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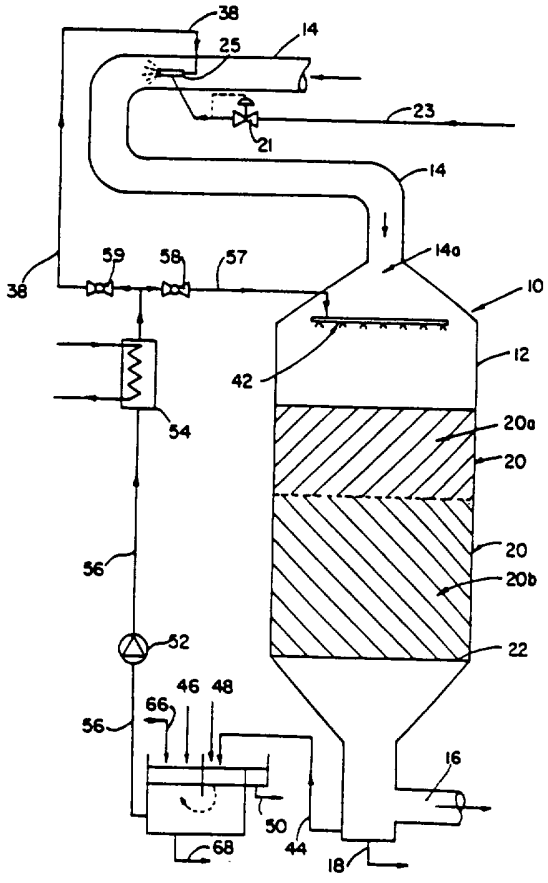
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(54) Title: BIOFILTRATION OF GASES

(57) Abstract

The present invention relates to the biofiltration of gases, specifically, to a packing material comprising a calcareous material of aquatic origin and to a biofilter bed (10) containing a calcareous material of aquatic origin as the packing material (20). The calcareous material may be derived from a marine alga or a marine calcareous sand and, preferably, the calcareous material is derived from Lithothamnium calcareum. The packing material (20) may consist essentially of calcareous material derived from Lithothamnium calcareum (20a) or, alternatively, the packing material may comprise calcareous material derived from Lithothamnium calcareum in admixture with a known packing material selected from peat, compost, wood chips, heather or coir (20b). The packing material (20) and biofilter bed (10) according to the invention may be used for cleaning gaseous effluents from industrial, municipal and agricultural plants.



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BIOFILTRATION OF GASES

The present invention relates to the biofiltration of gases, specifically, to a packing material for biofiltration of a gas and to a biofilter bed. The assembly of a packing material and one or more strains of micro-organism(s), if present, when located in a housing, is termed a biofilter bed.

Biofiltration involves the removal of components from the gas being treated by the dual action of filtration/adsorption onto the packing material and decomposition by the micro-organisms, primarily bacteria and fungi, which are present in or on the packing material. The components to be removed from the gas are usually adsorbed onto or into the packing material and are then decomposed by the micro-organisms present in a bio-layer in or on the packing material. Thorough contact of the gas and its components with the bio-layer is necessary.

In recent years biofiltration has been increasingly used for cleaning gases such as effluents from industrial and agricultural plants e.g. furnaces, abattoirs and rendering, food processing, pharmaceutical and chemical plants, and sewage works. Known packing materials in such biofilter beds are compost, fibrous peat (Eriophorum or peat fibre), nodular peat, wood chips, heather and coir (coconut fibre).

Suitable packing materials should act as a carrier for the micro-organisms(s), if present, and as a humidity reservoir and should also provide adsorption surfaces for the gas to be filtered. Factors which influence the biofilter bed's efficiency include

contaminant solubility; bed pH; bed humidity; efficiency of contact between the gas and the micro-organism(s); rate of reaction between the contaminants in the gas and the micro-organism(s); flow rate of the gas through the biofilter bed; back pressure (flow resistance); and the porosity and height of the biofilter bed.

Problems are often encountered with known packing materials, due partly to their relative lack of homogeneity. The natural structure of known packing materials, which typically consist of loose, low density materials, often prevents a uniform distribution of gas flow, as a result of which the biofilter bed cracks and short-circuiting channels develop in the packing material. This causes a considerable drop in the biofilter bed's effectiveness. Reducing irregularities in the packing material by the inclusion of light uniform non-degradable materials such as polystyrene reduces the risk of bed cracking. However, the inclusion of non-natural materials such as polystyrene in the biofilter bed gives rise to an environmentally unacceptable "waste" biofilter bed.

Other water absorbing packing materials can lead to problems in containing the packing material due to physical expansion of the biofilter bed arising from water absorption. Such expansion can cause excessive pressure on the biofilter bed housing often leading to rupture of the walls.

The known packing materials are all strongly subject to aging. Aging is poorly understood and is believed to be caused by pH extremes, temperature extremes, humidity extremes, rapid pH and/or temperature variations, physical breakdown as a result of expansion and contraction due to changes in water content,

decomposition by microbial and/or fungal action or adverse effects of contamination. In addition, some types of packing materials tend to lump, causing a reduction of their effective surface area.

According to the invention there is provided a packing material for the biofiltration of a gas containing at least one contaminant, the packing material comprising a calcareous material of aquatic origin.

