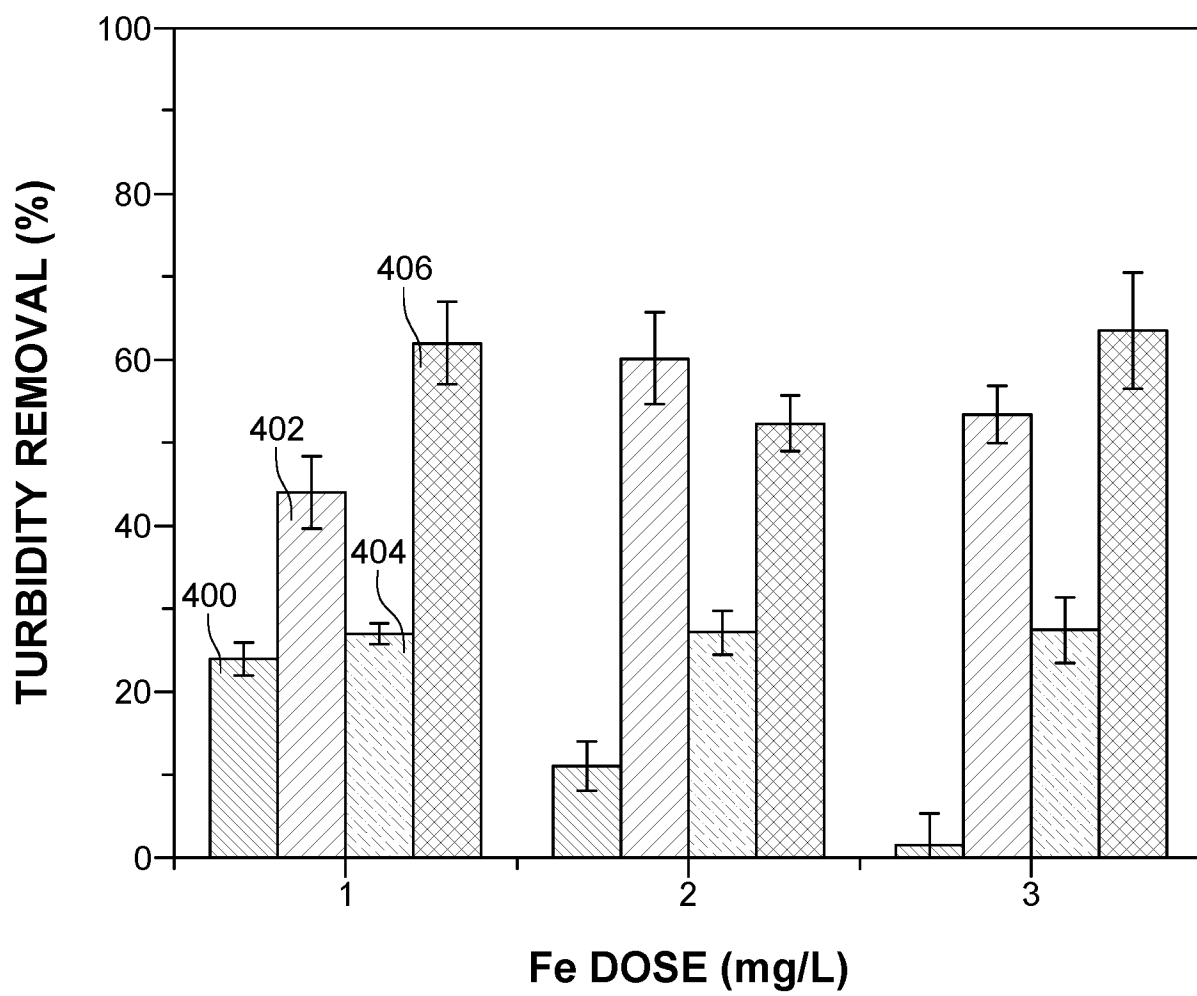


FIG. 4

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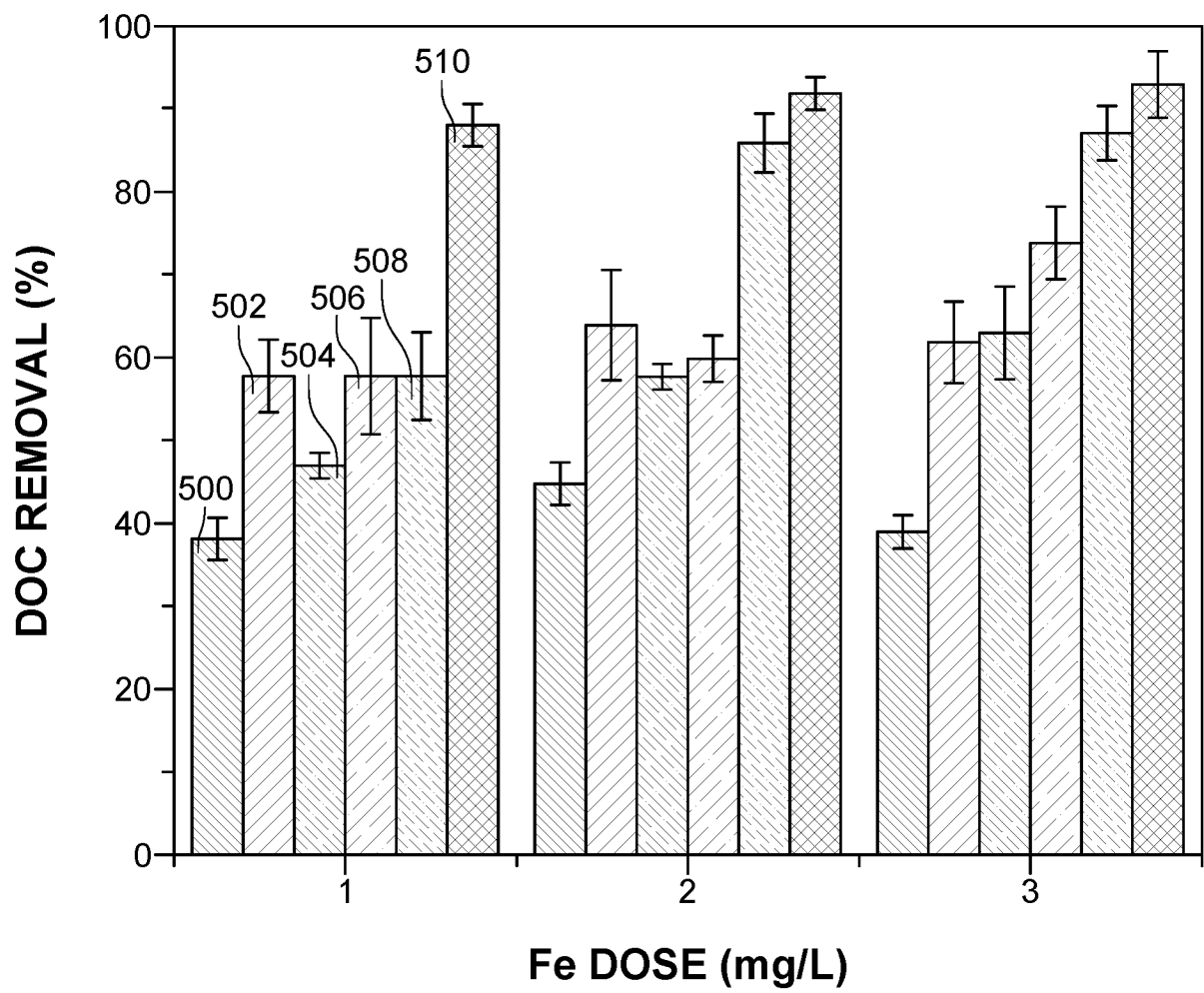


