(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
06 September 2024 (06.09.2024)

WIPO | PCT

(10) **International Publication Number**
WO 2024/182111 A1

(51) **International Patent Classification:**
C02F 3/00 (2023.01) ***B01D 63/02*** (2006.01)
C02F 3/30 (2023.01) ***B01D 53/56*** (2006.01)
C02F 3/10 (2023.01) ***B01D 53/86*** (2006.01)
C02F 3/12 (2023.01) *C02F 101/16* (2006.01)
B01D 61/00 (2006.01) *C02F 11/04* (2006.01)
B01D 53/22 (2006.01)

(21) **International Application Number:**
PCT/US2024/015425

(22) **International Filing Date:**
12 February 2024 (12.02.2024)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
102023000003423 27 February 2023 (27.02.2023) IT

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

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,

(54) Title: SYSTEM AND METHOD FOR SCAVENGING NITROUS OXIDE

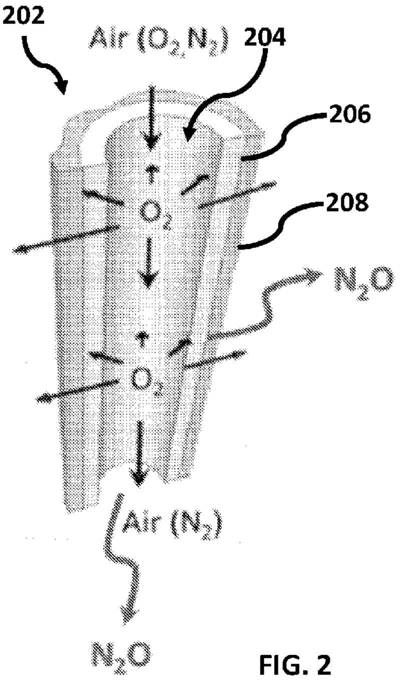

FIG. 2

(57) **Abstract:** A system and method for scavenging N_20 in a wastewater treatment process are provided. The method comprises operating a membrane aerated biofilm reactor (MABR) in a high ammonia concentration activated sludge process and collecting N_20 in the lumen of the MABR membrane. N_20 is driven into the lumen of the membranes by pressure adjustments. Pressure adjustments include total pressure of a process gas and partial pressure adjustments of components of a process gas. Collected N_20 may be recycled back into the wastewater treatment system or further treated downstream of the MABR.

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SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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

SYSTEM AND METHOD FOR SCAVENGING NITROUS OXIDE

RELATED APPLICATIONS

[0001] This application claims the benefit of Italian Patent Application No. 102023000003423, filed on February 27, 2023, which is incorporated herein by reference.

FIELD

[0002] The present invention relates to wastewater treatment processes and systems for reducing or eliminating nitrous oxide emissions from wastewater treatment systems.

BACKGROUND

[0003] As part of the Paris Climate Agreement, and the resulting push towards decarbonization of the economy, many countries have committed to exploring ways to achieve utility-wide carbon neutrality goals. In particular, there are signs that nitrous oxide (N_2O) may become a regulated component of water resource recovery facilities of the future. For example, in Denmark, the government has announced plans to introduce limits on N_2O emissions in treatment plants with a capacity equivalent to 30,000 PE or more.

[0004] International Patent Application WO 2022/184829 discloses a method to reduce or minimize N_2O emissions in the exhaust gas from a membrane aerated biofilm reactor (MABR) by monitoring one or more parameters of the wastewater and/or the exhaust gas and/or the feed gas and modulating the supply of feed gas to the membrane based on the one or more parameters in order to minimize or eliminate the N_2O in the exhaust gas.

INTRODUCTION

[0005] In an aspect of the invention, a membrane aerated biofilm reactor is used to intentionally scavenge N_2O that is produced in wastewater treatment processes. CO_2 may also be scavenged in the process. For example, CO_2 may coincidently be scavenged along with N_2O. The intentional scavenging may be effected by driving the N_2O into the MABR lumen. Once in the lumen, the N_2O may be sent to a secondary process for abatement, nitrogen recovery, enhancing treatment of the liquid line, energy production, or reducing the carbon footprint of the overall wastewater treatment facility.

[0006] A method according to this disclosure comprises operating an MABR in an anoxic zone of a wastewater treatment plant such that N_2O produced in the biofilm is preferentially driven into the lumen of the membrane and concentrated in exhaust gas. N_2O may be preferentially driven into the lumen of the membrane, for example, driven to a relatively greater extent into the lumen of the membrane relative to N_2O driven into the bulk liquid, by adjusting the partial pressure of components in a process gas inputted to the membrane. The exhaust gas comprising N_2O is not returned to the bulk liquid, for example as a mixing or scrubbing gas. The exhaust gas may be repurposed to another point in the wastewater treatment line or to another process within the same or another treatment facility, upstream or downstream of the MABR, scrubbed by other means, or otherwise treated, to use or reduce or eliminate N_2O in the gas.

