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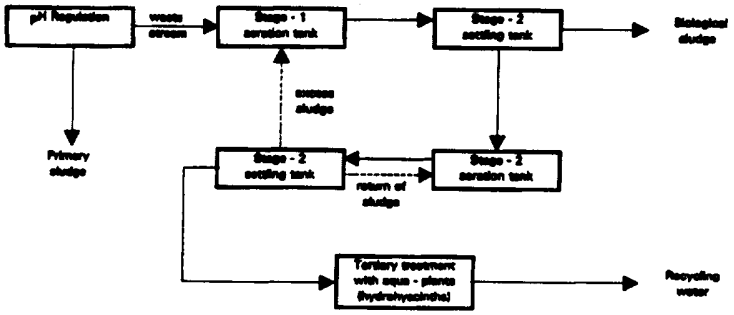

(57) Abstract

This invention refers to an original solution for the purification of contaminated water streams with the activated sludge method, involving: a) a two-stage aeration system operating at high rate and low rate conditions respectively, where the first stage operates in non acidic conditions promoting denitration, whereas the second stage operates under oxidant conditions so that nitrates are removed to an extent of 70 %; b) a system for moving the biological sludge, where the sludge produced in the first aeration tank is totally rejected, and that produced in the second aeration tank recycled to the first. By disposing the sludge from the first aeration tank, 70-80 % of the phosphate contents are removed and the system is relieved of toxicity; c) a system using special ion exchanging resins enclosed in a casing, which are inflatable in water by a factor of 200-350, which have a high ion exchange capacity, and which bind the total metal ions present; d) in the course of the biological treatment, the thermal activation of the biological culture is introduced by the recycle of the culture to the first aeration tank, where conditions of toxicity related biological stress develop on the culture, so that thermal activation and selectivity of species are promoted in it; e) following the above, the installation for cleaning contaminated water operates to specification with a very high and steady yield, achieving contaminated water purification to an extent of BOD reduction by 95 % and with the option for the application of tertiary purification with the development of aquatic plants, leading to the production of recycle water of BOD<5 and hardness <10 in a simple and cost-effective manner. The biological treatment process described constitutes indeed an intervention for optimising contaminated water purification installations operating with the activated sludge method. It is most suitable for use with installations located in warm climate regions where the oxygen supply ability in the aeration tanks is reduced due to the high temperatures of the contaminated water and where the needs for water recycle are maximal.

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METHOD FOR CLEANING CONTAMINATED WATER

Our invention refers to a method for cleaning contaminated domestic and industrial effluent water streams with the active sludge method and by the introduction of innovative processes for treating the ammoniate and phosphate contents of such streams and for the promotion of the activation of biological culture. The methods achieves a high degree of purification at a rapid rate. It results in obtaining recycle water of a high purity, using low installation and operating cost equipment.

The activated sludge method for cleaning contaminated water has a very wide range of applications and is often simply referred to as the method for biological treatment of contaminated water. It employs a tank for primary settling, an aeration tank and a tank for secondary settling. In the course of its development, multi-stage systems have been introduced, where two- or three- stage aeration is conducted. The two- stage aeration method is combined with the development of conditions for the growth of bacteria only in the primary settling tank and for the growth of higher micro-organisms (such as protozoa and other) in the secondary settling tank. This has also required the adjustment of the residence times in the to tanks. Furthermore, multi-stage systems for the treatment of ammoniates and phosphates present in the contaminated water stream have been developed.

The process of biological treatment of contaminated water with the activated sludge method is characterised by the residence times in high rate processes and low rate processes. The high rate process, with a residence time of 2.5 hours appears to favour the growth of bacteria principally, whereas the low rate process favours the growth of a variety of micro-organisms where bacteria and protozoa are the principal constituents, depending on the residence times, usually being in the range of 4 to 6 hours. The high rate process has a small oxygen

consumption and maintains a small concentration of a biological culture in the order of 500 kg./ liter. It responds positively to a rise in temperature up to 45 °C, achieves high degrees of purification, up to 70%, and requires a small consumption of energy. The low rate process, however, does not benefit from rising the temperature above 20 °C, operates in an excess biological culture concentration of 3000 kg / litter and has high operating costs associated with it.

It is also known that in warm - climate regions, the sewage or industrial waste end - up in aeration tanks where temperatures in excess of 30 °C prevail. Thus, air solubility in such tanks is limited. The saturation oxygen content at 15 Celsius is 10.4 kg/lit, whereas this drops to 6.6 kg/lit at 35 Celsius. Thus, extended aeration installations tend to underperform in such regions.