FIG. 5A

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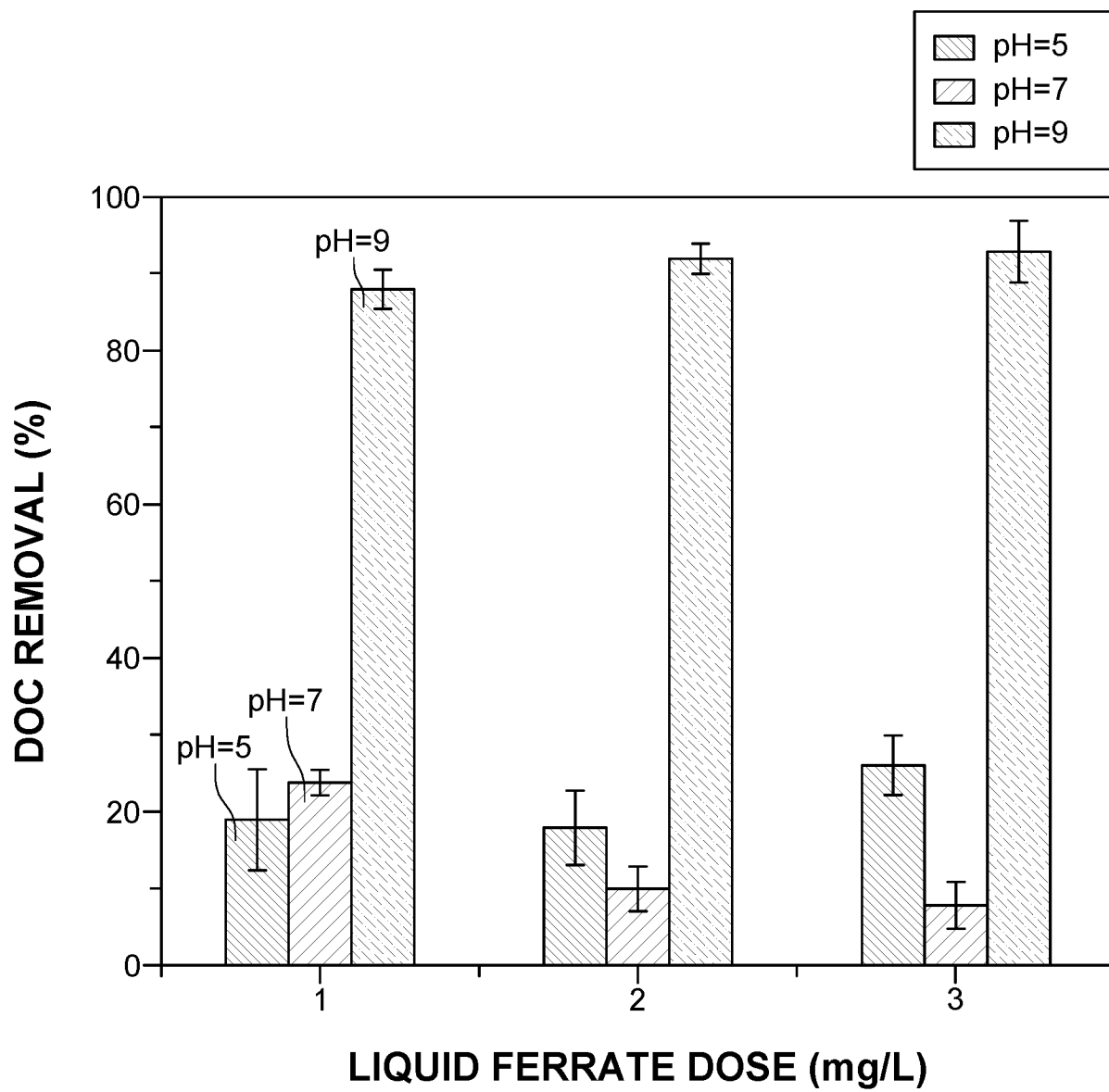


