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Beardwood et al.(10) **Pub. No.: US 2007/0081573 A1**(43) **Pub. Date: Apr. 12, 2007**(54) **PROCESS FOR INHIBITING BIOFILM
FORMATION ON AND/OR REMOVING
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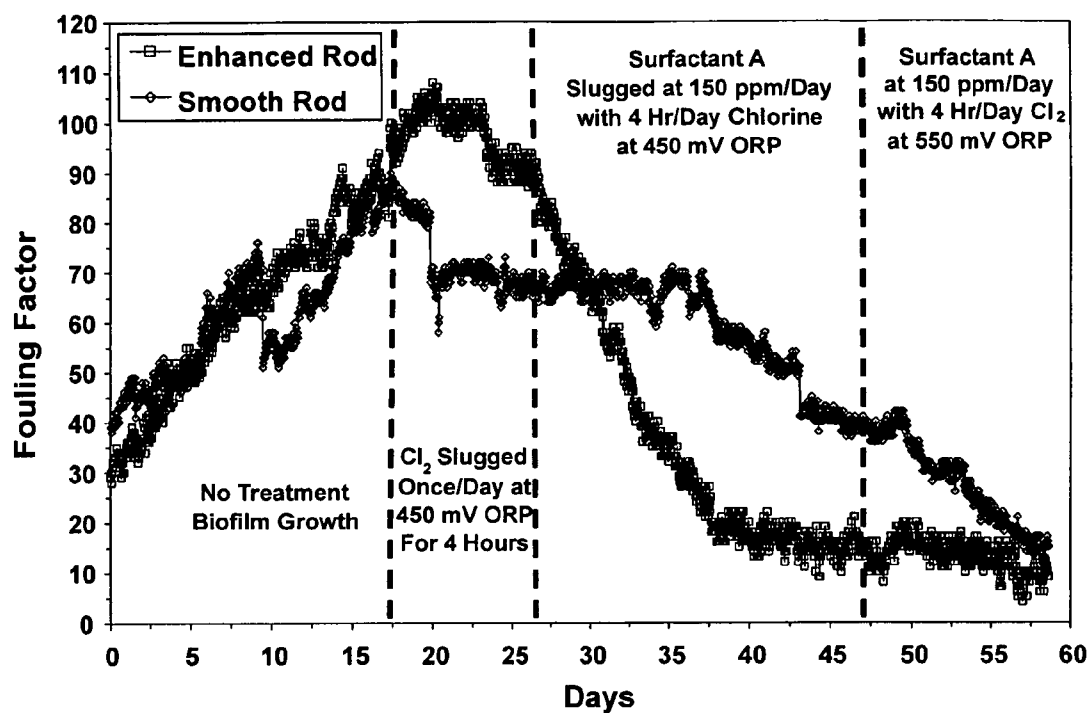
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31, 2005.**Publication Classification**(51) **Int. Cl.****G01N 25/00** (2006.01)**F28G 1/12** (2006.01)**F02M 23/14** (2006.01)(52) **U.S. Cl. 374/7; 165/95; 261/155; 261/DIG. 11**

(57)

ABSTRACT

This invention relates to a process for inhibiting the formation of biofilm and/or removing biofilm deposited on an enhanced tube of a heat exchanger in contact with an aqueous system. The process comprises feeding an oxidant selected from the group consisting of chlorine dioxide and stabilized bromine into an aqueous system such that the oxidant agent comes into contact with the enhanced tube.



