

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2005332342 B2**

(54) Title
A method for improving flux in a membrane bioreactor

(51) International Patent Classification(s)
C02F 3/30 (2006.01) **C02F 5/12** (2006.01)
B01D 61/16 (2006.01) **C02F 1/00** (2006.01)
C02F 1/56 (2006.01) **C02F 1/44** (2006.01)
C02F 3/12 (2006.01)

(21) Application No: **2005332342** (22) Date of Filing: **2005.07.26**

(87) WIPO No: **WO06/130163**

(30) Priority Data

(31) Number (32) Date (33) Country
11/142,745 **2005.06.01** **US**

(43) Publication Date: **2006.12.07**

(44) Accepted Journal Date: **2011.08.18**

(71) Applicant(s)
Nalco Company

(72) Inventor(s)
Koppes, Jeroen A.;Huisman, Ingmar H.;Yoon, Seong-Hoon;Collins, John H.

(74) Agent / Attorney
Pizzeys, Level 2, Woden Plaza Offices Woden Town Square Woden, Canberra, ACT, 2606

(56) Related Art
US 6517723
JP 62-221494
US 6428705
US 2003/0159990
US 7087170
US 6027649

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 December 2006 (07.12.2006)

PCT

(10) International Publication Number
WO 2006/130163 A1

(51) International Patent Classification:
C02F 3/30 (2006.01)

(74) Agent: **KEEFER, Timothy, J.**; Seyfarth Shaw LLP, 55 East Monroe, Suite 4200, Chicago, IL 60603 (US).

(21) International Application Number:
PCT/US2005/026481

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

(22) International Filing Date: 26 July 2005 (26.07.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/142,745 1 June 2005 (01.06.2005) US

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **NALCO COMPANY** [US/US]; 1601 West Diehl Road, Naperville, IL 60563-1198 (US).

(72) Inventors; and

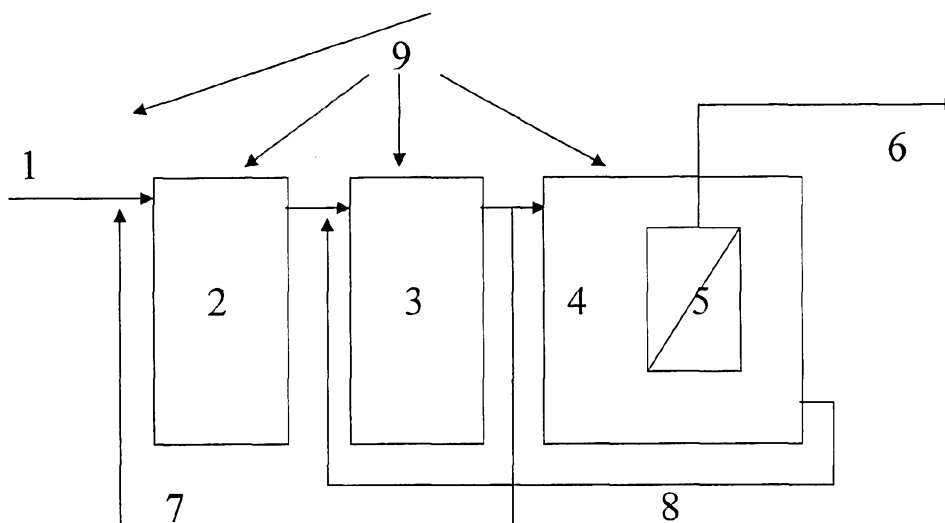
(75) Inventors/Applicants (*for US only*): **YOON, Seong-Hoon** [KR/US]; 2304 Kentuck Court, Naperville, IL 60564 (US). **COLLINS, John, H.** [US/US]; 389 Meadowlark Road, Bloomingdale, IL 60108 (US). **KOPPE, Jeroen, A.** [NL/NL]; Kapeynstraat 23,, NL-2313 RL Leiden (NL). **HUISMAN, Ingmar, H.** [NL/NL]; Crommelinlaan 5, NL-2627 AD Delft (NL).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR IMPROVING FLUX IN A MEMBRANE BIOREACTOR



(57) Abstract: The invention pertains to a method of improving flux in a membrane bioreactor (4) having membrane (5) by adding an effective amount of cationic, amphoteric, and zwitterionic polymers, or a combination thereof. The membrane bioreactor (4) is in a system also including an aerobic reactor (2) and anaerobic digester (3).

WO 2006/130163 A1

A METHOD FOR IMPROVING FLUX IN A MEMBRANE BIOREACTOR

TECHNICAL FIELD

5 This invention concerns the use of water soluble cationic, amphoteric or zwitterionic polymers, or a combination thereof to increase water flux through membranes in membrane bioreactors.

BACKGROUND OF THE INVENTION

10

 The membrane bioreactor (MBR) unit combines two basic processes: biological degradation and membrane separation-into a single process where suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit. The entire biomass is confined within the system, providing for both control of the residence time for the microorganisms in the reactor (mixed liquor age) and the disinfection of the effluent.