It is derived from the analysis above that the method for contaminated water purification by the activated sludge method is not effectively studied nor optimised as yet. Among functionality problems associated with it, one could list:

it has particular adaptation problems when the temperature of the contaminated water stream rises.

as sewage and industrial waste are complex materials always carrying toxicity, in the form of organic toxic matter and heavy toxic metals, to a higher or lesser degree, the approach is rather of theoretical importance

the toxicity has a variable composition and intensity and inhibits the development of the biological culture and the rate of the biological treatment, thus leading to serious economic and environmental drawbacks.

Taking into account the above mentioned advantageous and disadvantageous aspects of the biological treatment of contaminated water with the activated sludge method, the inventors have invented,

researched and operated pilot solutions which manage to handle all these aspects successfully and highly beneficially.

The inventors have proved that the process of biological treatment of contaminated water with the method of the activated sludge can be optimally operated in a two - stage aeration process in a process, where the first stage operates in a non-acidic environment with removal of nitrates and acting as a toxicity trap. According to this solution, the biological culture in the first aeration tank also acts as an adsorber of heavy metals and toxicity. This culture is totally removed and is not recycled into the system, Following disposition of the sludge from the first aeration tank, phosphate removal is also accomplished, to a degree in excess of 70%. Active sludge is developed and maintained in the second aeration tank which operates in highly oxidant conditions by promoting the oxidation of ammoniates to nitrates and by recycling the sludge for providing for sludge requirements in both aeration tanks.

During the purification process involving two-stage aeration, the sludge from the second stage is only employed. This sludge is entered into the first aeration tank which contains toxicity, thus resulting to the development of competition between micro-organisms for their survival. Thus, the most resilient and active of bacteria which express the higher energy levels of micro-organism development, prevail. These operating conditions are defined as thermophilic activation of the biological culture. This thermophilic activation will develop to a steady state for the whole purification system, where in the first tank development conditions will involve competition of species by the application of toxic stress, whereas in the second aeration tank seeds of activated biological culture will be conveyed and optimum conditions for the development of biological sludge will prevail.

The combination of a high rate and a low rate process developed and operating as a toxicity trap is an original and optimised solution applicable to the warm climate regions. It is also a highly original and simple solution leading to a high degree of nitrate and phosphate

removal. It has been shown that the rate of nitrate removal in a high rate process conditions, developing in a non-acidic environment with a continuous recycle of a water load with sludge from the second, low rate process tank (where oxidant conditions prevail leading to nitrate formation) is in the order of 60-80%. In parallel, as the biological sludge from the first aeration tank is totally rejected, a high fraction of the phosphates (60-80% of total contents) is also received.

The inventors have also invented, elaborated and operated solutions for the toxic relief of the installations for cleaning contaminated water with the activated sludge method, by introducing means for the selective binding of the heavy metals supplied and for the introduction of primary settling conditions for the reduction of the pollutant load in the tank.

The heavy metals in the form of ions are bound to ion-exchanging resins of a special type, invented and operated by the same inventors. Such resins are positioned onto a bed where from the contaminated water passes. The ion exchanging resins are polymer to macroplegmatic structure of an Mc value of 50,000 conversion products. Sulfonic and carboxylic groups have been inserted to these resins to a maximum density to ion exchange ratio near the theoretical 5.6 - 6.2 limit. Such resins are inflated in water 250-350 fold their weight, and, having low porosity, they bind rapidly the total of metal ions passing through, carried by the water.

The ion exchanging resins mentioned above are added to the aeration tanks. As they are inflated 250 - 350 fold in water, they bind the soluble metal ions, whereas due to their low porosity the sludge cannot flow through.

By the addition of alkaline water, the pH in the primary settling tank is regulated to a value of 8.3. Under such conditions it has been shown that the largest proportion of the suspended material settles, leading to a reduction of environmental load in the order of 40-50%,

with a total binding of phosphates by the calcium ions present. Thus, conditions for reducing the pollutant load in cases of intensive operation of the biological treatment plant are developed. Alkaline water is formed, by the treatment of the sludge in an anaerobic digestion process in the thermophilic region. This process is documented in patent 90117377/3/10 filed by the same inventors.

The improvements to the contaminated water treatment method of activated sludge proposed by this invention lead to the operation of such plants in an effective, trouble-free manner, achieving high rates of purification, a reduced operating cost and operation according to specifications.