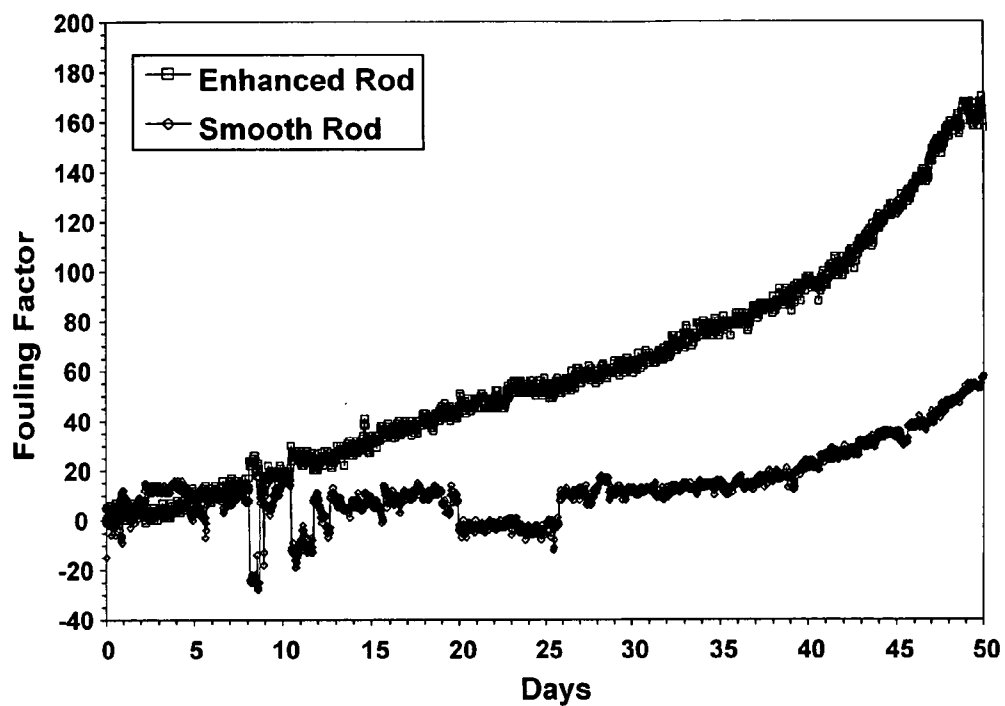


FIG. 1

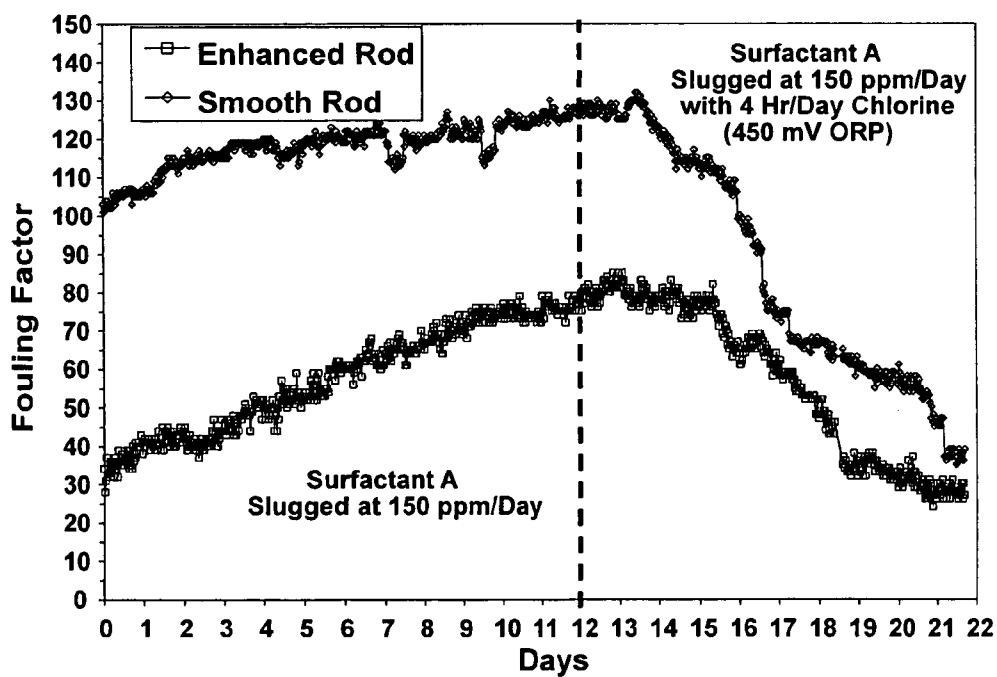
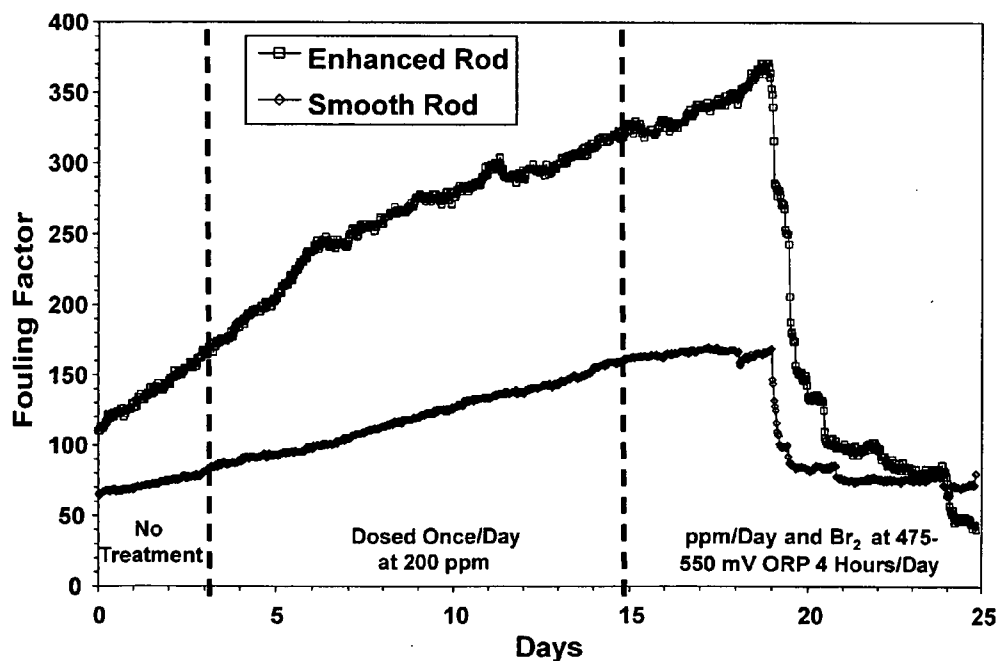
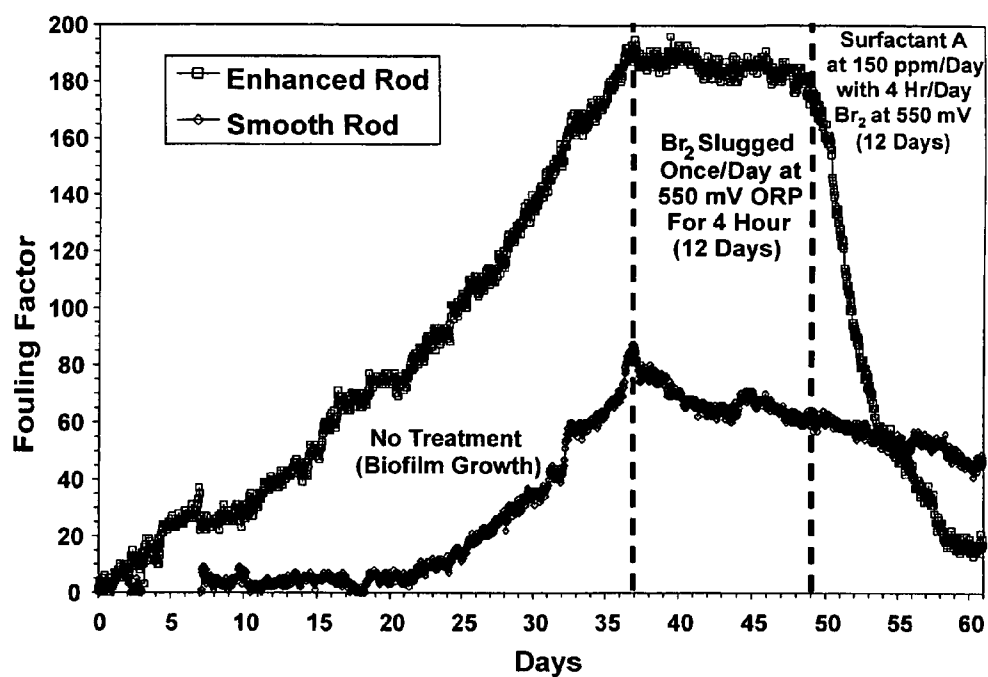