The term "calcareous material" is intended to embrace material comprising calcium and/or magnesium carbonate. The term "calcareous material" embraces, but is not limited to, material of plant or animal origin including, for example, material derived from algae, calcareous sands, sponges (Phylum Porifera, Class Calcarea), corals (Phylum Coelenterata, Class Anthozoa), shells (Phylum Mollusca) or colonial animals (Phylum Polyzoa (Bryozoa)).

The term "aquatic origin" is intended to mean originating from bodies of fresh and/or sea water, including, rivers, lakes, seas, oceans and the like. The term "aquatic origin" embraces originating from existing bodies of water, as well as, from those bodies of water that existed during the Palaeozoic, Mesozoic and Cenozoic Eras. The term "aquatic origin" embraces, but is not limited to, originating from the Irish Sea, Mediterranean Sea, Atlantic Ocean, Lough Neagh (Northern Ireland), Shannon River (Ireland), Lower Palaeozoic Seas, Carboniferous Seas and Jurassic Seas.

Preferably, the calcareous material is of marine origin. More preferably, the marine calcareous material is derived from a marine alga or a marine calcareous sand.

Advantageously, the packing material may be derived from *Lithothamnium calcareum*, a red alga from the taxonomic division Rhodophycophyta of the family Corallinaceae (also known collectively as maerl). Such packing material typically contains $MgCO_3$ and $CaCO_3$ in a ratio of 1:10-20 and has a minimum particle size of 37 μm, a porosity of 40-50%, an apparent density of 1.05-1.08, a true density of 2.7, a surface area of 1.5 m^2/g, a surface tension of 480 dyne/cm and a specific volume of 0.0176 cm^3/g.

The packing material may comprise calcareous material derived from, e.g., *Lithothamnium calcareum* alone, or in admixture with a known packing material selected from peat, compost, wood chips, heather or coir, preferably fibrous peat (peat fibre) or coir. Calcareous material derived from *Lithothamnium calcareum* may be introduced into the biofilter bed either in a separate layer, or in a single layer mixed with other packing materials such as fibrous peat, nodular peat, compost, wood chips, heather or coir, or in graded stages.

Calcareous material derived from *Lithothamnium calcareum* is a rigid material, which may be ground to a uniform particle size of from 37 microns to 20 mm, depending on the identity of the gas to be filtered. Calcareous material derived from *Lithothamnium calcareum* in the particle size range 2-12 mm is preferred - such a relatively homogeneous packing material reduces the likelihood of bed cracking due to a more uniform distribution of porosity in the biofilter bed. Typically, calcareous material derived from *Lithothamnium calcareum* may be used alone or mixed with known biofilter bed materials. The rigidity, resistance to compression, and structural stability of calcareous

material derived from *Lithothamnium calcareum* makes possible biofilter beds of increased bed height relative to biofilter beds containing traditional packing materials, thereby reducing the footprint area required by the biofilter bed.

The non-expanding nature of calcareous material derived from *Lithothamnium calcareum* even under wet conditions decreases the risk of the biofilter bed housing being damaged by biofilter bed expansion, which is frequently a problem caused by traditional bed materials.

Calcareous material derived from *Lithothamnium calcareum* has a high porosity, high surface area, good wettability and a rough surface. It is believed that these factors encourage the initial attachment of micro-organisms at the solid-liquid interface, so as to enhance the bio-layer. In general, rough surfaces promote thicker and more stable bio-layers, which are less prone to sloughing than bio-layers formed on smooth surfaces. The formation of thick stable bio-layers on calcareous material derived from *Lithothamnium calcareum* permits relatively high loading rates of the gas to be filtered, e.g., $100m^3/hr/m^3$.

Calcareous material derived from *Lithothamnium calcareum* has heat absorbing and heat resisting properties. Thus calcareous material derived from *Lithothamnium calcareum*, alone or in combination with other packing materials, acts as a heat sink, inhibiting the formation of dead areas within the biofilter bed resulting from temperature gradients. For the same reason, the addition of other heat resistant packing materials, for example, sintered glass or ceramic materials, to a biofilter bed comprising calcareous

material derived from *Lithothamnium calcareum* allows the biofilter bed to operate with thermophilic bacteria (Thermophilic bacteria have a minimum growth temperature requirement of 45-60°C). Calcareous material derived from *Lithothamnium calcareum* may also act as a heat exchanger, transferring excess heat into the aqueous solution, which is delivered via an irrigation spray means. This would obviate the need to cool the gas before the gas contacts the biofilter bed.

It will be appreciated that the use of calcareous material derived from *Lithothamnium calcareum*, being a natural material, in a biofilter bed gives rise to an environmentally acceptable "waste" biofilter bed.

Calcareous material derived from *Lithothamnium calcareum* is associated with a slow release of nutrients and trace elements which, when used in biofilter beds, stimulates the growth of micro-organisms within the biofilter bed, leading to increased microbial activity.

Calcareous material derived from *Lithothamnium calcareum* counteracts biofilter bed acidification, by the release of magnesium and/or calcium cations. Thus, calcareous material derived from *Lithothamnium calcareum*, by its pH buffering effect, improves the retention of acid-intolerant micro-organisms in the biofilter bed.