 In general, influent enters the bioreactor, where it is brought into contact with the biomass.

 The mixture is filtered through the membrane using a pump, water pressure or a combination of both. The permeate is discharged from the system while the entire biomass is maintained in the bioreactor

 The permeate is discharged from the system while the entire biomass is returned to the bioreactor. Excess mixed liquor is pumped out in order to maintain a constant mixed liquor age, and the membrane is regularly cleaned by backwashing, chemical washing, or both.

 Membranes used in the MBR unit include ultra- and microfiltration, inner and outer skin, hollow fiber, tubular, and flat, organic, metallic, ceramic, and the like. Preferred membranes for commercial application include hollow fiber with an outer skin ultrafilter, flat sheet ultrafilter and hollow fiber with an outer skin microfilter. Preferred membrane pore size is 0.01 – 5 micron.

In the aerobic membrane bioreactor (MBR) process, membrane fouling has always been a significant issue limiting the hydraulic performance of the process. Due to membrane fouling, MBR throughput or flux often decreases and more membranes are required to compensate for the throughput loss.

5 Recently, many research results (Nagaoka et al, 1996, 1998; Lee et al., 2002) have shown that one of the main causes of membrane fouling is biopolymers, which includes polysaccharides and proteins secreted by the biomass present in the mixed liquor of the MBR. In addition, a number of inorganic scales formed in bioreactors have been reported, where the salt concentrations in the influent were relatively high. As a result of
10 scale formation on the membrane surface, the membrane performance was significantly reduced (Huisman, 2005; Ognier, 2004).

To prevent membrane fouling caused by biopolymers, methods were developed using cationic polymers that do not react with negatively charged membranes in contact with the mixed liquor (Collins and Salmen, 2004). In this method, various
15 polymers are added directly to the aerobic MBR usually to the aeration tank and these polymers react with the biopolymers. The resulting particles, which consist of biopolymers and polymers, have considerably lower membrane fouling tendencies.

The same microbiologically produced polysaccharide and protein biopolymers produced in MBRs that cause membrane fouling are also known to cause foaming in the MBR mixed liquor. This is because these compounds contain many surface active functional groups that help stabilize foam at the air-
20 water interface. In addition, MBRs often contain significant amounts of filamentous microorganisms that have been correlated to foam formation. Both the biopolymers and filamentous microorganisms react with the cationic polymers described in this invention. Previous work has shown foam reduction or foam elimination always occurs at the same time that cationic polymer has been observed to improve membrane flux. (Richard, 2003).
25

In the mean time, anoxic and anaerobic tanks are increasingly being installed in MBRs to increase nitrogen and phosphorus removal efficiencies. In these conditions, the aerobic biomass will be periodically exposed to oxygen scarce conditions while the
30 anaerobic biomass will be exposed to aerobic conditions, since the mixed liquors are recycled between oxygen rich and oxygen scarce conditions. Therefore biomass will prod

uce more biopolymer due to oxygen stress. Apart from the accelerated biopolymer generation triggered by the cyclic oxygen concentrations, biopolymer generation also can be accelerated by low dissolved oxygen (DO) conditions in anoxic and anaerobic tanks (Calvo et al., 2001).

5 The most direct evidence of the accelerated membrane fouling at low DO situations was obtained in Kang *et al.*'s experiment (2003). In their experiment, nitrogen gas was used to continuously scour the submerged membranes, while air was supplied through separate nozzles to the area above which no membrane was placed. The permeate flow was constantly maintained at 20 L/m²/hr. As soon as air supply was
10 stopped, TMP started to increase and DO started to decrease.

 Accordingly, if anoxic and/or anaerobic tanks are installed in a MBR process, the biopolymer content in the mixed liquor will be higher than that in other MBRs having only aeration tanks. Therefore, if the MBR contains anoxic and anaerobic reactors, the previous method (John et al, 2004) will be considerably less effective in terms of dosage and flux improvement. In addition, the previous method would not be effective in
15 anaerobic MBRs, which includes anaerobic digester as a sole bioreactor or one of the bioreactors. A more effective and economic method, which allows better performance and lower dosage, is necessary.

 Apart from the biopolymer problem, recently, inorganic fouling has been
20 reported in a number of MBRs (Huisman, 2005; Ognier et al, 2002). This inorganic fouling often consists mainly of calcium carbonate (CaCO₃) and/or calcium phosphate, which may precipitate in the aerated biological wastewater treatment or directly onto the membrane ("scaling"). The inorganic fouling also includes iron oxides.

 Aeration in the treatment tank (and in the membrane tank) can lead to inorganic
25 fouling by various routes. For example, aeration drives the dissolved CO₂ out of the wastewater and this pushes the equilibrium of reaction (1) to the right.