[0007] A system according to this disclosure comprises an MABR with a gas-permeable membrane capable of supporting a counter diffusional biofilm. The MABR may be equipped with an exhaust valve for controlling the pressure of a process feed gas or the partial pressure of components of a process gas fed into the lumen of the membrane. The partial pressure of the components of the gas inside the lumen may be adjusted to promote or encourage N_2O to diffuse towards the interior of the lumen as opposed to diffusing into the bulk liquid. In some examples, some N_2O may diffuse into the bulk liquid so long as the denitrification capacity in the bulk liquid is sufficient to prevent N_2O emissions in off-gas from the bulk liquid.

BRIEF DESCRIPTION OF THE FIGURES

[0008] **FIG. 1** provides a schematic representation of a counter-diffusional biofilm.

[0009] **FIG. 2** shows an example membrane for use in a membrane aerated biofilm reactor.

DETAILED DESCRIPTION

[0010] In an aspect, the present invention provides a system and method for reducing or eliminating N_2O emissions from a wastewater treatment plant, for example to assist in reducing the overall carbon footprint for wastewater treatment. The method and system disclosed herein comprise scavenging N_2O in a lumen of the membrane of a membrane aerated biofilm reactor and, in another aspect, reusing the N_2O in upstream or downstream processes of the wastewater treatment plant or treating the N_2O downstream of the MABR.

[0011] In an example, the method comprises operating a membrane aerated biofilm reactor (MABR) in an unaerated zone, such as an anaerobic and preferably an anoxic zone, of a wastewater treatment system (WWTS). The unaerated zone may be for example an anoxic part of an activated sludge process with an elevated ammonia concentration in the bulk liquid. In an example, the elevated ammonia concentration may be 7 mg-N/L or more. The increased ammonia concentration can provide higher nitrification activity in the MABR and can produce more N_2O. The increased concentration of N_2O may be scavenged for re-use or additional treatment as further described herein.

[0012] In an example, the system and method as disclosed herein may be used for high-strength nitrogen removal, for example in mainstream or sidestream wastewater treatment. Minimizing airflow for post-treatment may be easier to do in sidestream as compared to mainstream environments. For example, use of anammox pathways may decrease the oxygen requirement for ammonia oxidation by approximately half. As a result, the sidestream ratio of oxygen demand to nitrogen load can be much lower than in the mainstream. MABR may further facilitate post-treatment of N_2O emissions by operating at very high oxygen transfer efficiencies, even exceeding 95% which can result in less airflow required to transfer the same amount of oxygen, and the airflow volume requiring post-treatment for removal of N_2O may be minimized. For example, the system and method disclosed herein may be used for treating centrate from digested sludge (i.e. after dewatering of aerobically or anaerobically digested sludges), or any high ammonia waste streams such as food and industrial wastes, with low carbon. For example, the MABR may be operated for short cut nitrogen removal processes to treat low carbon to nitrogen ratio wastewaters.

[0013] The membrane aerated biofilm reactor comprises a counter-diffusional biofilm. A counter diffusional biofilm may be, for example, grown on a gas-permeable membrane wherein electron acceptor and electron donor substrates are supplied from opposite sides of the biofilm (i.e. from the bulk liquid and from the lumen of the membrane). In contrast, co-diffusional biofilms grow on non-permeable substrates, where both electron donor and acceptor substrates are supplied from the bulk liquid. Figure 1 provides a representative counter-diffusional biofilm 100 comprising an aerobic/nitrifying layer 102 and an anoxic/denitrifying layer 104, showing substrate movement into and out of the biofilm. Figure 1 also shows the partitioning of N_2O produced in the biofilm, for example, N_2O may diffuse towards the membrane lumen 106 comprising the exhaust gas or to the bulk liquid 108. In the example of Figure 1, oxygen diffuses from the membrane lumen 106 through the membrane wall 110 to the aerobic/nitrifying layer 102 of the biofilm. N_2O produced in the nitrification process flows from the aerobic layer 102 back towards membrane lumen 106, and towards the bulk liquid 108 (which is also anoxic and provides denitrification). NH_4 may move towards the aerobic biofilm layer from the bulk liquid while COD moves toward the anoxic biofilm layer. NO_x from the aerobic layer moves to the anoxic biofilm layer and N_2 from the anoxic biofilm layer moves into the bulk liquid.

[0014] Figure 2 shows an example membrane 202 that may be used in an MABR. As seen in Figure 2, a process feed air may be inputted at a first end of the membrane into the lumen 204 of the membrane and an exhaust air may be expelled from a second end. The second end of the membrane may be, for example, at an end of the membrane that is opposite the input end of the membrane. The process feed gas may include oxygen, nitrogen and/or other components. In an example, the process feed gas may be air. The MABR comprising the membrane is preferably located in an anoxic zone of the reactor but may be located in an anaerobic or other unaerated zone. The oxygen depleted zone drives oxygen from the lumen of the membrane towards the bulk liquid where oxygen is not available. This allows for formation of a biofilm at the interface of the outer membrane wall and the bulk liquid as oxygen flows from an area of high oxygen concentration in the lumen towards an area of low oxygen concentration in the bulk liquid. In other words, oxygen from the process gas can diffuse through the permeable membrane walls 206 towards a counter-diffusional biofilm 208 growing on the outside of the membrane walls. The biofilm may comprise several layers, including both an aerobic layer closest to the membrane wall and an anoxic layer closest to the bulk liquid. This type of biofilm may promote both nitrification and denitrification pathways in the aerobic and anoxic layers, respectively. N_2O is a byproduct of secondary wastewater treatment that may be formed in the nitrification and denitrification pathways in the biofilm. The N_2O can diffuse out of the biofilm towards the lumen or towards the bulk liquid. In another example, other greenhouse gases, such as CO_2 for example, may be created and may diffuse out of the biofilm in a similar manner to N_2O.