FIG. 5B

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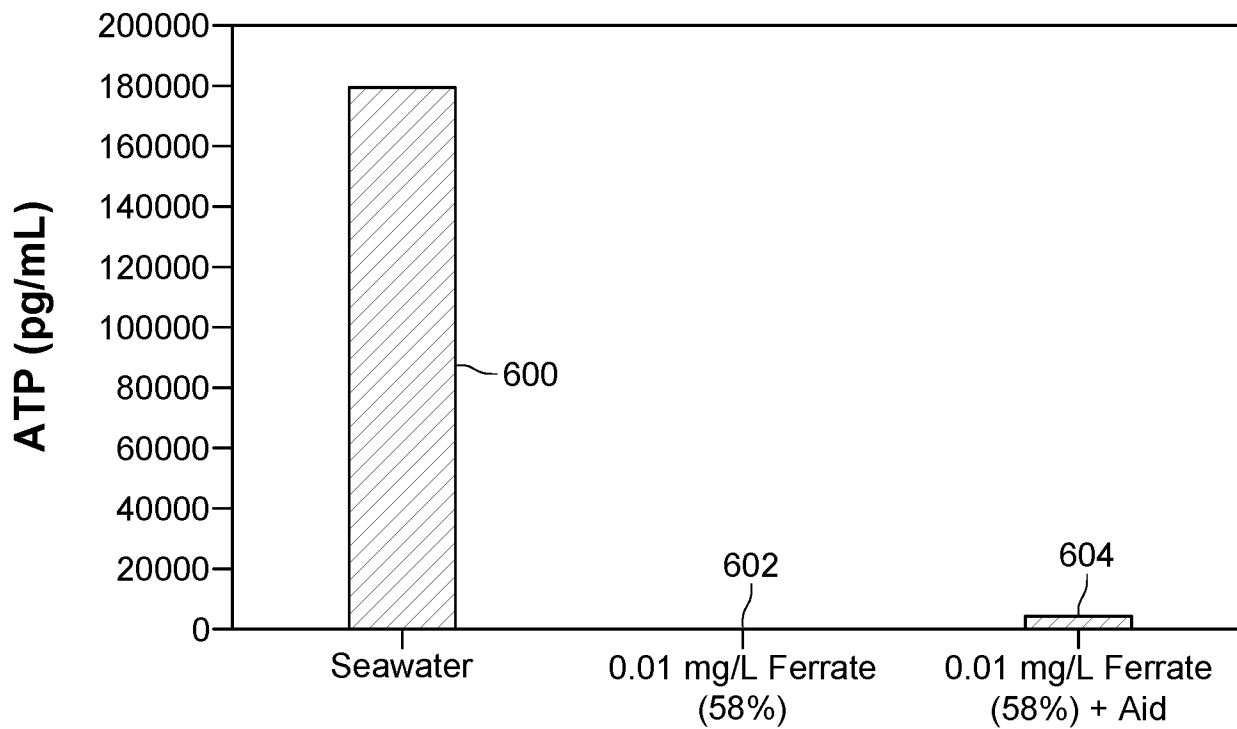


