

**PROCESS AND APPARATUS FOR NITRITATION USING MEMBRANE AERATED
BIOFILM REACTOR**

RELATED APPLICATIONS

- 5 **[0001]** This application claims the benefit of, and priority to, US Provisional Patent Application Number 62/972,719, Process and Apparatus for Nitritation Using Membrane Aerated Biofilm Reactor, filed on February 11, 2020, which is incorporated herein by reference.

10 **FIELD**

- [0002]** This specification relates to membrane aerated biofilm reactors (MABR) and related apparatus and to wastewater treatment using a membrane aerated biofilm.

BACKGROUND

- 15 **[0003]** Nitrogen compounds, often in the form of ammonia, is conventionally removed from wastewater by nitrification-denitrification. Conventional nitrification involves two steps: nitritation by ammonia oxidizing bacteria (AOB) to produce nitrite followed by the oxidation of nitrite to nitrate by nitrite oxidizing bacteria (NOB). Nitritation, alternatively called partial nitrification, proceeds through only the first step using AOB to produce nitrite. In nitritation-
- 20 denitrification, alternatively called short-cut denitrification, the nitrite is converted directly to gaseous nitrogen by ordinary heterotrophic bacteria (OHB) without producing nitrate. Anammox is an abbreviation for anaerobic ammonium oxidation, a microbial process in which nitrite and ammonium are converted into diatomic nitrogen and water. The abbreviation may also be used to refer to bacteria that perform the anammox process. Some
- 25 nitrate is also produced as a respiration product of the anammox bacteria. Deammonification (alternatively called partial nitrification - anammox ammonia oxidation) refers to a process including partial nitritation (i.e. nitritation of some but not all of the ammonium in a wastewater supply without significant production of nitrate) combined with anaerobic ammonium oxidation of the nitrite and remaining ammonium. Nitritation-denitrification and
- 30 deammonification are difficult processes to achieve in practice because NOB grow easily and tend to convert these processes to full nitrification-denitrification.

- [0004]** In membrane biofilm reactors (MBfR), a gas transfer membrane is used to support a biofilm while one or more gasses are supplied to the biofilm through the

membrane. Membrane-aerated biofilm reactors (MABR) are a subset of MBfR where an oxygen containing gas, typically air, is used in the bio-reaction. Efforts to use MABR for deammonification were recently reviewed by Li et al (2018). Efforts to address the challenge of suppressing NOB in the biofilm include controlling air pressure inside the membrane in an effort to match the ammonia and oxygen transfer rates (Gilmore et. al., 2013) and by periodically turning off the air (or oxygen) supply, for example turning the air off for 1 day out of a 1.5 day cycle. (Pellicer-Nacher 2010).

INTRODUCTION TO THE INVENTION

10 [0005] The following paragraphs are intended to introduce the reader to the invention and the detailed description to follow and not to limit or define any claimed invention.

[0006] The inventors have observed that methods of controlling NOB as described above are not efficient in practice. For example, controlling air pressure or air flow rate can avoid a significant growth of NOB in a biofilm during a reactor start up period (which may take a few months) and for several months thereafter. However, a significant population of NOB eventually appears and converts the process to full nitrification-denitrification. The reactor must then be shut down, usually for a period of 4-8 weeks, to destroy the NOB population in the biofilm. But after re-starting the reactor, the NOB population typically returns a few months later causing another reactor shut down. Shutting down the reactor for several weeks multiple times a year severely impacts the productivity of the process. Similarly, turning air off for 12-24 hours out of a 1.5-2 day cycle severely impacts the productivity of the process. While the air off periods can inhibit the growth of NOB, the AOB also do not convert ammonia to nitrite during the air off periods.

[0007] This specification describes processes for operating an MABR. The MABR may be used for the biological conversion of ammonia in water, for example through nitrification (without full nitrification) with or without a complete nitrification-denitrification or deammonification reaction. In these processes, it is useful to suppress or control the growth of NOB and, in the case of deammonification, to support the growth of anammox bacteria. A process includes providing a gas or gas mixture containing oxygen (optionally called process air) to an apparatus containing a membrane aerated biofilm media such as a gas transfer membrane (the apparatus optionally called an MABR unit) so as to inhibit the growth of NOB and, in some examples, to encourage the growth of anammox. This specification also describes an apparatus, for example an MABR or MABR unit. The apparatus includes

means, for example one or more of conduit networks, gages, valves, sensors and flow control devices, for providing air to a membrane aerated biofilm media as required to implement a process.

[0008] In some examples described herein, a process can include one or more of:

- 5 intermittent or batch feed of process air in short cycles; process air modulation; process air direction reversal; process air nitrogen enrichment (alternatively called process air oxygen dilution), for example by process air recycle; process air cascade flow; and, maintaining an exhaust air oxygen concentration below 4%. Process air is air provided to the inside of an MABR unit for transfer to a biofilm as opposed to air provided, for example, to produce
- 10 bubbles outside of the MABR unit to scour a biofilm. Exhaust air is the portion of process air that is not delivered to the biofilm and leaves an MABR unit. These processes may be used together in various permutations and combinations. For example, process air cascade flow may be combined with any other method, optionally in combination with an MABR media (i.e. one or more gas transfer membranes) or MABR unit that is less than 0.5 m long. In another
- 15 example, process airflow direction reversal can be combined with any of the other methods.

[0009] This specification describes a process of batch feed of process air in short cycles. In this process, air is provided to an MABR unit for a first period of time and then valves are closed upstream and downstream of the MABR unit for a second period of time. Optionally the total cycle time may be between 0.1 and 2 hours long.