[0015] Driving N_2O into the lumen of the membrane from the biofilm may comprise using a process feed gas with little or no N_2O, for example using a process feed gas such as ambient air pressurized by a blower without N_2O, or another gas with less than 25ppm N_2O. In this way, the lumen of the membrane may be operated with a lower concentration of N_2O

than the biofilm such that N_2O moves from a high concentration where it is being produced in the biofilm to an area of low concentration of N_2O in the lumen of the membrane. For example, during operation, the lumen may have a feed gas or be fed a feed gas with a lower concentration of N_2O than the biofilm. Some N_2O may be permitted to flow from the biofilm to the bulk liquid where it may be denitrified if sufficient readily biodegradable carbon is present. In another example, some N_2O that diffuses toward the bulk liquid may also be reduced to N_2 in the biofilm, for example in anoxic outer layers of the biofilm. If sufficient denitrification capacity is not present, the N_2O may be stripped to the atmosphere by bulk liquid aeration which is not desirable. N_2O and/or other components such as CO_2 may be driven into the lumen by selecting a feed or input gas (i.e. the process gas) that is low or absent that component. For example, the partial pressure of N_2O, and/or CO_2 in the process gas may be selected or adjusted to be less than the partial pressure of N_2O, and/or CO_2 in the bulk liquid. In an example, the process feed gas is selected such that it is absent N_2O and/or CO_2.

[0016] Some greenhouse gases such as N_2O or CO_2 may flow into the bulk liquid, particularly as the pressure differential between the biofilm and the lumen membrane approaches equilibrium. Some N_2O or CO_2 flowing into the bulk liquid is acceptable so long as there is enough denitrification capacity to remove the N_2O from the bulk liquid before it is emitted into the environment. The partial pressure of N_2O at a second end of the lumen (i.e. the end where the exhaust gas is expelled), may be adjusted by reducing the partial pressure of O_2 in the process feed gas. The partial pressure of oxygen may be reduced just enough to balance a limit in the nitrification and denitrification reactions in the biofilm to produce less N_2O with maintaining an efficient MABR system. In an example, the partial pressure of N_2O at the input end of the lumen is smallest or non-existent, and highest, for example to the point of equilibrium between the lumen and the biofilm, at an exhaust end of the lumen. In this way, the exhaust gas may be expelled from the lumen at its maximum capacity for the greenhouse gas, while limiting the amount of N_2O that back diffuses into the bulk liquid.

[0017] In an example, as N_2O diffuses from the biofilm into the lumen of the membrane, the concentration of N_2O along the length of the membrane may vary. For example, a higher concentration of N_2O may exist closer to a second end of the lumen, closest to where the exhaust gas is expelled. In an example, a process according to the present disclosure may include monitoring components in the exhaust gas such as N_2O, CO_2 and O_2, and based on these parameters, controlling the process by adjusting the pressure of the process feed gas or the backpressure into the lumen.

[0018] In an example, the pressure of the process feed gas into the lumen of the membrane may be adjusted. Increasing the pressure of the feed gas may be used to lower diffusion of greenhouse gases into the lumen of the membrane while decreasing pressure may increase diffusion of greenhouse gases into the lumen of the membrane.

[0019] In an aspect, the total flow rate of input process feed gas may be reduced to minimize the quantity or total flow rate of exhaust air over time that may need to be redirected to other process. In this case, the same per kg N_2O or kg CO_2 is produced in the system and may be driven into the lumen but the amount of gas that needs to be treated is lower, with lower O_2, which may result in easier treatment of the components. Reducing the input air may therefore reduce the amount of exhaust gas that is expelled from the lumen requiring further treatment, redirection.

[0020] In a further aspect, N_2O in the exhaust gas may be measured or monitored, to determine what adjustments, if any, need to be made to the process feed gas. For example, if N_2O in the exhaust gas increases above an upper threshold value, the process feed gas flowrate may be reduced. A reduced flowrate of process feed gas into the lumen of the membrane reduces the O_2 availability in the biofilm and increases the opportunity for reduction of N_2O to N_2 via denitrifiers in the biofilm. When the N_2O measurement or monitoring shows a reduced N_2O concentration in the exhaust gas, for example lower than a lower threshold value, the process feed gas flowrate may be increased such that the O_2 concentration in the biofilm is increased to promote more nitrification.