FIG. 6A

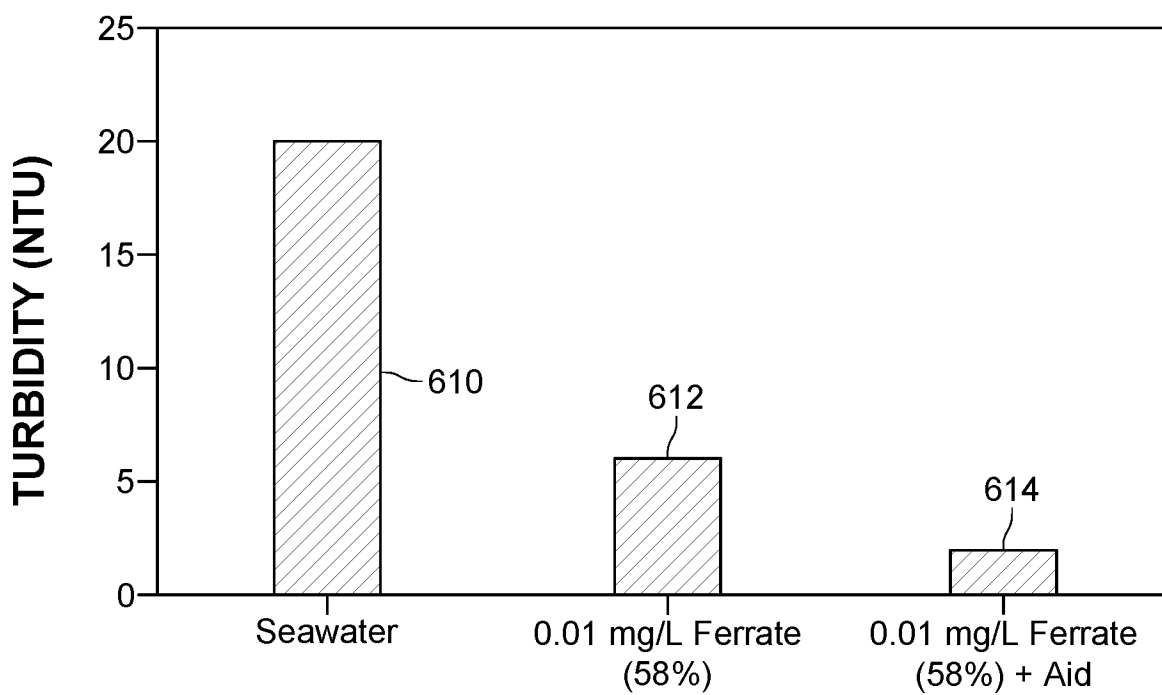


FIG. 6B

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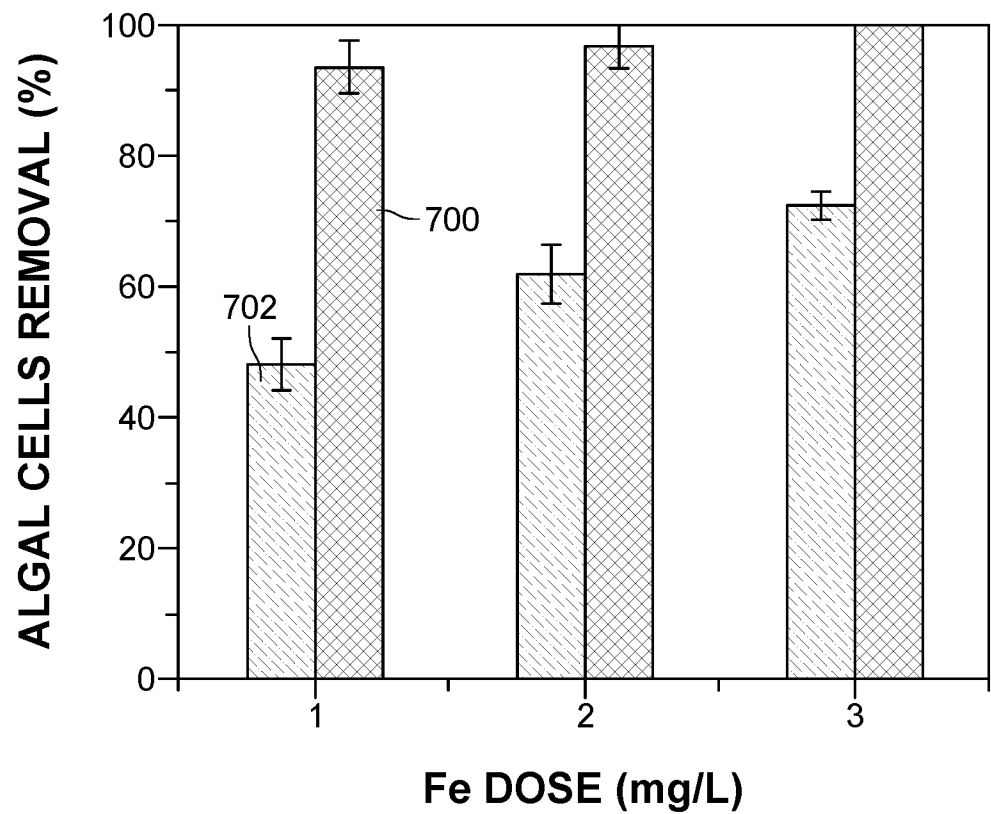