The invention also provides a biofilter bed for the biofiltration of a gas containing at least one contaminant, the bed comprising a housing; and a packing material in the housing, the packing material comprising a calcareous material of aquatic origin.

The packing material in the housing may be in one or in many separate layers.

The biofilter bed, which communicates with a gas inlet conduit, a gas outlet conduit and a drain outlet, may include a conditioning spray means to release a micro-organism into the gas inlet conduit. The conditioning spray means is selected to condition the gas and to bring the micro-organism into intimate contact with the contaminant(s) in the gas to be filtered. The term "condition" embraces altering the temperature and/or relative humidity and/or other parameter of the gas to be filtered. The conditioning spray means may be a mechanical scrubber or, alternatively, the spray means may be an atomising nozzle, an aerosol generator or an ejector Venturi scrubber followed by a forced mixing chamber to effect mechanical scrubbing.

Advantageously, at least one strain of micro-organism is provided in association with the packing material, the or each micro-organism being selected to degrade the or each contaminant in the gas.

Also, continuous or discontinuous introduction of the aqueous suspension containing the micro-organism(s) into the gas inlet conduit by the conditioning spray means causes intimate mixing of the micro-organism(s) and the gas. This allows biological decomposition to commence before the gas contacts the biofilter bed, thereby improving the efficiency of the biofilter bed. Micro-organism introduction by the conditioning spray means into the gas inlet conduit and/or through an irrigation spray means into the housing also permits an increased and/or replenished microbial population in the biofilter bed.

Continuous recirculation and incubation of the micro-organism in an irrigation storage tank permits selection of the specific micro-organism(s) adapted to degrade the contaminant(s) present in the gas. This is particularly advantageous for the treatment of malodourous air from sewage works, composting plants, livestock and the like, since such air is likely to contain contaminants whose identity and relative concentrations will vary from day to day.

The contaminant(s) can also be recovered and removed for other uses.

An embodiment of the invention will now be described, by way of example, with reference to the accompanying drawing, which is a diagrammatic view of a biofilter bed according to the invention, incorporating a packing material according to the invention.

Referring now to the accompanying drawing, there is illustrated a biofilter bed 10 according to the invention for the biofiltration of a gas containing at least one contaminant. The biofilter bed 10 comprises a housing 12 communicating with a gas inlet conduit 14, a gas outlet conduit 16 and a drain outlet 18.

The housing 12 contains a packing material 20 according to the invention. The packing material 20 is in two layers - a first layer 20a comprising calcareous material derived from *Lithothamnium calcareum*; and a second layer 20b comprising a mixture of calcareous material derived from *Lithothamnium calcareum* and of traditional packing materials such as compost, fibrous peat, nodular peat, coir, wood chips, heather or the like. A perforated bed support 22 is located under the second layer 20b. Alternatively, a single layer (not

shown) may incorporate mixtures of packing materials as desired and, in that event, the perforated bed support 22 is located under the single layer of packing material 20.

The packing material 20 is provided with micro-organisms in and on the packing material 20, the micro-organisms being selected to degrade at least one of the contaminants in the gas to be filtered. The micro-organisms in and on the packing material 20 of each of the layers 20a and 20b may be similar to or identical with each other.

Alternatively, thermophilic bacteria may be provided in and on the first layer 20a, thereby obviating the need to cool the gas before contacting the packing material 20a. Mesophilic bacteria (minimum growth temperature requirement of 20-45°C) may be provided in and on the second layer 20b. The packing material 20 for the first layer 20a may be calcareous material derived from *Lithothamnium calcareum*, alone or in combination with another heat resistant packing material such as sintered glass, stone, sand or ceramic materials, if thermophilic bacteria are to be provided in and on the first layer 20a.

The housing 12 is provided with an irrigation spray means 42 adjacent an outlet 14a of the gas inlet conduit 14. An irrigation outlet conduit 44 provides fluid communication between the housing 12 adjacent the drain outlet 18 and an irrigation storage tank 46. The irrigation storage tank 46 contains a chamber 48 with an outlet 50 for the removal of grease, oil or other contaminants. The irrigation storage tank 46 has a liquid inlet conduit 66, for the supply of appropriate solutions, for example, nutrient solutions and/or

suspensions of micro-organisms, into the irrigation storage tank 46. The irrigation storage tank 46 also has a liquid outlet conduit 68 for the removal of, for example, sediment suspensions from the irrigation storage tank 46. The irrigation storage tank 46 is, via a pipe 56, a pump 52, a heat exchanger 54 and a pipe 57 provided with a flow control valve 58, in fluid communication with the irrigation spray means 42. The irrigation storage tank 46 is also, via the pipe 56, the pump 52, the heat exchanger 54, and a pipe 38 having a flow control valve 59, in fluid communication with a conditioning spray means or gas conditioning two-phase nozzle 25 (e.g., a Turbotak Caldyn (Trade Mark) nozzle).

The contents of the irrigation storage tank 46 are heated to a temperature and for an incubation period sufficient to permit the selective growth of micro-organisms specific for the contaminants found in the gas for biofiltration. This facilitates the selection of a micro-organism population specifically adapted to decompose the actual contaminants found in the gas for biofiltration.

