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(71) **Applicant** *(for all designated States except US)*: **Amecon Environmental Consultancy** [NL/NL]; Tanthofdreef 21, NL-2623 EW Delft (NL).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **MULDER, Arnold** [NL/NL]; Henry Dunantlaan 31, NL-2614 GK Delft (NL).

(74) **Agent: WINCKELS, J.H.F.**; c/o VEREENIGDE, Johan de Wittlaan 7, NL-2517 JR The Hague (NL).

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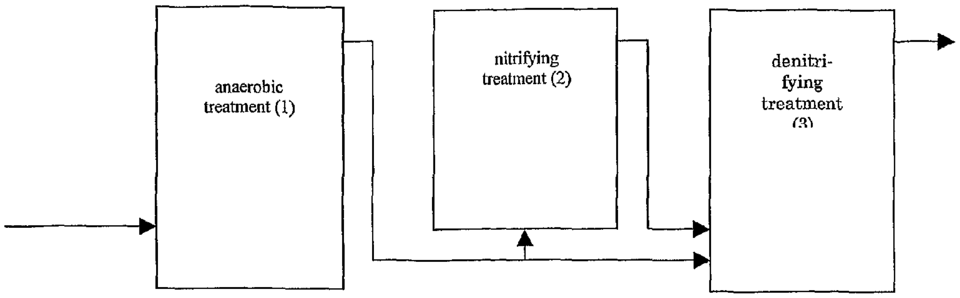
(54) **Title:** PROGRESS FOR THE BIOLOGICAL DENITRIFICATION OF AMMONIUM CONTAINING WASTEWATER



(57) **Abstract:** The invention is directed to a process for biological denitrification of waste water, comprising a nitrifying reactor and a denitrifying reactor, wherein an ammonium ion containing waste water stream is partly fed to the denitrifying reactor and partly to the nitrifying reactor, in which process the ammonium ion is biologically nitrified in the nitrifying reactor to nitrate, which nitrified waste water flow is subsequently fed to the denitrifying reactor. In the denitrifying reactor nitrate is denitrified through nitrite into di-nitrogen ($N_2$) gas by a consortium of bacteria which are oxidising concomitantly COD and ammonium.

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Title:

# PROCESS FOR THE BIOLOGICAL DENITRIFICATION OF AMMONIUM CONTAINING WASTEWATER

The invention is in the area of waste water treatment and more in particular in the area of denitrifying ammonium oxidation.

In WO-A 8907089 a process of this kind is described, wherein the ammonium ion is used as an electron donor in the denitrification of waste water. In this process the ammonium ion and the nitrate are simultaneously fed to a fluidized bed reactor and reacted therein. The said application is specifically directed to specific micro-organisms that are suitable for this process.

This process is also known as the Anammox process, or the anammox-pathway.

The reactor in said process is fed with effluent from an anaerobic reactor treating diluted yeast wastewater and the nitrate is supplied from an external sodium nitrate solution. Afterwards fundamental research at the Technical University of Delft disclosed that in this process ammonium is oxidized with nitrite in stead of nitrate.

Since then most applications of the Anammox process are focused on feeding the Anammox reactor with nitrite produced in an aerobic nitritification system (e.g. the Sharon- Anammox-process developed by TUD; WO-A 9807664)). Since its discovery the Anammox bacteria have been found on many locations in nature.

In the Sharon-Anammox process the Sharon reactor, where nitrite is produced by suspended growing biomass, is placed prior to the Anammox reactor. The feeding of the suspended growing biomass from the Sharon reactor (which is essential for this process) into the Anammox reactor may interfere with an appropriate biofilm formation in the Anammox reactor. It has been found that non-attaching microbes are able to hydrolyze the attachment polymers of attaching microbes. This means that this two stage system is characterized by a potential intrinsic instability with respect to attached growing microbes.

JP-A 2001/104992 a different embodiment of the Sharon process is disclosed, which process differs from the basic process in that part of the waste water bypasses the aerobic reactor in which nitrite is formed.

High nitrite levels as produced in the Sharon are known to be toxic, directly or through the formation of NO for microbes. This affects the performance of the Anammox process negatively.

These negative aspects show that there is a need for a more appropriate configuration with the Anammox process. It was unexpectedly found that the given shortcomings can be solved by the present invention.