FIG. 7A

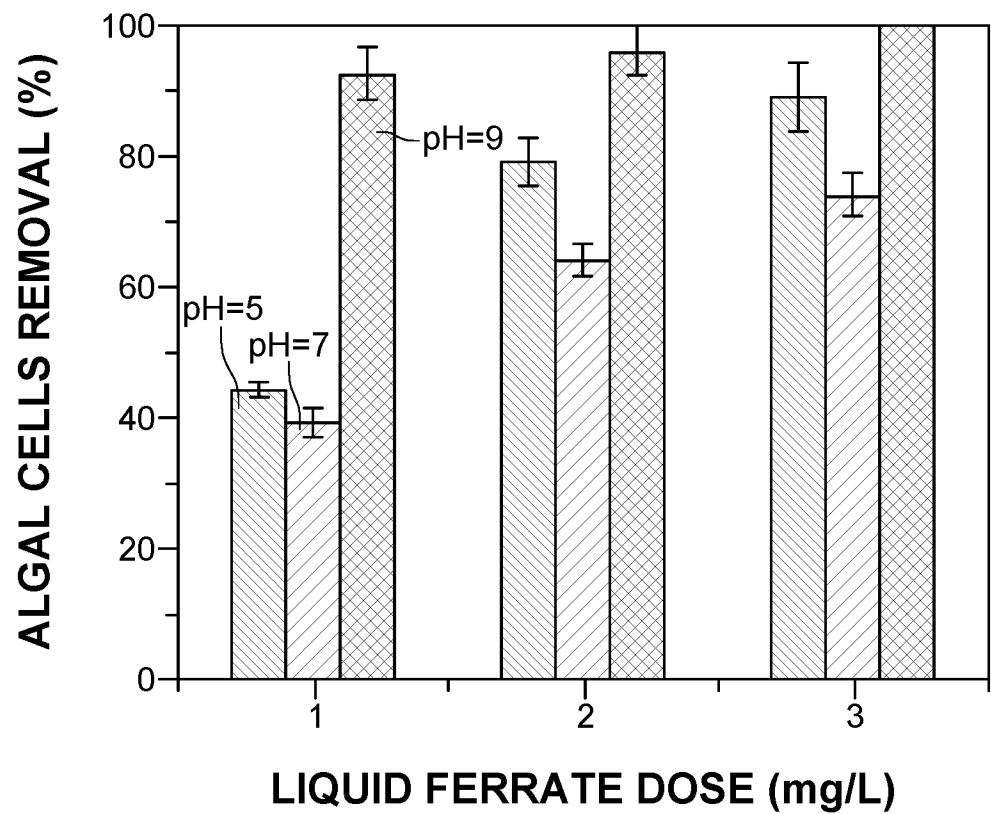


FIG. 7B

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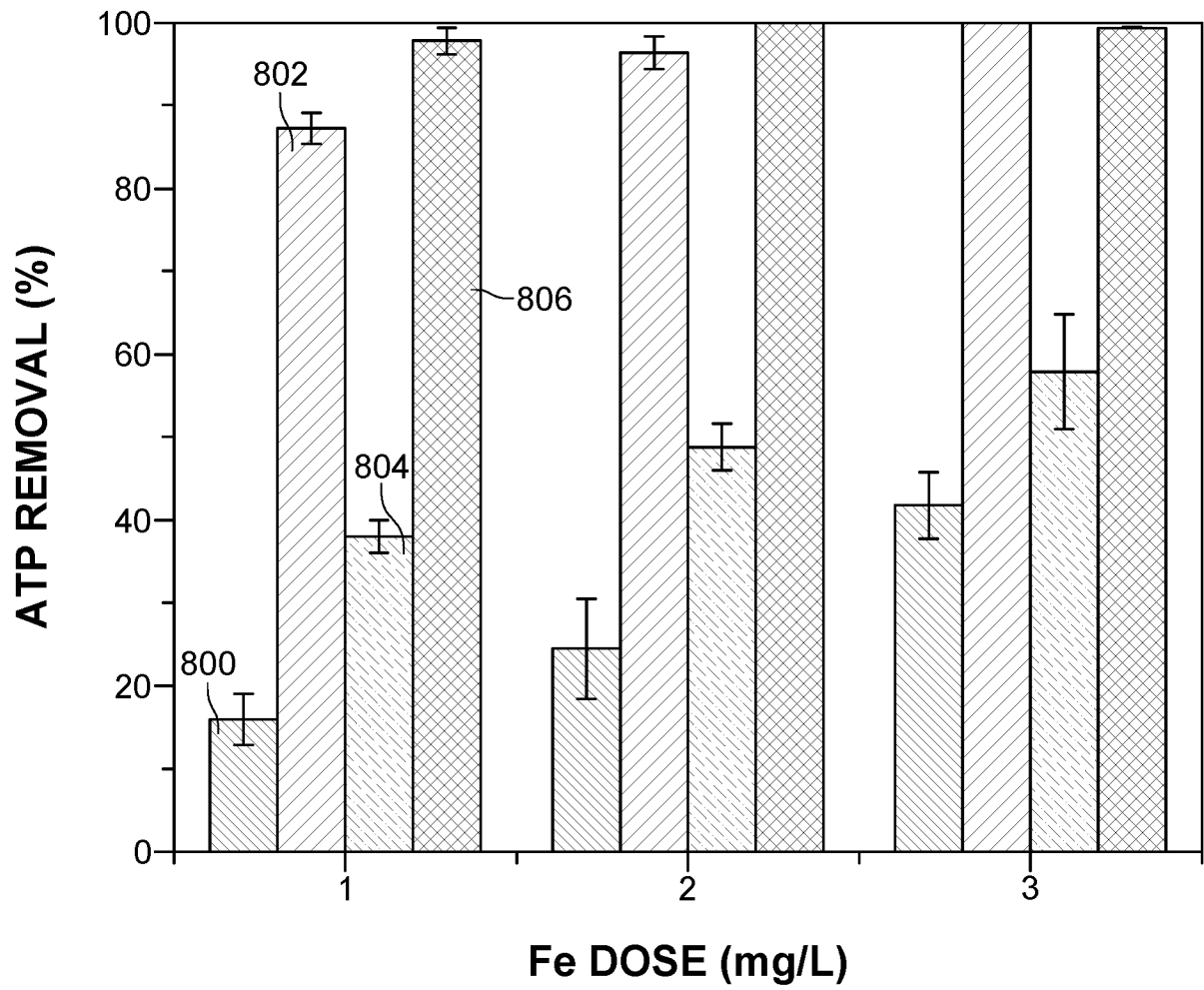