The gas, e.g. odorous air, for biofiltration is introduced into the biofilter bed 10 along the gas inlet conduit 14. Humidity alone or with one or more micro-organism(s) in suspension (along the pipe 38) and air, steam or compressed contaminated air (along a line 23 having a pressure control valve 21) are both introduced into the two-phase nozzle 25 located in the gas inlet conduit 14. The gas and humidity/micro-organism(s) are atomised and are intimately mixed by the two-phase nozzle 25. Further downstream, a centrifugal, radial-bladed mixing fan (e.g. S & P type CSB-60) may be installed at right angles to the gas flow, for use as a mechanical scrubber (not shown).

The gas/humidity/micro-organism(s) then passes along the gas inlet conduit 14 and enters the housing 12 at the outlet 14a. The gas/humidity/micro-organism(s) pass from top to bottom through the first and second layers 20a and 20b of the packing material 20. As the humidity/micro-organisms pass between the individual particles and fibres of the packing material 20, the humidity/micro-organisms are adsorbed onto the packing material 20 so as to replenish the bio-layer formed in and/or on the packing material 20. As the gas passes between the individual particles and fibres of the packing material 20, the contaminants in the gas are adsorbed onto and/or into the bio-layer of the packing material 20, where the micro-organisms degrade the contaminants. The biofiltered gas passes through the perforated bed support 22 and out of the housing 12, via the gas outlet conduit 16. Sediment suspensions are removed via the drain outlet 18.

The packing material 20 is irrigated by introducing an aqueous solution, via the irrigation spray means 42 and/or nozzle 25, into the housing 12. The aqueous solution may, optionally, contain nutrients and/or trace elements for assisting micro-organism growth. The aqueous solution passes successively through the first and second layers 20a and 20b of the packing material 20 and out of the housing 12, via the irrigation outlet conduit 44. The residual aqueous solution for recirculation then passes into the chamber 48 of the irrigation storage tank 46.

The grease and/or oil or other contaminants are continuously removed, via the outlet 50. The aqueous solution then passes, via the pipe 56, the pump 52 and the heat exchanger 54, to the irrigation spray means 42 via the pipe 57 and/or to the nozzle 25 via the pipe 38.

The irrigation solution introduced via the irrigation spray means 42 or the nozzle 25 is cooled or heated using the heat exchanger 54, as required. The recirculation of irrigation solution permits the recirculation of micro-organisms which have washed off the packing material 20 during the irrigation process and permits temperature control in the biofilter bed.

The biofilter bed 10 has a co-flow configuration, where the gas to be biofiltered and the irrigation solution both pass downwards through the packing material 20. If fluidisation of the packing material 20 is desired, the direction of co-flow may be reversed, so that the gas to be biofiltered and the irrigation solution both pass upwards through the packing material 20. Alternatively, a counter-flow configuration, where the gas and irrigation solution pass in opposite directions, may be desirable.

Where the gas contains a high quantity of contaminants, additional nozzles 25, located in sequence in the gas inlet conduit 14 (not shown), may be used to increase the number of contact zones between the contaminants in the gas and the micro-organisms. In addition, the length of the gas inlet conduit 14 may be increased to increase the duration of contact prior to entry into the biofilter bed.

EXAMPLE

Three packing or test materials were evaluated in duplicate using a test rig consisting of six "laboratory-scale" filters of 1m height and 200mm diameter connected in parallel. Hydrogen sulphide was chosen as the test gas, since it is a common component of malodourous gaseous emissions from both sewage

treatment plants and the food industry. Experiments were carried out under three test regimes of hydrogen sulphide (H_2S) concentration and gas loading rate. The performance of the test materials with respect to H_2S removal was monitored. In addition, measurements of back pressure, pH and microbial counts were carried out.

The test rig comprised six acrylic columns of 200mm diameter and 1.5m height. Each column was filled to a height of 1m with test materials which were supported on a perforated perspex disc. Duplicate columns were filled with each of the test materials described below:

(i) Calcareous material derived from *Lithothamnium calcareum*;

(ii) 40:60 mixture (vol:vol) of calcareous material derived from *Lithothamnium calcareum* and of mature fibrous peat (peat fibre); or

(iii) 40:60 mixture (vol:vol) of calcareous material derived from *Lithothamnium calcareum* and of coir.

Calcareous material derived from *Lithothamnium calcareum* is supplied, under the Trade Mark SeaCal Calcified Seaweed, by Celtic Sea Minerals Ltd., of Enterprise House, Marina Commercial Park, Marina, County Cork, Ireland. SeaCal Calcified Seaweed contains approximately 87.5% $CaCO_3$. This calcareous material is identified as "*Lithothamnium calcareum*" hereinafter. Calcareous particles derived from *Lithothamnium calcareum* of between 2mm and 12mm were used in these tests. The mature or black fibrous peat is supplied by Bord na Mona of Newbridge, County Kildare, Ireland and the coir is supplied as fibre strands by Rawson Fillings Ltd., of Castle Bank Mills, Portobello Road, Wakefield, Yorkshire WF1 5PS, England.

