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(54) Title: METHODS OF REMOVING MICROBES FROM SURFACES

(57) Abstract: A method has been found for the inhibition of microbial biofilm on surfaces in contact with systems, such as aqueous systems. In accordance with the method, an effective amount of a modified starch polymer is fed to the system water. The modified starch polymer may be a cationic quaternary ammonium starch.



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METHODS OF REMOVING MICROBES FROM SURFACES

FIELD OF INVENTION

[0001] The field of the invention relates to methods for inhibiting microbial biofilm on surfaces in contact with systems, including but not limited to aqueous systems. More particularly, the invention relates to the use of a modified starch biofilm control agent for inhibiting microbial biofilm.

BACKGROUND OF THE INVENTION

[0002] Industrial process- or operating-water systems, such as, open or closed water-cycle systems, in particular cooling-water systems, offer suitable conditions for the growth of microorganisms, with the result that a slime known as biofilm is formed on the surfaces of water-bearing systems. In the case of cooling water systems in particular, these biofilm deposits can lead to reduced heat exchange efficiency, pipeline damage and corrosion within the systems. Adverse effects on process control are possible, which can ultimately reduce the efficiency of the industrial process in question and impair product quality. In addition to this, biofilm or slime deposits generally lead to higher energy consumption.

[0003] The deposition of the bacterial slimes can most effectively be controlled with biocides; the effect of these biocides being based on the fact that they kill off the microorganisms in the operating water and thus prevent slime production. However, biocide concentrations needed to control biofilm are much higher than that needed to control planktonic bacteria. Thus, biocides to control biofilm increase expenses, raise doubts on ecological grounds, and, because of their toxicity, pose considerable dangers when handled. For this reason, alternative ways of eliminating biofilm have been sought in the past.

[0004] Industrial efforts to prevent colonization or to clean fouled surfaces amount to costly expenditures in many industries. Often such expenditures are made for cleaning programs that include the use of surfactants. Surfactants are regularly applied in water treatment programs as agents believed to play a role in the removal

of organic masses from surfaces, in the enhancement of biocide efficacy or in the assistance in the water miscibility of various biocidal agents. The more non-toxic surfactants often require higher levels of concentrations to achieve their purpose, thereby making them uneconomical due to huge amount of water treated. These surfactants are also prone to forming high level of unwanted foam, and are toxic to non-target aquatic organisms upon discharge to common receiving bodies of water.

[0005] Beyond the higher levels of concentration, another issue of most non-toxic surfactants is foaming which results in the need to feed antifoam compositions to the system. Foam, even with feeding antifoam compositions, is not preferred in some industrial applications like air separation processes. In fact, U.S. Patent Nos. 6,054,054 and 5,128,100 refer to water soluble polymers, such as polydiallyldimethylammonium chloride (PDADMAC) and ionene polymer, which reputedly do not foam when fed to the system for microbial control functions.

SUMMARY OF THE INVENTION

[0006] In one exemplary embodiment of the invention, a method is provided for inhibiting the growth of microbial biofilm on surfaces in contact with aqueous systems. The method comprises adding an effective amount of a modified, naturally occurring polymer to the aqueous system. In one embodiment, this modified naturally occurring polymer is a water soluble cationic quaternary ammonium starch. The aqueous system may, for example, be a cooling water system.

[0007] In accordance with one aspect of the invention, the biofilm treatment agent may be fed to the cooling water system in an amount of about 1 ppm to about 400 ppm with an alternative range of from about 5 to about 200 ppm and a further embodiment of about 10 to about 100 ppm. It is noted that any range or ranges disclosed in this specification are deemed to include and provide support for sub-ranges within the stated range or ranges. Any range or ranges disclosed in the description are deemed to include and provide support for any point or points within that range or ranges.

[0008] The various features of novelty that characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this

disclosure. Changes to and substitutions of the components of the invention can of course be made. The invention resides as well in sub-combinations and sub-systems of the elements described, and in methods of using them.

DETAILED DESCRIPTION

[0009] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about”, are not limited to the precise value specified. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Range limitations may be combined and/or interchanged, and such ranges are identified and include all the sub-ranges included herein unless context or language indicates otherwise. Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions and the like, used in the specification and the claims, are to be understood as modified in all instances by the term “about”.