FIG. 2



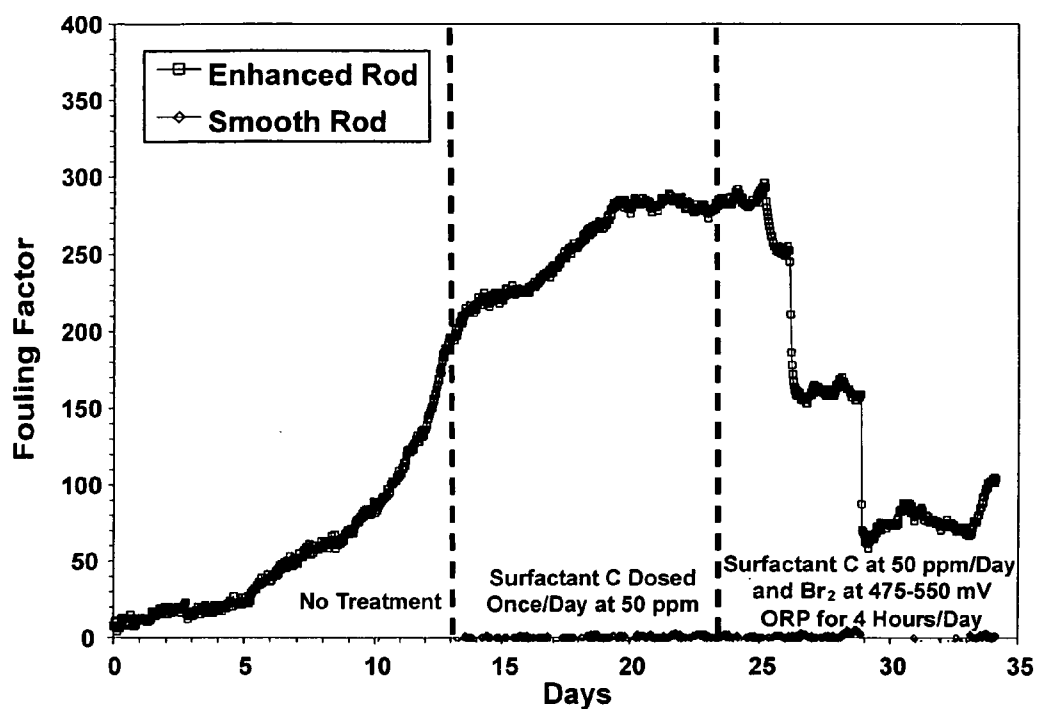


FIG. 5

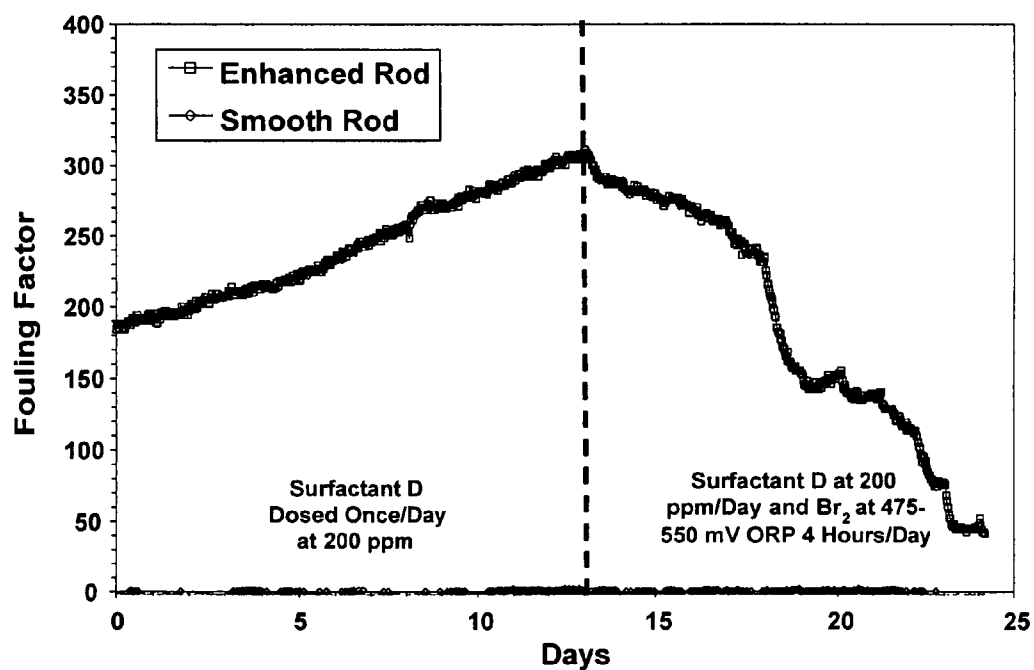
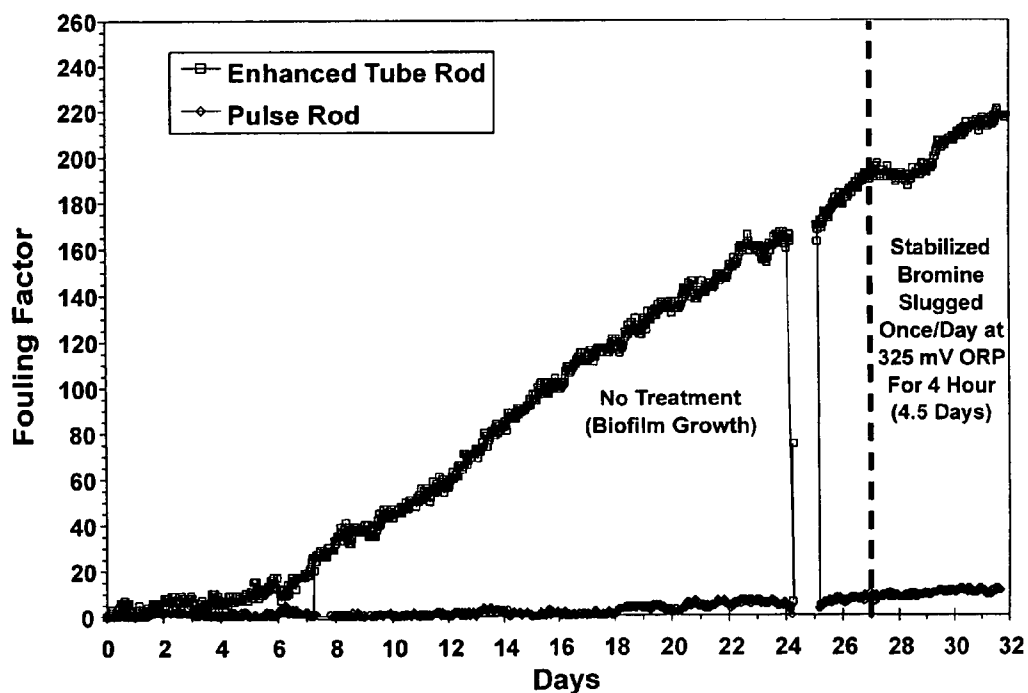
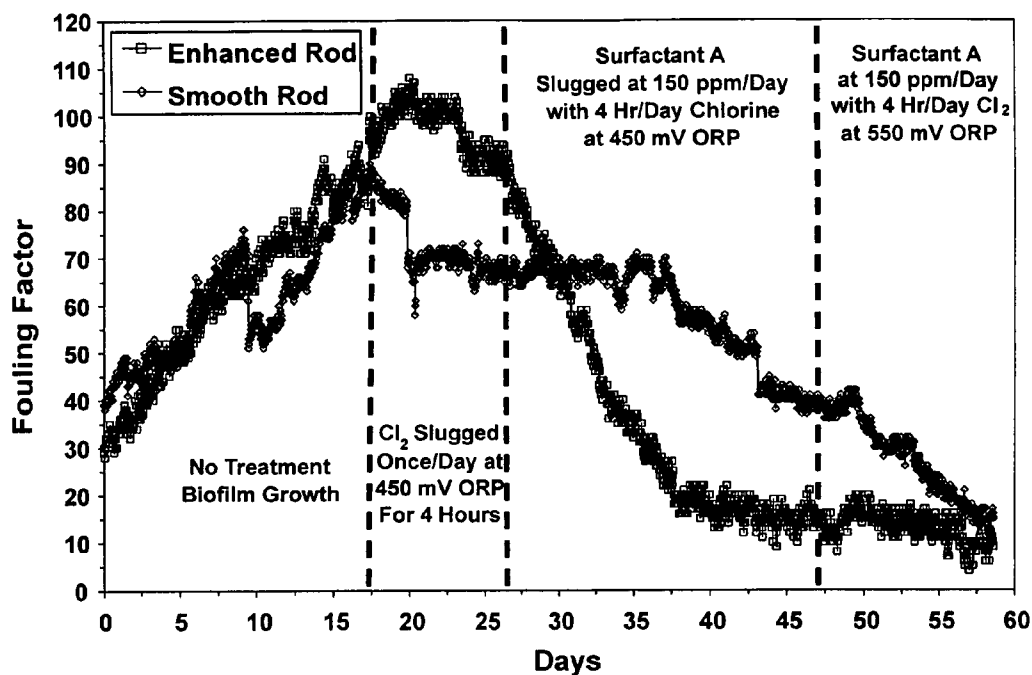