 The carbonate (CO₃²⁻) formed by reaction (1) precipitates with calcium that is present in the wastewater to form CaCO₃ (limestone). Moreover, reaction (1) will
30 cause an increase in pH, which will favor calcium phosphate and iron oxide precipitation. The precipitation of carbonates and phosphates will partly take place in the bulk wastewater and this will form small particles, of which most will be retained

by the membranes. This precipitation will also take place on all surfaces, among which is the membrane surface.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common
5 general knowledge in the field.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

SUMMARY OF THE INVENTION

10

According to a first aspect the present invention provides a method for improving flux in a membrane bioreactor system comprising one or more anoxic reactors and one or more aeration tanks of which the influent has a concentration of salts or inorganic oxides comprising adding one or more cationic, amphoteric or zwitterionic polymers, or
15 a combination thereof to said membrane bioreactor system.

According to a second aspect the present invention provides a method for improving flux in a membrane bioreactor comprising the steps of:

providing said membrane bioreactor which comprises a combination of at least two of the following types of reactors: anaerobic reactors, anoxic reactors, and aerobic
20 reactors; and

adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the anaerobic and/or anoxic reactors, directly or indirectly through a feed stream.

According to a third aspect the present invention provides a method for
25 improving flux in a membrane bioreactor comprises the steps of:

providing said membrane bioreactor which comprises one or more anaerobic digesters

adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the
30 anaerobic digesters, directly or indirectly through a feed stream.

According to a fourth aspect the present invention provides a method for improving flux in a membrane bioreactor comprises the steps of:

providing said membrane bioreactor which comprises a combination of one or more anaerobic digesters and one or more aerobic reactors; and

adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the
5 anaerobic digesters, directly or indirectly through a feed stream.

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

10 In one aspect the present invention provides for a method of improving flux in a membrane bioreactor of which the influent has a concentration of salts of inorganic oxides sufficient to cause scaling or inorganic fouling conditions by adding an effective amount of one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor. The membrane bioreactor may also comprise one
15 or more aerobic reactors. The membrane reactor may also comprise a combination of at least two of the following reactors: anaerobic, anoxic, and aerobic reactors.

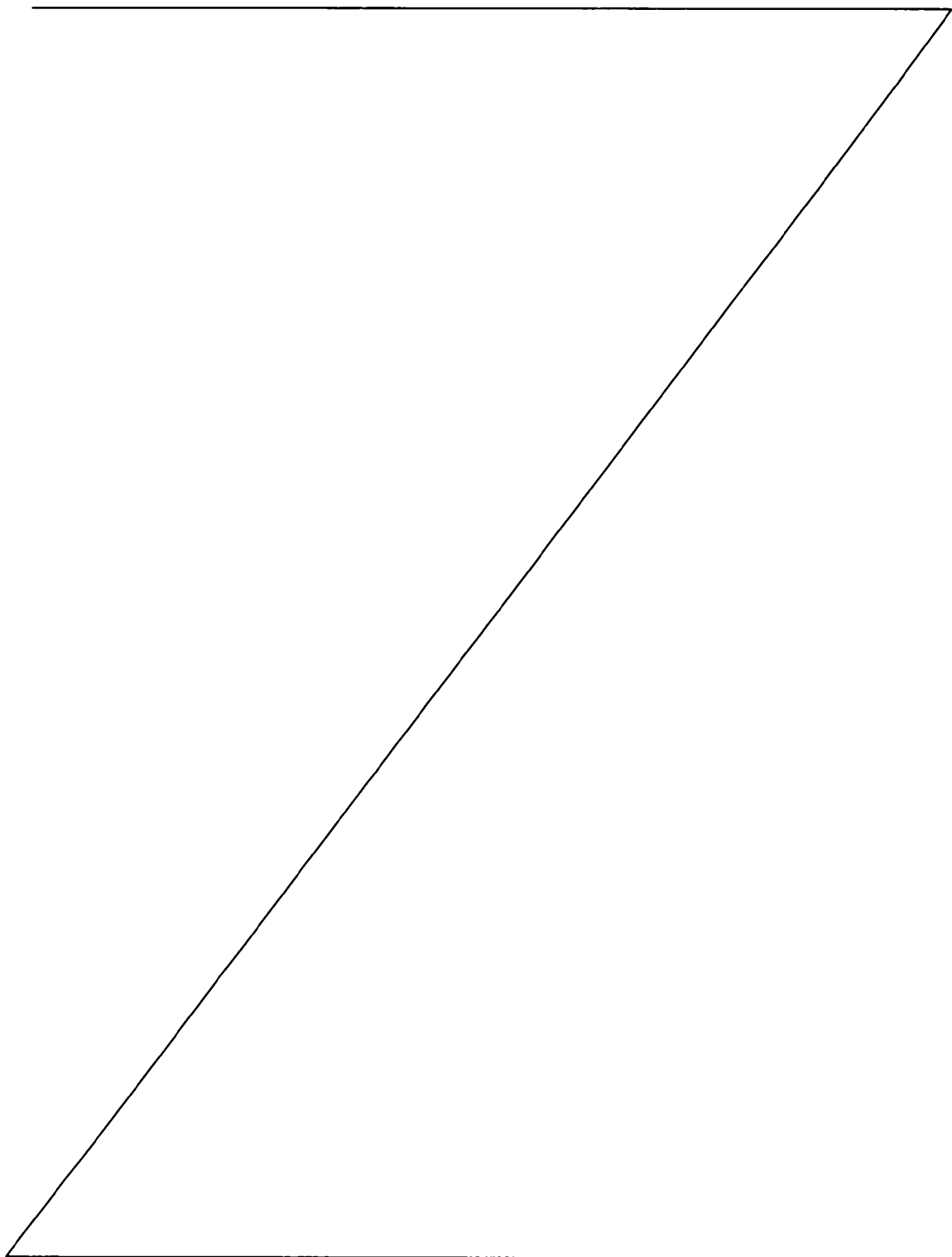
In another aspect the present invention also provides for a method of improving flux in a membrane bioreactor that is made of at least two of the following types of reactors: anaerobic, anoxic, and aerobic reactors. An effective amount of one or more
20 cationic, amphoteric, or zwitterionic polymers or combination thereof is added to this type of membrane bioreactor.

