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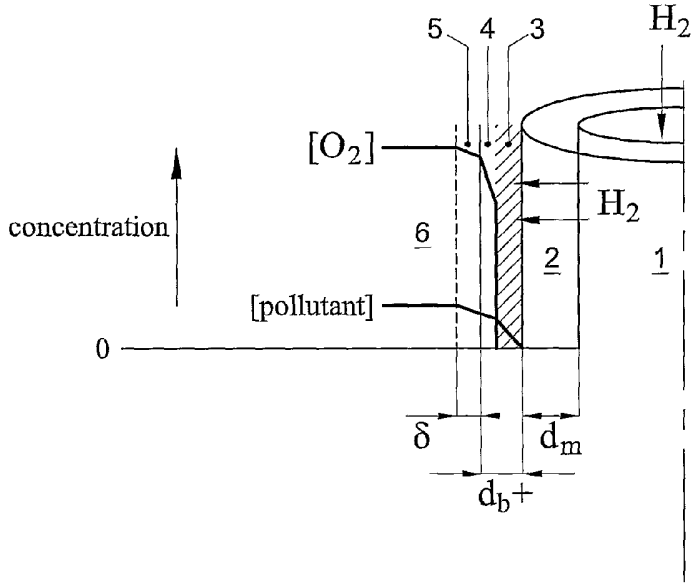
(54) Title: METHOD FOR REMOVING A POLLUTANT FROM AN AQUEOUS MEDIUM USING A MEMBRANE



(57) Abstract: The invention relates to a method for removing a pollutant from an aqueous medium using a membrane (2) provided with a biofilm (3, 4), comprising -contacting hydrogen gas with the aqueous medium using the membrane (2) -reducing oxygen, nitrite and/or nitrate present with hydrogen, thereby forming water and/or nitrogen - anaerobically biologically converting a pollutant by reduction with hydrogen.

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Title: Method for removing a pollutant from an aqueous medium using a membrane

The invention relates to a method for removing a pollutant from an aqueous medium using a membrane.

Aqueous media, such as drinking water, groundwater and surface water are often polluted with inorganic and/or organic pollutants which are undesirable with a view to public health and/or environment. Due to *inter alia* agriculture and industrial activities, such substances may end up in the groundwater and surface water on a large scale and, consequently, also in the water that is derived therefrom, particularly in drinking water. In addition, as a result of process steps such as oxidation in water treatment, undesired harmful by-products may be formed which still need to be removed. Known techniques for the removal of at least a number of such pollutants are ion exchange and electrodialysis (for ionic pollutants), reverse osmosis, nanofiltration (for relatively large molecules), oxidation/ozonization (for oxidizable compounds), adsorption to active carbon, biological conversion and combinations thereof.

Biological treatment of aqueous media is relatively inexpensive and suitable for the removal of many types of pollutants. The biological conversion may, for instance, be carried out in a biofilm of bacteria which have been immobilized in a packed-bed reactor, a tubular reactor or a fluidized-bed reactor.

For the degradation of many pollutants, anaerobic or anoxic conditions are necessary. Examples of such pollutants are NO_3^-, NO_2^-, pesticides, chlorocarbons, azo dyes, (per)chlorate and bromate.

In addition, for reducing pollutants, an electron donor is necessary. If this is insufficiently present, this needs to be added to the flow to be treated. Examples of suitable electron donors are methanol, ethanol and acetic acid.

In US-B-6 387 262, it is proposed to remove nitrate and/or nitrite from water by treatment in a hollow-fiber membrane provided with a biofilm. For this purpose, hydrogen gas is supplied as a reductor.

In EP-A-1 178 017, a method is described for removing nitrate from water, in which use is made of catalyst particles comprising a metal such as palladium on a porous particle such as a porous oxide, an expanded polymer or (preferably) carbon flakes with a size of a few mm. As a reductor, hydrogen may be used.

However, there is a need for alternative methods for the removal of organic and/or inorganic pollutants.

It has now been found that such an alternative is provided by a method for removing a pollutant (particularly having it react away by means of reduction) from an aqueous medium using a membrane provided with a biofilm and with a specific catalyst.

Therefore, the present invention relates to a method for removing a pollutant from an aqueous medium using a membrane provided with a biofilm comprising a zone with anaerobic bacteria and provided with a catalyst which is, under the method conditions, capable of catalyzing the conversion from oxygen and hydrogen to water, comprising

- contacting hydrogen gas with the aqueous medium using the membrane;
- reducing at least one compound present chosen from the group of oxygen, nitrate and nitrite with hydrogen to the catalyst, thereby forming water or nitrogen; and
- anaerobically converting the pollutant by biological reduction with the hydrogen in the zone with anaerobic bacteria.