[0021] Process feed gas that has not diffused through the membrane walls towards the bulk liquid and any components that have diffused into the lumen of the membrane from the biofilm may be concentrated in the lumen as an exhaust gas. The exhaust gas will have a higher N_2O concentration as compared to the process feed gas. For example, the exhaust gas may comprise N_2O and other components that diffuse from the bulk liquid, and/or the biofilm into the lumen of the membrane. The exhaust gas may be sent for additional treatment, or redirected to another part of the wastewater treatment system. In an example, redirecting the exhaust gas may be used to leverage denitrification capacity in the bulk liquid around the MABR. N_2O in the exhaust gas may be used as a means of determining an anoxic zone's capacity to denitrify any N_2O that is produced by the MABR and diffused to the bulk liquid.. For example, the denitrification capacity in the anoxic zone of the bulk liquid may be used to determine the N_2O denitrification capacity. The N_2O in the exhaust gas may indicate the driving force of N_2O into the lumen of the membrane, wherein the higher the driving force of N_2O into the lumen, the higher the N_2O concentration is in the bulk liquid. The higher concentration of N_2O in the bulk liquid may be tied to nitrates and nitrites, for example as a consequence of excessive nitrates and nitrites, being returned to the anoxic zone. By controlling the nitrate and nitrite return to the anoxic zone, there may be more denitrification capacity to remove N_2O produced by the MABR in the bulk liquid. In an example, a target exhaust N_2O band (for example to define an upper limit) may be selected such that if the N_2O exceeds the upper limit, the MABR system may be controlled to target one or more of i) a lower percent of internal mixed liquor recycle, ii) the addition or adjustment of an intermittent aeration regime in the bulk liquid, and iii) a percent increase of carbon addition to the bulk liquid.

[0022] In an example, at least a portion of N_2O enriched exhaust gas may be directed to downstream treatment. Downstream treatment may include a wet scrubber, which may for example be used with raw sewage or primary effluent as a liquid source, or in cases where carbon is not available such as some food waste applications, may be used with supplemental carbon, for example in the form of acetate or methanol. Other downstream treatments may include N_2O abatement or reduction treatments, catalysis, N_2O absorption and N_2O adsorption.

[0023] In another example, the N_2O enriched exhaust gas may be used to enhance energy production through combustion. For example, the fuel-to-air ratio may be adjusted to minimize nitrogen oxide emissions associated with N_2O from wastewater treatment processes. In another example, treatment of the exhaust gas may be effected by adsorption, such as by using titanium coated carbon with UV light (for example, from the sun) to treat the N_2O or in another example, using a catalyst and heating the exhaust gas up to 200+ °C. In another example, the exhaust gas may be diffused into a denitrifying submerged biological process, such as for example a fixed bed, or denitrification filter.

[0024] In another aspect, the exhaust gas enriched in N_2O may be used to control the bulk liquid in the anoxic zone, aerobic zone and/or other zones in the wastewater treatment system. For example, the exhaust gas may be used to control return activated sludge recycle rates or internal mixed liquor recycle rates. The exhaust gas enriched with N_2O may be used to control oxidation-reduction potential (ORP) in the anoxic zone of the wastewater treatment system or to control intermittent aeration in the aerobic zone. In yet another example, the N_2O enriched exhaust gas may be used to control the target effluent nitrate/nitrite at the end of either the aerobic zone or plant effluent such as to try to limit the amount of nitrogen oxides being returned in return activated sludge. Leveraging the potential of the N_2O in the exhaust gas may also be beneficial to maintaining the denitrification capacity of the bulk liquid, for example to treat any N_2O flowing from the biofilm into the bulk liquid (rather than into the lumen of the membrane). For example, the denitrification capacity in the bulk liquid may be maintained by controlling the mixed liquor recycle, ORP, and dissolved oxygen in the anoxic and/or aerobic zones of the wastewater treatment plant.

[0025] In an aspect, exhaust gas is de-coupled from the scouring or mixing gas dedicated for the MABR operation, for example scouring or mixing gas directed at the bulk liquid. In this way, N_2O or CO_2 or other greenhouse gases driven into the lumen of the membrane are not returned to the liquid phase of the system. The exhaust gas enriched with undesirable greenhouse gases may be removed from the system and/or treated or reused to leverage the potential of N_2O, for example as described herein. The mixing or scouring gas may be received from an alternative source. In this way the denitrification capacity of the bulk liquid only needs to account for the N_2O diffusing from the biofilm into the bulk liquid, and not from N_2O being reintroduced via the bulk liquid aeration (i.e. mixing or scouring) system.

[0026] In another aspect, the intensity or frequency of scouring or mixing gas in bulk liquid may be controlled to manage biofilm thickness. A thicker biofilm may provide for larger anoxic and aerobic layers that may be used to directly treat N_2O in the biofilm, which may help to reduce the total amount of N_2O flowing out of the biofilm (in either direction). In another example, the frequency or intensity of scouring or mixing gas may be adjusted to encourage substrate renewal in the liquid phase to promote further growth of the biofilm.