FIG. 6



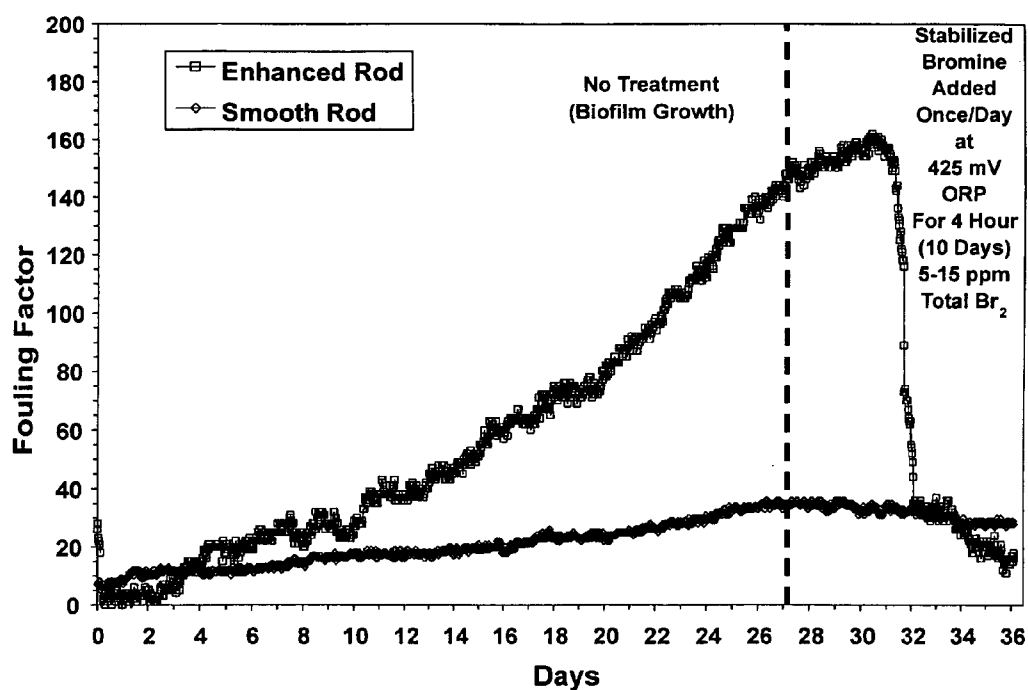


FIG. 9

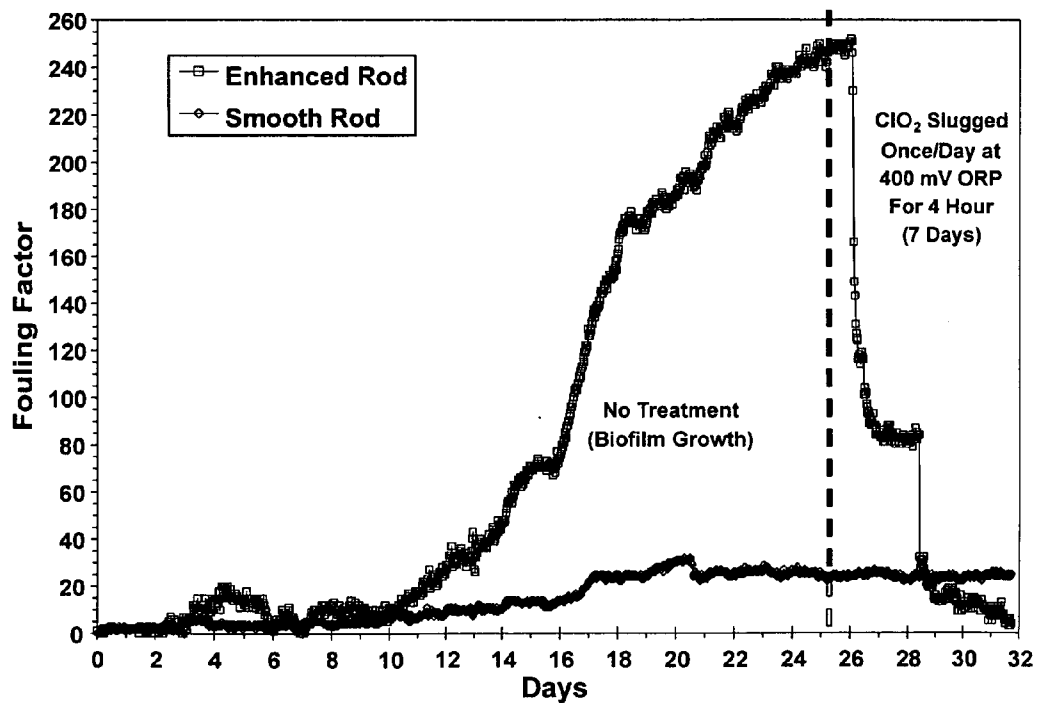


FIG. 10

PROCESS FOR INHIBITING BIOFILM FORMATION ON AND/OR REMOVING BIOFILM FROM AN ENHANCED TUBE

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 60/666,750 filed on Mar. 31, 2005, entitled Heat Transfer Test Assembly for an Apparatus for Monitoring Fouling of Aqueous Systems, the contents of which are hereby incorporated into this application.