Fig. 1 diagrammatically shows a membrane during the carrying out of a method according to the invention (Fig. 1A) and a membrane according to the state of the art, without catalyst (Fig. 1B).

The biofilm usually comprises a zone with a very low oxygen concentration in which the anaerobic conversion takes place. The zone is referred to as the anaerobic zone.

Herein, anaerobic means that, on location, insufficient oxygen (in the form of O_2) is present to inhibit the biological reduction of pollutants. More in particular, anaerobic is understood to mean that the oxygen concentration on location is less than 1 μg/l, with great preference 1 ng/l to 1μg/l.

In addition, the biofilm usually comprises a zone located between the bulk of the aqueous medium on the one side and the anaerobic zone and the membrane on the other side in which the oxygen concentration is between the oxygen concentrations of the anaerobic zone and the bulk. This zone is referred to as the aerobic zone.

A method according to the invention has been found very suitable for the treatment of groundwater, drinking water or surface water, and in particular for the treatment of an aqueous medium (such as already partly purified groundwater or surface water) in the preparation of drinking water.

It has been found that, in known methods for removing a pollutant from aqueous media, oxygen is often present in the aqueous medium – for instance in the range of between 1 and 9 mg/l – which has a considerable adverse effect on the desired anaerobic biological conversion. It has been found that, under such conditions, particularly the removal of pollutants to a concentration (far) below the oxygen and/or nitrate concentration is hampered or becomes unfeasible with a known method.

It has now surprisingly been found that this problem can be obviated by making use of a method according to the invention in which the membrane has been provided with a catalyst which catalyzes the conversion

of oxygen to water in the presence of the hydrogen. It has been found that, as a result, the oxygen concentration can be kept sufficiently low to remove, with a good effectiveness, in addition to or instead of nitrate and/or nitrite, one or more other pollutants. For this reduction, microorganisms can use the H_2 dosed via the membrane as an electron donor.

Thus, the invention is eminently suitable for the treatment of an aqueous medium, with the weight content of oxygen and/or nitrate in the aqueous medium in the bulk at the start of the conversion being higher than the weight content of pollutants to be converted, preferably at least 5 times higher, more preferably 10 to 1000 times higher.

The invention is very suitable for the removal of nitrogen oxides such as NO_3^-, NO_2^- and/or N_2O.

The invention has been found eminently suitable for removing one or more reducible inorganic pollutants, in particular at least one pollutant chosen from the group consisting of bromate, chlorate, perchlorate and sulfate.

In principle, the invention can be used for degrading all types of aromatic pollutants, including the aromates (that is, hydrocarbons with at least one benzene ring) found on the so-called "black list" published by the Netherlands Ministry of Housing, Spatial Planning and the Environment ("Target values and intervention values for soil remediation", Netherlands Government Gazette, No. 39, February 24, 2000, pp. 8-16), which list is understood to be inserted herein.

The invention has been found very suitable for removing one or more reducible organic pollutants, in particular carbon compounds with at least one substituent selected from the group consisting of halogen, sulphoxy, nitro and azo groups, more in particular chloroaliphates such as per, tri and dichloroethene, vinyl chloride, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, chloroform and tetrachloromethane and chlorobenzenes, chlorophenols and the like.

The invention is very suitable for removing one or more pesticides, in particular one or more pesticides chosen from the group consisting of atrazine, ametryn, terbutryn, prometryn, cyanazine, propazine, simazine, simeton, cyromazine, amidine, melamine, DCP (1,2-dichloropropane) bromacil, bentazon, mecoprop, amitrole, MCPA (4-chloro-2-methylphenoxy acetic acid), DDT (dichlorodiphenyltrichloroethane), methoxychlor, lindane and TBA (trichlorobenzoic acid).

By means of the invention, it has been found possible to reduce the weight content of at least one convertible pollutant, for instance bromate, from a content in the range of, for instance, 20-100 ppb to a range of maximally 10 ppb, preferably to a content in the range of approximately 0.1-1 ppb, for instance approximately 0.5 ppb.