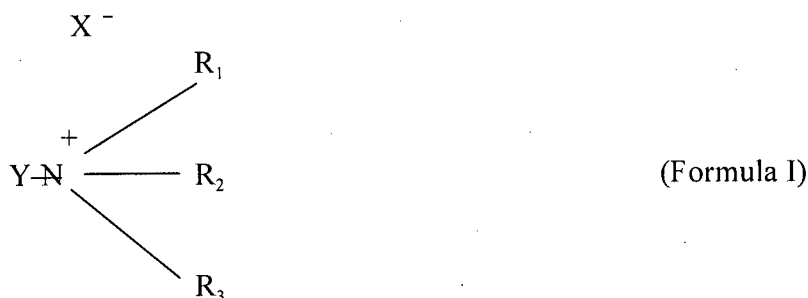
[0010] As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article or apparatus that comprises a list of elements is not necessarily limited to only those elements, but may include other elements not expressly listed or inherent to such process, method article or apparatus. The phrase “modified naturally occurring polymer” means a naturally occurring polymer that has been chemically modified, preferably to contain cationic moieties, such as quaternary ammonium groups bonded to the polymer backbone.

[0011] In one embodiment of the present invention, the modified starch biofilm control agent removes or reduces microbial slime from surfaces in contact with aqueous systems better than that caused by water alone. As used throughout the specification and claims, the words inhibit and/or inhibition are intended to refer both to the function of removing biofilm from structural surfaces in contact with system waters and to the retardation or growth diminishment of the biofilms.

[0012] One embodiment of the present invention provides a method for inhibiting the growth of microbial biofilm on surfaces in contact with systems, including, but not limited to aqueous systems such as cooling water systems such as open recirculating, closed recirculating and once through cooling systems, pulping and papermaking systems, water transport pipelines, reverse osmosis systems, air washer systems, shower water systems, hydrocarbon storage systems, hydrocarbon transport pipelines, aqueous metal working systems and aqueous mineral processing systems.

[0013] In one aspect of the invention, the biofilm treatment agent in accordance with the invention is a water soluble cationic quaternary ammonium starch. As to the cationic quaternary starches (CQS) that may be employed, these are described in U.S. Patent 4,088,600 which disclosure is incorporated by reference herein in its entirety. Basically, as is set forth in U.S. Patent 4,088,600, the CQS consists mainly of two moieties, namely a starch group and a quaternary ammonium salt group. The starch group may be prepared from a host of starches and starch fractions including acid or enzyme modified corn or waxy starches. Exemplary starches include those prepared from corn, potato, tapioca, sago, rice, wheat, waxy maize, grain sorghum, grain starches in raw or modified forms such as those modified with acids, oxidizing agents and the like; to amylose and amylopectin and to the linear and branched components respectively, of cornstarch and also to dextrans.

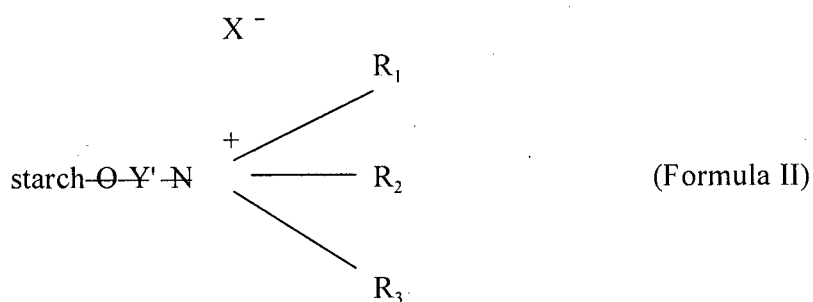
[0014] The quaternary ammonium compound used to form the CQS is generally of the formula:



in which X^- is any monovalent anion, e.g., chloride, bromide, iodide, or methyl sulfate; Y is from the group consisting of 2,3-epoxy propyl, 3-halo-2-hydroxy propyl,

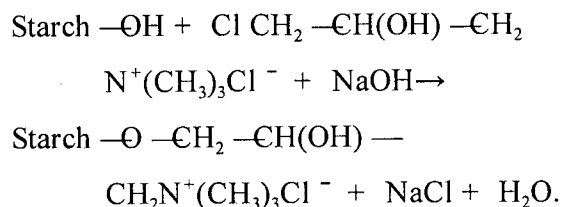
2 haloethyl, *o*, *p*, or *m* (α hydroxy – β halo ethyl) benzyl; R_1 , R_2 , and R_3 are from the group consisting of hydrogen, hydroxyl, alkyl, substituted alkyl, aryl and aralkyl; in which two of the R 's may be joined to form a heterocyclic or homocyclic ring compound; in which the total number of carbons in all three of R_1 , R_2 , and R_3 should not exceed about 14 carbons. If all three of R_1 , R_2 and R_3 are different, and R_3 contains more than 3 carbon atoms but not more than 12, then R_1 and R_2 should preferably be from the group consisting of methyl and ethyl; and if R_1 and R_2 are joined to form a ring compound, R_3 should preferably not be greater than ethyl.