[0027] A method of reducing or eliminating N_2O emission from a wastewater treatment system according to aspects as disclosed herein is provided. For example, the method may comprise operating an MABR in a location within a wastewater treatment plant where the ammonia concentration is high or highest, for example in an anoxic zone upstream of an aerobic zone or in sidestream treatment of centrate from dewatered digester digestate. The MABR membranes comprise a hollow interior lumen with an inlet for introducing a process gas as a feed gas to the system and an outlet for expelling an exhaust gas. The feed gas may provide, for example, oxygen, that diffuses through the walls of the lumen to the opposite side of the membrane walls where a biofilm forms. The biofilm may comprise both anoxic and aerobic zones that promote both nitrification and denitrification. The nitrification and denitrification pathways produce N_2O. The higher the nitrogen or ammonia content in the bulk liquid surrounding the MABR, the more N_2O that may be produced in the biofilm. The feed gas is low and preferably completely depleted of N_2O. N_2O may be driven by partial pressure adjustments into the lumen of the membrane. Some N_2O may flow into the bulk liquid. N_2O driven into the exhaust gas may be reused in the wastewater treatment system to maintain or leverage sufficient denitrification capacity in the bulk liquid, as previously described herein. This recycle may be used to address any N_2O flowing into the bulk liquid before N_2O diffuses into the atmosphere, such as in off-gas from bulk aeration. N_2O enriched exhaust gas may alternatively or additionally be treated to reduce or eliminate the N_2O, for example by using a wet scrubber, by adsorption or using other submerged biological processes.

[0028] In another aspect of the invention, a system for scavenging N_2O from a wastewater treatment plant is provided. The system comprises a membrane aerated biofilm reactor adapted to grow a counter-diffusional biofilm that produces N_2O in nitrification and/or denitrification pathways. The membranes used in the MABR comprise a lumen and permeable membrane walls, for example the membranes may be hollow fiber membranes. The lumen may be used to concentrate N_2O diffusing into the lumen from biofilm grown on the outer membrane walls. The lumen may comprise a process feed gas input end and an exhaust gas output end. The exhaust gas output end may be connected to a downstream N_2O treatment step or a recycle stream to redirect the exhaust gas to another part of the wastewater treatment system.

[0029] In an example, the MABR comprises an exhaust valve for controlling the partial pressure of components of the process feed gas being introduced into the lumen of the membrane. The partial pressure of the components may be adjusted to promote diffusion of N_2O from a high concentration of N_2O in the biofilm to a low partial-pressure environment in the lumen of the membrane. For example, the N_2O partial pressure in the lumen may be adjusted such that the driving pressure of N2O from the bulk liquid is maintained or elevated. In an example, the process gas being introduced into the lumen is completely depleted of N_2O. In an example, the lumen of the membrane may comprise a partial pressure gradient with a partial pressure of N_2O being lowest at the input end of the lumen and highest at the output end.

[0030] Downstream N_2O treatment may comprise treatment with a wet scrubber such as with raw sewage or primary effluent as a liquid source, or with supplemental carbon. In another example, treatment of the exhaust gas comprising N_2O may be achieved by adsorption or by diffusing the exhaust gas into a denitrifying submerged biological process.

Analyzing the N2O enriched exhaust gas may comprise a recycle control system that manipulates the performance of the activated sludge process to have lower N2O concentrations in the bulk liquor. Recycle or re-use of the N_2O enriched exhaust gas may comprise a recycle conduit such as to allow the exhaust gas to be used to i) control return activate sludge rates or internal mixed liquor recycle rates, ii) control ORP in the anoxic or aerobic zones, iii) control aeration in an aerobic zone and/or iv) control target effluent nitrate/nitrite at the end of either an aerobic zone or plant effluent to limit the amount of nitrogen oxides being returned in return activated sludge.

[0031] According to the above disclosure, a system and method is provided for driving N_2O that is produced in the biofilm into the MABR lumen to facilitate downstream treatment. In addition, as disclosed herein, the system and method further provide for re-use of N_2O in various processes. The invention as disclosed herein may therefore be beneficial in limiting the greenhouse gas emissions from the wastewater industry while also promoting more efficient processes within the wastewater industry.

CLAIMS:

We claim:

1. A method of treating a wastewater, the method comprising,

operating a membrane aerated biofilm reactor (MABR) in an unaerated zone of a wastewater treatment system (WWTS) including introducing a process feed gas into a first end of a lumen of a membrane of the MABR and expelling an exhaust gas from a second end;

producing N_2O in a biofilm grown on the membrane of the MABR;

driving N_2O into the lumen of the membrane;

expelling the exhaust gas from the lumen of the membrane, wherein the exhaust gas has a higher concentration of N_2O compared to the process feed gas.

2. The method of claim 1 further comprising producing and driving CO_2 in the same manner as N_2O.

3. The method of claim 1 or 2 wherein driving N_2O and/or CO_2 to the lumen of the membrane comprises one or more of i) adjusting partial pressures of components of the process feed gas and ii) adjusting pressure of process feed gas being introduced to the inside of the lumen of the membrane.

4. The method of claim 3 wherein adjusting the partial pressure of components of the process feed gas comprises reducing the partial pressure of N_2O and/or CO_2 in the process feed gas to less than the partial pressure of N_2O and/or CO_2 in a bulk liquid around the MABR.

5. The method of any one of claims 1 to 4 further comprising monitoring the N_2O concentration in the exhaust gas until an upper threshold value is reached and then reducing O_2 introduced to the lumen of the membrane by the process feed gas.

6. The method of claim 5 comprising increasing the O_2 introduced to the lumen of the membrane by the process feed gas when the N_2O concentration in the exhaust gas decreases to below a lower threshold value.