A special advantage of a method by means of the invention is further the possibility to very effectively remove a pollutant using a membrane on which a relatively thin biofilm is present compared to a known method, preferably having a thickness of approximately 0.01-100 μm, more preferably of approximately 1-100 μm, still more preferably of approximately 10-100 μm. A thin biofilm means less biomass in the system and a lower diffusion resistance from the bulk to the anaerobic zone for the substances to be converted, which allows the use of a less large membrane surface, which requires lower investment costs. In addition, the release of the biomass to the flow to be treated can be lower (lower erosion).

As a membrane, a hollow-fiber membrane is very suitable. Here, preferably, hydrogen gas is led through the lumen of the hollow fiber, where the gas can diffuse outwards through the porous wall and then contacts the catalyst, the biofilm and the aqueous medium. An example of such a fiber in an aqueous medium which is being purified is diagrammatically shown in Fig. 1, in which a hollow fiber is shown whose wall 2 is hydrogen-permeable, has a wall thickness d_m and a central lumen 1 through which the hydrogen

gas is led. The curves designated "O_2" and "pollutant", respectively, diagrammatically show the gradients of these components.

Fig. 1A shows a membrane in a method according to the invention.

On the outside of fiber wall 2, there is a porous catalyst layer (hatched layer in zone 3) in which anaerobic bacteria are also present. This layer has a very low oxygen content compared to the bulk water flow 6 and forms the so-called anaerobic zone 3 here. During the method, the oxygen content is kept sufficiently low under the influence of the catalyst.

Contiguous to the anaerobic zone 3, which comprises the catalyst layer, a so-called aerobic zone 4 with bacteria may be present, in which the oxygen concentration is high compared to the anaerobic zone. During a method according to the invention, this zone 4 may, without any problems, be eroded by the bulk water flowing by. This allows high flow velocities.

The aerobic and anaerobic zones with bacteria together form the biofilm with thickness d_b^+. In Fig. 1B, this is designated d_b. In a method using a membrane according to Fig. 1B, the thickness of the biofilm, and particularly the aerobic zone therein, is generally considerably larger. Here, the anaerobic zone is free from a catalyst layer.

Contiguous to the aerobic zone, there is a hydrodynamic boundary layer 5 having thickness δ, over which there may be another oxygen gradient. Contiguous to the hydrodynamic boundary layer, the bulk water flow is found with an at least virtually gradientless oxygen concentration.

The biofilm preferably extends over at least a part of the membrane wall side which is closest to the aqueous medium (usually the outside in the case of a hollow-fiber membrane), more preferably over essentially the whole side. The thickness, specific activity and composition of the biofilm (thickness and specific activity/composition) will adjust automatically if the right nutrients (including the pollutant) are present.

Suitable bacteria are generally naturally present in the fluid to be purified and can contribute to a suitable biofilm without special measures being necessary.

Examples of bacteria of which preferably at least one species is present are *Ralstonia eutropia* (such as ATCC 17697), *Pseudomana fluorescens, Xantthomonas maltophila, Flavobacterium indologenes, Alcaligens eutrophus, Pseudomonas maltophila* and *Pseudomanas putrefaciens.*

The zone with anaerobic bacteria and the catalyst are preferably at least partly mixed with each other (or, are interwoven with each other) and are preferably in or on the side of the wall of the membrane which is closest to the aqueous medium. It has thus been found that an extremely good fixation of the biofilm and/or the catalyst occurs, so that erosion of at least a substantially anaerobic zone of the biofilm and/or the catalyst is suppressed to a considerable extent or even (virtually) completely prevented.

The membrane is preferably based on a hydrophobic carrier material, in particular in the case of a porous carrier material. Herein, hydrophobic is defined as a material which has a contact angle with water of more than 90 degrees, preferably to virtually 180 degrees. In general, this means that force needs to be exerted (work needs to be performed) to make water penetrate into the pores.

Very suitable is a membrane with a polymer chosen from polypropene (PP), polyethene (PE), polytetrafluoroethene (PTFE) and polyvinylidene fluoride (PVDF) as a carrier material for the catalyst and the biofilm.

The wall of the membrane is usually porous. The porosity can be chosen within broad limits, in general such that, under the method conditions, the hydrogen gas can flow through it and the aqueous medium at least substantially cannot. Preferably, the number average pore diameter

is less than 0.5 μm. Very good results have been achieved with a number average pore diameter in the range of approximately 0.05-0.2 μm.

By the conversion of oxygen, nitrate and/or nitrite, the catalyst supports the anaerobicity/anoxicity to the membrane in an aerobic environment.

