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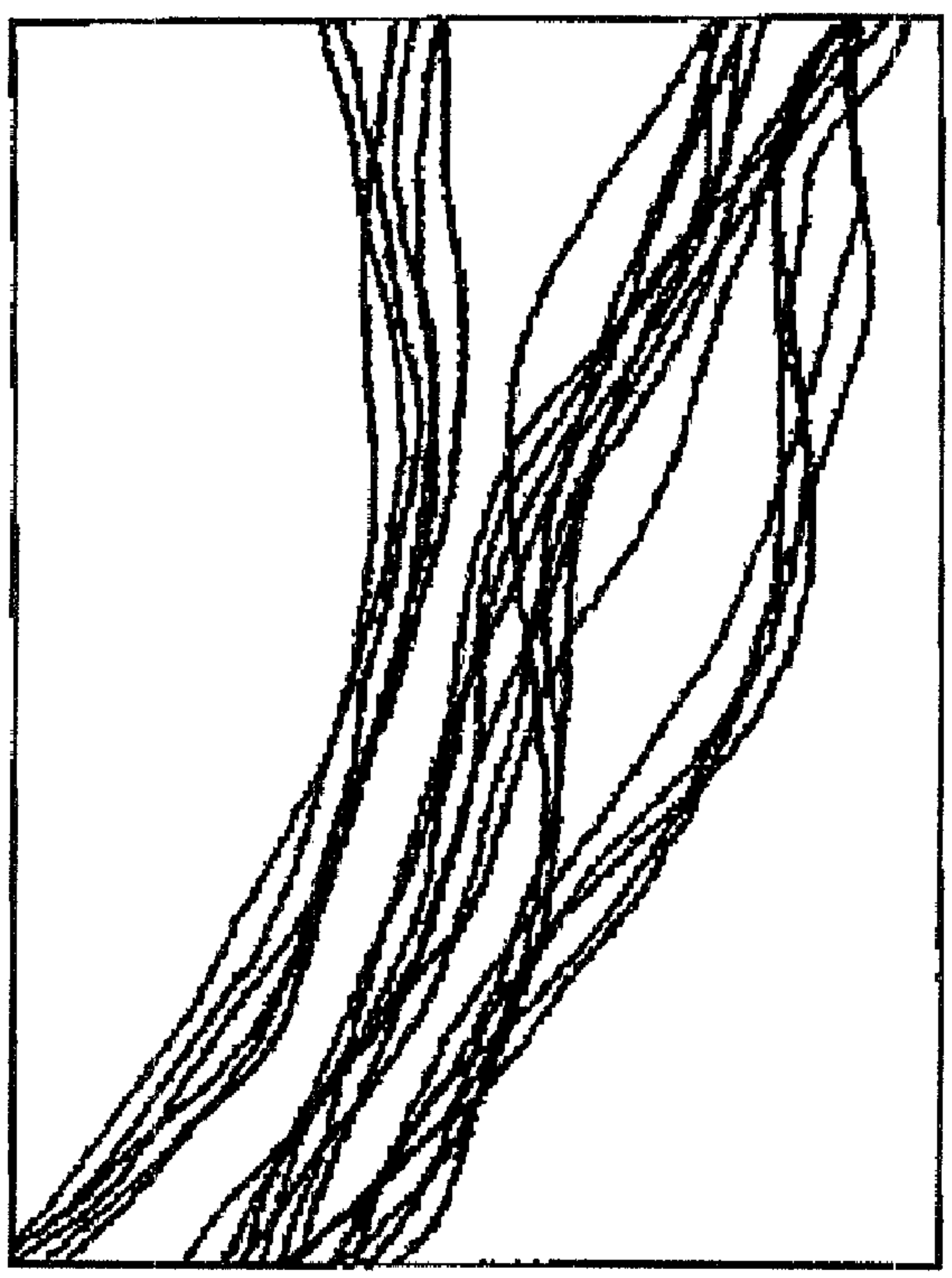
(54) Titre : METHODE A BASE DE FILM BIOLOGIQUE SUR MEMBRANE POUR EFFECTUER LA REDUCTION AUTOTROPHE

(54) Title: MEMBRANE SUPPORTED BIOFILM PROCESS FOR AUTOTROPHIC REDUCTION



PMP Textile Fibre

(57) Abrégé/Abstract:
A hollow gas transfer fibre is arranged in tows and potted into a module. The module may be used to treat wastewater by supplying hydrogen containing gas via the interior of the fibers to a biofilm present on an exterior surface of the fibers.

ABSTRACT OF THE DISCLOSURE

A hollow gas transfer fibre is arranged in tows and potted into a module. The module may be used to treat wastewater by supplying hydrogen containing gas via the interior of the fibers to a biofilm present on an exterior surface of the fibers.

Title: Membrane supported biofilm process for autotrophic reduction

Field of the invention

[0001] This invention relates to membrane supported biofilm processes and apparatus generally, and to autotrophic denitrification using such apparatus in particular.

Background of the invention

[0002] U.S. Patent No. 5,116,506 to Williamson et al. describes a gas permeable membrane which divides a reactor vessel into a liquid compartment and a gas compartment. A biofilm is grown on the gas permeable membrane on the liquid side of the membrane. The gas permeable membrane is supported by the structure of the membrane itself. The biofilm is chosen from bacteria to degrade certain pollutants by means of anaerobic fermentation, aerobic heterotrophic oxidation, dehalogenation, and hydrocarbon oxidation. This is accomplished by means of oxygen and alternate gases (i.e., methane) through the gas permeable membrane to certain bacteria growing on the liquid side of the gas permeable membrane.

Summary of the invention

[0003] It is an object of the present invention to improve on the prior art. It is another object of the present invention to provide a gas transfer module made using tows of a hollow fibre membrane. It is another object of the present invention to provide a membrane supported biofilm module for treating wastewater, particularly wastewater rich in nitrates and other oxidized species.