In a further aspect the present invention also provides for a method of improving flux in a membrane bioreactor which comprises one or more anaerobic digesters. An effective amount of one or more cationic, amphoteric, or zwitterionic polymers or
25 combination thereof is added to this type of membrane bioreactor.

In a related aspect the present invention also provides for a method of improving flux in a membrane bioreactor which comprises one or more anaerobic digesters, and one or more aerobic reactors. An effective amount of one or more cationic, amphoteric, or zwitterionic polymers or combination thereof is added to this type of membrane
30 bioreactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of a typical example of MBR, which consists of an aeration tank alone, and where 1 correlates to wastewater (COD=50-30,000 mg/L),



2 correlates to an aeration tank, 3 correlates to membranes, 4 correlates to effluent obtained by pumps or gravity, and 5 correlates to polymer addition.

Figure 2 is a schematic of typical example of MBR, which consists of aeration and anoxic tanks. Reactor sizes in the schematic do not represent the volume ratio of reactors and 1 correlates to wastewater (COD=50-30,000 mg/L), 2 correlates to an anoxic tank, 3 correlates to an aeration tank, 4 correlates to membranes, 5 correlates to internal sludge recycle from aeration tank to anoxic tank, 6 correlates to effluent obtained by pumps or gravity, and 7 correlates to polyelectrolyte addition.

Figure 3 is a schematic of a typical example of an MBR, which consists of aeration, anoxic, and anaerobic tanks. Reactor sizes in the schematic do not represent the volume ratio of reactors, and where 1 correlates to wastewater (COD=50-30,000 mg/L), 2 correlates to anaerobic tank (no aeration), 3 correlates to anoxic tank (no aeration), 4 correlates to aeration tank, 5 correlates to membranes, 6 correlates to effluent obtained by pumps or gravity, 7 correlates to internal sludge recycle from anoxic tank to anaerobic tank, 8 correlates to internal sludge recycle from aeration tank to anoxic tank, and 9 correlates to polyelectrolyte addition.

Figure 4 is a schematic of an anaerobic MBR and where 1 correlates to wastewater (COD=200-100,000 mg/L), 2 correlates to polyelectrolyte addition (it can also be added any place in the streamline in membrane side), 3 correlates to a mixer (optional), 4 correlates to headspace, 5 correlates to anaerobic tank, 6 correlates to membranes, 7 correlates to effluent, 8 correlates to gas recycle from head space to the bottom of membranes, and 9 correlates to sludge recirculation pump.

DETAILED DESCRIPTION OF THE INVENTION

25

Definitions of Terms

“About” means nearly or equal to.

As used herein, the following abbreviations and terms have the following meanings: MBR for Membrane Bioreactor; AcAM for acrylamide; and DMAEA•MCQ for dimethylaminoethylacrylate methyl chloride quaternary salt.

30

“Amphoteric polymer” means a polymer derived from both cationic monomers and anionic monomers, and, possibly, other non-ionic monomer(s). Amphoteric polymers can have a net positive or negative charge. The amphoteric polymer may also be derived from zwitterionic monomers and cationic or anionic monomers and possibly nonionic monomers. The amphoteric polymer is water soluble.

“Cationic polymer” means a polymer having an overall positive charge. The cationic polymers of this invention are prepared by polymerizing one or more cationic monomers, by copolymerizing one or more nonionic monomers and one or more cationic monomers, by condensing epichlorohydrin and a diamine or polyamine or condensing ethylenedichloride and ammonia or formaldehyde and an amine salt. The cationic polymer is water soluble.