The catalyst preferably comprises at least one precious metal from group VIII of the periodic system, with great preference at least palladium. This has been found to have a good oxygen-converting activity under conditions in which the biofilm is active.

The amount of catalyst in relation to the weight of the carrier material of the membrane can be chosen within broad limits and is with preference less than 10 wt.%, with great preference 0.1-1 wt.%.

Optionally, one or more other metals may be added to the catalyst, such as for instance copper, preferably in a total content of less than 10 wt.% in relation to the catalytically active component. The addition of copper and the like has been found to favorably influence the selectivity of the conversion reaction of nitrate and nitrite to nitrogen.

The catalyst can be provided on the carrier material in any manner, and is preferably present as a (finely divided) porous layer. In practice, the porosity of the catalyst layer is such that it is permeable to the hydrogen gas, oxygen as well as water. Very suitable is a membrane on which the catalyst has been provided by means of *electroless plating*. Very good results have been achieved with a membrane obtained by means of such a method as described in Dutch patent application no. 1 023 364.

Very good results have been achieved with a membrane where a coating layer has been provided on the catalyst, which coating layer is permeable to oxygen and also to hydrogen, nitrogen and water. Such a layer protects the catalyst against pollutants in the aqueous medium and/or products secreted by the bacteria.

Preferably, the coating layer is a polymeric layer, which may be provided, for instance, by dip coating from a diluted solution of the polymer and then evaporating the solvent. In particular, a polymeric layer appears to contribute to keeping the catalyst clean. In this connection, very good results have been achieved with a polypropene oxide (PPO) and the like.

In a method according to the invention, the aqueous medium is preferably maintained at overpressure in relation to the hydrogen gas pressure. In this manner, bubble formation is suppressed or completely prevented, which limits the gas transfer to diffusion and prevents hydrogen gas loss due to bubble formation, and/or favorably influences the integrity of the biofilm. With great preference, the overpressure is at least approximately 0.05 bar, with greater preference approximately 0.1 to 0.5 bar.

In principle, a method can be applied at any temperature at which the catalyst and the biofilm are active. A skilled person will know how to choose this temperature on the basis of the catalyst and bacteria present. Generally suitable is a method in which at least the anaerobic conversion – and preferably also the conversion of oxygen – takes place at a temperature in the range of 4-90°C. For practical reasons (for instance with a view to energy consumption) a temperature in the range of 15-30°C is particularly preferred.

As already mentioned hereinabove, the invention may very suitably be carried out at a high flow velocity, for instance flow velocities corresponding to a Reynold's number (Re) of approximately 1 to 500, with great preference of approximately 10 to 500. Herein, Re is based on the interstitial linear velocity, that is, the actual fluid velocity along the membrane surface. The characteristic length in the calculation of Re is determined by the system and is, in particular in the case of a system with hollow-fiber membranes, the outer diameter of the fibers.

An advantage of a high flow velocity is that the aerobic layer 4 (which generally does not materially contribute to the anaerobic removal of pollutants) remains relatively thin and a very good mass transfer takes place. This allows the surface of the biofilm (formed by the anaerobic zone and the aerobic zone) and the membrane to be relatively low, which is advantageous from an investment point of view.

For compounds which are removed by a sequential conversion by aerobic and anaerobic compounds, such as for the removal of halogenated aromates, the flow velocity is preferably relatively low compared to a method for removing compounds in which the aerobic bacteria play no part or only a minor part. For removing a compound by means of a sequential conversion by aerobic and anaerobic compounds, very good results have been achieved with a method in which the flow velocity corresponds to a Re in the range of 1 to 100.

The aqueous medium may contain one or more minerals, trace elements and/or vitamins. Examples hereof are described in Dutch patent application no. 1 021 458.

Very suitable is a method in which the aqueous medium comprises at least one mineral, preferably chosen from the group of phosphates, sulfates, nitrates. As counterions, one or more cations from the group formed by cations of magnesium, potassium and sodium are very suitable.

Very suitable is a method in which the aqueous medium comprises at least trace elements such as (i) the cations of iron, zinc, manganese, cobalt, nickel and/or copper; and/or (ii) acids and/or salts of molybdates (salts of MoO_4^{2-}), tungstates (salts of WO_4^{2-}), selenates (salts of SeO_3^{2-}) and/or borates. With great preference, essentially all these trace elements are present.