- 20 **[0010]** This specification describes a process of process air modulation. In this process, air is provided to an MABR unit at a first rate for a first period of time and at a second rate for a second period of time. Optionally the total cycle time may be between 0.5 and 10 days long.

- [0011]** This specification describes a process of process air direction reversal. In this
- 25 process, process air flows in one direction through an MABR unit for a first period of time, and then flows in the opposite direction through the MABR unit for a second period of time. Optionally, the total cycle time may be between 0.5 and 10 days long.

- [0012]** The specification describes a process of process air nitrogen enrichment. In process air nitrogen enrichment, nitrogen enriched (or oxygen diluted) air is provided to an
- 30 MABR for a period of time. The nitrogen enriched air may be provided continuously. Optionally, the nitrogen enriched air is provided to the MABR unit for a first period of time and ambient air is provided to the MABR unit for a second period of time, for example with a total cycle time between 0.5 and 10 days long. In some examples, the nitrogen enriched air is

provided by process air recycle, i.e. flowing at least some of the exhaust gas from an outlet of an MABR unit into an inlet of the MABR unit. Optionally, the process air flow rate in the second period of time is not reduced relative to the first period of time such that the flow rate of air through the MABR unit increase during the period of exhaust gas recycle.

5 [0013] This specification describes a process of process air cascade flow. In some examples, process air is provided to multiple MABR units in series, for example by connecting a port of one MABR unit to a port of another MABR unit.

[0014] A short startup period also benefits the use of deammonification to treat water since anammox are slow growing microorganisms of low yields, and the start-up time of a
10 deammonification reactor is typically significant. In some examples, this specification describes a process useful for shortening the start-up time of a reactor or for shortening the time required for a reactor to recover from an upset involving loss of anammox bacteria. The process can include adding a seed sludge containing anammox to a reactor, optionally after pre-treatment and selection of the seed sludge, optionally after seeding the reactor with a
15 nitrifying sludge. Alternatively or additionally, the process can include pre-seeding the MABR media or unit separately from seeding the reactor.

[0015] Without intending to be limited by theory, the methods described herein stress NOB by causing at least some, but preferably most or all, of the biofilm attached to an MABR unit to periodically experience low oxygen availability. However, the MABR unit as a whole is
20 rarely, if ever, entirely exposed to low oxygen availability so the AOB remain active. In some examples, the process takes advantage of spatial differences in the MABR unit, for example that upstream parts of the MABR unit receive process air with a higher oxygen concentration than downstream parts of the MABR unit. Processes such as process air cascade flow, process air batch feed, process air modulation, and process air nitrogen enrichment can help
25 ensure that a downstream part of the MABR unit is at least temporarily exposed to air with a low oxygen concentration, for example 4% oxygen or less. Process air direction reversal or exhaust gas recycle can cause the area of low oxygen concentration to move to the formerly upstream end of the MABR unit such that the NOB are inhibited throughout most or all of the biofilm.

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BRIEF DESCRIPTION OF THE FIGURES

[0016] Figure 1 is a graph of DO and O₂ flux along membrane cords in a pilot plant.

- [0017] Figure 2 is a graph of oxygen flux change in the batch feed of process air at a frequency.
- [0018] Figure 3 is a graph of oxygen flux over time in a process air modulation process.
- 5 [0019] Figure 4 is a graph of oxygen flux profile along the membrane length in process airflow direction reversal.
- [0020] Figure 5 is a graph of oxygen flux along the membrane length with and without process air recycle.
- [0021] Figures 6A and 6B are diagrams of batch feed of process air with open ended
10 media and dead ended media respectively.
- [0022] Figure 7 is a diagram of process air modulation with continuous but low process air flow on the left and intermittent but high process air flow on the right
- [0023] Figure 8 is a diagram of process airflow direction reversal.
- [0024] Figures 9A and 9B are diagrams of process air recycle with continuous
15 process air with recycle and batch feed of pure oxygen with recycle on the right.
- [0025] Figures 10A, 10B and 10C are diagrams of process air cascade flow, process air cascade flow with recycle, and process air cascade flow with process air direction reversal respectively.
- [0026] Figures 11A, 11B and 11C are schematic diagrams of an experimental MABR
20 configured for start up, process air direction reversal and process air batch feed respectively.
- [0027] Figure 12 is a graph of experimental results during operation of the MABR of Figure 11A.
- [0028] Figure 13 is a graph of experimental results during operation of the MABR of Figure 11B.
- 25 [0029] Figure 14 is a graph of experimental results during operation of the MABR of Figure 11C.
- [0030] Figure 15 is a graph of experimental results of an MABR with process air modulation and, in some cases, process air direction reversal.
- [0031] Figure 16 shows an experimental MABR with process air direction reversal.
- 30 [0032] Figure 17 shows the experimental MABR of Figure 16 configured with process air direction reversal and process air cascade flow.
- [0033] Figure 18 is a graph of experimental results for the MABR of Figures 16 and 17.

[0034] Figure 19 is a graph of experimental results during the start up of another MABR.

[0035] Figure 20 is a graph of experimental results of the MABR of Figure 19 including a period of process air direction reversal.

5 [0036] Figure 21 is a graph of experimental results of the MABR of Figure 19 including a period of process air nitrogen enrichment.