“Cationic monomer” means a monomer which possesses a net positive charge.

“Solution polymer” means a water soluble polymer in a water continuous solution.

“Aerobic tank” means a bioreactor having higher than 0.5 ppm of dissolved oxygen to grow aerobic bacteria. Under this condition bacteria can actively oxidize organic materials contained in influent using the dissolved oxygen.

“Anoxic tank” means a bioreactor having less than 0.5 ppm of dissolved oxygen. This reactor is typically fed with a mixed liquor having higher than 3 ppm of nitrate (NO_3^-) ion as nitrogen. Under this condition, most of heterotrophic bacteria can breathe with the combined oxygen in the nitrate and reduce the nitrate to nitrogen gas that eventually discharges to the air.

“Anaerobic tank” means a bioreactor having less than 0.1 ppm of dissolved oxygen and less than 3 ppm of nitrate ion.

“Anaerobic digester” means a bioreactor that is completely isolated from the air with top cover to grow strict anaerobic bacteria which produces methane gas.

“Zwitterionic polymer” means a polymer composed from zwitterionic monomers and, possibly, other non-ionic monomer(s). In zwitterionic polymers, all the polymer chains and segments within those chains are rigorously electrically neutral. Therefore, zwitterionic polymers represent a subset of amphoteric polymers, necessarily maintaining charge neutrality across all polymer chains and segments

because both anionic charge and cationic charge are introduced within the same zwitterionic monomer. The zwitterionic polymer is water soluble.

“Zwitterionic monomer” means a polymerizable molecule containing cationic and anionic (charged) functionality in equal proportions, so that the molecule is net
5 neutral overall.

Preferred Embodiments

The cationic, amphoteric, and zwitterionic polymers or a combination
10 thereof are introduced directly into one of the bioreactors or any liquid stream flowing to one of the bioreactors by various means.

In all cases, the polymer should be reasonably mixed with the mixed liquor in the bioreactor to maximize adsorption. This may be accomplished by feeding the polymer into an area of the bioreactor where an aeration nozzle is located. So-called
15 “dead” zones in the bioreactor having little to no flow should be avoided. In some cases, a submerged propeller mixer may be needed to increase mixing in the basin, or the mixed liquor can be re-circulated through a side arm loop.

Solution polymers can be dosed using a chemical metering pump such as the LMI Model 121 from Milton Roy (Acton, MA).

20 In one embodiment, the membrane bioreactor influent has concentration of salts or inorganic oxides that is sufficient to cause scaling and organic fouling. The salts and inorganic oxides are selected from the group consisting of: magnesium, calcium, silicon and iron. In another embodiment, both magnesium and calcium salts or inorganic oxides may have a concentration of about 5 ppm or greater, iron salts or
25 inorganic oxides have a concentration of about 0.1 ppm or greater, and silicon salts or inorganic oxides have a concentration of about 5 ppm or greater. In yet another embodiment, the salts are selected from the group consisting of: carbonates, phosphates, oxylates, and sulfates.

In another embodiment, the amount of cationic polymer that is added to a
30 membrane bioreactor is about 10 to about 2,000 ppm as active based on the total membrane bioreactor volume.

In another embodiment, the cationic polymer that is added to a membrane bioreactor has a molecular weight of about 25,000 Da or more.

In another embodiment, the cationic polymer that is added to a membrane bioreactor has about 10% mole charge or more.

5 In another embodiment, the cationic polymer that is added to a membrane bioreactor is 25,000 Da or more and has about 10% mole charge or more.

In another embodiment, the cationic polymer added to a membrane bioreactor is selected from the group consisting of a polymer of epichlorhydrin-dimethylamine crosslinked with either ammonia or ethylenediamine; a linear polymer of
10 epichlorohydrin and dimethylamine, a homopolymer of polyethyleneimine; polydiallyldimethylammonium chloride; homopolymer of DMAEM·H₂SO₄; polymerized triethanolamine/methyl chloride quat, polymerized triethanolamine and tall oil fatty acid/methyl chloride quat, polyethylenedichloride/ammonia, and modified polyethyleneimine.

15 In another embodiment, the cationic polymer added to a membrane bioreactor is a polymer of (meth)acrylamide and one or more cationic monomers include dialkylaminoalkyl acrylates and methacrylates and their quaternary or acid salts, including, but not limited to, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl
20 acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate
25 hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts such as acrylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl
30 methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt,

diethylaminoethylacrylate, diethylaminoethylmethacrylate, diallyldiethylammonium chloride and diallyldimethyl ammonium chloride.

In another embodiment, the cationic polymer added to a membrane bioreactor is diallyldimethylammonium chloride/acryamide copolymer.