FIG. 8

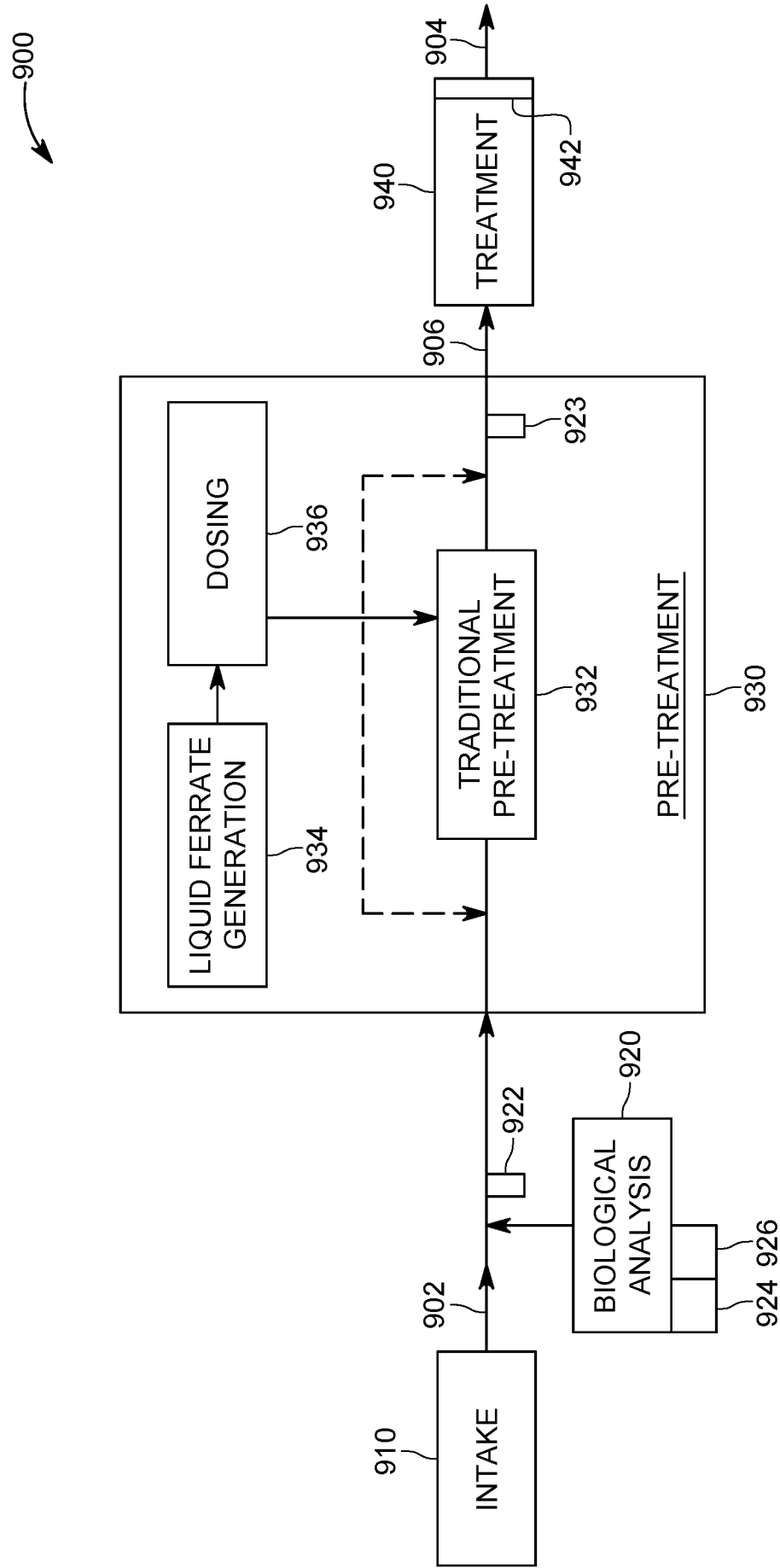


FIG. 9

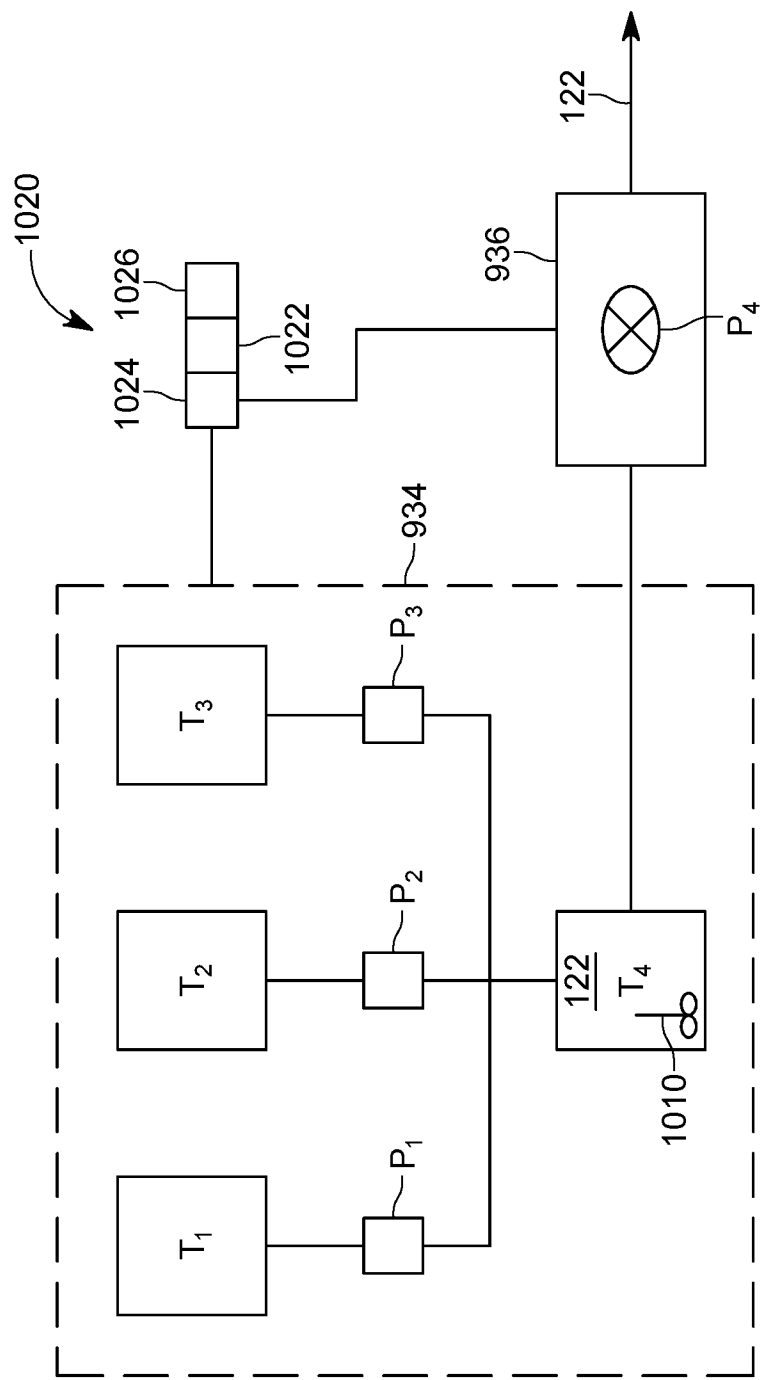


FIG. 10

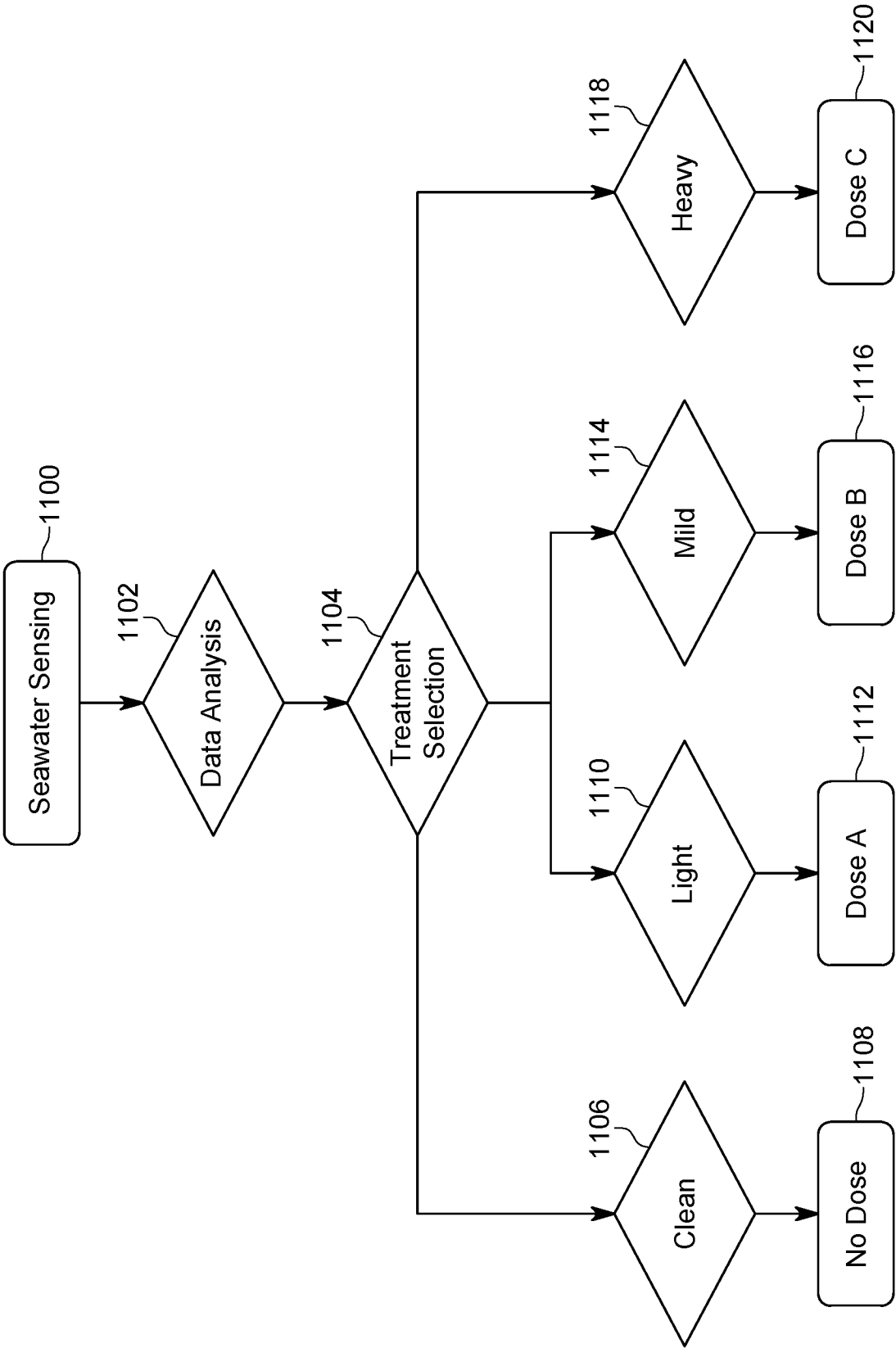


FIG. 11

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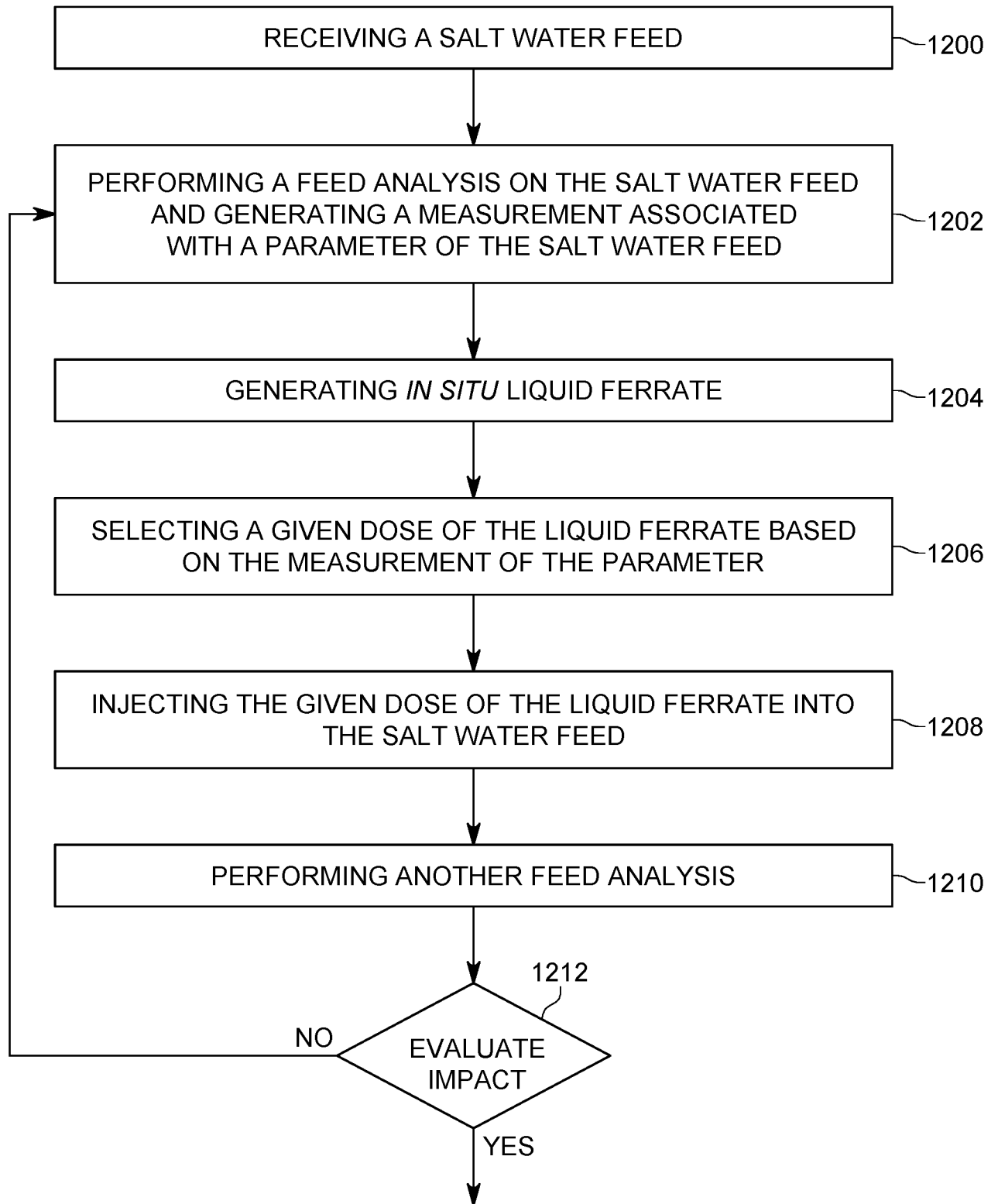


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/053093

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/52 C02F1/44 C02F1/72 B01D61/04
ADD. C02F103/08 B01D61/02

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 B01D

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 2005/271575 A1 (CIAMPI LEE E [US] ET AL) 8 December 2005 (2005-12-08) paragraphs [0002], [0008] - [0011], [0042] - [0068], [0099] - [0102], [0157] - [0187], [0208] - [0209], [0222] - [0232], [0247] paragraphs [0250] - [0260], [0293] - [0316], [0428], [0446] - [0451] ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

2 July 2020

Date of mailing of the international search report

17/07/2020