The invention is based on the surprising discovery, that the these and other advantages could be overcome by oxidising the ammonia in the nitrifying reactor to nitrate or mainly to nitrate and feeding part of the ammonium ion containing waste water directly into the denitrifying reactor, and the remaining part to the nitrifying reactor. In this process the nitrite is not formed in the nitrifying reactor, but in the denitrifying reactor from nitrate.

Accordingly the invention concerns a process for biological denitrification of waste water, preferably having a COD/N ratio between 0.5 and 3.5, comprising a nitrifying reactor and a denitrifying reactor, wherein an ammonium ion containing waste water stream is partly fed to the denitrifying reactor and partly to the nitrifying reactor, in which process the ammonium ion is biologically nitrified in the nitrifying reactor to nitrate, which nitrified waste water flow is subsequently fed to the denitrifying reactor, where nitrate is reduced and COD and ammonium are concomitantly oxidised.

Surprisingly it has been found that with this process the disadvantages of the prior art are overcome, whereas further no complex process control is required for the production of nitrite in a reactor prior the reactor with the denitrifying process. Also the denitrifying conditions in the denitrifying reactor will enhance the growth of granules which will stimulate the development of the denitrifying process.

Further it is an advantage that there are no high nitrite levels which may be toxic, reactive and result in the unwanted emission of volatile nitrogen oxides ($N_2O$, NO, $NO_2$) which are greenhouse gasses.

An added advantage resides therein that the first reactor can be made substantially smaller that the Sharon reactor of the prior art, as the flow through the reactor is only part of the total flow.

The process of the invention is especially useful for waste water having a COD/N ratio of $> 0.5$ and $< 3.5$. The COD/N ratio is defined by weight and determined using the Standard Methods for Examination of Water and Wastewater, 20th Edition 1998, American Public Health Association, Washington DC. Within these ranges an optimal purification effect is obtained, better than with the Sharon process and the conventional nitrification-denitrification process. For the conventional nitrification-denitrification a COD/N ratio $> 3.5$-4 is required. The COD used is the degradable COD, as defined in the Examples.

The most relevant conversions in the nitrogen removal process of the invention are given below. The ammonium in the water stream passing the nitrifying system will be nitrified according to the conventional nitrification reactions (1) and (2).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad (2)$$

In the process of the invention it is possible to produce nitrate in the first, nitrifying, reaction step. In a preferred embodiment the reaction goes mainly to nitrate.

Full nitrification is preferred, although some nitrite in the effluent of the nitrifying reactor (about 5-10% of the influent ammonium concentration) can be tolerated.

The required nitrite for the ammonium oxidation is produced under denitrifying conditions in the denitrifying reactor from nitrate.

The nitrate produced in the nitrifying system will be reduced to nitrite according to reaction (3) in which [H] stands for the reduction equivalents originating from sulfide or organic components. This reduction takes place in the biomass in the denitrifying reactor, where a very effective and efficient "interspecies nitrite transfer" occurs.

The nitrite produced will then be used by the anammox bacteria to oxidize ammonium, which is let directly into the denitrifying reactor, according to reaction (4). The induction of nitrite may also proceed through the oxidation of manganese into manganese oxide (Vandenabeele, J. et al, (1995). Influence of nitrate on manganese removing microbial consortia from sand filters. Wat. Res. 29, 579-587). Manganese compounds may be present in the effluent of a methane reactor. Also the presence of sulfides or carboxylic acids lead to nitrite formation from nitrate.

$$NO_3^- + 2[H] \rightarrow NO_2^- + H_2O \qquad (3)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \qquad (4)$$

The direct flow of ammonia containing effluent into the nitrifying reactor will result in decrease of potential methane emission.

The denitrification reactor is partially fed directly with the ammonium ion containing effluent, for example an anaerobic effluent, such as from a methanogenic pre-treatment. The distribution ratio between the nitrifying and the denitrifying reactor is determined by the composition of the wastewater in especially by the concentration of the individual electron donors (sulfide, organic compounds and ammonium) in comparison with the amount of ammonium ion.

The nitrite production in the denitrifying reactor is preferably controlled and stimulated by a characteristic feeding pattern based on a discontinuous loaded substrate gradient (DLG). The discontinuous loaded gradient may be realized by two modes. First in the denitrifying reactor there is a separate inlet for the effluent and the outlet of the nitrification process. The separate inlet will result in a substrate gradient in the reactor. Secondly the partition of the total flow (from the methanogenic reactor) over the nitrification reactor and the direct flow into the reactor is alternating (Figure 2). This operating mode surprisingly results in a good process performance, especially with respect to absence of nitrite accumulation. DLG has the result that substantially no nitrite accumulation occurs, thereby further reducing any problems that may occur due to the presence of nitrite in the system. The actual feeding pattern in the Sharon-Anammox process is based on a continuous flow. However for the process of the present invention it is also possible to use the DLG only during start-up. However the intermittent feed supply is important for a fast and efficient induction of the Deamox process.