5 In another embodiment, the amphoteric polymer added to a membrane bioreactor is selected from the group consisting of: dimethylaminoethyl acrylate methyl chloride quaternary salt/acrylic acid copolymer, diallyldimethylammonium chloride/acrylic acid copolymer, dimethylaminoethyl acrylate methyl chloride salt/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine copolymer,
10 acrylic acid/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine copolymer and DMAEA-MCQ/Acrylic acid/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine terpolymer.

In another embodiment, the zwitterionic polymer added to a membrane bioreactor is about 99 mole percent and composed of N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine and about 1 mole percent
15 of more nonionic monomers.

The following examples are not meant to limit the invention.

20 Example 1

In Fig. 2, membranes (3) are directly submerged in the aeration tank (2). The aeration tank can be divided by multiple numbers of reactors. Membranes can be submerged to one of the reactors or can be installed outside of the reactor. The MLSS of the mixed liquor can be maintained between 3,000 mg/L and 30,000 mg/L. When influent (1)
25) has higher than 5 ppm of calcium ion and/or higher than 5 ppm of magnesium and/or higher than 10 ppm of silica and/or higher than 0.1 ppm iron, scale formation or inorganic fouling can occur on the membrane surface. Cationic polymers having a MW of 10,000-20,000,000 Da and charge of 1-100% can be added directly to the one of the tanks (5) or any of the streams flowing to
30 one of the reactors at a concentration of 10-2,000 ppm as active polymer. The upper limit of MW is limited only by the solubility or dispersibility of the polymer in water.

Example 2

In Fig. 2 anoxic tank (2) is added to the aeration tank (3) and mixed liquor in the aeration tank is recycled to the anoxic tank, where no air is supplied to maintain dissolved oxygen level at <0.5 mg/L. The nitrogen compounds contained in wastewater are oxidized to nitrate in the aeration tank (3) and recycled to anoxic tank (2). In the anoxic tank, some denitrifying bacteria utilize the combined oxygen contained in the nitrate ions and produce nitrogen gas. The membrane configuration can be flat sheet, hollow fiber, tubular, or combinations of these. Optionally membranes can be placed outside of membrane tank and the sludge in one of the tanks can be circulated to the membrane system by pump(s). When influent (1) has higher than 5 ppm of calcium ion and/or higher than 5 ppm of magnesium and/or higher than 0.1 ppm of iron and/or higher than 10 ppm of silica, scale formation or inorganic fouling can occur on the membrane surface.

Though a broad range of cationic polymers are helpful to prevent membrane fouling, high M.W. ($>50,000$ Da) and high mole charge ($>10\%$) polymers will be particularly effective. One or multiple number of different polymers can be added to the anoxic tank and/or the aeration tank and/or any flow stream flowing to one of the reactors.

Example 3

In Fig. 3, an anaerobic (2) and an anoxic (3) tank are added to the aeration tank (4) together for maximum phosphorous removal. Though the mixed liquor recycled from the anoxic tank to the anaerobic tank (7) contains some nitrate ions, the overall oxygen supply is extremely limited since DO level is less than 0.1 mg/L. Even in this environment, some phosphorous accumulation organisms (PAOs) can obtain energy by hydrolyzing the polymeric form of phosphorous that was accumulated in the cell. Once PAOs move to aeration tank through the anoxic tank, they overly accumulate phosphorous for the future use, which is the so called "Luxury Uptake". The overly accumulated phosphorous is eventually removed when excess biosolids are removed from the system. The membrane configuration can be flat sheet, hollow fiber, tubular, or a combination of these. Optionally the membranes can be placed outside of the tanks and the sludge can be circulated through the membranes to the tanks by pumps. When

influent (1) has higher than 5 ppm of calcium ion and/or higher than 5 ppm of magnesium and/or higher than 0.1 ppm of iron and/or higher than 10 ppm silica, scale formation or inorganic fouling can occur on the membrane surface.

Though a broad range of cationic polymers are helpful to prevent membrane
5 fouling, high M.W. (>50,000 Da) and high mole charge (>10%) polymers will be particularly effective. One or multiple number of different polymers can be added to the anoxic tank and/or the aeration tank and/or any flow stream flowing to one of the reactors.