[0004] In one aspect, the invention provides a tow of hollow fibers. The fibers are fine, for example with an outside diameter (OD) of 100 μm or less. To facilitate building modules with minimal reduction in the effective surface area of the fibres, the fibres are processed or used as tows over a significant portion, for example one half or more, of their length. Modules may be made directly from the tows without first making a fabric. The tows may also be made into open fabrics to facilitate potting, for example along the edges of the fabric sheet, while leaving significant portions of the fibres as tows, for example a portion between the edges of the fabric sheet. The modules made from tows may be potted at both ends, or one end only with the other end left unpotted with fibre ends open to permit exhaust gas to escape. A single header module may have lower cost than a double header module. A single header module may be inserted in a vertical configuration with the header at the bottom and the fibres floating upwards. Such a module may be aerated from outside the module to remove accumulations of trash and solids. Feed may also be screened, for example through a 0.5 mm screen, to reduce trash in the feed before it enters the reactor. Where the tow module is used in a downstream stage of a multi-stage reactor, the upstream stage may also reduce the amount of trash fed to the tow module reactor. More preferably, this reactor may be used to treat secondary effluent in a municipal or industrial wastewater treatment plant, which is rich in nitrates and other oxidized species but is relatively free of trash.

[0005] In another aspect, a reactor is provided for treating wastewater rich in nitrates and other oxidized species, but poor in COD, for example 100 mg/L or less or 20 mg/L or less of COD. The reactor can include a module having an hydrogen transfer area of equal to or over 10 times the outer surface area of a biofilm attached to the fibres. A pure hydrogen or hydrogen containing gas stream can be fed to the lumen of the module, with reaction occurring in the biofilm grown on the surface of the fibre. Hydrogen depleted gas can be discharged after or without incineration, depending content of impurities.

[0006] In another aspect, a reactor is used to grow autotrophic microorganisms on the outside surface of the fibres and tows by supplying hydrogen to the lumen of the fibre. Wastewater containing oxidized species, particularly nitrates present in secondary wastewater effluent, can be fed to this reactor and denitrification reaction can occur in the biofilm. Harmless nitrogen gas is generated and can be discharged to the environment.

Wastewater with very low nitrate nitrogen concentration (< 10 mg/L, or < 2 mg/L) can be safely discharged to the receiving stream.

[0007] In another aspect of this invention, the biofilm surface area is adapted to ensure that the hydrogen to microorganism ratio (H/M) is such that the endogenous respiration of microorganisms is comparable in magnitude to microbial growth rate to maintain a stable biofilm.

[0008] In another aspect of this invention, the autotrophic reduction reactor is fed a gas from anaerobic digester on site. This gas may contain hydrogen, carbon dioxide and methane. The gas is passed through the lumen of hollow fibre. Hydrogen and some methane can be consumed by the autotrophic microorganisms and the gas leaving the membrane lumen can be returned to the anaerobic digester gas systems for further heat recovery or burn-off to destroy these gases prior to discharge. Such gas may be treated to remove mist, and cooled to remove excess moisture, but may require no or little other purification step to increase hydrogen enrichment. The fibre described in the invention may provide the hydrogen purification step.

[0009] In another aspect of this invention, the anaerobic digester may be modified to insert an acid conversion stage to maximize production of hydrogen.

[0010] In another aspect of this invention, the methane rich gas produced in an anaerobic digester may be converted to a hydrogen and carbon dioxide rich stream by the commonly known and practiced steam reforming process. However, such gas may not be further purified by removing carbon dioxide and a mixture of hydrogen and carbon dioxide may be fed directly to the lumen side of the module described in this invention. The exhaust gas may contain some unreacted hydrogen and may be burned off to destroy this prior to discharge.

[0011] In another aspect of this invention, natural gas or liquefied petroleum gas may be converted to a hydrogen and carbon dioxide rich stream by the commonly known and practiced steam reforming process.

However, such gas may not be further purified by removing carbon dioxide and a mixture of hydrogen and carbon dioxide may be fed directly to the lumen side of the module described in this invention. The exhaust gas may contain some unreacted hydrogen and may be burned off to destroy this prior to discharge.

[0012] In another aspect of this invention, the bioreactor described above may be operated as a continuously stirred tank reactor with generally oxidized species concentration, and particularly nitrate concentration in secondary effluent close to the discharge concentration to ensure uniform rate of reaction at the biofilm surface.

[0013] In another aspect of this invention, the bioreactor may be operated under plug flow conditions to maximize reaction rates. This is particularly true of wastewater streams containing very low concentrations of toxic species such as chlorates and arsenates.

Brief description of the drawings

[0014] Embodiments of the invention will be described below with reference to the following figures.

[0015] Figure 1 is a photograph of a membrane fiber.

[0016] Figure 2 is an elevation view of the fibres potted as tows.

[0017] Figure 3 is a photograph of a bench scale test module using tows of fibres.

[0018] Figure 4a is a photograph of an open fabric made of tows.

[0019] Figure 4b is a top view of a sheet module using sheets of the fabric of Figure 4a.

[0020] Figures 5 is a graph showing the results of experiments with the module of Figure 4b.

Detailed description of the embodiments

[0021] Figure 1 shows a textile polymethyl pentene (PMP) fibre with 45 micron outside diameter and 15 to 30 micron inside diameter. The fibre is made by a melt extrusion process in which the PMP is melted and drawn through an annular spinnerette. The raw polymer used was MX-001, produced by Mitsui Petrochemical. The fibres are hollow inside but non-porous with dense walls. Other fibres may also be used, for example stretched microporous PE or PP fibres, treated to be hydrophobic, may be used. The fibres may have various diameters and may be fine fibers having outside diameters of less than 100 microns, for example between 30 and 100 microns or between 50 and 60 microns. Oxygen or other gases may travel through the fibre walls.