DETAILED DESCRIPTION

[0037] A membrane aerated biofilm media (optionally called MABR media) typically
10 includes one or more gas transfer membranes. Gas transfer membranes can be hydrophobic porous membranes, a dense walled material or a material with pores small enough (i.e. < 40 Angstroms) to prevent bulk water flow. The gas transfer membranes can have any form factor. For example, the gas transfer membranes can be in the form of a flat sheet, for example as in products made by Fluence, or in the form of discrete hollow fibres,
15 for example as in products made by 3M or Oxymem. Alternatively, the gas transfer membranes may be a plurality of hollow fiber gas transfer membranes in a cord as in the ZeeLung™ product sold by Suez. Such a cord is described in International Publication Number WO 2015/142,586 A2, which is incorporated herein by reference. In the case of a cord, or another structure with multiple gas transfer membranes smaller than the expected
20 biofilm thickness, the gas transfer surface can be represented by a smooth surface covering the individual membranes. The use of a cord to support nitrification is described in International Publication Number WO 2020/086,407 A2, which is incorporated herein by reference. The MABR media can be deployed in a tank with or without suspended biomass. Nitrification, nitrification-denitrification, or deammonification can occur in the biofilm.

25 [0038] Factors that inhibit or wash out NOB include, for example, solids retention time (SRT), dissolved oxygen (DO) concentration (especially during different lag phases of AOBs and NOBs), temperature, pH, alkalinity, free nitrous acid and free ammonia. However, many of these factors are either impractical or difficult to adjust in an MABR. Limiting oxygen supply may be used for NOB control in an MABR. However, an overly limited oxygen supply
30 will also reduce the ability of AOB's to convert ammonia to nitrite. Further, limiting oxygen supply alone is not typically effective to achieve and maintain high-rate nitrification while minimizing complete nitrification in an MABR for an extended period of time.

[0039] In a membrane aerated biofilm process, oxygen diffuses across the membrane wall into the biofilm while substrates, such as ammonium, come into the biofilm from the bulk liquid in the opposite direction, a phenomenon called counter-diffusion.

Oxygen accumulates at the base of the biofilm if the oxygen is not consumed immediately.

5 When the local oxygen level becomes high enough, NOB start to grow and may proliferate at the base of the biofilm. It is a dilemma in MABR that a higher airflow rate might increase the oxygen transfer rate (OTR) but it might also cause more oxygen accumulation at the base of the biofilm. Even with a controlled, low air flow rate, after a long period of operation a substantial population of NOB may become established in the biofilm.

10 **[0040]** In particular, even with a low airflow rate, NOB might proliferate near the entrance of an MABR unit. The oxygen concentration of process air, and therefore the oxygen transfer driving force, is higher at the entrance of an MABR unit. Figure 1, shows the oxygen flux and DO concentration at the base of the biofilm along the length of a hollow fiber gas transfer membrane. As can be seen from Figure 1, the oxygen flux and DO
15 concentration are higher near the entrance of the MABR unit (i.e. at the entrance to the gas transfer membrane) and became lower at the exit. Although the overall process conditions (i.e. the average oxygen flux or DO concentration) may be optimized to selected for NOB suppression, the oxygen flux and DO concentration near the entrance of the MABR unit are still high, which might result in NOB growth in the long term starting from one end of the
20 membrane. However, some or all of the processes described below help to suppress NOB growth in the long term and minimally reduce, or may optionally increase, the overall oxygen transfer rate (OTR).

[0041] An intermittent or batch feed of process air, for example over a time period of 0.1 to 2 hours, creates a cycle of OTR change over time in the biofilm, including a period of
25 high OTR (aeration-on period), a period of OTR decreasing to zero (aeration-transition period), and optionally a short period of OTR maintained at zero (aeration-off period). An example of the change in oxygen flow through the membrane is shown in Figure 2. The durations of the aeration on and off periods are the controllable parameters for the process success and can be optimized for a particular plant. In general, the duration of the aeration-off period should be 25% or less, or 10% or less, of the total cycle time. The total duration of
30 the cycle is optionally 30 minutes or less. The process air conditions during the aeration-on period, including process airflow rate and operational pressure, can be higher than for a process with continuous process air selected to inhibit NOB. In this way, the overall OTR

and the treatment capacity of an MABR unit with batch feed of process air is not necessarily reduced relative to a process with continuous process air.

[0042] Figures 6A and 6B shows two methods of providing the aeration-transition period. In one method, shown in Figure 6A, the supply of process air 15 to the MABR unit 6 is stopped, for example by closing inlet valve 20, while an exhaust 18 outlet from the MABR unit is left open. In another method, shown in Figure 6B, the supply of process air 15 to the MABR unit 6 is stopped, for example by closing an inlet valve 20, and an exhaust outlet from the MABR unit is also closed, for example by closing an exhaust valve 22. The naming of the inlet and outlet of the MABR unit 6 is relative to the direction of process air flowing through the MABR unit 6, which may be changed as described further below. However, the inlet and outlet are on opposite ends of gas transfer membranes in the MABR unit 6. Accordingly, when the inlet valve 20 and exhaust valve 22 are closed, process air is trapped inside the MABR unit and the oxygen continues to permeate through the gas transfer membranes to the biofilm. Within a short cycle, the resulting aeration-transition period can continue to the next aeration-on period such that there is no aeration-off period. In the arrangement of Figure 6A, there is often a pressure control valve at the outlet of an MABR unit 6. This valve can be modulated to extend the aeration-transition period such that any aeration-off period is less than 25%, optionally less than 10%, of the total cycle time. However, in either case (Figure 6A or 6B) the total cycle time may be 2 hours or less, or 30 minutes or less, since in a longer cycle the aeration-transition period is not likely to be a material part of the cycle. The aeration-transition period, and the aeration-off period if any, inhibit the growth of NOB.