The process of the invention may be based on any biological nitrification and denitrification system using micro-organisms, such as suspended sludge systems and is preferably based on systems using a biofilm in granules (e.g. EGSB or UASB) or on a supporting matrix (filter or fluidized bed systems). The ammonium oxidation under denitrifying conditions is operates optimal by a consortium of microbes in a biofilm where the intermediate nitrite concentration is kept surprisingly low. This shows that the process proceeds through a very effective and efficient interspecies nitrite transfer in the granules.

A typical flow diagram with the process of the invention is given in Figure 1. In the methane treatment (1) (UASB-reactor) biodegradable organic components are largely removed and the effluent contains only residual organic components and sulfide (when the influent contains sulfate). The effluent of the methane reactor is divided over the nitrifying treatment (2) and the denitrifying treatment (3). This division is preferably discontinuous (see Figure 2) and the ratio is determined by the composition of the wastewater, especially by the concentration of the reduction equivalents and nitrogen. It is to be noted that it is also possible to use more than one reactor for both the nitrifying and the denitrifying step, either parallel or subsequent. After nitrification the separate streams are combined in the denitrification reactor through separated feeding lines in order to create the intended substrate gradient in the reactor. The separate inlet and the discontinuous division will realize the required discontinuous loaded substrate gradient which triggers and control the denitrifying ammonium oxidation. The denitrification process is appropriate for treatment of nitrogen (i.e. ammonium) containing wastewater which contains a too low concentration of electron donors for conventional denitrification (anaerobic treated yeast wastewater, leachate etc.).

For both the nitrifying and the denitrifying systems any conventional system can be applied:

1) activated sludge (SBR etc) and
2) trickling filter.

For the loading rate of the process of the invention the following values may apply:

| | | |
|---|---|---|
| Denitrification capacity: | 0.7 - 2 | kg $NO_x$-N/m$^3$.d |
| Anammox capacity | 0.5 - 1.5 | kg $NH_4$-N/m$^3$.d |
| Total N-removal capacity | 1.2 - 3.5 | kg N/m$^3$.d |

Based on the wastewater composition the required hydraulic retention can be calculated. The preferred technology for the denitrifying-reactor (DEAMOX-reactor) is UASB or EGSB. For start-up activated sludge from nitrifying / denitrifying treatment plant can be used. The reactor is generally filled nearly completely, unwanted sludge will be washed out and under denitrifying conditions granulating sludge will develop gradually. If no anaerobic pre-treatment is used, for example in case of leachate, it can be seeded with a small fraction methanogenic sludge (10%). After start-up the system can be seeded with acclimatized denitrification-sludge.

The invention is now elucidated on by the following example, which is intended as elucidation and not as limitation.

EXAMPLE 1

In a process set-up as described in fig 1, waste water having the following composition: total COD 4.53 g/l, COD after centrifugation 3.86 g/l and sulfate 135 mg S-$SO_4$/l was fed to reactor (1) wherein an anaerobic treatment took place. The effluent of the anaerobic reactor had the following composition: total COD 1.2 g/l, COD after centrifugation 0.98 g/l, sulfate 0 mg S-$SO_4$/l and N-$NH_4$ 382 mg N/l. The COD/N ratio in the effluent based on biodegradable COD was 1.2 (Table 1). The hydraulic retention time in the anaerobic reactor was 28 h and the COD loading rate was 3.92 g COD $_{total}$/l/d.

50% of the said effluent was fed to the nitrification reactor (2) and the remaining 50% bypassed the said reactor (2) and was fed to denitrification reactor (3).