The installations for cleaning contaminated water as developed by this invention achieves the full removal of toxicity, a high rate of evolution, and a low operating cost. It can operate without a primary settling tank, especially when the solids suspended in the contaminated water stream have a concentration inferior than 5000 kg./litter. The process as a whole achieves purification to a degree of BOD reduction in the order of 98% and can be combined with a unit for the development of aquatic plants where auxiliary nitrate, phosphate and pollutant removal develops. Such a combination has a small installation and operation cost and can achieve the production of recycle water meeting high purity specifications and a quality biological evolution. In general, what has been described and developed in this invention is a modern approach for the evolution of installations for contaminated water purification which has a highest economic, scientific and environmental significance.

Example No 1

In the pilot plant of the attached drawing, which is located at the end of the central sewage duct of the Greater Athens area, and which is fed at a flowrate of 20 lit/h., the effectiveness of the water cleaning process was investigated: The contaminated water stream was fed with a BOD load of 320+/-100, a suspended solids concentration of 520+/-140 containing heavy metals at a concentration of 200 kg. /lit, ammoniates at 100 kg./lt., and phosphates at a quantity of 60 kg./lt. The pilot unit operated for 45 days with no problems at the following operating parameters:

Suspended solids in the first aeration tank : 480+/- 50 kg./litter

Suspended solids in the second aeration tank : 5300+/- 150 kg./litter

Aeration in the first aeration tank: 1-1.1 cu.m./h

Aeration in the second aeration tank: 1.4-1.7 cu.m./h

The outlet stream had a BOD load of 30+/-5 and a COD load of 45+/-10. 65 +/- 5% of heavy metals were bound in the first aeration tank, nitrate removal at 82% was achieved, whereas phosphate binding by the rejected sludge was in the order of 72%.

Example No 2

A second pilot unit involving a single aeration tank of a size equal to the total of the two tanks of the first unit was operated for the treatment of a supply of 20 litters/hour, as well, The relative performance of the two units was investigated in terms of BOD reduction at the outlet.

Results are summarised below:

	Pilot Unit of drawing attached	Second pilot unit involving single stage aeration
24 hrs	60+/-10	180+/-50
48 hrs	40+/-5	150+/-60
72 hrs	25+/-5	150+/-60

Example No 3

In the pilot unit illustrated in the drawing attached, a quantity of 50 gram of ion exchange resin was placed in a casing suspended in the aeration tank.. This resin was inflatable in water up to 300 fold. with a dehardening ability of 5.2 degrees. The result of this addition was the total elimination of metals during the experiment. Furthermore, the biological culture in the second tank developed without any disruption, resulting in a significant improvement of the rate and the degree of purification. During the 25 days of operation of the unit at conditions similar to those of experiment 1, the outlet BOD was 15 +/- 5 with a steady yield since the first day of operation and an air consumption of 2.3 cu. m. / minute.

Following the end of the experiment, the ion exchange resins exhibited a reduced ion exchange ability. They were removed, reactivated by submersion in salted water (sea water) and reset to operation. At these conditions, the influence of the residence time on the degree of purification was investigated with the following results:

Flowrate, lit/h.	Outlet BOD	Air Consumption, cu.m./h.
20	18+/-5	2.2
23	20+/-6	2.3
26	20.5+/-6	2.3
30	19.8+/-8	2.3

It was found that with an increase in the flow by 50%, the cleaning system is adapted to optimum operating conditions and that the degree of purification remains steady.

Example No 4

In the pilot unit illustrated in the attached Drawing, fed at a flowrate of 20 litters/hour at a contaminated water stream composition of the experiment no 1, the influence of the rate and time of recycle on the degree of purification in the two aeration tanks was investigated;

Aeration tank No 1:

Sludge production: 3750 +/- 200 kg./h.

Quantity and rate of sludge recycle

	Own sludge %	from tank 2	Outlet BOD
1-48 h.	100%	0	290 +/- 10
1-48 h.	50%	50%	220 +/- 20
1-48 h.	0	100%	140 +/- 10
1-48 h.	0	100%	290 +/- 10

Aeration tank No 2:

Sludge production: 4000 +/- 300 kg./h.

Outlet BOD	aeration, cu.m./h.	
160+/-8	3.8	Note a)
130+/-6	3.2	Note b)
35+/-5	2.7	Note c)
25+/-5	2.2	Note d)

a) After 5 hours of operation the aeration tank does not exhibit biological activity

b) The operation of the aeration tank exhibits reduced biological activity

c) The sludge in the aeration tank has some activity and a light colour

d) Following placement of a casing with ion exchange resins in the second aeration tank.