Very good results have been achieved with a method in which the total content of minerals plus trace elements is 0.1-10 g/l.

Good results have *inter alia* been achieved with a method in which the aqueous medium contains one or more vitamins. The one or more vitamins are preferably chosen from the group consisting of para-aminobenzoic acid, folic acid, DT-lipoic acid, riboflavin, nicotinic acid amide, pyridoxine, pantothenate, vitamin B_{12} and biotin. Preferably, essentially all these vitamins are present.

Very good results have been achieved with a total vitamin content of approximately 0.1-10 mg/l.

The minerals, trace elements and vitamins contribute to the desired growth of bacteria. A suitable amount can routinely be determined by a skilled person on the basis of general professional knowledge.

The pH can be chosen in a suitable manner on the basis of the catalyst used, bacteria used and the pollutant(s) to be converted. In general, a range of approximately 4.5 to 8.5 is very suitable, although a pH outside this range is also possible. If desired, the medium can be brought to pH in a usual manner, for instance by addition of CO_2 or a corresponding base.

Optionally, the invention may be used in combination with one or more purification procedures for removing undesired components. Such procedures are generally known in the field.

The invention is, for instance, very suitable to be applied to an aqueous medium which has first been subjected to ozonization. In ozonization, usually, some bromate, chlorate and/or another pollutant is formed. A pollutant formed during ozonization can then be removed by means of the invention.

The invention further relates to the use of a membrane as defined in the specification and/or the claims in the preparation of drinking water, process water, wastewater or ultrapure water (such as demineralized and/or distilled water).

The invention further relates to the use of a membrane as defined in the specification and/or claims for maintaining (virtually) anaerobic

conditions in a biofilm for removal of a reducible pollutant, and in particular to the use of this membrane for removing oxygen in the biofilm.

CLAIMS

1. A method for removing a pollutant from an aqueous medium using a membrane provided with a biofilm comprising an anaerobic zone with anaerobic bacteria and provided with a catalyst which is capable of catalyzing the conversion of oxygen and hydrogen to water under the method conditions, comprising:
- contacting hydrogen gas with the aqueous medium using the membrane
- reducing oxygen, nitrite and/or nitrate present with hydrogen to the catalyst, thereby forming water and/or nitrogen
- anaerobically biologically converting a pollutant by reduction with the hydrogen in the anaerobic zone with anaerobic bacteria.

2. A method according to claim 1, wherein the aqueous medium is maintained at overpressure in relation to the hydrogen gas pressure, preferably at an overpressure of 0.05 to 0.5 bar.

3. A method according to any one of the preceding claims, wherein the temperature is in the range of approximately 4-90°C, preferably of approximately 15-30°C.

4. A method according to any one of the preceding claims, wherein the pH of the aqueous medium is in the range of approximately 4.5 to 8.5.

5. A method according to any one of the preceding claims, wherein the membrane is a hollow-fiber membrane.

6. A method according to any one of the preceding claims, wherein the catalyst comprises at least one precious metal from group VIII of the periodic system, preferably at least palladium.

7. A method according to any one of the preceding claims, wherein the anaerobic zone with anaerobic bacteria and the catalyst are at least partly mixed with each other.

8. A method according to any one of the preceding claims, wherein at least one pollutant is converted chosen from the group consisting of bromate, chlorate, perchlorate, nitrate, nitrite, sulfate, N_2O and carbon compounds with at least one substituent selected from the group consisting of halogen groups, preferably chloro groups, sulfoxy, nitro and azo groups.

9. A method according to any one of the preceding claims, wherein the weight content of oxygen and/or nitrate in the aqueous medium at the start of the anaerobic conversion is higher than the weight content of pollutants to be converted, preferably at least 5 times higher, more preferably 10 to 1000 times higher.

10. A method according to any one of the preceding claims, wherein the aqueous medium is subjected to an ozonization prior to the anaerobic conversion of the pollutant.

11. A method according to any one of the preceding claims, wherein the catalyst is provided with a protective coating layer.

12. A method according to any one of the preceding claims, wherein the flow velocity of the aqueous medium with respect to the membrane corresponds to a Reynold's number (Re) of approximately 1 to 500, preferably of approximately 10 to 500.

13. Use of a membrane as defined in any one of claims 1, 5-7 or 11 in the preparation of drinking water, process water, wastewater or ultrapure water.

14. Use of a membrane as defined in any one of claims 1, 5-7 or 11 for maintaining anaerobic conditions in a biofilm for removal of a reducible pollutant.