FIELD OF THE INVENTION

[0002] This invention relates to a process for inhibiting the formation of biofilm and/or removing biofilm deposited on an enhanced tube of a heat exchanger in contact with an aqueous system. The process comprises feeding an oxidant selected from the group consisting of chlorine dioxide and stabilized bromine into an aqueous system such that the oxidant comes into contact with the enhanced tube.

BACKGROUND OF THE INVENTION

[0003] In water treatment systems that utilize a heat exchanger, it is desirable to reduce the capital costs of the heat exchanger by reducing the physical size of the heat exchanger, while maintaining the same heat transfer area. In order to accomplish this objective, some or all of the "smooth tubes", traditionally used in heat exchangers, are replaced by "enhanced tubes".

[0004] When water, or some other liquid, is used as the coolant, it circulates inside the enhanced tube. In these systems, the enhancements are found inside the tube. The internal enhancements are typically helical flutes or fins, which increase the surface area of the heat exchanger, and thus promote more efficient heat exchange. By using the enhanced tubes to increase the surface area of the heat exchanger, it is possible to decrease the size of the heat exchanger.

[0005] The problem with using heat exchangers that have enhanced tubes is that the enhancements promote the precipitation of solids from the aqueous stream in contact with the enhanced tubes, which provides an ideal environment for the growth of biofilm. Thus, the enhancements may become fouled with a biofilm rather quickly and to such an extent that most or all of the benefits of associated with using the enhanced tubes are neutralized.

[0006] Biofouling is an extremely complex phenomenon in open recycling cooling systems. Biofouling of heat transfer equipment occurs when microorganisms attach to the surface of heat transfer equipment. Biofouling results in the deposit of a "biofilm" which is comprised of any or all of the following classes of materials: biomass, scale, corrosion products, insoluble materials (silt, etc.), and/or water formed sludge. Factors that influence the biofouling of enhanced tubes are well-known from the literature related to heat exchangers containing enhanced tubes. Numerous attempts have been made to adapt standard treatment chemistries for use with heat exchangers containing enhanced tubes to eliminate or reduce biofouling, but unfortunately results have been inconsistent. Therefore, there is a need for a process, which inhibits the formation of biofilm on an enhanced tube and/or removes biofilm deposited on an enhanced tube.

[0007] All citations referred to in this application are expressly incorporated by reference.

SUMMARY OF THE INVENTION

[0008] This invention relates to a process for inhibiting the formation of biofilm and/or removing biofilm deposited on an enhanced tube of a heat exchanger in contact with an aqueous system. The process comprises:

[0009] feeding an effective amount of an oxidant selected from the group consisting of chlorine dioxide and stabilized bromine into said aqueous system in contact with a heat exchanger containing one or more enhanced tubes, such that the oxidant inhibits the formation of biofilm on the enhanced tube and/or removes biofilm deposited on the enhanced tube.

[0010] It was surprising that the use of chlorine dioxide or stabilized bromine as the oxidant inhibits the formation of biofilm on the enhanced tube and/or removes biofilm deposited on the enhanced tube. Experimental tests indicate that the use of other oxidants was not as effective as chlorine dioxide or stabilized bromine. It was also surprising that chlorine dioxide or stabilized bromine could be used effectively without using a biocides dispersant. And it was surprising that these effects were more pronounced on enhanced tubes than on smooth tubes.

[0011] Based on the data generated from experiments, it is evident that the described process is a non-corrosive process, which effectively removes biological and biologically entrapped foulants from enhanced tubes without jeopardizing the integrity of the tubes. Chlorine dioxide or stabilized bromine effectively attacks the root cause of deposit formation on the surface of heat transfer equipment, which is biofouling. When deposits caused by biofouling are released, other foulants are also released from the surface of the heat transfer equipment.

[0012] Experimental data showed that chlorine dioxide was the most chemically effective and cost effective oxidant, because biofouling could be inhibited and/or reduced more effectively when chlorine dioxide was used as the oxidant without a dispersant. Concentration rates and treatment times could be reduced when chlorine dioxide was used as the oxidant.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly.

[0014] FIG. 2 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly, which shows the effect of using Dispersant A to treat the aqueous system, followed by chlorine and Dispersant A combination.

[0015] FIG. 3 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly, where bromine is first used to treat the system followed by the use of bromine in combination with Dispersant A.

[0016] FIGS. 4-6 are plots showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly, Dispersants B, C, and D are first used to treat the system followed by the use of bromine in combination with Dispersants B, C, and D respectively.

[0017] FIG. 7 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly, where chlorine is first used to treat the system followed by the use of chlorine in combination with Dispersant A.

[0018] FIG. 8 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly where stabilized bromine is used to treat the aqueous system and the ORP of the oxidizing aqueous system is about 325 mV.

[0019] FIG. 9 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly where stabilized bromine is used to treat the aqueous system and the ORP of the oxidizing aqueous system is about 425 mV.

[0020] FIG. 10 is a plot showing experimental biofouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly, where chlorine dioxide is used to treat the aqueous system, the ORP of the oxidizing aqueous system is about 400 mV.

DESCRIPTION OF THE INVENTION

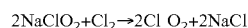
[0021] An enhanced tube is a tube used in a heat exchanger that increases the surface area of the heat exchanger when compared to the use of a similar tube, which is smooth, in the heat exchanger. Typically, the internal enhancements to the enhanced tube are grooves, ribs, fins, and the like, which typically form helical flutes and the like.

[0022] Although the heat exchanger containing one or more enhanced tubes may be found in a variety of places through which water flows and is treated, e.g. open recirculating cooling water systems with cooling towers, once-through cooling water systems and closed cooling water systems. Heat exchangers that may employ enhanced tubes include, but are not limited to chillers and condensers on refrigeration machines, compressor intercoolers and after-coolers, and various chemical, petrochemical and hydrocarbon process streams. Typically, the tubes in any individual heat exchanger will be of the same type, either smooth or enhanced, but there is no design limitation to prevent the mixture of tube types in the same heat exchanger. However, in any given cooling water circuit, there may be multiple heat exchangers some of which have enhanced tubes, while others have smooth tubes.