[0022] Figure 2 shows a module with fibres arranged and potted in tows of fibres. The tows are made of a loose collection of a plurality of fibres 10, for example between 1 and 200 or 16 to 96 fibres. The fibres may be lightly twisted together or left untwisted. The fibres may be curled, crimped or undulating to provide three dimensional structure to the each potted row. Curling may be achieved by re-winding the fibres onto a bobbin while varying the tension on the fibres. The individual fibres remain separable from each other in the tow. Such a tow, when coated with a thin biofilm, for example of less than 1 mm thickness, may provide a ratio of gas transfer area through the fibre walls to biofilm outer surface area ($SA_{oxygen}/SA_{biofilm}$) of less than 2.5, less than 1 or between 0.1 or 0.2 and 1. Inert fibres may be added to the tow to strengthen it if required.

[0023] Each tow is potted into a plug of resin so that its ends are open at one face of the resin. The plug of resin is glued into a plastic header enclosure having a port which forms a header connecting the port to the open ends of the fibers through a cavity. There are two headers, one associated with each end of the fibres, although modules with only an inlet header may also be made. With two headers, air or other gases may be input into one header, flow through the fibres and exhaust from the second header. Tows are potted in a resin such as polyurethane, and the potted ends are cut to expose the fibre lumen. Alternately, a fugitive potting material may be used to block off fibre ends, as described in U.S. Patent No. 6,592,759, or other potting methods may be used. In Figure 2, the number of tows and the number of fibers per tow are both small for clarity in the drawing and may be much larger in practice.

[0024] Figure 3 shows a bench scale module made by potting 100 tows, each of 96 fibres as shown in Figure 1, into an opposed pair of headers. The module was tested to treat a feed water in a batch process. In the test process, the module was located in a tank filled to 4 L of synthetic wastewater. The tank was drained and filled with fresh feed every 2 to 7 days. Air was applied to the module at 30 mL/min. A biofilm of stable thickness grew on the module for a period of over 6 months. The biofilm was essentially endogenous, its rate of growth generally equal to its rate of decay, except that a small part of the biofilm broke off and was discharged with some of the tank drains.

[0025] The module and reactor of Figure 3, with autotrophic microorganisms grown on the surface of the fibre, could be used to treat wastewater streams containing oxidized species such as secondary effluent from a wastewater treatment plant containing a high level of nitrate. Our calculations based on kinetics of autotrophic denitrification, show that the hydrogen to microorganism ratio must be less than 0.05 g hydrogen consumed/ g volatile suspended solids (VSS) per day, and preferably less than 0.026 g of hydrogen/g VSS /d to maintain conditions such that endogenous respiration of microorganisms generally equals growth, resulting in a stable biofilm.

[0026] Figure 4a shows an open fabric made by weaving tows through the shuttle of a loom and crossing the tows with an inert fibre only along the edges of the fabric. The fabric is approximately 1.3 m wide, that is it has active fibres of about 1.3 m long, and has inert fibers woven perpendicularly to the tows in a strip of about 2 cm along the edges. The tows remain unrestrained between these strips. The resulting roll of fabric is cut into sections of about 20-200 cm or 30-60 cm width to make individual sheets. The sheets are cut along the woven edges to open the ends of the fibres and potted with a 0 to 10 mm space between them into one or a pair of opposed headers. Depending on the potting method used, the fibres may be cut open either before or after they are inserted into the potting resin.

[0027] Referring to Figure 4b, 1 to 100 or 8-20 sheets may be potted into a pair of headers to produce a sheet-style tow module (also referred to herein simply as a "sheet module"). The sheet module may be assembled in cassettes and placed in a bioreactor to which a nitrate rich stream is introduced. Hydrogen rich gas may be introduced in the lumen and the wastewater treated to reduce nitrate prior to discharge on the autotrophic biofilm grown on the surface.

[0028] In a batch process, the concentration of the wastewater generally decreases towards the end of each processing period. Demand for hydrogen supplied to the biofilm also decreases and so the gas supply to the modules may be reduced. Modules using fibres at least partially in the form of tows allows a very high surface area for hydrogen transfer and biofilm growth. Tow modules (whether or not sheet-style) are particularly useful in treating wastewater having a low nitrate concentration, 100 mg/L or less of COD and 50 mg/L or less of nitrates, and 5 mg/L or less of chlorates, because they provide large surface areas. Pressure loss through the fine fibre lumens is not limiting with the amount of air supply required to deliver oxygen to a biofilm treating low oxidant wastewater.

[0029] Although tow modules may be useful for treating other wastewaters as well, tow modules can be used where the initial feed has a low oxidant concentration, or as a second or third stage behind other treatment processes or apparatus that reduce the oxidant concentration of stronger feedwaters. With industrial wastewater or secondary effluent or other feeds, for example feeds having a nitrate of 1,000 mg/L or more, a two stage apparatus may be used. In a first stage, membrane supported biofilm modules in the form of a fabric sheet are used as described in U.S. Provisional Application No. 60/447,025, which is incorporated herein in its entirety by this reference to it. The outlet from a reactor containing these modules is fed to a reactor containing tow modules as described in this document which provides second stage treatment.

Example 1

[0030] A batch H_2 denitrification process was tested in a small sheet reactor similar to that described in U.S. Provisional Application No. 60/447,025. In the present example, the reactor was provided with sheet modules constructed of tows, similar to that of Figure 4b (above). The test involved growing autotrophic microorganisms (biofilm) on the surface of the sheet by providing hydrogen to the lumens of the fibers of the tows. The reactor working volume was 20 litres, the effective sheet area was 0.108 m^2, and the temperature was about 20°C. The hydrogen pressure was about 2 psi.