[0043] Figures 3 and 7 show process air modulation. Process air modulation is conducted over longer cycles, for example cycles between 0.5 and 10 days long, or between 1 and 7 days long. Process air modulation does not have an aeration-off period. As shown in Figure 3, the process air flow rate is modulated between a relatively higher rate and a relatively lower rate in repeated cycles. As shown in Figure 7, the high flow rate periods typically correspond with a higher pressure inside the MABR unit 6 (right side of Figure 7) compared to the pressure inside the MABR unit 6 during the low flow rate periods (left side of Figure 7). The lower OTR period in process air modulation is controlled at a level that NOB is inhibited, i.e. at a level that limits the growth of NOB, optionally temporarily stopping or reversing the growth of NOB, in at least part of the MABR unit 6. The higher OTR periods increase the average OTR without causing an over-proliferation of NOB. Optionally, process

air modulation can be combined with batch feed of process air to produce a process having periods of high OTR, periods of low OTR, aeration-transitions periods and aeration-off periods. Optionally, process air modulation is combined with process air direction reversal (described below). In this case, the lower flow rate may be selected such that NOB are inhibited only in a downstream end of the MABR unit 6.

5 [0044] The threshold for a low OTR that limits NOB growth is a function of many parameters, including the membrane material and configuration, and operational conditions, such as temperature, pH, DO and ammonium concentration in the bulk. The accepted level of complete nitrification also impacts the selected threshold of OTR. Therefore, the operational conditions to achieve a low OTR may vary according to the changes of the affecting parameters. However, the inventors have observed that NOB may be inhibited in at least part of an MABR unit when the exhaust gas has an oxygen concentration of 4% or less. NOB are very likely to be inhibited in at least a downstream part of an MABR when the exhaust gas has an oxygen concentration of 2% or less.

10 [0045] Referring to Figure 8, in process air direction reversal, in a first period of time process air 15 enters a first port 24 of an MABR unit 6 and exhaust gas 18 leaves from a second port 26 of the MABR unit 6 (left side of Figure 8). In a second period of time (right side of Figure 8) process air 15 enters the second port 26 of the MABR unit 6 and exhaust gas 18 leaves from the first port 24 of the MABR unit 6. The air flow direction through the membrane aerated biofilm media (i.e. hollow fiber membranes or cords) is reversed in repeated cycles.

20 [0046] As discussed above, a stable nitrification can be achieved under continuous but relatively low process airflow rate. However, a compromise is often made with continuous aeration in that a certain level of complete nitrification may be allowed to maximize the OTR (and the conversion of ammonia to nitrite) while keeping NOB only partially under control. The complete nitrification might mainly take place in the biofilm near the upstream end of an MABR unit 6, where process air 15 is introduced into the membrane aerated biofilm media, a phenomenon called 'entrance effect' hereafter. The entrance effect occurs because the oxygen flux is higher at the entrance and becomes lower at the exit of the MABR unit 6 as the oxygen partial pressure decreases along the gas flow direction in the MABR unit 6.

30 [0047] As shown in Figure 4, the oxygen flux profile along the length of a gas transfer membrane is switched when the process airflow direction is reversed. The biofilm at both ends of the membrane only receives a relatively high oxygen flux intermittently, and this is

followed by a period of relatively low oxygen flux. NOB populations do not become established at either end of the membrane if the periods of low oxygen flux are long enough to damage any NOB that may have started to grow in the biofilm during the period of high oxygen flux. The frequency of the reversal operation may vary between plants but generally should not exceed 20 days between reversals. Optionally, the total process time (i.e. the sum of the first period of time and the second period of time) is in the range of 0.5 to 10 days or 1-7 days. The overall process air conditions may also be selected to increase OTR relative to a process with continuous process air. To implement process air direction reversal, an appropriate network of valves and pipes may be connected to the MABR unit 6 and a controller to provide an automated reversal of flow through the membranes.

[0048] Process air direction reversal may be more effective when there is a large gradient in OTR along the length of the media, for example due to a variation in oxygen concentration along the length of a membrane. A large partial pressure difference along the length of a membrane creates a non-uniform DO profile in the attached biofilm along the length of the membrane. With process air direction reversal, the areas near the upstream and downstream ends of an MABR unit 6 have a non-uniform DO profile over time. The temporary presence of very low DO is manageable for AOB, but detrimental to NOB. However, a large portion of the biofilm has a higher DO, with active AOB, at all times in the process. A non-uniform DO profile within the biofilm along the length of a membrane, combined with process air direction reversal, helps to inhibit NOB growth in a critical part of the biofilm near the inlet of an MABR unit 6 without reducing activity within the MABR unit 6 as a whole.

[0049] The concentration of oxygen in exhaust gas 18 can be used as an indicator of whether there is a materially non-uniform DO profile along the length of the biofilm. For example, the oxygen concentration in the exhaust gas may be 0.5-4% or less, or 0.5-2% or less, optionally about 1-2%. In an automated process, a sensor can be used to measure the oxygen concentration in the exhaust gas 18. A control process may use an exhaust gas oxygen concentration set point, for example in range of 1-2%, to control the flow rate and/or pressure of the process air 15. Automating the process air flow based on the exhaust gas oxygen concentration helps to provide a stable and reliable process.