Example 4

The fourth application example is an anaerobic MBR (Fig. 4), which operates between ambient temperatures and 70 °C. This MBR has a cover on the top of the reactor and no air is supplied. Optionally mechanical agitation can be performed
15 using the mixer (3). In the case of submerged membrane (Fig. 4a), gases in the headspace (4) can be recycled to the bottom of the tank to scour the membranes. If membranes are externally equipped (Fig. 4b), sludge circulation pumps (9) should be used. This anaerobic digester can be used solely or used with a combination of aerobic reactor. The mixed liquor suspended solids (MLSS) level is maintained at 3,000-
20 30,000 mg/L and the influent COD is 200-100,000 mg/L.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for improving flux in a membrane bioreactor system comprising one or more anoxic reactors and one or more aeration tanks of which the influent has a concentration of salts or inorganic oxides comprising adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor system.
2. The method according to claim 1 wherein said salts or inorganic oxides are selected from the group consisting of: magnesium, calcium, silicon and iron.
3. The method according to claim 2 wherein said magnesium or said calcium has a concentration of about 5 ppm or greater, or said iron has a concentration of about 0.1 ppm or greater, or said silicon has a concentration of about 5 ppm or greater.
4. The method according to any one of the preceding claims wherein said amount of cationic polymer is about 10 to about 2,000 ppm as active based on the total membrane bioreactor volume.
5. The method according to any one of the preceding claims wherein said membrane bioreactor system further comprises at least one of the following types of reactors: anaerobic reactors, and aerobic reactors.
6. The method according to any one of claims 1 to 4 wherein said membrane bioreactor comprises one or more aerobic reactors.
7. A method for improving flux in a membrane bioreactor comprising the steps of:
providing said membrane bioreactor which comprises a combination of at least two of the following types of reactors: anaerobic reactors, anoxic reactors, and aerobic reactors; and
adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the anaerobic and/or anoxic reactors, directly or indirectly through a feed stream.
8. The method of claim 7 wherein said amount of cationic polymer is about 10 to about 2,000 ppm as active based on the total membrane bioreactor volume.

9. The method according to claim 7 or claim 8 wherein said cationic polymer that is added to said membrane bioreactor has a molecular weight of about 25,000 Da or more.
10. The method according to any one of claims 7 to 9 wherein said cationic polymer that is added to said membrane bioreactor has about 10% mole charge or more.
11. The method according to claim 7 or claim 8 wherein said cationic polymer that is added to said polymer is about 25,000 Da or more and has about 10% mole charge or more.
12. The method according to any one of claims 7 to 11 wherein said cationic polymer is selected from the group consisting of a polymer of epichlorhydrin-
10 dimethylamine crosslinked with either ammonia or ethylenediamine; a linear polymer of epichlorohydrin and dimethylamine, a homopolymer of polyethyleneimine; polydiallyldimethylammonium chloride; homopolymer of DMAEMH₂SO₄ polymerized triethanolamine/methyl chloride quat, polymerized triethanolamine and tall oil fatty acid/methyl chloride quat, polyethylenedichloride/ammonia, and modified
15 polyethyleneimine.
13. The method according to any one of claims 7 to 12 wherein said cationic polymer is a polymer of (meth)acrylamide and one or more cationic monomers selected from the group consisting of: dialkylaminoalkyl acrylates and their quaternary or acid salts, dialkylaminoalkyl methacrylates and their quaternary or acid salts,
20 dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt,
25 dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts, acrylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt,
30 dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl

methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate, diallyldiethylammonium chloride, and diallyldimethyl ammonium chloride.

- 5 14. The method according to any one of claims 7 to 13 wherein said cationic polymer is diallyldimethylammonium chloride/acrylamide copolymer.
15. The method according to any one of claims 7 to 14 wherein said amphoteric polymer is selected from the group consisting of: dimethylaminoethyl acrylate methyl chloride quaternary salt/acrylic acid copolymer, diallyldimethylammonium
- 10 chloride/acrylic acid copolymer, dimethylaminoethyl acrylate methyl chloride salt/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine copolymer, acrylic acid/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine copolymer and DMAEA-MCQ/Acrylic acid/N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine terpolymer.
- 15 16. The method according to any one of claims 7 to 15 wherein said zwitterionic polymer is composed of about to 99 mole percent of N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine and about 1 mole percent of more nonionic monomers.
17. A method for improving flux in a membrane bioreactor comprises the steps of:
- 20 providing said membrane bioreactor which comprises one or more anaerobic digesters
- adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the anaerobic digesters, directly or indirectly through a feed stream.
- 25 18. A method for improving flux in a membrane bioreactor comprises the steps of: providing said membrane bioreactor which comprises a combination of one or more anaerobic digesters and one or more aerobic reactors; and
- adding one or more cationic, amphoteric or zwitterionic polymers, or a combination thereof to said membrane bioreactor, wherein the polymers are added to the
- 30 anaerobic digesters, directly or indirectly through a feed stream.

19. The method according to any one of claims 1 to 6 wherein said salts are selected from the group consisting of: carbonates, phosphates, oxylates, and sulfates.
20. A method for improving flux in a membrane bioreactor substantially as herein described with reference to any one of the embodiments of the invention illustrated in
5 the accompanying drawings and/or examples.