The effluent of the nitrification reactor (2) had the following composition: total COD 0.94 g/l, COD after centrifugation 0.78 g/l, sulfate 77 mg S-$SO_4$/l, N-$NH_4$ 31 mg N/l, N-$NO_2$ 5 mg N/l and N-$NO_3$ 194 mg/l, and was also fed to the denitrification reactor (3) The total flow through the anaerobic reactor and Deamox reactor was constant, however the actual distribution of the flow through the nitrifying system and the flow from the methane reactor direct to the Deamox reactor was discontinuous (see Fig. 2). In a cycle of 1 h during 30 minutes 95% of the flow was pumped direct into the Deamox reactor and 5 % flowed through the nitrifying system. For the next 30 minutes 100 % of the flow was directed into the nitrifying reactor and the direct flow was zero. As averaged result of this feeding pattern 47.5 % of the total flow passes direct from the methane reactor into the denitrifying Deamox reactor and 52.5 % flows through the nitrifying reactor into the Deamox reactor. The influent of the Deamox reactor (3) had the following composition:

total COD 1.07 g/l COD after centrifugation 0.87 g/l, sulfate 39 mg $S\text{-}SO_4$/l, $N\text{-}NH_4$ 197 mg N/l, $N\text{-}NO_2$ 2 mg N/l and $N\text{-}NO_3$ 102 mg/l. The final effluent of reactor (3) had the composition: total COD 0.75 g/l COD after centrifugation 0.73 g/l, sulfate 62 mg $S\text{-}SO_4$/l, $N\text{-}NH_4$ 93 mg N/l, $N\text{-}NO_2$ 0 mg N/l and $N\text{-}NO_3$ 55 mg/l. From these data it can seen that in the Deamox reactor ammonium is removed with a concomitant removal of nitrate and nitrite. The Deamox reactor had a volume of 2.73 l and the hydraulic retention time was 28.8 h.

Table 1. Summary of the process data of the treatment configuration with the Deamox process from example 1.

| **Parameter** | **Unit** | **UASB (1)** | | **Nitrifying system (2)** | **Deamox (3)** | |
|---|---|---|---|---|---|---|
| | | **Influent** | **Effluent** | | **Influent** | **Effluent** |
| $COD_{total}$ | g/l | 4.53 | 1.2 | 0.94 | 1.07 | 0.75 |
| $COD_{centrifuged}$ | g/l | 3.86 | 0.98 | 0.78 | 0.87 | 0.73 |
| $S\text{-}SO_4$ | mg/l | 135 | 0 | 77 | 39 | 62 |
| $N\text{-}NH_4$ | mg/l | - | 382 | 31 | 197 | 93 |
| $COD_{degradable}/N$ 1) | g/g | | 1.2 | - | - | - |
| $N\text{-}NO_2$ | mg/l | - | - | 5 | 2 | 0 |
| $N\text{-}NO_3$ | mg/l | - | - | 194 | 102 | 55 |
| Volume reactor | l | 2.53 | | - | 2.73 | |
| HRT | h | 28 | | | 28.8 | |
| COD loading rate | g COD/l.d | 3.92 | | - | - | |

1. The ratio COD/N is related to the biodegradable COD: $COD_{degradable} = COD_{total}$ effluent UASB - $COD_{total}$ effluent Deamox = 1.2 - 0.75 = 0.45 g/l.

## EXAMPLE 2

In a second example with a similar process set-up as described in fig 1 the loading rates were increased. Waste water having the following composition: total COD 4.73 g/l and sulfate 167 mg $S\text{-}SO_4$/l (Table 2), was fed to reactor (1) wherein an anaerobic treatment took place. The effluent of the anaerobic reactor had the following composition: total COD 1.4 g/l, sulfate 0 mg S-$SO_4$/l, sulfide 161 mg S-$H_2S$/l and N-$NH_4$ 232 mg N/l. The COD/N ratio in the effluent based on biodegradable COD was 3.3 (Table 2). The hydraulic retention time in the anaerobic reactor was 18 h and the COD loading rate was 6.26 g COD $_{total}$/l/d.

50% of the said effluent was fed to the nitrification reactor (2) and the remaining 50% bypassed the said reactor (2) and was fed to denitrification reactor (3).