7. The method of any one of claims 1 to 6 further comprising adjusting the frequency of mixing or scouring gas directed to a bulk liquid around the MABR.

8. The method of claim 7 wherein the exhaust gas is separate from, and has a higher concentration of N_2O compared to, the mixing or scouring gas.

9. The method of any one of claims 1 to 8 wherein the unaerated zone is part of an activated sludge process with an elevated ammonia concentration in the bulk liquid.

10. The method of claim 9 wherein the ammonia concentration is 7mg-N/L or more.

11. The method of any one of claims 1 to 10 further comprising reducing the flow rate of the process feed gas introduced into the lumens at the first end to reduce the flow rate of the exhaust gas outputted from the second end of the lumen.

12. The method of any one of claims 1 to 11 wherein the unaerated zone is an anoxic zone.

13. The method of any one of claims 1 to 12 further comprising directing at least a portion of the exhaust gas comprising N_2O to a downstream treatment, or to recycling to another portion of the WWTS, wherein the downstream treatment or recycling comprises any one or more of:

a) an N_2O abatement treatment;

b) treatment with a wet scrubber with i) use of raw sewage or primary effluent as a liquid source, or ii) use of supplemental carbon;

c) treatment of N2O by catalysis;

d) treatment of the exhaust gas comprising N_2O by adsorption;

e) diffusing the exhaust gas into a denitrifying submerged biological process; and,

f) using the exhaust gas to enhance energy production through combustion by adjusting fuel-to-air ratios to minimize nitrogen oxide emissions associated with N_2O from the WWTS.

14. The method of any one of claims 1 to 12 comprising using N_2O in the lumen of the membrane to control:

a) return activated sludge recycle rates or internal mixed liquor recycle rates;

b) control oxidation-reduction potential (ORP) in the unaerated zone;

c) intermittent aeration in an aerobic zone;

d) target effluent nitrate/nitrite at the end of either an aerobic zone or plant effluent to limit the amount of nitrogen oxides being returned in return activated sludge.

15. A system for scavenging N_2O from a wastewater treatment system (WWTS), the system comprising,

a membrane aerated biofilm reactor (MABR) in an unaerated zone of an activated sludge process with a high concentration of ammonia, the MABR comprising a membrane adapted to grow a biofilm that produces N_2O when in use;

the membrane further comprising a lumen adapted to collect an exhaust gas enriched with N_2O, the lumen comprising an input end and an output end; and,

a membrane exhaust gas output connecting the output end of the lumen to (i) a downstream N_2O treatment or (ii) a recycle conduit to another portion of the WWTS.

16. The system of claim 15 wherein the biofilm is a counter-diffusional biofilm.

17. The system of claim 15 or 16 comprising an exhaust valve for controlling pressure of gas introduced at the input end of the lumen.

18. The system of claim 17 wherein the exhaust valve is adapted to control partial pressures of components in the gas introduced at the input end of the lumen.

19. The system of any one of claims 15 to 19 wherein the unaerated zone is an anoxic zone.

20. The system of any one of claims 15 to 19 wherein the downstream N_2O treatment comprises:

a) an N2O abatement treatment;

b) treatment by catalysis;

c) treatment with a wet scrubber with i) use of raw sewage or primary effluent as a liquid source, or ii) use of supplemental carbon;

d) treatment of the exhaust gas comprising N_2O by adsorption;

e) diffusing the exhaust gas into a denitrifying submerged biological process.

21. The system of any one of claims 15 to 20 wherein the recycle conduit to another portion of the WWTS is used to provide the exhaust gas to:

a) control return activated sludge recycle rates or internal mixed liquor recycle rates;

b) control oxidation-reduction potential (ORP) in the anoxic zone;

c) control intermittent aeration in an aerobic zone;

d) control target effluent nitrate/nitrite at the end of either an aerobic zone or plant effluent to limit the amount of nitrogen oxides being returned in return activated sludge.