[0023] Chlorine dioxide or stabilized bromine is used as the oxidant. Stabilized bromine is hypobromite stabilized by the addition of a halogen stabilizer such as a sulfamate.

[0024] Although the chlorine dioxide can be generated by any of the methods known in the art, it is typically generated on site by reacting sodium chlorite with gaseous chlorine or acidified sodium hypochlorite as follows:

(1) Gaseous chlorine Generation



(2) Acidified sodium hypochlorite Generation



[0025] Specific practices for generating chlorine dioxide according to these methods are well known in the art, including the electrolytic/membrane process. Examples of generation equipment suitable for use in the process are described in U.S. Pat. Nos. 4,013,761 and 4,147,115. Various means may be used to control the delivery of sodium chlorite and other chemicals to the generator. Such means include, but are not limited to, variable rate pumps, valves, eductors and metering devices. The precursor chemicals are typically pumped or educted into motive or dilution water. Then they are mixed in a mixing chamber or sent directly to the reaction chamber of the chlorine dioxide generator. Mixing the precursor chemicals first provides better yields of chlorine dioxide.

[0026] The chlorine dioxide or stabilized bromine may be added to the aqueous system either continuously or in batch feed over one or more hours. Typically batch feed is used. The residual amount of chlorine dioxide or stabilized bromine present in the aqueous system containing the heat exchanger with enhanced tubes is typically from 0.05 ppm to 1.0 ppm, preferably from 0.10 ppm to 0.25 ppm depending on the level of microbial contamination in the aqueous stream.

[0027] Biodispersants may also be fed to the aqueous system in order to eliminate or reduce the deposition of biofilm on the enhanced tubes of the heat exchanger. Examples of biodispersants include terpenes, nonionic esters, nonionic ethoxylates, amide-based dispersants, as well as any nonionic, cationic or anionic surfactant. They are all efficacious, however the active concentration and contact time varies between these chemistries.

[0028] Although the pH of the aqueous system treated may vary over wide ranges, the pH of the aqueous system typically ranges from 6.0 to 9.5, more typically from 6.6 to 9.2.

[0029] Although the oxidation-reduction potential (ORP) of the aqueous system treated may vary over wide ranges, the ORP of the aqueous system typically ranges from -100 to +250 without the addition of any oxidant, during the feed of chlorine dioxide, the ORP of the aqueous system will be raised to a range of from +350 to +650, typically to a range of +400 to +500. The ORP is typically measured with an ORP monitor such as those supplied by Rosemont, Honeywell, Foxboro, etc.

[0030] The pH, ORP, and other parameters of the system can be monitored, preferably continuously and automatically, by methods well-known in the water treatment industry. It is particularly useful to control the feed and feedrate of chlorine dioxide by systems comprising ORP technology analyzers, sensors, and a Master Control Unit. See, for example, U.S. Pat. No. 5,227,306, which describes how to proportionally feed ClO_2 to an aqueous system. The total control system consists of a Master Control Unit, which is a PLC (programmable logic controller)-based system comprising control logic and an operator interface. Any PLC and operator interface-based system can be used.

[0031] Abbreviations and Definitions:

[0032] Dispersant A ENV IROPLUS® 8100, a biodegradable terpene dispersant, sold by Drew Industrial of Ashland Inc.

[0033] Dispersant B DREWSPERSE® 739, a nonionic ester dispersant, sold by Drew Industrial of Ashland Inc.

[0034] Dispersant C DREWSPERSE® 1930, an amide-based dispersant, sold by Drew Industrial of Ashland Inc.

[0035] Dispersant D DREWSPERSE® 738, a nonionic ethoxylated dispersant, sold by Drew Industrial of Ashland Inc.

[0036] Stabilized bromine STABROM 909, a hypobromite stabilized by the addition of a halogen stabilizer such as a sulfamate, sold by Albemarle.

EXAMPLES

[0037] The Examples will illustrate specific embodiments of the invention. These Examples are not intended to cover all possible embodiments of the invention, and those skilled in the art will understand that many variations are possible without departing from the scope of the invention. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims. In this application all units are in the metric system and all amounts in milligrams per liter, unless otherwise expressly indicated.

[0038] In order to test the effect of various biodispersants and/or oxidants on the formation of biofilm on an enhanced tube, an automated, laboratory scale cooling tower system comprising the following components was constructed: (a) a circulating pump, (b) a small water-to-water heat exchanger, which is used to supply a heat load to allow the tower water to concentrate, and (d) a modified, laboratory version of Ashland's online P.U.L.S.E. analyzer cooling water monitor¹, containing one enhanced tube² and one smooth tube.

[0039] The operating parameters of the cooling water system and the make-up water tested are set forth in Table I. During these tests, a portion of the circulating water was bypassed to the tower basin to maintain the cold water temperature (temperature drop across the cooling tower with the limited heat input). The concentration of circulating water was maintained by conductivity control. In addition, fouling factor, pH, and ORP were constantly monitored.

¹ The modified version of the P-U-L-S-E® fouling monitor (see U.S. Pat. Nos. 4,339,945, Re. 33,346, 4,346,587, and Re. 33,468) was designed to more effectively measure the biofouling of enhanced tubes found in a heat exchanger in contact with an aqueous system. The fouling tendency of the fluid on the enhanced tube is evaluated by the passage of water from the aqueous system tested through the heat transfer test assembly under controlled rates of flow and heat output from the heating element. A side stream from the aqueous stream tested, which is in contact with the enhanced tube, is diverted to the modified heat transfer test assembly in order to measure the biofilm on the enhanced tube in the contact with the aqueous system tested. The significant modification of the P-U-L-S-E® fouling monitor involved replacing the smooth tube the P-U-L-S-E® fouling monitor with an enhanced tube. Measurement of temperature drops between the tube in the test assembly and the aqueous system tested are correlated with the formation and reduction of fouling. The modified P-U-L-S-E® fouling in monitor was designed to emulate the same tube-side flow conditions.

² The enhanced tube with externally enhanced with helical flutes.

TABLE I

Test Cooling Tower Operating Design Conditions	
System volume	0.22 m ³ (58 gallons)
Recirculation rate	4.542 m ³ /hr (20 gpm)
Volume to recirculation ratio	3:1
Cooling tower temperature drop (ΔT)	2.8° C.