Bulk air flow through the test rig was generated by means of a fan and the air was heated to 15-20°C. Hydrogen sulphide gas was injected into the air stream at controlled concentrations by means of a pressure regulator and rotameter. Downstream of the H_2S injection point, mains water and compressed air were supplied to an in-line nozzle at a pressure of 3.5 bar, in order to humidify the air to more than 90% relative humidity. Further downstream, a centrifugal, radial bladed, mixing fan was installed at right angles to the gas flow, for use as a mechanical scrubber.

The air flow rate into the six individual columns was regulated by means of needle valves and adjustable flow meters. Each column was equipped with sampling ports for the collection of samples of inlet and outlet gases and of test materials. Each column was fitted with an irrigation spray means to permit periodical sprinkling of the test material with mains water. Excess liquid collected into a drainage system beneath the columns.

Prior to installation, the test materials were analysed for total viable microbial counts and subsequently inoculated with a sulphur-oxidising bacteria, *Thiosphaera pantotropha*. Solutions containing nutrients (nitrogen, phosphorus, potassium) were also added to the test materials. These nutrients were added as NH_4Cl (212.6g/m^3), KH_2PO_4 (10.6g/m^3) and K_2HPO_4 (41.9g/m^3).

The test materials were installed in the columns and acclimatised for several weeks to approximately 10ppm of hydrogen sulphide, prior to commencement of the test programme. Prior to each of the three individual performance tests, the columns were acclimatised to the

test concentration of hydrogen sulphide for a number of days.

Back Pressure

The pressure differences across each column were measured using a manometer at a gas flow rate through each column of $100m^3/hr/m^3$. These measurements were carried out on three occasions, at the test programme start date, during the test programme and at the test programme final date.

TABLE 1: BACK PRESSURE MEASUREMENTS (mbar)

Test Material	Time of Sampling	Column 1	Column 2
"*Lithothamnium calcareum*"	Start	0.43	0.49
	During Test	0.44	0.42
	Finish	0.72	0.64
"*Lithothamnium calcareum*" - peat fibre	Start	4.52	3.36*
	During Test	4.16	3.30
	Finish	4.13	4.07
"*Lithothamnium calcareum*" - coir	Start	0.22	0.20
	During Test	0.17	0.16
	Finish	0.30	0.23

Note: * Test material compacted

The measured total pressure drop across duplicate columns containing calcareous material derived from *Lithothamnium calcareum* only (at $100m^3/hr/m^3$) ranged from 0.46mbar (average) at installation to 0.68mbar (average) after final tests were completed.

The measured total pressure drop across duplicate columns containing the "*Lithothamnium calcareum*" and coir mixture (at $100m^3/hr/m^3$) ranged from 0.21mbar (average) at installation to 0.27mbar (average) after completion of the final tests. Similarly, the measured total pressure drop across duplicate columns containing the "*Lithothamnium calcareum*" and peat fibre mixture (at $100m^3/hr/m^3$) ranged from 3.94mbar (average) at installation to 4.1mbar (average) after final tests were completed.

The pressure differences across columns containing "*Lithothamnium calcareum*" - coir mixture or "*Lithothamnium calcareum*" alone were low, with significantly higher back pressures in the columns containing the "*Lithothamnium calcareum*" - peat fibre mixture. The back pressure of all columns increased gradually during the test programme.

pH Measurements

Samples of test materials were collected from two ports in each column on three occasions - at the test programme start date, during the test programme and at the test programme final date. The pH of the samples was measured by rehydrating one part sample in nine parts distilled water and shaking for 10 minutes. The pH of the hydrated samples was measured using a pH meter and electrode.

TABLE 2: pH MEASUREMENTS

Test Material	Time of Sampling	Column 1		Column 2	
		Top	Bottom	Top	Bottom
"Lithothamnium calcareum"	Start	9.9	10.0	9.8	9.9
	During Test	9.5	9.8	9.8	9.9
	Finish	8.9	10.0	10.1	10.0
"Lithothamnium calcareum" - peat fibre	Start	9.1	8.7	9.1	9.1
	During Test	9.2	9.1	9.0	9.1
	Finish	9.1	9.1	9.4	9.3
"Lithothamnium calcareum" - coir	Start	8.3	9.2	8.9	9.1
	During Test	9.1	9.3	8.9	9.5
	Finish	9.3	9.6	8.8	9.4

The pH of each test material was quite high due to the presence of calcareous material. Although microbial degradation of H_2S results in the formation of sulphuric acid which can cause a decrease in the pH of packing materials, each test material displayed a stable pH over the duration of the test programme. It would be expected that these packing materials, being pH stable, would be less susceptible to aging phenomena.

Microbiological Analysis

Samples of test materials were analysed for total microbial count prior to installation in the columns. Materials were also collected from each column on the final test date. These samples were analysed for both total microbial and total fungal counts. Total

microbial counts were determined by plating 1ml of suitably diluted samples on yeast extract agar. Agar plates were incubated at 30°C for 3 days before counting. The microbial population is expressed as the number of colony-forming units per gram (wet wt.) of test material (cfu/g), which allows the calculation of the total microbial count in terms of the number of colony-forming units per m^3 of test material (cfu/m^3) (assuming the apparent relative densities of calcareous material derived from *Lithothamnium calcareum* and of peat fibre are 1.05 - 1.08 and 0.3, respectively). Since the apparent relative density of calcareous material derived from *Lithothamnium calcareum* is considerably higher than that of peat fibre, namely, 1.05-1.08 compared with 0.3, expression of the total microbial counts per unit volume (m^3) permits direct comparison of the microbial counts for these packing materials.