Name and mailing address of the ISA/

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Authorized officer

Rozanska, Agnieszka

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/053093

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BHASKAR JYOTI DEKA ET AL: "Mitigation of algal organic matter released from Chaetoceros affinis and Hymenomonas by in situ generated ferrate", CHEMOSPHERE., vol. 206, 10 March 2018 (2018-03-10), pages 718-726, XP055710306, GB ISSN: 0045-6535, DOI: 10.1016/j.chemosphere.2018.05.052 pages 719-720 -----	1-20
X	YU WENZHENG ET AL: "Evaluation of ferrate as a coagulant aid/oxidant pretreatment for mitigating submerged ultrafiltration membrane fouling in drinking water treatment", CHEMICAL ENGINEERING JOURNAL, ELSEVIER, AMSTERDAM, NL, vol. 298, 24 March 2016 (2016-03-24), pages 234-242, XP029538316, ISSN: 1385-8947, DOI: 10.1016/J.CEJ.2016.03.080 pages 234-242 -----	1-20
X,P	ALSHAHRI ABDULLAH H ET AL: "Advanced coagulation using in-situ generated liquid ferrate, Fe (VI), for enhanced pretreatment in seawater RO desalination during algal blooms", SCIENCE OF THE TOTAL ENVIRONMENT, ELSEVIER, AMSTERDAM, NL, vol. 685, 19 June 2019 (2019-06-19), pages 1193-1200, XP085753243, ISSN: 0048-9697, DOI: 10.1016/J.SCITOTENV.2019.06.286 [retrieved on 2019-06-19] the whole document -----	1-20
A	KR 101 589 412 B1 (ILSHIN ENVIRONMENTAL ENGINEERING CO LTD [KR]; ECO G TECH [KR] ET AL.) 27 January 2016 (2016-01-27) the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2020/053093

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2005271575	A1	08-12-2005	US 2005271575 A1	08-12-2005
			US 2009120802 A1	14-05-2009
			US 2011036725 A1	17-02-2011
			US 2012175314 A1	12-07-2012
			US 2013175224 A1	11-07-2013
			US 2014042101 A1	13-02-2014
			US 2016031732 A1	04-02-2016
			US 2017334753 A1	23-11-2017
			WO 2006073433 A2	13-07-2006

KR 101589412	B1	27-01-2016	NONE	