TABLE I-continued

Apparent Cooling Water Apparent Time	Approximately 22 to 23 hours
Cold Water Temperature	33° C.
Maximum circulation	76 L/m (20 gpm)
Standard Uncycled Make-up Water Chemistry	
Calcium, mg/L as CaCO ₃	81
Magnesium mg/L as CaCO ₃	48
Total Alkalinity, mg/L as CaCO ₃	96
Bicarbonate Alkalinity, mg/L as CaCO ₃	96
Chloride mg/L as chlorine	58
Sulfate, mg/L as SO ₄	46
pH	7.4

[0040] Control

[0041] (Preparing a Contaminated Enhanced Tube)

[0042] In order to determine the effect of various biodispersants and/or oxidizing agents on the formation of biofouling deposits on the smooth tubes and enhanced tubes having flutes (grooves between adjacent ribs). The enhanced tube was the controlling test. That is, since the two tubes were running in parallel in the same test rig, the runs started and stopped at the same time and were exposed to the same cooling water. The test heat exchanger was exposed to cooling water, which was inoculated with *Pseudomonas aeruginosa* (ATCC 27853), a known slime forming aerobic bacterium, in order to contaminate the enhanced tube with biofilm.

[0043] Nutrient broth was added to the tower daily at a dose of 50 mg/L. Chemistry and data associated with this test run are provided in Table II. Although biofouling was observable by the naked eye by the seventh day into the run, it was actually detected as an increasing trend on the third and fifth day by the enhanced tube. The enhanced rod fouled at a linear rate of 0.439 m²-°K/Watt-sec. The tests were run until the enhanced rod flutes (grooves between adjacent ribs) were filled with foulants and there was a significant trend differentiating the enhanced tube from the smooth tube. All of the runs lasted 20 to 36 days, which is within the typical range (14 to 45 days) for biofilm grow-up on surfaces and P-U-L-S-E fouling runs.

[0044] FIG. 1 shows the biological fouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly. The data indicate that the enhanced tube fouls more rapidly than the smooth tube.

TABLE II

Water chemistry and data related to control (contaminated water)	
pH	7.0
"P" Alkalinity, mg/L as CaCO ₃	0
Carbonate, mg/L as CaCO ₃	0
Total Alkalinity, mg/L as CaCO ₃	54
Bicarbonate, mg/L as CaCO ₃	54
Calcium Hardness, mg/L as CaCO ₃	162
Magnesium Hardness, mg/L as CaCO ₃	96
Chloride, mg/L as chlorine	116
Sulfate, mg/L as SO ₄	230
Conductivity, μS/cm ²	936

Aerobic Bacteria added - *Pseudomonas aeruginosa* - 4.55 × 10⁶ CFU/mL
 Difco Nutrient Broth (37.5% Beef Extract + 62.5% Peptone) - 50 mg/L/day
 Tube velocity, m/sec - 1.6-1.68
 Skin Temperature ° C. - 37.8

Example 1

[0045] (Use of Dispersant A to Treat the Aqueous System)

[0046] In this example, Dispersant A was used to treat the aqueous system to determine its effect on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube. The water chemistry used for the experimental runs is listed in Table III.

TABLE III

Generalized Experimental Biofouling Runs-Water Chemistry and Data	
pH	8.5
"P" Alkalinity, mg/L as CaCO ₃	14
Carbonate, mg/L as CaCO ₃	28
Total Alkalinity, mg/L as CaCO ₃	186
Bicarbonate, mg/L as CaCO ₃	158
Calcium Hardness, mg/L as CaCO ₃	243
Magnesium Hardness, mg/L as CaCO ₃	144
Chloride, mg/L as chlorine	174
Sulfate, mg/L as SO ₄	240
Conductivity, $\mu\text{S}/\text{cm}^2$	1404

Note:

Aerobic Bacteria, nutrient broth, tube velocity and skin temperature data remain the same as shown in Table I

[0047] After the contaminating the water with aerobic bacteria, Dispersant A was slug fed at 150 ppm for 12 days.

[0048] FIG. 2 shows the fouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly after feeding with Dispersant A during this twelve day period. The data show that the enhanced tube exhibits greater fouling than the smooth tube. The data also indicate that use of Dispersant A alone has little or no effect on inhibiting and/or removing biofilm.

Example 2

[0049] (Use of bromine as Oxidant)

[0050] In this example, bromine was used as the oxidant, and its effect on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube was investigated. The water chemistry used for the experimental runs is listed in Table III.

TABLE III

Generalized Experimental Biofouling Runs-Water Chemistry and Data	
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Magnesium Hardness, mg/L as CaCO ₃	144
Chloride, mg/L as chlorine	174
Sulfate, mg/L as SO ₄	240
Conductivity, $\mu\text{S}/\text{cm}^2$	1404

Note:

Aerobic Bacteria, nutrient broth, tube velocity and skin temperature data remain The same as show in Table I

[0051] After the contaminating the water with aerobic bacteria, bromine alone was slug fed for 4 hours per day to +550 mV ORP for nine days.

[0052] FIG. 3 shows the fouling data for a heat transfer test assembly containing a smooth tube and enhanced tube

in a heat transfer test assembly after bromine alone was first used to treat the aqueous system for nine days. The data again confirm that the enhanced tube fouls more rapidly than the smooth tube. The data also indicate that use of bromine alone has little effect on inhibiting and/or removing biofilm.

Example 3

[0053] (Effect of using bromine with different biodispersants on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube)

[0054] In this example, the use bromine as the oxidant with different biodispersants and their effects on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube were investigated. The water chemistry used for these experimental runs is also listed in Table III.

[0055] After the contaminating the water with aerobic bacteria, bromine oxidant was slug fed 4 hours per day to maintain +475 to +550 mV ORP. Then Dispersants A, B, C and D were separately slug fed into the aqueous system in the amounts set forth in Table IV.

[0056] FIGS. 3-6 show the fouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly when the dispersants after bromine alone was first used to treat the aqueous system for nine days. The data again confirm that the enhanced tube fouls more rapidly than the smooth tube. The data indicate improved effectiveness in inhibiting and/or removing biofilm if the bromine is used in conjunction with a biodispersant. Nevertheless, the results, which are summarized in Table IV, indicate that the use of bromine in conjunction with a biodispersant still takes several days to clean the enhanced tube of the test apparatus. And obviously, the use of a dispersant in conjunction with the bromine increases the treatment costs.

TABLE IV

Biodispersant	Dosage, mg/L	Time to Clean (Days)
Dispersant A	150	7
Dispersant B	200	5
Dispersant C	50	6
Dispersant D	200	12

Example 4

[0057] (Use of chlorine as Oxidant)

[0058] In this example, chlorine was used as the oxidant, and its effect on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube was investigated. The water chemistry used for the experimental runs is listed in Table III.

[0059] After the contaminating the water with aerobic bacteria, biodispersant A was slug fed into the cooling tower at 150 ppm daily. After 12 days, both the enhanced and smooth rods continued to foul, though at a slower rate.