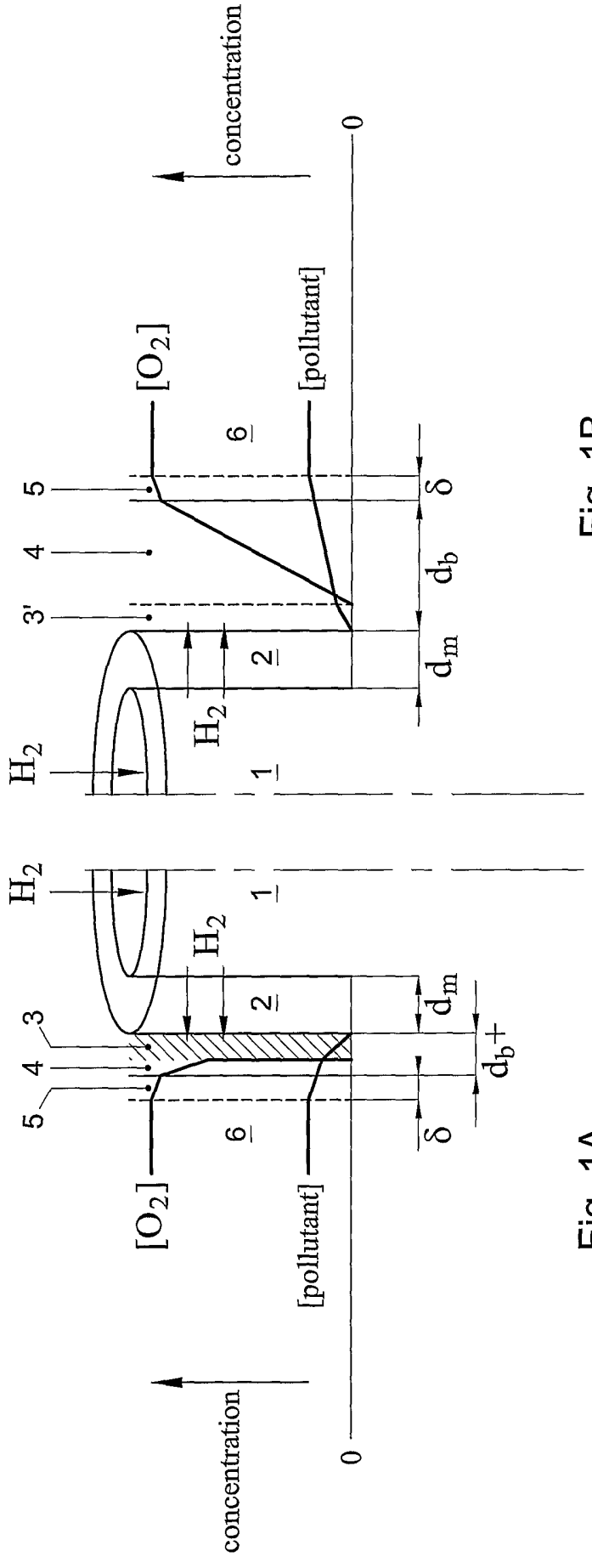
concentration
0
[pollutant]
[O2]
6
5
4
3'
2
1
H2
H2
δ
db
dm
H2
1
H2
2
3
4
5
dm
db+
δ
6
[O2]
[pollutant]
0
concentration

Fig. 1B

Fig. 1A

INTERNATIONAL SEARCH REPORT

Application No
PCT/NL2004/000347

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F3/10 C02F1/70 C02F3/28

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, WPI Data, PAJ, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 387 262 B1 (LEE KUAN-CHUN ET AL) 14 May 2002 (2002-05-14) cited in the application the whole document	1-8,13
Y	DE 195 05 436 A (SOLVAY UMWELTCHEMIE GMBH) 22 August 1996 (1996-08-22) page 5, line 22 - page 6, line 15	1-8,13
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A	US 5 116 506 A (STRAND STUART E ET AL) 26 May 1992 (1992-05-26) abstract	1-14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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 document but published on or after the international filing date
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2004	22/10/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gonzalez Arias, M

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INTERNATIONAL SEARCH REPORT

Application No
PCT/NL2004/000347

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/16660 A (MACASKIE LYNNE ELAINE ;ROWSON NEIL ANTHONY (GB); YONG PING (GB); H) 28 February 2002 (2002-02-28) abstract page 4	1,6

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