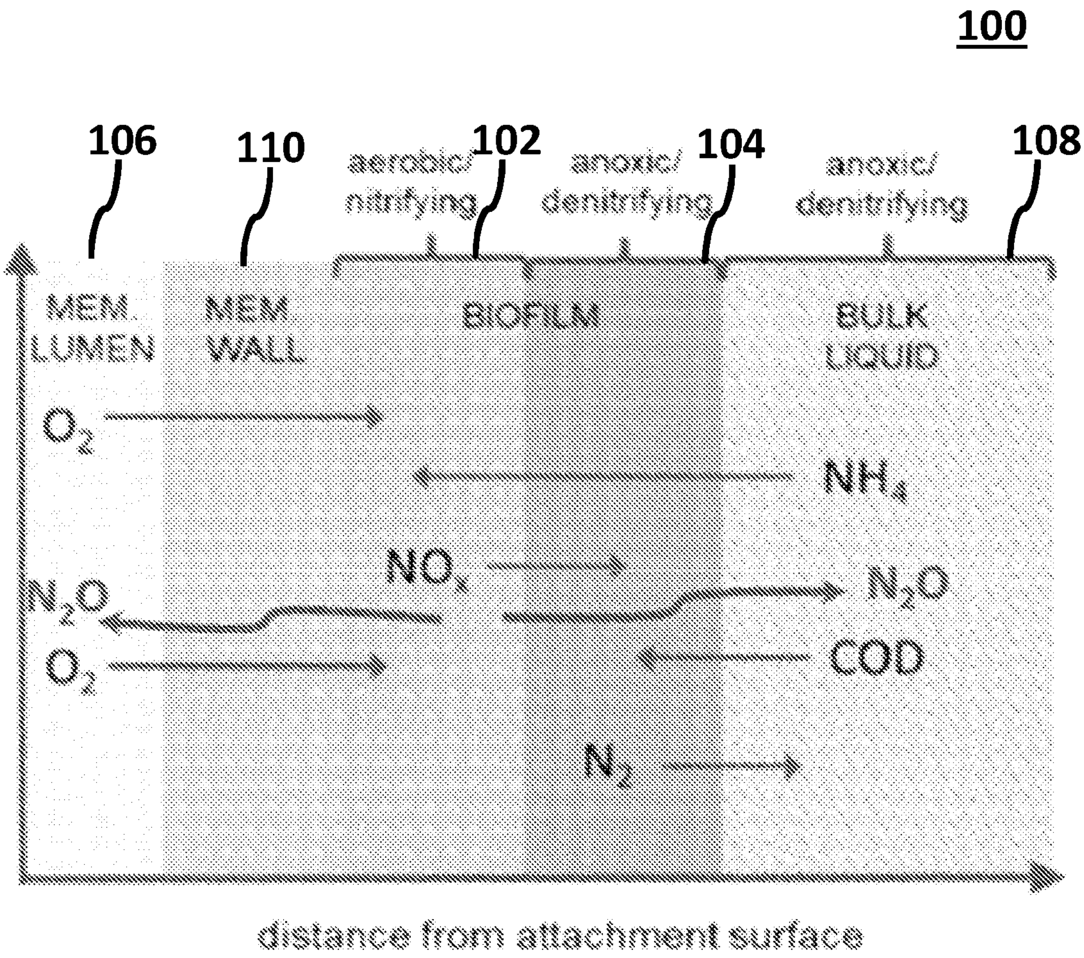
100
106
110
aerobic/
nitrifying
102
anoxic/
denitrifying
104
anoxic/
denitrifying
108
MEM.
LUMEN
MEM.
WALL
BIOFILM
BULK
LIQUID
O_2
NH_4
NO_x
N_2O
N_2O
O_2
COD
N_2
distance from attachment surface

FIG. 1

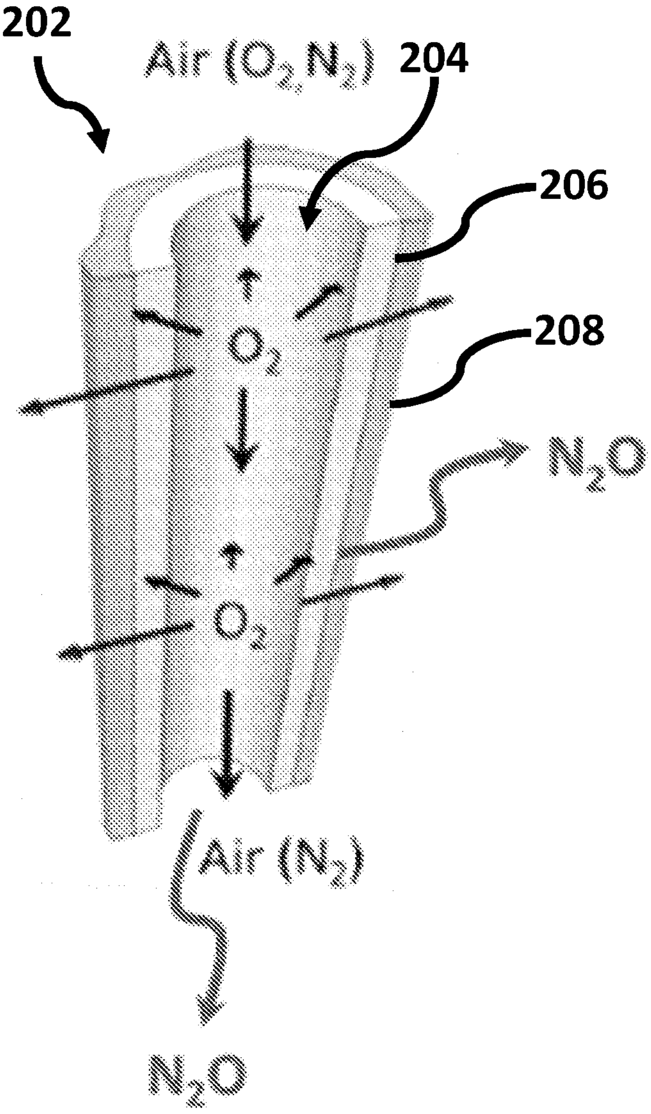

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/015425

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F3/00 C02F3/30 C02F3/10 C02F3/12 B01D61/00
B01D53/22 B01D63/02 B01D53/56 B01D53/86
ADD. C02F101/16 C02F11/04