EXAMPLE No 5

The effluent water from the purification installations with a BOD of 20 - 100 is passed to a tank for the development of aquatic plants (aquatic hyacinths, aquatic celery, etc.) operating at greenhouse conditions covered with a transparent polymer which permits the sun-rays to pass. The aquatic plants develop very rapidly and the final outflow water has a BOD less than 2 and a hardening factor of 10. Thus, it is a high quality recycle water. The aquatic plants can be cut and transferred to the anaerobic digestion unit or be used for making animal foodstuffs.

CLAIMS

1. A method for cleaning contaminated water with the activated sludge method which consists of:

   a) A two-stage aeration system operating at high rate and low rate conditions respectively

   b) A system for moving the biological sludge, so that the sludge produced in the first aeration tank is rejected, at the same time removing 70-80% of the phosphate contents and so that the cleaning system is covered in terms of biological culture by the sludge produced at the second aeration tank

   c) A two-stage aeration system, where the first stage operates in non acidic conditions, whereas the second stage operates under oxidant conditions so that nitrates are removed to an extent of 70%.

   d) A system using special ion exchanging resins which are inflatable in water by a factor of 200-350 and which bind the total metal ions present.

   e) An installation for the development of aquatic plants for the production of high purity recycle water.

   With the above, the installation for cleaning contaminated water operates with a continuous activation of the biological culture without any effects from the toxicity supplied.

2. A method according to claim 1, where the toxicity supplied to the system is adsorbed by the rejected sludge of the first aeration tank which is fed with sludge recycled from the second aeration tank. Thus conditions of biological selectivity are created with a continuous activation of the biological culture.

3. A method according to claim 1, where the second aeration tank operates at optimised biological conditions, free of the toxicity supplied in the form of heavy metals, as ion exchanging resins inflatable up to 350 fold in water are located and binding the total quantity of metal ions supplied.

4. A method according to claims 1,2, and 3 where the toxicity supplied being of a varying intensity, creates a varied intensity toxic stress to the biological sludge, creating conditions for species competition and resulting in maintaining a steady functionality to the system.

5. A method according to the previous claims, where the purification system evolves towards steady state operation, where in the first aeration tank conditions for the selection of the biological activity of selected thermophilic bacteria which in the form of grains or biologically activated complexes are transferred to a second aeration tank, where their development under optimised conditions is rapid.

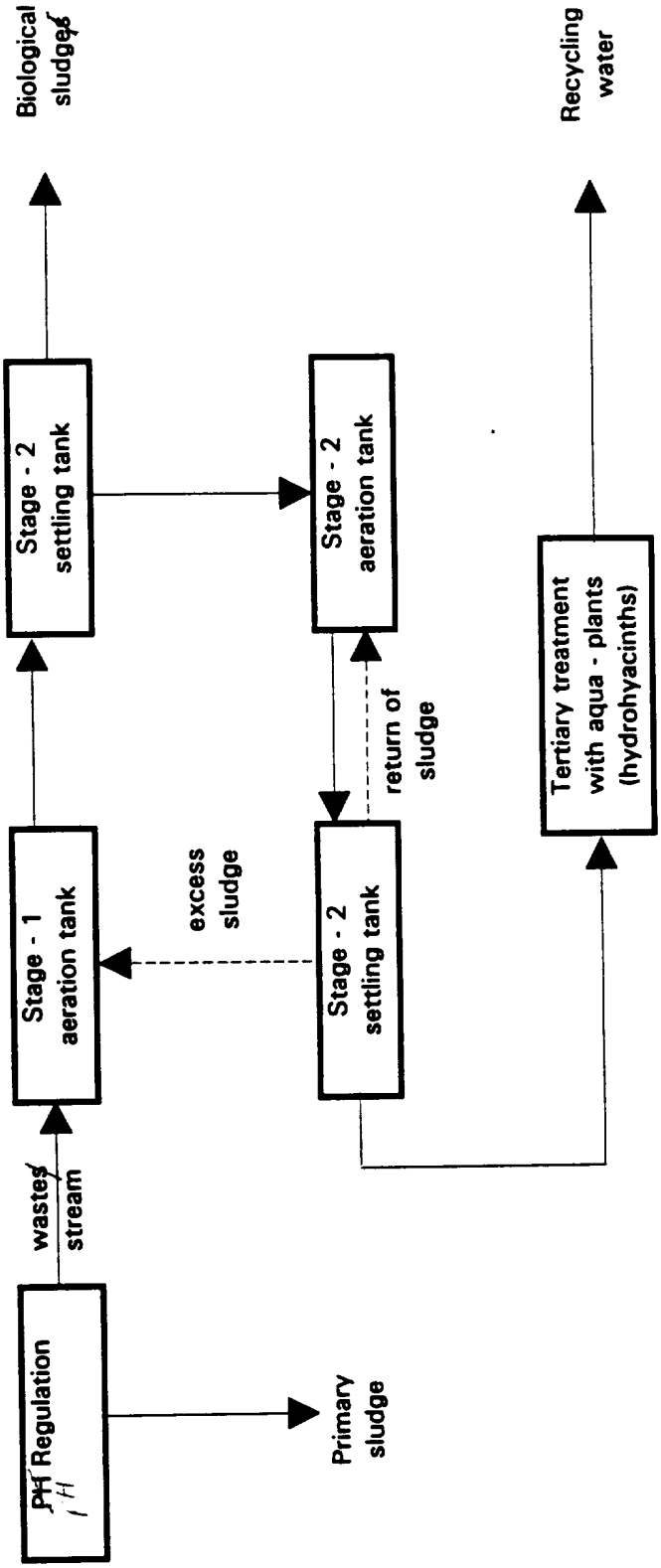
6. A method according to claims 2,4 and 5 where the activation of the biological culture is promoted in parallel by the thermophilic selection of a range of thermophilic micro-organisms, thus increasing the rate and the effectiveness of the contaminated water cleaning system