[0050] The entrance effect can also be mitigated by temporary or continuous process air nitrogen enrichment. The process air is relatively nitrogen rich, or oxygen diluted, relative to ambient air. For example, the oxygen concentration in the process air may be in the range

of 5-15% at the inlet to a MABR unit. Nitrogen enriched process air can be provided, for example, by flowing the process air through a gas exchange membrane unit or by adding nitrogen to the process air. Optionally, process air nitrogen enrichment can be provided by exhaust gas recycle. The exhaust gas is depleted in oxygen, or nitrogen enriched. Figure 9A shows one method of process air recycle. In this method, some of the exhaust gas 18 is continuously mixed with fresh process air 15. A nitrogen enriched mixture of fresh process air 15 and exhaust gas 18 flows through the MABR unit 6. Figure 9B shows another method of process air recycle. In this method, a batch of process air 15 is pumped into the MABR unit 6. Inlet valve 20 and exhaust valve 22 are closed and the exhaust gas 18 is recycled through the MABR unit 6 for a period of time, optionally with some process air 15 added to make up in volume for oxygen permeating out of the MABR unit 6. After a period of time, a new batch of fresh process air 15 is added. The method of Figure 9A produces a continuous supply of nitrogen enriched process air, at a generally constant nitrogen concentration, for the duration of the process air nitrogen enrichment. The method of Figure 9B produces process air with an increasing concentration of nitrogen over the duration of the process air nitrogen enrichment. Optionally, process air nitrogen enrichment can be provided for a first period time and then withdrawn for a second period of time in repeated cycles, for example of 0.5-10 days or 1-7 days.

[0051] Figure 5 shows a comparison of the oxygen flux along the membrane length with and without process air nitrogen enrichment. In this example, the flow of fresh process air is not reduced when nitrogen or recycled exhaust gas is added. In this way the total mass flow rate through the MABR unit increases but the oxygen mass transfer flow rate does not increase, or does not increase to the same extent. When the process air is recycled (or diluted with nitrogen), oxygen partial pressure at the entrance of a membrane becomes lower and, if the mass flow rate is increased, the gas velocity becomes higher in the membrane. This results in lower oxygen flux at the entrance of the membrane and more evenly distributed oxygen flux along the membrane length. The overall OTR rate may be retained while inhibiting the growth of NOB at the upstream end of the membranes.

[0052] Process air recycle can be implemented as in Figure 9A by using a gas pump 28 to recycle the exhaust gas 18 to the inlet 24 of the MABR unit 6, for example by connecting the exhaust gas line to a process air line or directly to membrane headers of the MABR unit 6. However, the process air recycle might be carried out in different ways depending on the source of oxygen. If air is used as the oxygen source, a continuous

process air flow rate might be used with continuous exhaust recycle in a system as shown in Figure 9A. If pure oxygen is used as the oxygen source, a batch feed of pure oxygen might be used with recycle as shown in the Figure 9B. If an inert gas such as nitrogen is added to dilute the process air, an additional gas line and flow control are added.

5 [0053] Figures 10A, 10B and 10C show three alternative methods of process air cascade flow, which, generally speaking, is to run two or more MABR units 6 in series, using the exhaust air 18 of the first MABR unit as the feed air of the next MABR unit 6. In Figure 10A, the outlet 26 of one MABR unit is connected to the inlet 24 of another MABR unit. The designations of inlets 24 and outlets 26 can be varied according to the reference direction of
10 gas flow in an MABR unit. For example, while the gas flows downwards in both MABR units 6 in Figure 10A, the gas could alternatively flow downwards in one MABR unit 6 and upwards in another MABR unit 6. Optionally, as shown in Figure 10B, some of the exhaust air 18 can also be recycled to the inlet 24 of the first MABR, while another portion of the exhaust gas 18 flows to the next MABR unit 6. Optionally, the process air direction, through one or both of
15 the MABR units 6 and/or the order of the MABR units, may be changed. As shown in Figure 10C, the process air 15 flows in reverse order, and in a reverse direction, through the MABR units 6 relative to Figure 10A. Process air cascade flow can be combined with any one or more of the other methods described herein. For example, process air cascade flow is combined with process air direction reversal by alternating between the configuration of
20 Figure 10A and the configuration of Figure 10C in repeated cycles. The repeated cycles may be, for example, 0.5-10 days long or 1-7 days long.

[0054] Some strategies for quick startup include optimizing conditions and selection and pretreatment of seed sludges. Quantitative Polymerase Chain Reaction (qPCR) techniques can be used to identify and quantify the different anammox or other species in the
25 seed sludge and in the biofilm. Seed sludge rich in fast growing anammox species, such as *Ca. Brocadia Sinica*, can shorten the startup time. In addition, a pretreatment of breaking up the seed sludge into small particles will enhance the initial attachment and therefore shorten the startup time as well.

[0055] In another process, off-site startup is used to speed up on-site startup in full-
30 scale applications by providing a portion of pre-seeded MABR units, and in some cases, to eliminate the on-site startup by providing all pre-seeded MABR units.

[0056] Deammonification was performed in a lab scale pilot using synthetic wastewater of high-strength ammonium as the feed at temperature in the range of 30-35°C.

Stable deammonification at optimized process air conditions (optimal process airflow and pressure) was achieved. Two strategies of quickly forming a single biofilm containing both ammonium oxidizing bacteria (AOB) and Anammox on ZeeLung membrane cords were tested and proved successful. The two strategies were (1) forming AOB in the biofilm first and then Anammox, and (2) forming Anammox in the biofilm first and then AOB. TIN removal was around 3.5gN/m²/d. TIN removal appears to be limited by the nitrite generation rate in the biofilm. To increase the nitrite generation rate, higher process airflow rates than the optimal continuous process airflow can be provided intermittently. Merely increasing the airflow rate from the optimal continuous airflow rate results in poor nitrification.

5 [0057] In cycles described herein the duration of a first period of time to the duration of a second period of time may be in the range of 1:4 to 4:1, or in the range of 1:2 to 2:1, or about 1:1.