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	WO 2013/025792 A2 (UNIV LELAND STANFORD JUNIOR [US]; SCHERSON YANIV D [US] ET AL.) 21 February 2013 (2013-02-21) figures 1,2,10a page 2, lines 1-8 page 3, line 27 - page 5, line 19 page 7, line 14 - page 8, line 9 page 11, line 16 - page 12, line 2 page 20, line 12 - page 24, line 24 ----- -/--	1-21

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search 8 April 2024	Date of mailing of the international search report 19/04/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Rozanska, Agnieszka

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SABBA FABRIZIO ET AL: "Nitrous oxide emissions from biofilm processes for wastewater treatment", APPLIED MICROBIOLOGY AND BIOTECHNOLOGY, SPRINGER BERLIN HEIDELBERG, BERLIN/HEIDELBERG, vol. 102, no. 22, 10 September 2018 (2018-09-10), pages 9815-9829, XP036623087, ISSN: 0175-7598, DOI: 10.1007/S00253-018-9332-7 [retrieved on 2018-09-10] abstract page 9821, column 2 - page 9824, column 1 -----	1-21
X	WO 2022/184829 A1 (OXYMEM LTD [IE]) 9 September 2022 (2022-09-09) cited in the application figure 1 page 1, lines 8-12 page 1, line 28 - page 2, line 30 page 3, line 13 - page 4, line 4 page 4, line 24 - page 5, line 32 page 6, line 36 - page 7, line 34 page 8, line 6 - page 12, line 32 -----	1-21
X	HNIN YU KHIN: "Nitric oxide and nitrite removal by partial denitrifying hollow-fiber membrane biofilm reactor coupled with nitrous oxide generation as energy recovery", ENVIRONMENTAL TECHNOLOGY , vol. 43, 2022, no. 19 11 April 2021 (2021-04-11), pages 2934-2947, XP093052700, Retrieved from the Internet: URL:https://www.tandfonline.com/doi/full/10.1080/09593330.2021.1910348?scroll=top&needAccess=true&role=tab&aria-labelledby=full-article [retrieved on 2023-06-07] abstract figure 1 page 2935 - page 2937 page 2940 page 2944 -----	1-21
X	US 2006/037896 A1 (COTE PIERRE L [CA] ET AL) 23 February 2006 (2006-02-23) figures 16-18,20 paragraphs [0002], [0006], [0012], [0014], [0015], [0019], [0090] - [0125] -----	1-21
	-/--	

12

1

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/163184 A1 (BL TECHNOLOGIES INC [US]) 19 August 2021 (2021-08-19) figures 11a-11c paragraphs [0002] - [0004], [0006] - [0012], [0037] - [0052], [0056] - [0082] -----	1-21
A	WO 2020/225709 A1 (ARBOREA LTD [GB]) 12 November 2020 (2020-11-12) the whole document -----	1-21
A	CN 112 320 940 A (UNIV XIAN ARCHITECTUR & TECH) 5 February 2021 (2021-02-05) the whole document -----	1-21
A	CN 112 320 933 A (UNIV XIAN ARCHITECTUR & TECH) 5 February 2021 (2021-02-05) the whole document -----	1-21

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/015425

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013025792 A2	21-02-2013	AU 2012296626 A1	30-01-2014
		CA 2841574 A1	21-02-2013
		CN 103827285 A	28-05-2014
		EP 2744886 A2	25-06-2014
		JP 2014524256 A	22-09-2014
		KR 20140070544 A	10-06-2014
		US 2012309071 A1	06-12-2012
		WO 2013025792 A2	21-02-2013
WO 2022184829 A1	09-09-2022	AU 2022230740 A1	21-09-2023
		CA 3210138 A1	09-09-2022
		CN 117279866 A	22-12-2023
		EP 4301704 A1	10-01-2024
		GB 2606128 A	02-11-2022
		JP 2024512292 A	19-03-2024
		KR 20230173082 A	26-12-2023
		WO 2022184829 A1	09-09-2022
US 2006037896 A1	23-02-2006	US 2006037896 A1	23-02-2006
		US 2006163157 A1	27-07-2006
		US 2008110827 A1	15-05-2008
WO 2021163184 A1	19-08-2021	AU 2021219694 A1	01-09-2022
		CA 3170534 A1	19-08-2021
		CN 115315414 A	08-11-2022
		EP 4103520 A1	21-12-2022
		KR 20220134022 A	05-10-2022
		US 2023079372 A1	16-03-2023
		WO 2021163184 A1	19-08-2021
WO 2020225709 A1	12-11-2020	AU 2020269611 A1	18-11-2021
		CL 2021002730 A1	08-07-2022
		CN 113795570 A	14-12-2021
		EP 3963045 A1	09-03-2022
		IL 287346 A	01-12-2021
		JP 2022533800 A	25-07-2022
		MA 55820 A	09-03-2022
		SG 11202111899P A	29-11-2021
		US 2022213427 A1	07-07-2022
		WO 2020225709 A1	12-11-2020
CN 112320940 A	05-02-2021	NONE	
CN 112320933 A	05-02-2021	NONE	