[0031] Biofilm on the sheet was generated aerobically to a thickness of about 1 mm using synthetic sewage. The biofilm was acclimated with pure hydrogen gas for two days before the first run. The gas discharge port on the module was closed to feed hydrogen in a dead-end manner. Municipal tapwater, spiked with $NaNO_3$ (45 mg/L NO_3-N) and $NaCO_3$ (100 mg/L $CaCO_3$) was used as the substrate. No agitation was used. The sheet was removed to stir the tank immediately prior to sampling (once per day). The reaction rate was steady at approximately 2 g NO_3-N/m^2/d from 45 to 3 mg/L. The reaction rate dropped to about 0.3 g/m^2/d at final concentration of 0.6 g/L.

[0032] Figure 5 shows the concentration of nitrate (as total nitrogen in mg/L) as a function of time in the reactor. Generally, in biofilm processes, the rate of reaction in the biofilm is directly proportional to the concentration of the substrate. To the inventor's surprise, the above results show that the relationship between time and concentration of nitrate, expressed as Total Nitrogen, is constant down to 2 mg/L. It is therefore possible to use a continuously stirred tank, operating at a concentration of 2 mg/L of nitrate expressed as Total Nitrogen. Advantageously, a constant reaction rate throughout the biofilm is achieved, providing uniform biofilm growth and maintenance. Overall treatment rates can be controlled to below a rate at which endogenous respiration equals microbial growth to maintain self-sustaining biofilm, while producing high quality effluent at a high rate.

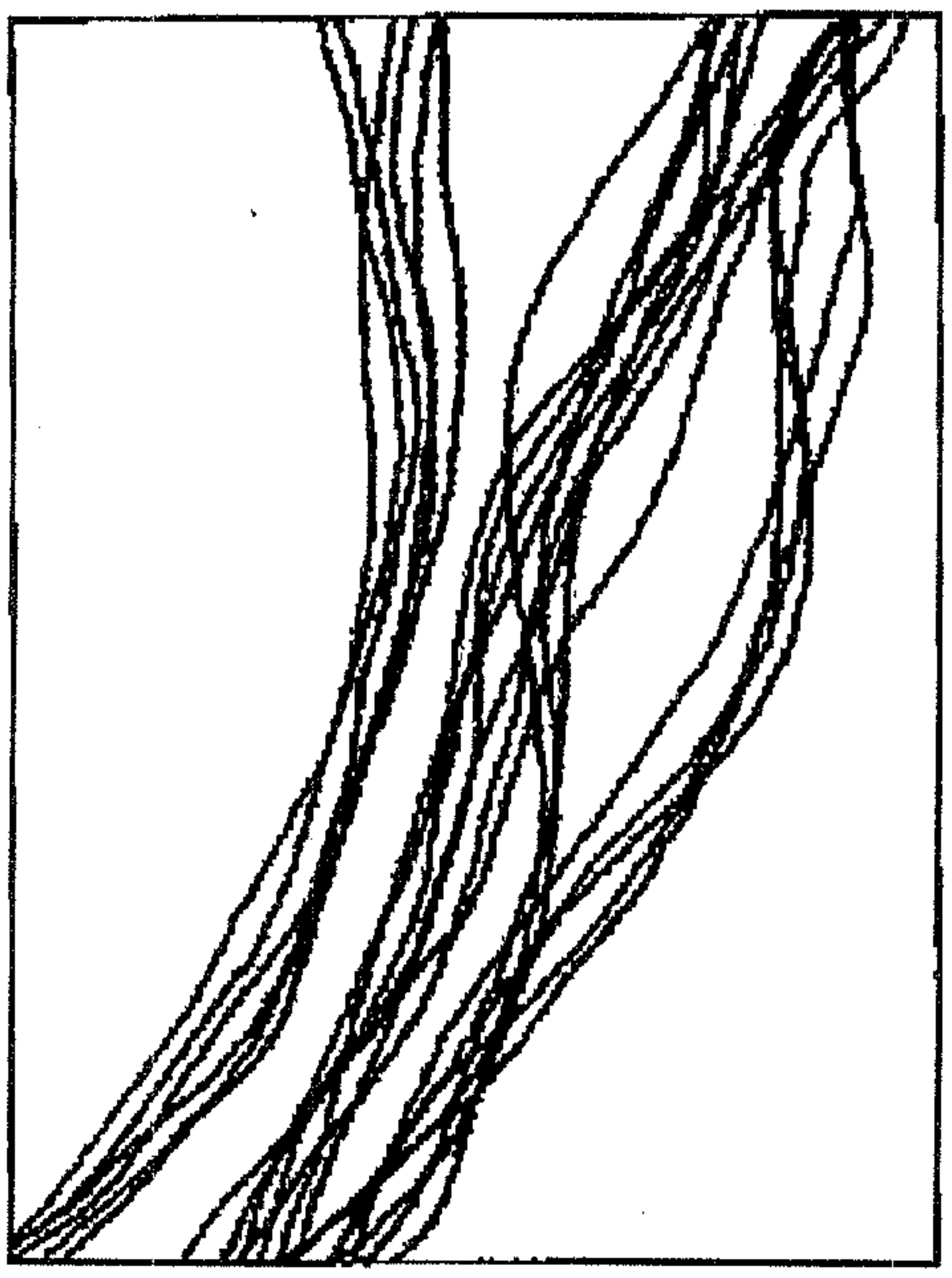
Claims:

We claim:

1. A method of treating wastewater comprising:

a) providing a module having tows of fibers, the fibers each having an exterior surface exposed to the wastewater, a hollow interior, and a gas permeable wall between the interior and exterior surface;

b) providing at least one of hydrogen and methane gas to the hollow interiors of the fibers, the gas penetrating the walls for feeding biofilm on the exterior surface of fibers.