Example 1

15 [0058] Figures 11A, 11B and 11C show a pilot scale membrane aerated biofilm reactor configured for operating in three different modes. In Figure 11A, the reactor is configured to operate with a continuous supply of process air to an MABR. In Figure 11B, the reactor is configured to operate with process air modulation and process air reversal. In Figure 11C, the reactor is configured to provide an intermittent supply of process air.

20 [0059] Referring to Figure 11A, wastewater is supplied from a feed tank 1 by a feed pump 2 through a valve 3 to an open tank 4. Feed water is treated in the tank 4 and leaves the tank as effluent 17. An MABR unit 6 is located in the tank 4 and kept submerged in feed water. In this example, the MABR unit 6 is a ZeeLung™ membrane module from Suez. Process air 15 is compressed and fed to the inlet of the MABR unit 6 through a mass flow controller 5. The process air flows from the inlet through the lumens of gas transfer membranes in the MABR unit 6 to an outlet of the MABR unit 6. As the process air passes through the MABR unit, oxygen passes through the gas transfer membranes to the feedwater to a biofilm on the outside of the gas transfer membranes. Process air flows from the outlet of the MABR unit 6 through a pressure gauge 7, a mass flow meter 8 and a needle valve 9 to be released as exhaust gas 18. The outside of the MABR unit 6 is scoured periodically with nitrogen bubbles to remove excess biofilm. To produce the bubbles, compressed nitrogen 16 is supplied through a pressure regulator 10 and a rotameter 11 to a coarse bubble aerator 13.

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[0060] The reactor in Figure 11B is similar to the reactor in Figure 11A. The reference numbers in Figure 11B refer to elements as described for Figure 11A. In addition, the reactor in Figure 11B has two three-way valves 13 and associated piping. The three-way valves can be configured to alternately (a) provide process air 15 to the inlet of the MABR unit 6 and release exhaust gas 18 from the outlet of the MABR unit 6 or b) provide process air 15 to the outlet of the MABR unit 6 and release exhaust gas 18 from the inlet of the MABR unit 6.

[0061] The reactor in Figure 11C is similar to the reactor in Figure 11A. The reference numbers in Figure 11C refer to elements as described for Figure 11A. In addition, the reactor in Figure 11C has solenoid valves 14. The solenoid valves can be configured to alternately (a) provide process air to the inlet of the MABR unit 6 and release exhaust gas 18 from the outlet of the MABR unit 6 or b) seal the inlet and outlet of the MABR unit 6.

[0062] The reactor was started up in the configuration of Figure 11A. Process air 15 was supplied to the MABR unit 6 continuously. Feed water was supplied to the tank 4 except while the reactor was seeded with a nitrifying sludge and an anammox sludge, as described below. The feedwater was a synthetic wastewater containing $\text{NH}_4\text{-N}$ at a concentration of about 100 mgN/L and NaHCO_3 . The feed water flow rate was adjusted to keep the $\text{NH}_4\text{-N}$ concentration in the tank 4 above 50 mgN/L, except while the reactor was being seeded. The temperature of water in the tank 4 was 30 to 35°C. The pH of water in the tank 4 was above 6.7 and most of the time above 7.5. The continuous process airflow rate was 4.2 L/m²/h (based on the area of gas transfer membranes in the MABR unit 6). Pressure in the MABR unit, as measured by pressure gage 7, was about 3psi (21 kPa).

[0063] At the beginning of the process, nitrifying seed sludge from an activated sludge membrane bioreactor was added to the tank 4. After seeding, the mixed liquor suspended solids (MLSS) concentration in the reactor was about 3g MLSS/L. The reactor was operated in batch mode for 10 days to keep the seed sludge in the tank 4. After 10 days of batch operation, the feed water pump 2 was started and the reactor was changed to a continuous feed and bleed operation. The suspended solids from the nitrifying seed sludge washed out of the reactor in a couple of days.

[0064] On the 46th day of operation, the flow of feed water was stopped and the tank 4 was seeded with an anammox sludge taken from a DemonTM granular sludge reactor. After seeding, the MLSS concentration in the reactor was around 3g MLSS/L. The reactor was operated in batch mode for 30 days to keep the seed sludge in the tank 4. After 30 days

of batch operation, the feed water pump 2 was started and the reactor was changed to a continuous flow through operation. The suspended solids from the nitrifying seed sludge washed out of the reactor in a couple of days.

[0065] Figure 12 shows results of operating the reactor for 150 days. the total
5 inorganic nitrogen (TIN) removal rate began to increase after the seeding with anammox sludge on day 46. The results in Figure 12 indicate that a partial nitrification/anammox (PN/A) biofilm was established in about 80 days with the sequential seeding of nitrifying seed sludge at day 0 followed by seeding with anammox sludge starting at day 46. Before seeding the reactor with anammox sludge, the TIN removal was approximately zero, which indicates that
10 there was no anammox activity for nitrogen removal in the reactor. The TIN removal rate began increasing during the anammox sludge seeding period (days 46-76). TIN removal was stable after discharging the anammox seed sludge at about day 80.

[0066] A ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ near 1.0 indicates that NOB are completely suppressed. A ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ near 0 indicates that NOB are not suppressed. There was a decrease
15 in the ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ during the anammox seeding. However, the ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ recovered after the reactor returned to normal operation and the anammox sludge was discharged.