[0015] The reaction to make the cationic starch involves the hydroxyl groups on the starch molecule and the reactive Y group of the quaternary ammonium reactant, so that the resulting cationic starch product has the formula



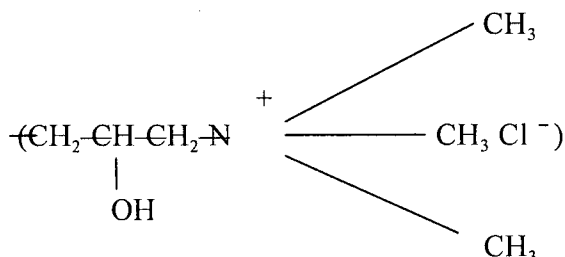
in which Y' is the reaction residue of Y and X and the R 's are unaltered. Y' would thus be (typically) 2 hydroxyl propyl, ethyl, or *o*, *p* or *m* (α hydroxy- β halo ethyl) benzyl.

[0016] In a typical case using N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, the reaction may proceed simplistically as



[0017] In one exemplary embodiment, a number of quaternary ammonium cationic starches may be prepared by reacting modified cornstarch with varying amounts of N-(3-chloro-2-hydroxy propyl) trimethylammonium chloride, with sodium hydroxide as catalyst. The degree of substitution (D.S.) of these products is

calculated theoretically and is found to be in the range of 0.01 to about 0.75 and more preferably from 0.1 to 0.45. The degree of substitution is defined as a number of moles of quaternary ammonium substituent, in this case



per anhydroglucose unit.

[0018] Exemplary quaternary ammonium cationic starches include those wherein the degree of substitution can be within the range of about 0.01 to 0.75 quaternary units conforming to Formula II given above, per anhydroglucose unit in the starch group. Preferably, it is about 0.1-0.45. One preferred CQS is prepared via reaction of 3-chloro-2-hydroxypropyltrimethylammoniumchloride and “Melogel” corn starch. The corn starch is present in an amount of about 13.9% (by weight), and the polymer product contains about 31% actives (by weight). The quat component is present in an amount of about 18.2 wt%. Another exemplary CQS is prepared via reaction of 3-chloro-2-hydroxypropyltrimethyl ammonium chloride and a hydrolyzed starch. The acid hydrolyzed starch is present in an amount of about 16.6 wt%, and the product contains about 27% actives by weight. The “quat” is present in an amount of about 5.4 wt%. Some commercially available CQS are sold commercially by GE under the Klaraid PC2710 and Klaraid 2712 designations.

[0019] In one exemplary embodiment, from about 1 ppm to about 400 ppm (or any range within this range) of the modified starch biofilm control agent is added to the aqueous system. The aqueous system may preferably have a pH from about 3.5 to about 10.5 and, as stated above, varying amounts of the modified tannin may be provided such as from about 5 ppm to about 200 ppm with an even more specific

range of about 10-100 ppm. Preliminary investigation reveals that about 50 ppm appears optimal.

[0020] The modified starch, in one aspect of the invention, does not foam at working concentrations in aqueous systems. Therefore, in this aspect of the invention, substantially no antifoam is needed.

EXAMPLES

Example 1

[0021] In order to demonstrate the efficacy of the modified starch in inhibiting the growth of biofilms, microplate assay tests were undertaken on *pseudomonas aeruginosa* bacteria. The *pseudomonas aeruginosa* biofilms were grown in 96 well plates overnight and treated with the candidate treatments in 15 ppm (actives) treatment amounts. Results are shown in Table 1.0.

Table 1.0

Pseudomonas Aeruginosa

<u>Treatment</u>	<u>Biofilm Removal %</u>
(15 ppm active)	
C-1	51%
C-2	85%
C-3	92%
C-4	76%
A-1	67%
C-5	76%

C-1 = acrylamide/DADMAC copolymer - DADMAC is diallyldimethylammonium chloride

C-2 = AETAC/tannin copolymer - AETAC is acryloxyethyltrimethyl ammonium chloride - 57.5% cationic charge density

C-3 = AETAC/tannin copolymer; cationic charge density = 70%

C-4 = ethanolamine/formaldehyde/tannin Mannich reaction product

A-1 = modified starch; quaternary ammonium cationic starch; prepared via reaction of 3-chloro-2-hydroxypropyltrimethyl - ammonium chloride and "Melogel" corn starch. The polymer product contains about 31% actives by weight. The quat is present in an amount of about 18.2 wt%. The corn starch is present in an amount of about 13.9% (by wt.).