PMP Textile Fibre

FIG. 1

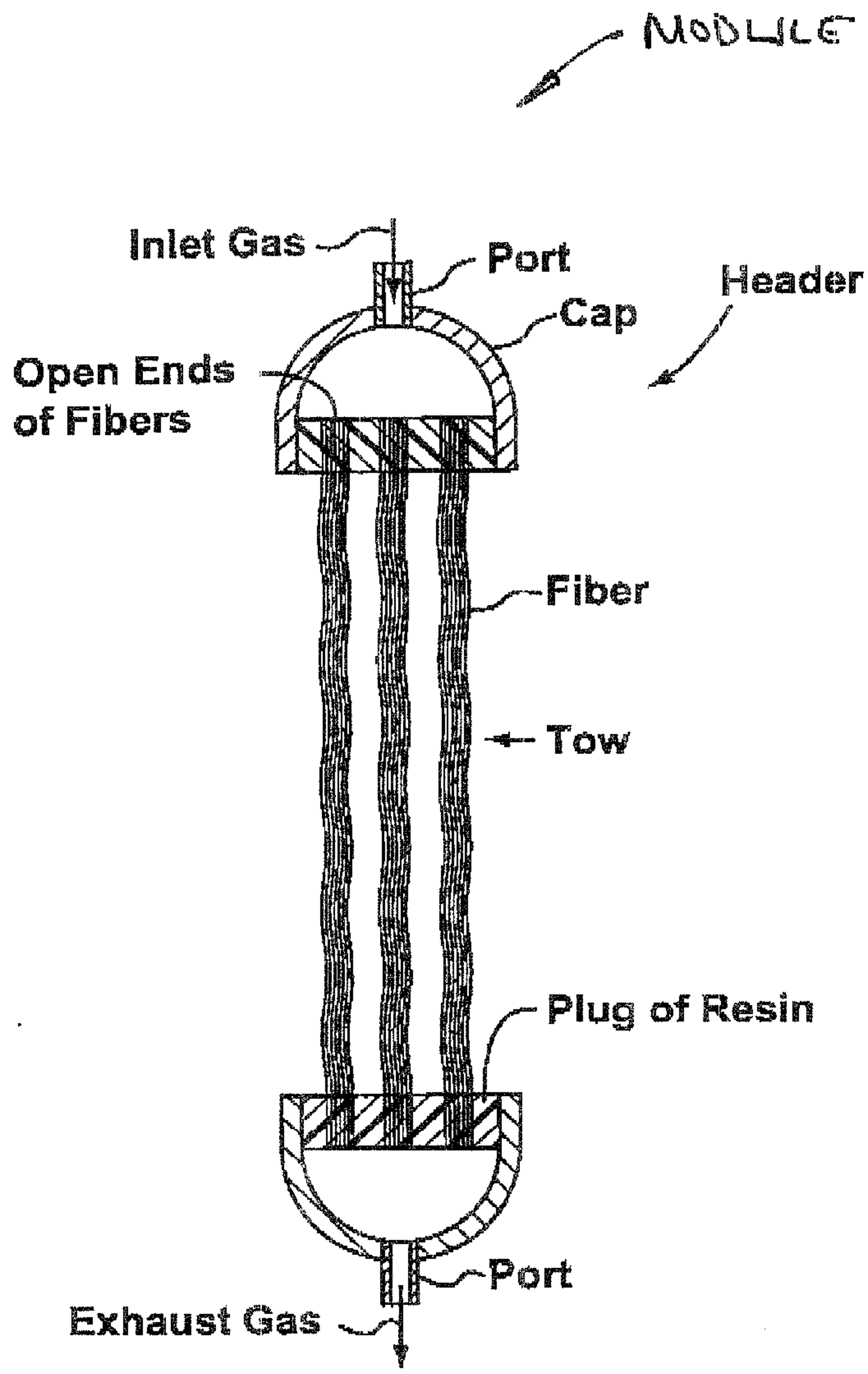

MODULE
Inlet Gas
Port
Header
Cap
Open Ends
of Fibers
Fiber
Tow
Plug of Resin
Port
Exhaust Gas