The effluent of the nitrification reactor (2) had the following composition: total COD 0.78 g/l, sulfate 135 mg S-$SO_4$/l, N-$NH_4$ 0 mg N/l, N-$NO_2$ 12 mg N/l and N-$NO_3$ 200 mg/l, and was also fed to the denitrification reactor (3) The total flow through the anaerobic reactor and Deamox reactor was constant, however the actual distribution of the flow through the nitrifying system and the flow from the methane reactor direct to the Deamox reactor was discontinuous (see Fig. 2). In a cycle of 1 h during 30 minutes 95% of the flow was pumped direct into the Deamox reactor and 5 % flowed through the nitrifying system. For the next 30 minutes 100 % of the flow was directed into the nitrifying reactor and the direct flow was zero. As averaged result of this feeding pattern 47.5 % of the total flow passes direct from the methane reactor into the denitrifying Deamox reactor and 52.5 % flows through the nitrifying reactor into the Deamox reactor. The influent of the Deamox reactor (3) had the following composition: total COD 1.03 g/l, sulfide 71 mg S-$H_2S$/l, sulfate 78 mg S-$SO_4$/l, N-$NH_4$ 99 mg N/l, N-$NO_2$ 12 mg N/l and N-$NO_3$ 112 mg/l. The final effluent of reactor (3) had the composition: total COD 0.64 g/l, sulfide 0 mg S/l, sulfate 138 mg S-$SO_4$/l, N-$NH_4$ 17 mg N/l, N-$NO_2$ 0 mg N/l and N-$NO_3$ 4 mg/l. From these data it can seen that in the Deamox reactor ammonium is removed with a concomitant removal of nitrate and nitrite. The $N_{inorganic}$ removal efficiency in the Deamox reactor was 90% and the $NH_4$-N removal efficiency was 83% (Table 2). The Deamox reactor had a volume of 0.97 l and the hydraulic retention time was 7 h. The $N_{inorganic}$ loading rate of the Deamox reactor was 0.76 g N/l.d.

Table 2. Summary of the process data of the treatment configuration with the Deamox process from example 2.

| **Parameter** | **Unit** | **UASB(1)** | | **Nitrifying system(2)** | **Deamox(3)** | |
|---|---|---|---|---|---|---|
| | | **Influent** | **Effluent** | | **Influent** | **Effluent** |
| $COD_{total}$ | g/l | 4.73 | 1.4 | 0.78 | 1.03 | 0.64 |
| S-$SO_4$ | mg/l | 167 | 4 | 135 | 78 | 138 |
| S-$H_2S$ | mg/l | - | 161 | 0 | 71 | 0 |
| N-$NH_4$ | mg/l | 4.5 | 232 | 0 | 99 | 17 |
| $COD_{degradable}$/N [1)] | g/g | - | 3.3 | - | - | - |
| N-$NO_2$ | mg/l | - | - | 12 | 7 | 0 |
| N-$NO_3$ | mg/l | - | - | 200 | 112 | 4 |
| Volume reactor | l | 2.53 | | 3.42 | 0.97 | |
| HRT | h | 18 | | 44 | 7 | |
| COD loading rate | g COD/l.d | 6.26 | | 0.76 | 3.57 | |
| $N_{inorganic}$ loading rate | g N/l.d | - | | - | 0.76 | |
| $NH_4$-N loading rate | g N/l.d | - | | 0.13 | 0.34 | |
| $N_{total}$ removal efficiency | % | - | | 7 | 90 | |
| $NH_4$ removal efficiency | % | - | | 100 | 83 | |

1 The ratio COD/N is related to the biodegradable COD: $COD_{degradable} = COD_{total}$ effluent UASB - $COD_{total}$ effluent Deamox = 1.4 - 0.64 = 0.76 g/l.

## Claims

1. Process for biological denitrification of waste water, preferably having a COD/N ratio between 0.5 and 3.5, comprising a nitrifying reactor and a denitrifying reactor, wherein an ammonium ion containing waste water stream is partly fed to the denitrifying reactor and partly to the nitrifying reactor, in which process the ammonium ion is biologically nitrified in the nitrifying reactor to nitrate, which nitrified waste water flow is subsequently fed to the denitrifying reactor, where nitrate is reduced and COD and ammonium are concomitantly oxidised.

2. Process according to claim 1, wherein the feed to the denitrifying reactor is based on an intermittent feeding pattern resulting in a discontinuous loaded substrate gradient, especially during start-up.

3. Process according to claim 1 or 2, wherein the ammonium ion containing waste water stream originates from an upstream anaerobic treatment.

4. Process according to claim 1-3, wherein the feed to the nitrifying reactor amounts to 10 to 90, preferably 25 to 75 % of the total of the combined amount of the feed to the nitrifying and the denitrifying reactors.

5. Process according to claim 1-4, wherein in the nitrifying reactor 80 to 95 % of the ammonium is nitrified to nitrate.

6. Process according to claim 1-5, wherein the distribution of the said ammonium ion containing waste water stream between the nitrifying and the denitrifying reactor is determined by the composition of the wastewater, preferably by the concentration of the individual electron donors, such as sulfide, organic compounds and ammonium.