C-5 = polyethyleneimine.

[0022] While we have shown and described herein certain embodiments of the invention, it is intended that these be covered as well any change or modification therein which may be made without departing from the spirit and scope of the invention as defined in the appended claims.

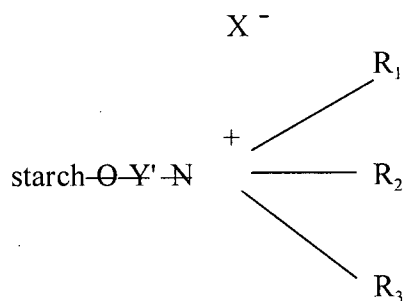
[0023] What is claimed is:

CLAIMS

1. A method for inhibiting the growth of microbial biofilm on surfaces in contact with an aqueous system which comprises adding an effective amount of a modified naturally occurring polymer to said aqueous system.

2. A method as recited in claim 1 wherein said modified naturally occurring polymer is a water soluble cationic quaternary ammonium starch (CQS), said aqueous system being a cooling water system, said CQS being fed to said cooling water system in an amount of about 1 ppm to about 400 ppm.

3. A method as recited in claim 2 wherein said CQS is fed to said cooling water system in an amount of from about 10-100 ppm, said CQS having the formula



wherein X is any monovalent anion including, chloride, bromide, iodide, methyl sulfate; Y' is selected from the group consisting of 2 hydroxypropyl, ethyl or o, p, or m (α hydroxy- β halo ethyl) benzyl; R₁, R₂, and R₃ are independently selected from the group consisting of hydrogen, hydroxyl, alkyl, substituted alkyl, aryl and araalkyl, and in which two of the Rs may be joined to form a heterocyclic ring compound or a homocyclic ring compound, further in which the total number of carbons in all three of R₁, R₂, and R₃ does not exceed about 14 carbons, with the proviso that if all three of R₁, R₂, and R₃ are different and R₃ contains more than 3 carbon atoms but not more than 12, then R₁ and R₂ are from the group consisting of methyl and ethyl; and if R₁ and R₂ are joined to form a ring compound, R₃ is an alkyl group not greater than ethyl.

4. A method according to claim 3 wherein the starch is selected from the group consisting of corn, potato tapioca, sago, wheat, waxy maize, grain sorghum, grain starches, and dextrin.

5. A method according to claim 3 wherein the degree of substitution of the CQS is in the range of 0.01 to 0.75.

6. A method according to claim 3 wherein the degree of substitution of the CQS is in the range of 0.1 to 0.45.

7. A method as recited in claim 1 wherein said aqueous system has a pH of about 3.5 to about 10.5.

8. A method as recited in claim 1 wherein said modified naturally occurring polymer is fed to said aqueous system in an amount of about 1 ppm to about 400 ppm.

9. A method as recited in claim 1 wherein said modified naturally occurring polymer is fed to said aqueous system in an amount of about 5 ppm to about 200 ppm.

10. A method as recited in claim 1 wherein said modified naturally occurring polymer is fed to said aqueous system in an amount of about 10-100 ppm.

11. A method as recited in claim 3 wherein X^- is a monovalent anion selected from the group consisting of chloride, bromide, iodide or methylsulfate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2010/002123

A. CLASSIFICATION OF SUBJECT MATTER

C02F1/50 (2006.01)i

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)

IPC: C02F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI,EPODOC,CNKI, CNPAT: Biofilm?, biological 4d fouling, bacterial 4d adhesion, , inhibit+, prevent+, deter+, treat+, starch??. cellulose?, polysaccharides?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO2010/117406 A1 (ANTI-N), 14 Oct.2010 (14.10.2010) page 1, lines 7-10, page 6, line 29, page 12, lines 12-14 of the description, examples 2 and 3, claims 1,10,23,25	1,7-10
A		2-6,11
A	US2010158852 A1 (GENE), 24 Jun. 2010 (24.06.2010) The whole document	1-11
A	US5783092 A (BIOB-N), 21 Jul. 1998 (21.07.1998) The whole document	1-11
A	DE19935230 A1 (FEIN-N), 08 Feb. 2001(08.02.2001) The whole document	1-11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 30 Aug. 2011(30.08.2011)	Date of mailing of the international search report 13 Oct. 2011 (13.10.2011)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer WANG Mingsong Telephone No. (86-10)82245909

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