FIG. 2

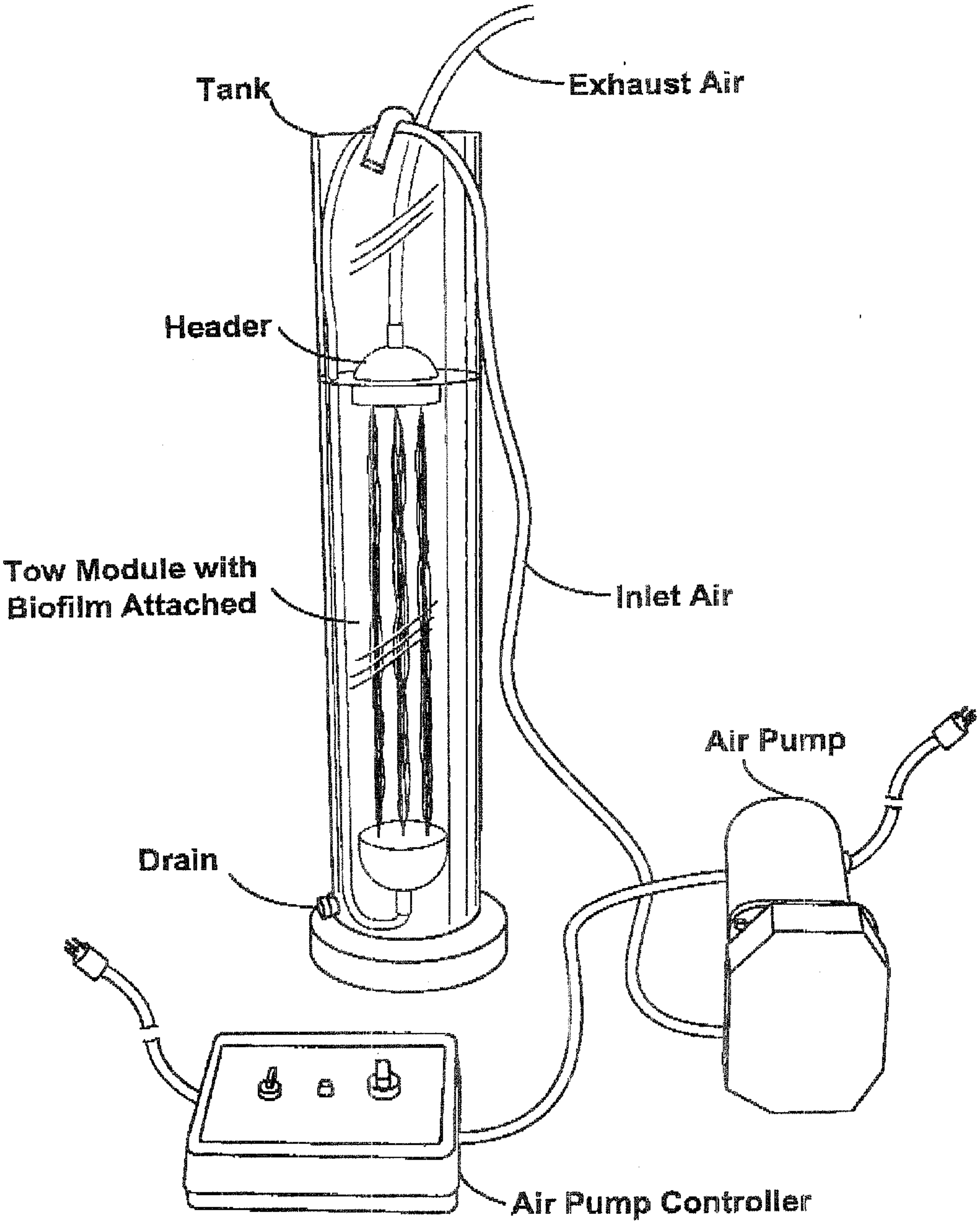

Tank
Exhaust Air
Header
Tow Module with
Biofilm Attached
Inlet Air
Air Pump
Drain
Air Pump Controller