7. A method according to claim 1, where in the case that the contaminated water stream for processing contains a high proportion of metal ions, or in the case that a source of such toxicity supply exists, the conditions for the binding of the said metal ions is achieved by the introduction of inflatable in water ion exchanging resins in the course of such supply or in the primary settlement tank of the purification system

8. A method according to claims 1, 2, 3 and 5 where the first aeration tank operates under non-acidic conditions permitting the conversion of nitrates to nitrogen by denitration, whereas the second aeration tank operates in oxidant conditions enabling the conversion of ammoniates to nitrates which re continuously recycled with the sludge to the first aeration tank. Thus, the cleaning system achieves a binding 70 - 75% of the nitrogen containing material and, following the disposal of the sludge from the first aeration tank, a removal of 60-75% of phosphates.

9. A method for cleaning contaminated water according to claims 1 - 8, where the contaminated water is supplied to a system for biological treatment operating in the activated sludge method involving two-stage aeration. Primary and secondary settling may or may not be applied. In this process the first aeration tank acts as a toxicity trap, also achieving nitrates removal. The sludge produced in this tank is rejected after having received 60 - 75% of the phosphates contents. Active sludge from the second aeration tank is recycled to the first aeration tank. Thus, biological stress develops in the first tank due to the toxicity, leading to a survival competition of micro-organisms which are activated. A thermophilic biological cultivation is developed in the second aeration tank of the contaminated water purification system. The toxic heavy metal ions present are bound with the use of special ion exchanging resins which are inflatable in water by a factor of 300 and which are placed in the second aeration tank or in the course of the metal ions flow in suitable quantities, so that the contaminated water purification system operates at a maximum rate, in a steady and optimised manner. This system requires reduced installation and operation costs. Following the addition of simple retrofit installations for the development of aquatic plants, the system can produce high purity recycle water.

Drawing


Biological sludges
Recycling water
Stage - 2 settling tank
Stage - 2 aeration tank
Tertiary treatment with aqua - plants (hydrohyacinths)
return of sludge
excess sludge
Stage - 1 aeration tank
Stage - 2 settling tank
wastes stream
PH Regulation
Primary sludge

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GR 95/00017

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C02F3/30 B01J39/04 C02F3/32

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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,A,40 36 548 (BÖHNKE, BOTHO) 21 May 1992 see column 2, line 45 - column 4, line 18; figure	1,2,8,9
Y	DE,A,39 39 732 (PREUSSAG AG) 6 June 1991 see the whole document	1,2,8,9
Y	EP,A,0 368 814 (GIANNOTTI, MAURIZIO) 16 May 1990 see page 5; claims 1,2,11-13	1,2,8,9
A	FR,A,2 456 712 (DEGREMONT) 12 December 1980 see page 3, line 12 - page 4, line 28; figure 1	1,2,8,9

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

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 December 1995	15.12.95

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

International Application No
PCT/GR 95/00017

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,39 12 921 (OSWALD SCHULZE GMBH & CO KG) 25 October 1990 see column 4, line 1 - line 45; figure -----	1,2,8,9

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte nal Application No
PCT/GR 95/00017

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		ES-A-	2046099	16-01-94
		IT-B-	1251780	24-05-95
DE-A-3939732	06-06-91	NONE		
EP-A-368814	16-05-90	NONE		
FR-A-2456712	12-12-80	NONE		
DE-A-3912921	25-10-90	NONE		