Figure 1

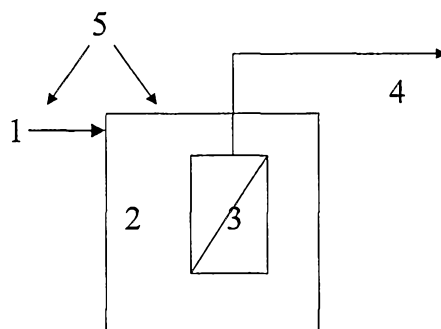
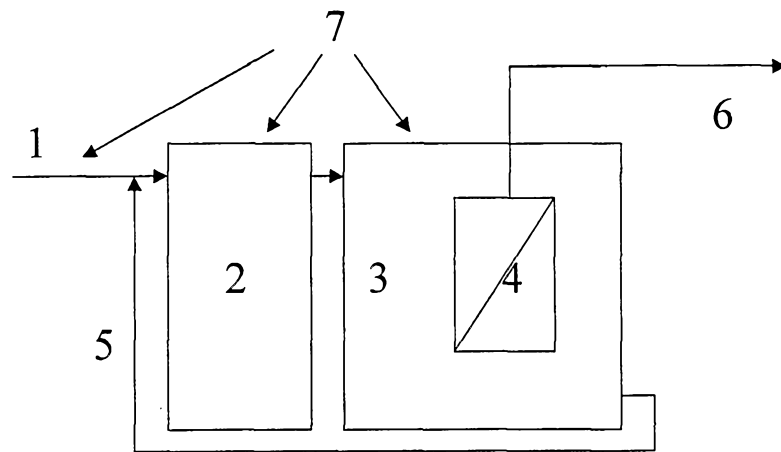


Figure 2



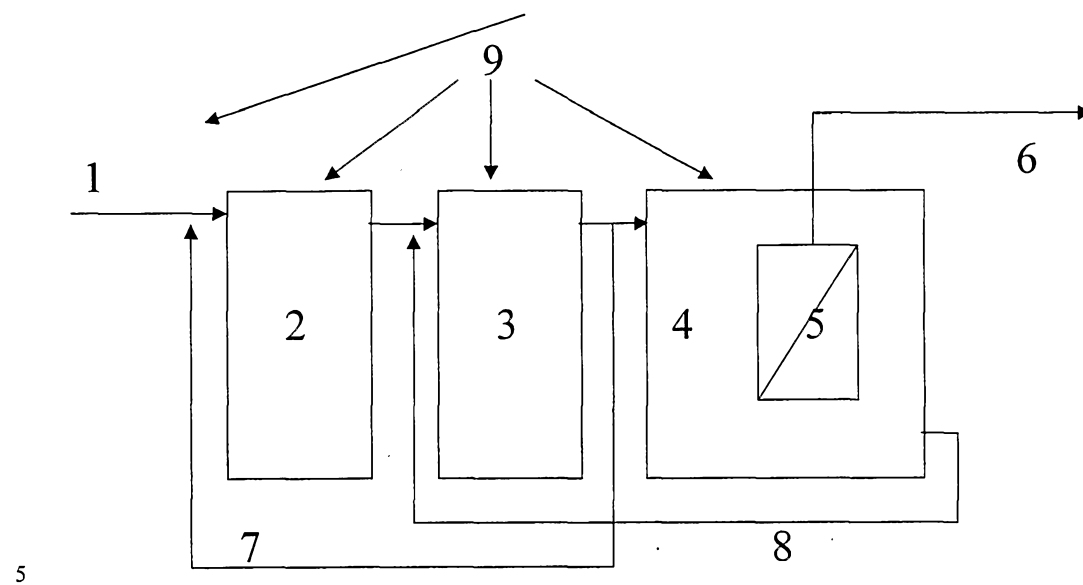
5

10

15

20

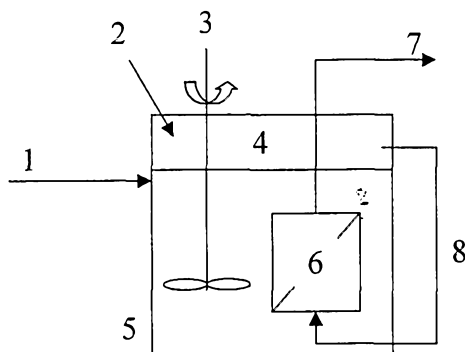
Figure 3



10

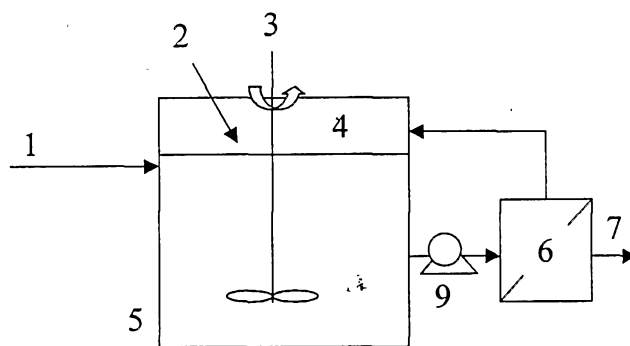
15

Figure 4



5

a) Anaerobic MBR equipped with submerged membranes



b) Anaerobic MBR equipped with side stream (or cross flow)

membranes