FIG. 3

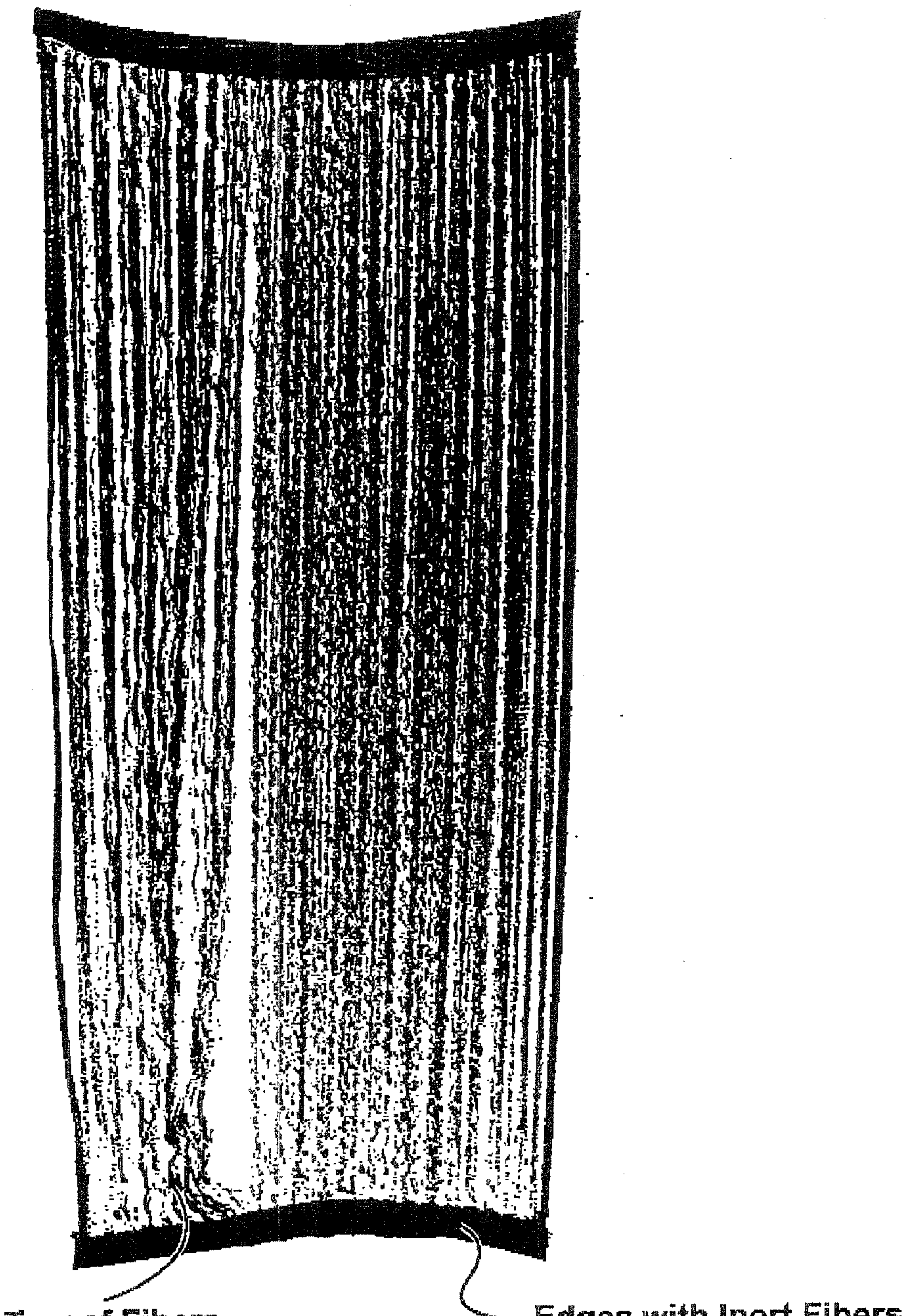

Tow of Fibers
Edges with Inert Fibers
Perpendicular to Tows

FIG. 4a

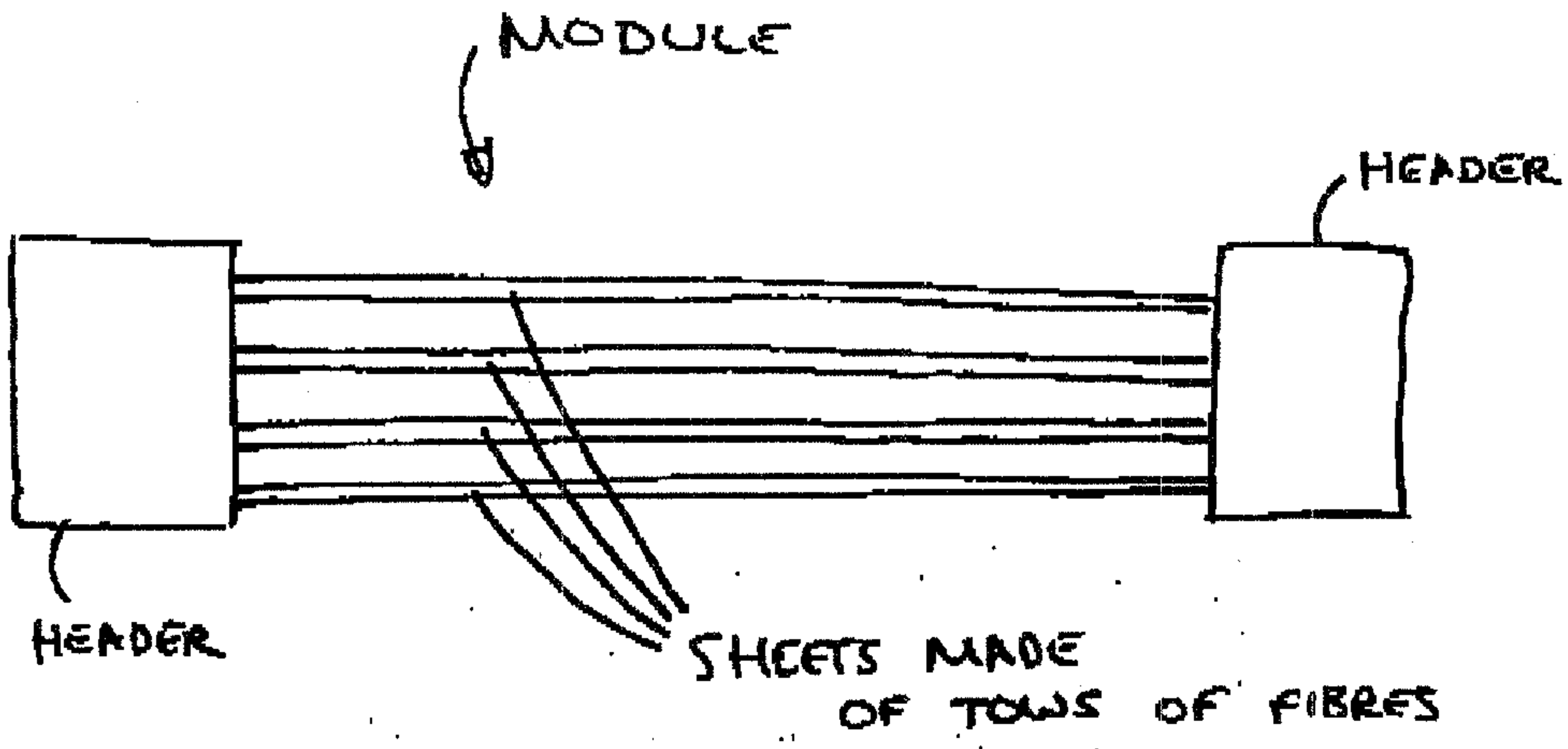