[0060] Beginning on the 13th day, chlorine was slugged over a 4 hour period/day to maintain an ORP of +450 mV. The fouling factors on both tubes dropped as illustrated in FIG. 32.

[0061] At this point, (FIG. 7) the biofilm was allowed to grow-up once again in the absence of dispersant or oxidant. On the 17th day, chlorine addition was re-instituted. The use of chlorine alone was only able to contain the fouling on the enhanced rod.

[0062] For the final 25 days, Dispersant A was again slug fed at 150 mg/l/day along with the daily slug of chlorine. Clean-up rates of the remaining biofilm were 82% for the enhanced rod.

[0063] FIG. 7 shows the fouling data for a heat transfer test assembly containing a smooth tube and enhanced tube in a heat transfer test assembly after chlorine alone was first used to treat the aqueous system for nine days. The data again confirm that the enhanced tube fouls more rapidly than the smooth tube. The data also indicate that use of chlorine alone has little effect on inhibiting and/or removing biofilm.

[0064] FIG. 7 also shows the fouling data the heat transfer test assembly when Dispersant A was slug fed after chlorine alone was first used to treat the aqueous system for nine days. The data also indicate improved effectiveness in inhibiting and/or removing biofilm if the chlorine is used in conjunction with a biodispersant. Nevertheless, the results indicate that the use of chlorine in conjunction with a Biodispersant A still takes several days to clean the enhanced tube of the test apparatus. And obviously, the use of a dispersant in conjunction with the chlorine increases the treatment costs.

Example 5

[0065] (Use of Stabilized bromine as Oxidant)

[0066] In this example, stabilized bromine was used as the oxidant, and its effect on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube was investigated. The water chemistry used for the experimental runs is listed in Table III.

[0067] After the contaminating the water with aerobic bacteria, stabilized bromine was slug fed for 4 hours per day without a dispersant. Initially, the oxidant slug feed was performed to maintain +325 mV ORP, which did not halt biofilm growth on the heat transfer rod (FIG. 8). An increase in oxidant feed to maintain +425 mV ORP followed. At this oxidant residual, the fouling associated with biofilm growth was terminated, which resulted in an on-line clean-up of the heat transfer rod (FIG. 9).

[0068] The data again confirm that the enhanced tube fouls more rapidly than the smooth tube. The data also indicate that use of stabilized bromine alone is effective at inhibiting and/or removing biofilm, particularly if the ORP of the oxidizing aqueous system is at least about 425 mV. Thus, it is possible to effectively inhibit and/or remove biofilm from the enhanced tube of the test apparatus using stabilized bromine alone without a biodispersant.

Example 6

[0069] (Use of chlorine dioxide as Oxidant)

[0070] In this example, chlorine oxide was used as the oxidant, and its effect on reducing the deposit of biofilm on a fouled enhanced tube and smooth tube was investigated. The water chemistry used for the experimental runs is listed in Table III.

[0071] After the contaminating the water with aerobic bacteria, chlorine dioxide was slug fed for 4 hours/day to maintain an ORP of 400 mV.

[0072] The results of the test are shown in FIG. 10. The data again confirm that the enhanced tube fouls more rapidly than the smooth tube. The data also indicate that use of chlorine dioxide is effective at inhibiting and/or removing biofilm, even when the ORP of the oxidizing aqueous system as low as 400 mV. Thus, chlorine dioxide is more effective than stabilized bromine as an oxidant for inhibiting and/or removing biofilm from the enhanced tube of the test apparatus, and can be used effectively without a biodispersant.

[0073] Summary of Test Results

[0074] Simulation of cooling waters under fouling conditions was achieved with the dynamic pilot system in the laboratory. Experimental investigations provided information regarding the fouling behavior of enhanced tubes compared to smooth bore tubes, the effect of using different oxidants, dispersants, and combinations thereof. The following observations were noted:

[0075] 1. Enhanced tubes foul faster and to a higher degree than smooth tubes when the potential for bio-fouling is present.

[0076] 2. Biodispersants alone are not sufficiently effective in the reduction of biofilm deposits on smooth tubes or enhanced tubes. There is more effective reduction of biofilms if an oxidant is also used.

[0077] 3. Conventional oxidants, such as chlorine or bromine, at dosing rates that afford planktonic bacteria control while avoiding the potential to initiate localized corrosion of copper alloy heat exchanger tubes, are not effective alone at reducing biofilms (sessile bacteria) when present on smooth tubes and enhanced tubes. There is more effective reduction of biofilms if a biodispersant is also used. But even when these oxidants are combined with a dispersant, the inhibition and/or reduction of biofilm is not accomplished in a technically effective and cost effective manner.

[0078] 4. Chlorine dioxide, and stabilized bromine to a lesser degree, when used alone, reduce the deposit of biofilm deposited on enhanced tubes.

[0079] 5. Chlorine dioxide alone is the most chemically and cost effective oxidant for reducing the deposit of biofilm deposited on enhance tubes.

We claim:

1. A process for inhibiting biofilm on and/or removing biofilm deposited on an enhanced tube of a heat exchanger in contact with an aqueous system, which comprises:

feeding an effective amount of an oxidant selected from the group consisting of chlorine dioxide and stabilized bromine into an aqueous system in contact with a heat exchanger containing one or more enhanced tubes, such that the oxidant inhibits the formation of biofilm on the enhanced tube and/or removes biofilm deposited on the enhanced tube.

2. The process of claim 1 which is carried out in the absence of a biodispersant.

3. The process of claim 2 wherein the amount of oxidant maintained in said aqueous system is from 0.05 ppm to 1.0 ppm.

4. The process of claim 3 wherein the pH of said aqueous system is from 6.0 to 9.5.

5. The process of claim 4 wherein the ORP of the oxidizing aqueous system is from 350 mV to 650 mV.

6. The process of claim 5 wherein the oxidant is stabilized bromine and the ORP of the oxidizing aqueous system is from 425 mV to 550 mV.

7. The process of claim 5 wherein the oxidant is chlorine dioxide and the ORP of the oxidizing aqueous system is from 400 mV to 550 mV.

8. The process of claim 6 or 7 wherein the enhancement to the enhanced tube comprises helical flutes.

9. The process of claim 8 wherein the heat exchanger is a component of a cooling tower.

10. The process of claim 9 wherein the helical flutes are located inside the tube.

11. The process of claim 10 where the heat exchanger is used in a cooling water system.

12. The process of claim 11 wherein the cooling system is an open recirculating cooling water system.

13. The process of claim 9 wherein the cooling system is a closed recirculating cooling water system.

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