Total fungal counts were determined by plating 1ml of suitably diluted samples on potato dextrose agar. Plates were incubated at 22°C for 5 days. The fungal population is expressed as the number of colony-forming units per gram (wet wt.) of test material (cfu/g).

TABLE 3: MICROBIOLOGICAL ANALYSIS

Time of Sampling	Test Material	Total microbial count (cfu/g)	Total fungal count (cfu/g)	Estimated total microbial count (cfu/m^3)
Start	*"Lithothamnium calcareum"*	$2.9 \times 10^{6*}$	nd	$3045 \times 10^{9*}$
	Peat Fibre	$1.5 \times 10^{5**}$	nd	$45 \times 10^{9**}$
	Coir	3.3×10^{4}	nd	nd
	"Lithothamnium calcareum"/peat	$2.08 \times 10^{6***}$	nd	$1245 \times 10^{9***}$
	"Lithothamnium calcareum"/coir	nd	nd	nd
Finish	*"Lithothamnium calcareum"* Column 1	3.6×10^{6}	3.2×10^{4}	3780×10^{9}
	"Lithothamnium calcareum" Column 2	4.4×10^{6}	7.9×10^{4}	4620×10^{9}
	"Lithothamnium calcareum"/peat Column 1	5.5×10^{6}	5.0×10^{4}	3300×10^{9}
	"Lithothamnium calcareum"/peat Column 2	6.0×10^{6}	6.0×10^{4}	3600×10^{9}
	"Lithothamnium calcareum"/coir Column 1	3.5×10^{5}	1.8×10^{6}	nd
	"Lithothamnium calcareum"/coir Column 2	8.0×10^{6}	2.8×10^{6}	nd

Notes:
* All moulds present
** Few moulds present
*** Calculated on the basis of a 40:60 mixture (by volume)
nd Not determined

The total microbial counts increased throughout the test programme for each test material. Dry, untreated calcareous material derived from *Lithothamnium calcareum* provides a poor substrate for bacterial growth and, initially, mainly moulds were present. However, as a result of wetting and the addition of nutrients, the bacterial population became dominant with only about 1-2% fungi (>90% being moulds) present. A similar situation was found for the calcareous material derived from *Lithothamnium calcareum*-peat fibre mixture, with a two-three fold increase in the total microbial population during the test programme and about 1% fungi (>90% being moulds) present at the completion of the test programme. The microbial population in the "*Lithothamnium calcareum*"-coir mixture was largely comprised of moulds. Coir appears to be a poor substrate for bacterial growth, as evidenced by a poor initial microbial count of 3.3×10^4 cfu/g - this may be due to the poor water absorption capacity of coir.

The microbial counts for each of the test materials were, at the end of the test programme, at the lower end of the range for other test materials, e.g., peat fibre alone as a test material can have a microbial count of $10^7 - 10^9$ cfu/g or $3{,}000\text{-}300{,}000 \times 10^9$ cfu/m^3. This may be explained by the pH of the test materials (8.3 - 10.1), the optimum pH range for growth and activity of *Thiosphaera pantotropha* being 8.0 - 8.2. It will be appreciated that alteration of the mixture of test materials used could result in higher microbial counts and perhaps better performance results.

Performance Measurements

The performance of the test materials with respect to hydrogen sulphide removal was assessed by

comparing the concentrations of H_2S in the inlet gas stream at the column inlet and in the foot spaces of the columns. The gas samples were collected by evacuation of 250ml glass bulbs using a hand pump. Analysis was carried out using a Hewlett Packard 5890 gas chromatograph coupled with a flame photometric detector.

The following three test regimes were used:

Test 1	Inlet gas concentration:	104ppm H_2S
	Gas loading rate:	100m^3/hr/m^3
	Spray nozzle on.	
	Mixing fan off.	
Test 2	Inlet gas concentration:	131.8ppm H_2S
	Gas loading rate:	100m^3/hr/m^3
	Spray nozzle on.	
	Mixing fan off.	
Test 3	Inlet gas concentration:	109ppm H_2S
	Gas loading rate:	150m^3/hr/m^3
	Spray nozzle on.	
	Mixing fan on.	

The results of performance tests with respect to H_2S removal are shown in Table 4 below. Similar results were obtained for "*Lithothamnium calcareum*" alone and the "*Lithothamnium calcareum*"-coir mixture - the performance was poor at a loading of 100m^3/hr/m^3 and an inlet H_2S concentration of 132ppm (Test 2). At the lower H_2S concentration of 104 or 109 ppm, the performance was excellent at a loading of 100m^3/hr/m^3 (Test 1) but decreased to 59.7% removal (average) at a higher loading of 150m^3/hr/m^3 (Test 3). In the case of the "*Lithothamnium calcareum*"-peat fibre mixture, performance was somewhat variable between duplicate

columns, with column 1 giving consistently better performance, and there was evidence of good performance of this test material at higher H_2S concentrations than for other test materials. However, this test material demonstrated a higher back pressure.