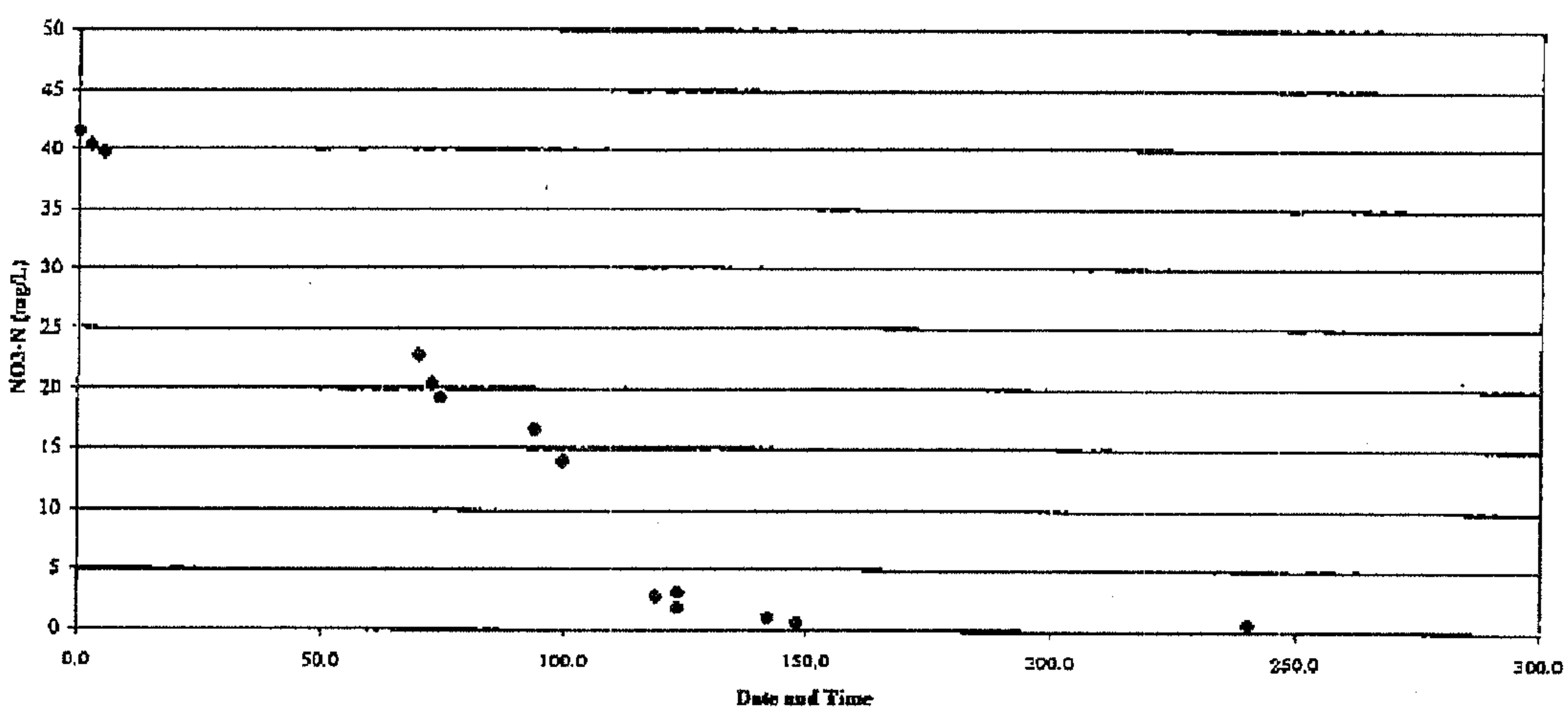
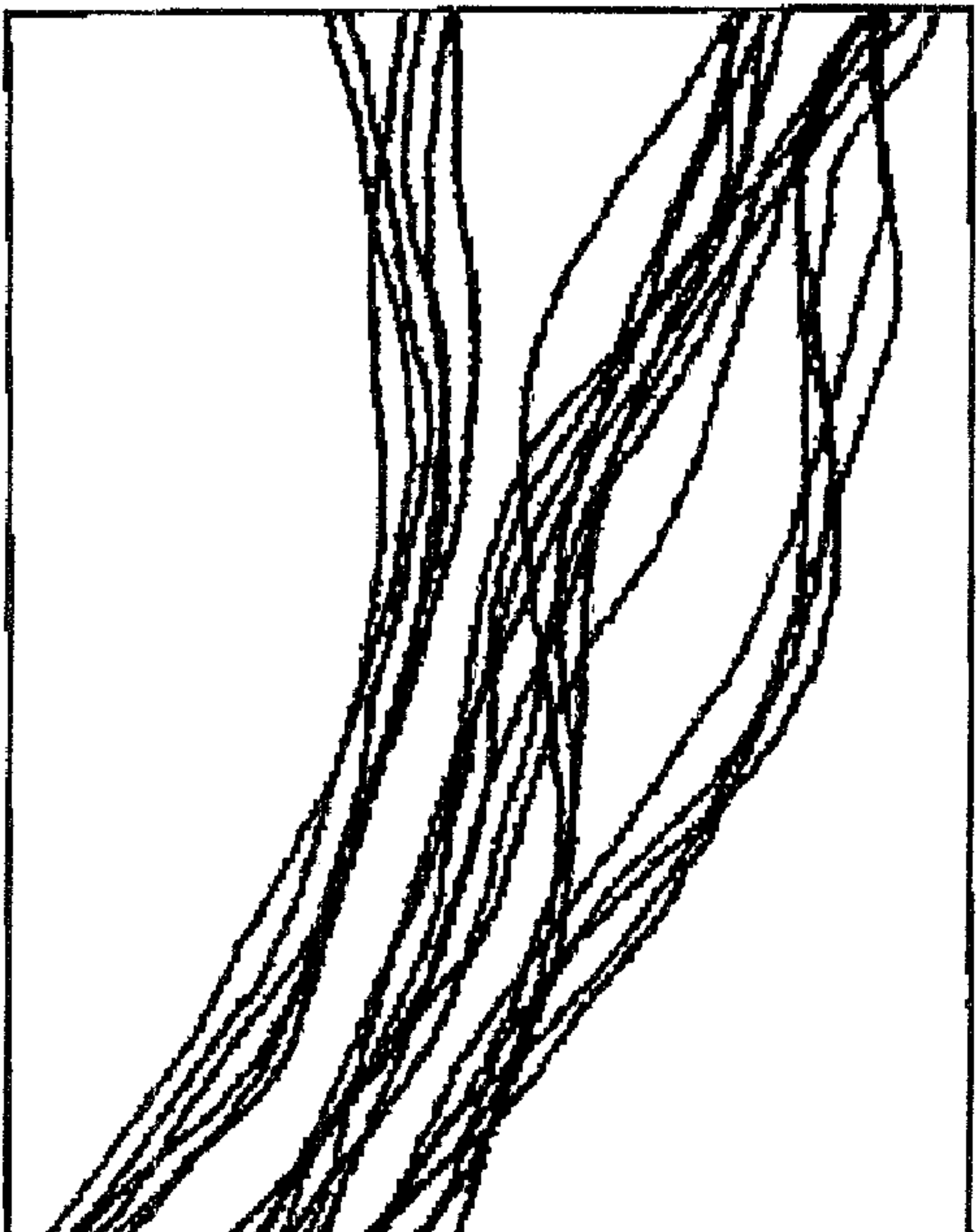


FIG. 46

Figure 5: Results of autotrophic denitrification





PMP Textile Fibre