7. Process according to claim 1-6, wherein the reactors are based on systems using a biofilm in granules, such as EGSB or UASB, or on a supporting matrix, such as filter or fluidized bed systems.

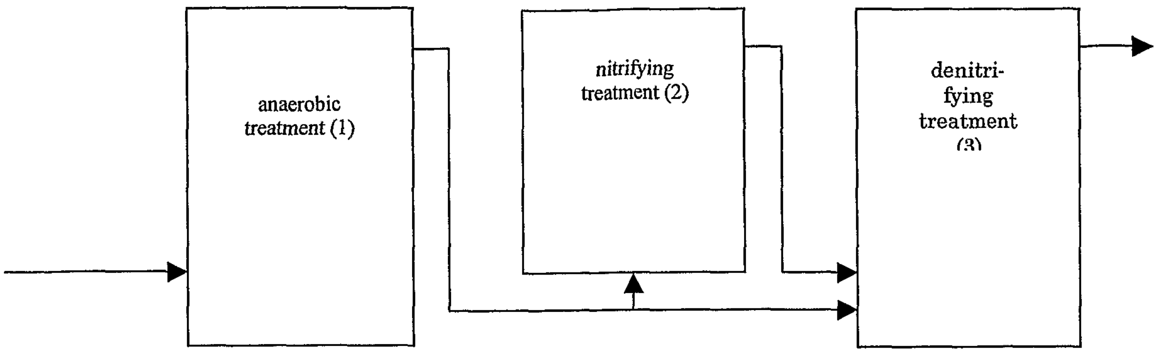
anaerobic treatment (1)
nitrifying treatment (2)
denitri-fying treatment (3)

Fig. 1

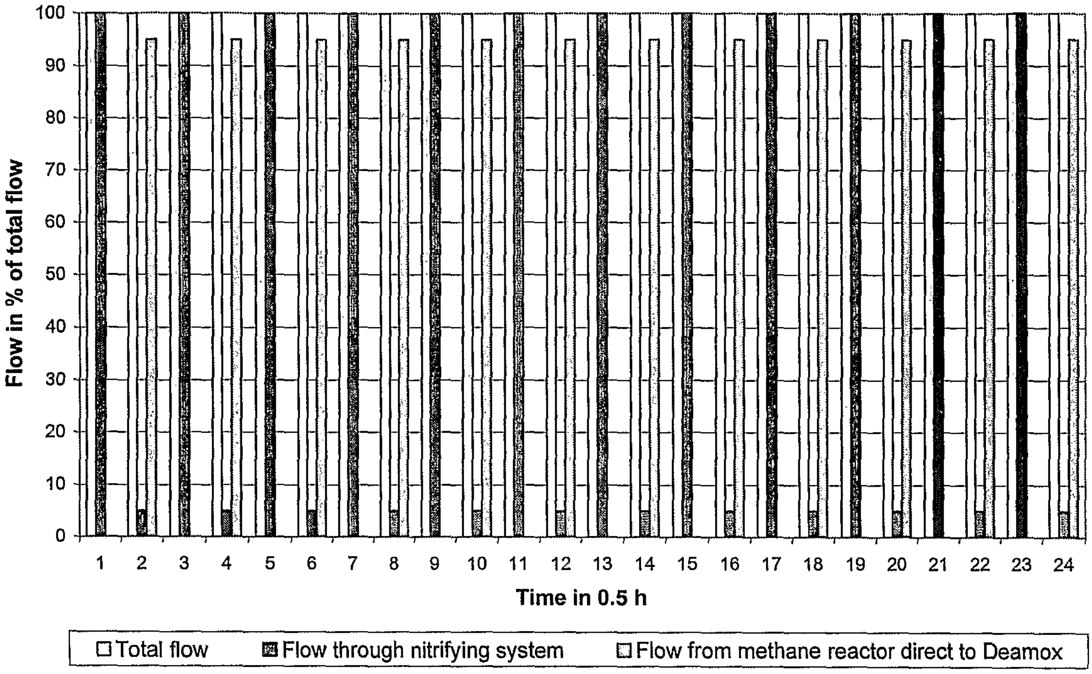
Flow in % of total flow
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
Time in 0.5 h
□ Total flow
▨ Flow through nitrifying system
□ Flow from methane reactor direct to Deamox

Fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL2005/000606

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C02F3/30

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F

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

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

EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| | |
|---|---|
| Date of the actual completion of the international search<br>31 October 2005 | Date of mailing of the international search report<br>07/11/2005 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Authorized officer<br>González Arias, M |

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

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