[0067] The reactor was operated for 450 days, including the 150 day period described above. Continuous process air was provided for about 325 days. The ratio of
20 $\text{NO}_2\text{-N}/\text{NO}_x$ was about 0.7 for the first 200 days of operation but decline to about 0.3 on day 325 when process air modulation and process air reversal were both started. The reactor was configured as shown in Figure 11B. According to process air modulation, process air was supplied at 3.2 L/m²/h for 3 days and then at 1.6 L/m²/h for 3 days, in repeated cycles. The direction of the process air flow was reversed once per day, i.e. the process air travelled
25 from the inlet of the MABR 6 to the outlet of the MABR 6 for 1 day and then from the outlet to the inlet for 1 day, in repeated cycles. Referring to Figure 13, the ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ began to increase when process air modulation and process air direction reversal were introduced. The ratio of $\text{NO}_2\text{-N}/\text{NO}_x$ was over 0.9 by day 450. $\text{NO}_2\text{-N}$ generation also increased when process air modulation and process air direction reversal were introduced.

[0068] A second reactor was set up and operated as described for the reactor except
30 that the reactor was configured as shown in Figure 11C. In addition, during the start up of this reactor, process air was provided in batches instead of continuously. In particular, process air was provided at 13.2 L/m²/h for 8 minutes, and then the solenoid valves 14 were

closed to hold the pressurized process air inside the MABR module for 10 minutes, in repeated cycles. Figure 14 compares the NO₂-N/NO_x ratio during startup between the second reactor with process air supplied in batches and the first reactor with process air supplied continuously. NOB were almost completely suppressed during startup with process
5 air provided in batches while there was some NOB in the biofilm when continuous air was supplied during startup.

Example 2

[0069] A pilot scale MABR reactor was operated and fed with lagoon supernatant
10 from an anaerobic digestion process. The reactor had three ZeeLung™ MABR units in a single reactor tank. The reactor tank was fed the lagoon supernatant at a constant rate. Each MABR unit had independent process air control, allowing for different airflow conditions in each MABR unit. Each MABR unit had exhaust gas monitoring for oxygen concentration. The reactor temperature was maintained using a recirculation loop and inline heater. The
15 process was started up by seeding the reactor with 3 g/L of nitrifying MLSS, which was diluted out of the system after five days. After the initial seeding, the pilot reactor was operated in a flow-through configuration.

[0070] The reactor had configuration and operating conditions as described in Table
1. MABR unit 1 was operated with process air direction reversal every 24 hours. MABR unit
20 2 was operated with process air direction reversal every 48 hours. MABR unit 3 was operated without process air direction reversal. The exhaust gas oxygen concentration was measured as an indicator of biofilm growth. In particular a low, for example 2% or less, exhaust gas oxygen concentration, indicates stable partial nitrification and out-selection of nitrite oxidizing bacteria (NOB).

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Table 1

Parameter	Value	Units
Number of MABR Units	3	#
Surface Area Per MABR Unit	40	m ²
Total Membrane Surface Area	120	m ²
Feed Flow Rate	50	L/h
Influent Ammonia Concentration	900	mg/L
Process Air Flow Rate	1.35	L/m ² /h
Inlet gas pressure	45	kPa
Exhaust gas pressure	20	kPa
MABR 1 air reversal frequency	24	Hours
MABR 2 air reversal frequency	48	Hours
MABR 3 air reversal frequency	N/A	Hours
Reactor Temperature	30	°C

[0071] Figure 15 shows the exhaust oxygen concentration from each of the three MABR units along with the ratio of nitrite produced to total NO_x produced for the entire reactor. MABR units 1 and 2 achieved low exhaust oxygen concentration the fastest and most consistently. MABR unit 3 did not achieve as low exhaust oxygen concentration. These results demonstrate that air reversal achieves lower exhaust oxygen concentration for a given airflow, indicating a more effective NOB suppression with process air direction reversal.

The reactor achieved a nitrate to NO_x ratio over 0.85, also indicating effective NOB suppression.

Example 3

[0072] A lab scale MABR reactor was operated to treat high strength centrate from the dewatering of anaerobic digestion sludge at a municipal wastewater treatment plant. The reactor consisted of four lab scale MABR units 6 in a single tank 4. The lab scale MABR units 6 are 0.5 m long (measured as the length of membrane between the headers that is exposed to water). In contrast, a ZeeLung™ MABR unit is 2.0 m long. The tank 4 was temperature controlled using an electric heating blanket. The centrate (feed water 1) was pumped into the tank 4 on a continuous basis. An initial configuration had the four MABR

units 6 configured in parallel as shown in Figure 16. Process air direction reversal was applied every 24-hours (i.e. a 2 day total cycle time) by changing the positions of three-way valves 27. The reactor was initially seeded with 3 g/L of nitrifying MLSS, which was then purged out of the system after 3 days.

- 5 **[0073]** After three months of operation, the reactor was reconfigured as shown in Figure 17 such that the MABR units 6 operated with process air cascade flow (i.e. process air flow in series). The MABR units 6 were connected in series with the outlet 26 of one MARB unit 6 connected to the inlet 24 of the next MABR unit 6. Process air direction reversal was also applied every 24 hours (2 day total cycle time) by changing the positions of
- 10 three-way valves 27. Operating conditions for the reactor are summarized in Table 2.