In the case of "*Lithothamnium calcareum*" on its own and the "*Lithothamnium calcareum*"-coir mixture, there was evidence of good performance at higher flow-rates. Both these test materials exhibited a more consistent performance than the "*Lithothamnium calcareum*"-peat fibre mixture. In addition, both these test materials demonstrated lower back pressures.

TABLE 4: PERFORMANCE TESTS

Test	Gas loading ($m^3/hr/m^3$)	Inlet conc. (ppm)	Test Material	Column	Outlet Conc. (ppm)	Removal (%)
1	100	104.0	"*Lithothamnium calcareum*"	1	2.6	97.4
				2	n.d.	>99.9
			"*Lithothamnium calcareum*" - Peat Fibre	1	1.9	98.1
				2	3.1	97.0
			"*Lithothamnium calcareum*" - Coir	1	22.4	78.5
				2	4.7	95.5
2	100	131.8	"*Lithothamnium calcareum*"	1	100.0	24.1
				2	109.6	16.8
			"*Lithothamnium calcareum*" - Peat Fibre	1	46.8	64.5
				2	95.5	25.5
			"*Lithothamnium calcareum*" - Coir	1	109.6	16.8
				2	107.2	18.7
3	150	109.0	"*Lithothamnium calcareum*"	1	43.7	59.9
				2	44.7	59.0
			"*Lithothamnium calcareum*" - Peat Fibre	1	33.9	68.9
				2	77.6	28.8*
			"*Lithothamnium calcareum*" - Coir	1	43.6	60.0
				2	43.7	59.9

Notes: n.d.: none detected (<0.05ppm)

* : Possibly caused by some short-circuiting resulting from the taking of physical samples for pH analysis. The lower back pressure for column 2 in Table 1 would support this explanation.

All three test materials were found to be high performance packing materials for the biofiltration of H_2S up to a concentration of about 100ppm H_2S at a gas loading of $100m^3/hr/m^3$, with an average H_2S removal at 94.4% and typical H_2S removal rates of >97%.

Both "*Lithothamnium calcareum*" and the "*Lithothamnium calcareum*"-peat fibre mixture were found to be suitable substrates for bacterial growth and had a similar microbial count per unit volume at the end of the test programme. Final microbial counts for these test materials were just within the range of values normally found in treated peat fibre alone. Higher microbial counts might be achieved if the pH was lowered somewhat to, e.g., pH 8.0 - 8.2. The growth and activity of *Thiosphaera pantotropha* is higher at a pH below its optimum pH range (e.g., pH 7) than above its optimum pH range (e.g., pH 9-10). The pH of the test material might be reduced by lowering the proportion of "*Lithothamnium calcareum*" in the mixture. Continuous exposure to high concentrations of H_2S might also result in a pH reduction. Alternatively, use of a sulphur-oxidising bacteria with a higher optimum pH range might be considered.

The back pressures of "*Lithothamnium calcareum*" and of the "*Lithothamnium calcareum*"-coir mixture were very low, which makes them very suited for biofilter beds. The back pressure of the "*Lithothamnium*

calcareum"-peat fibre mixture was somewhat higher than that of the other materials tested and also than that obtained for a peat fibre/heather mixture under the same conditions (0.2 mbar). The back pressure of the "*Lithothamnium calcareum*"-peat fibre mixture could be reduced by altering the ratio of packing materials in the biofilter bed. It will be appreciated that the back pressure of any packing material can be altered by changing the ratio of packing materials in the biofilter bed.

CLAIMS:

1. A packing material for biofiltration of a gas containing at least one contaminant, the packing material comprising a calcareous material of aquatic origin.

2. A packing material according to Claim 1, in which the calcareous material is of marine origin.

3. A packing material according to Claim 2, in which the marine calcareous material is derived from a marine alga or a marine calcareous sand.

4. A packing material according to Claim 3, in which the marine calcareous material is derived from *Lithothamnium calcareum*.

5. A packing material according to Claim 4, which comprises calcareous material derived from *Lithothamnium calcareum* in admixture with a known packing material selected from the group consisting of peat, compost, wood chips, heather and coir, the calcareous material derived from *Lithothamnium calcareum* being present in an amount of 20%-60% (vol).

6. A packing material according to Claim 5, in which the calcareous material derived from *Lithothamnium calcareum* is present in an amount of 40% (vol).