Table 2

Parameter	Value	Units
Number of MABR units	4	#
Surface Area Per MABR unit	0.25	m ²
Total Membrane Surface Area	1	m ²
Centrate Flow Rate	0.5	L/h
Influent Ammonia Concentration	750	mg/L
Process Air Flow Rate	0.5	L/m ² /h
Inlet gas pressure	45-55	kPa
Exhaust gas pressure	25-50	kPa
Air reversal frequency	24	hours
Reactor Temperature	34	°C

- [0074]** Figure 18 shows the nitrogen species generated as a result of ammonia conversion along with the exhaust oxygen concentration from the MABR units. While the four MABR units received oxygen in parallel, a high exhaust oxygen concentration was observed. Initially, the reactor had good nitritation, as shown in Figure 18 by the large proportion of nitrite produced during the first two months of operation. Loss of nitritation, and a conversion full nitrification, occurred at about 2 months as shown in Figure 18 by the increasing proportion of nitrate produced and decreasing proportion of nitrite produced. Reconfiguring the four MABR units in series, resulting in a longer effective membrane length, resulted in a reduced exhaust oxygen concentration, recovery of nitritation and subsequent growth of
- 15
- 20

anammox. Growth of anammox was indicated by an increasing portion of ammonia converted to nitrogen gas, indicating nitrification by AOB and conversion of ammonia and nitrite by anammox.

[0075] The combination of MABR units operated in series, low exhaust oxygen concentration, and air flow direction reversal led to the indigenous growth of anammox bacteria, indicating that the NOB population was controlled and appropriate conditions for growth of anammox were provided.

Example 4

[0076] A pilot plant was operated to treat high strength centrate from the dewatering of anaerobic digestion sludge at a municipal wastewater treatment plant. The pilot plant consisted of three ZeeLung™ MABR units in a single reactor tank and was fed centrate at a constant rate. The MABR units had a common process air feed and exhaust and the process air was distributed evenly between the three modules. The reactor temperature was maintained using a recirculation loop and inline heater. The process was started up by seeding the reactor with 3 g/L of nitrifying MLSS, which was diluted out of the system after five days. After the initial seeding, the pilot was operated in flow-through configuration

[0077] The pilot reactor was reconfigured to test the effects of process air direction reversal and process air nitrogen enrichment. During process air nitrogen enrichment, a dilution stream of nitrogen gas was added to the process air before feeding the nitrogen enriched process air to the MABR units. The gas flows were arranged such that the MABR units had the same oxygen mass flow but a lower oxygen concentration where the process air enters the lumens of the gas transfer membranes. The reactor was operated under the conditions shown in Table 3.

Table 3

Parameter	Value	Units
Number of MABR Units	3	#
Surface Area Per MABR Unit	40	m ²
Total Membrane Surface Area	120	m ²
Centrate Flow Rate	40-50	L/h
Influent Ammonia Concentration	500-700	mg/L
Air Flow Rate	1.6	L/m ² /h
Process gas dilution flow rate (when applied)	1.6	L/m ² /h
Inlet gas pressure	40	kPa
Exhaust gas pressure	28	kPa
Air reversal frequency	24	hours
Reactor Temperature	31	°C

[0078] After seeding, the reactor was run in a feed water flow through mode. The MABR units were initially operated by introducing process air at the top of the MABR units and collecting exhaust from the bottom of the MABR units. Nitritation was stable throughout the first 60 days of operation without nitrate accumulation. However, over time NOB acclimated to the process conditions and nitrate accumulation occurred. As shown in Figure 19, nitrate accumulation started around day 80 and continues to around day 120. During this stretch of time the nitrate concentrations exceeded 100 mgN/L.

[0079] Beginning on day 120, air flow direction reversal was implemented. In the reverse direction, process air was fed to the bottom of the MABR unit and exhausted from the top of the MABR unit. The process air flow direction was reversed every 24 hours. Up to day 120, the exhaust oxygen concentration was <2%, meaning that the bacteria at the bottom of the MABR unit where receiving oxygen transfer from a gas with an oxygen concentration less than 2%. It is likely that the ecology at the bottom of the MABR units was conditioned to out-select NOB's, which are sensitive to anoxia, due to the low oxygen concentration while the AOB's could consume the limited oxygen to oxidize ammonia.

[0080] When the process air direction was reversed and air with 20.9% oxygen was introduced to the bottom of MABR unit, nitrate production from the MABR unit decreased

immediately, but slowly re-accumulated over time. With the airflow direction switched, the top of the module sees low oxygen concentration, creating NOB limiting conditions. The strategy, then, is to leverage the periods of anoxia at the top versus bottom of the module as a way of avoiding NOB activity and, in turn, nitrate accumulation.

5 **[0081]** Figure 20 shows the impact of reversing the process air direction on a regular basis (i.e. every 24 hours). In the period between July 14 and August 23, nitrite concentrations reached 250 mgN/L but nitrate reached concentrations greater than 100 mgN/L. August 23 to October was a transitional period in which process air direction reversal was implemented intermittently. Continuous operation with process air direction reversal
10 occurred between October 22 and December 1. During this period, nitrite concentrations again reached 250 mg-N/L, but nitrate concentrations leveled off and were maintained around 70 mgN/L.

[0082] Referring to Figure 21, between August 14 and September 2, the pilot was reconfigured to test the effect of process air nitrogen enrichment. There was no process air
15 direction reversal during the process air nitrogen enrichment. There were two tests of process air nitrogen enrichment in the periods highlighted in Figure 21. The air dilution tests resulted in high ammonia and nitrogen removal rates. The 90th percentile of performance data for ammonia and nitrogen removal rates between day 90 and day 110 and were 0.62 kg/d/m³ and 0.47 kg-N/d/m³, respectively. During the first period of dilution, the 25th percentile
20 for ammonia and nitrogen removal rates were 0.65 kg-N/d/m³ and 0.45 kg-N/d/m³, respectively, demonstrating that the removal rates were much higher than the 90th percentile removal rates for the period without air dilution. The performance during the periods of air dilution showed a material change in performance of the reactor in ammonia and nitrogen removal, which was reversed when the dilution was removed. A second shorter period of
25 process air dilution showed the same trend.