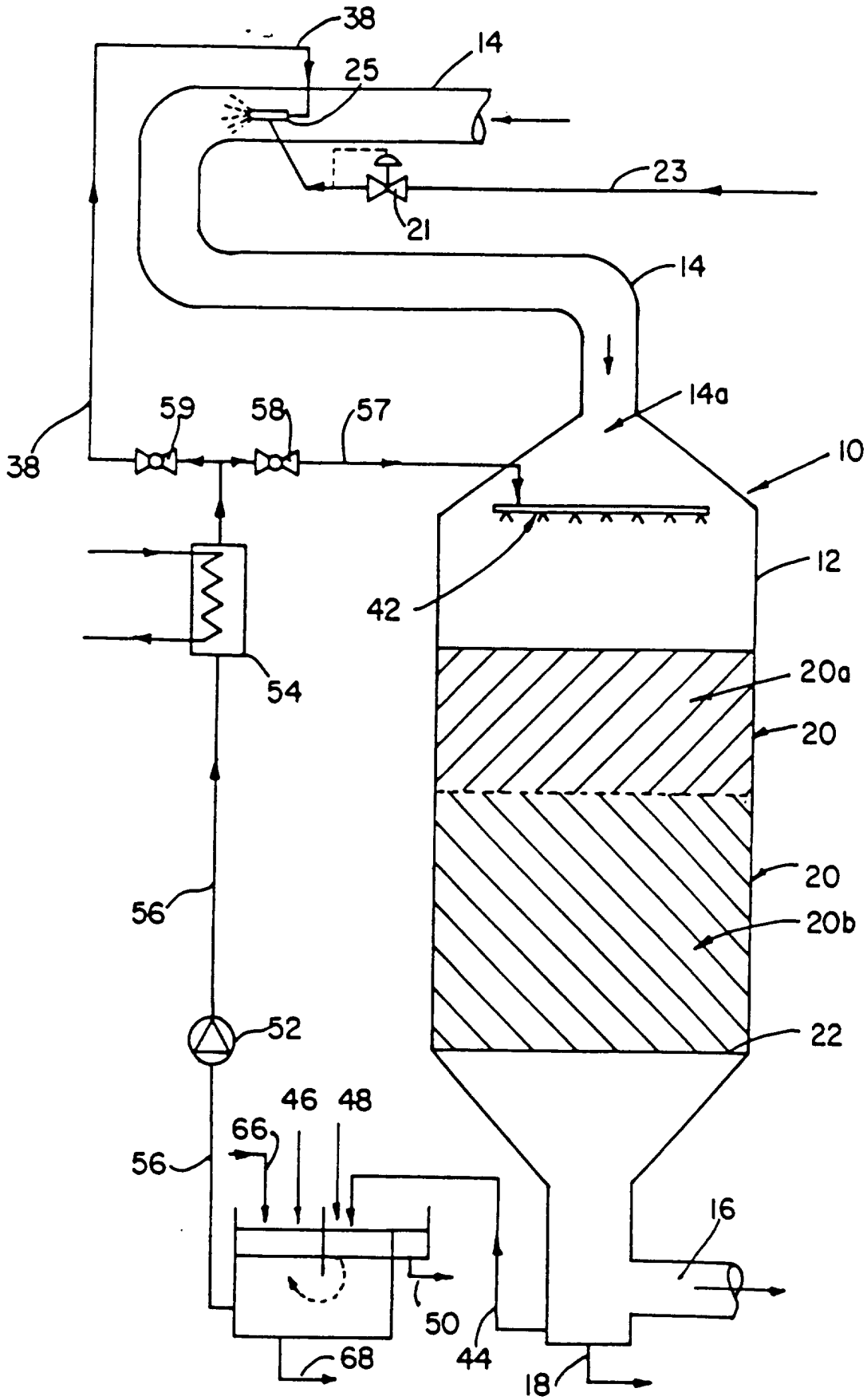
7. A packing material according to Claim 1, the packing material consisting essentially of calcareous material derived from *Lithothamnium calcareum*.

8. A biofilter bed for the biofiltration of a gas containing at least one contaminant, the bed comprising a housing; and a packing material in the housing, the

packing material comprising a calcareous material of aquatic origin.

9. A biofilter bed according to Claim 8, in which at least one strain of micro-organism is provided in association with the packing material, the or each strain being selected to degrade the or each contaminant in the gas.

10. A biofilter bed according to Claim 9, in which the contaminant is H_2S and the micro-organism is *Thiosphaera pantotropha*.


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INTERNATIONAL SEARCH REPORT

International Application No PCT/IE 93/00030

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01D53/00; B01J20/24

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01D ; B01J ; C02F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	WO,A,8 910 179 (EWERS ET AL.) 2 November 1989 see page 4, paragraph 5 - page 5, paragraph 1; claims 1-8	1-4,7
Y		5,8,9

X	FR,A,2 655 563 (SAPS ANTI-CORROSION SA) 14 June 1991 see page 5, line 10 - line 35 see page 7, line 21 - line 25; claims 1-17; figure 1	1-3,8,9
Y		4,7,10

X	DATABASE WPI Section Ch, Week 8847, Derwent Publications Ltd., London, GB; Class D22, AN 88-334706 & JP,A,63 248 436 (SANO M) 14 October 1988 see abstract	1-3

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° Special categories of cited documents :[10]

"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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

1

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
25 AUGUST 1993	16.09.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	EIJKENBOOM T.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	FR,A,2 608 587 (TIMAC SA) 24 June 1988. see page 1, line 1 - page 2, line 9; claims 1-3	4,7
Y	EP,A,0 237 091 (SHELL INT RES MIJ) 16 September 1987 see claims 1-7	10
Y	FR,A,2 591 122 (SAPS ANTICORROSION) 12 June 1987 see page 3, line 14 - line 16; claims 1-10; figure 1	5,8,9
A	WO,A,8 607 346 (SOCIETE LEMAIRE) 18 December 1986 see the whole document	1-5,7,8
A	FR,A,2 460 710 (BASSET) 30 January 1981 see claims 1-9	1-4,7,8

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

IE 9300030
SA 74330

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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FR-A-2608587	24-06-88	None	
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