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(71) Applicant
Ionics Italba Spa

(Incorporated in Italy)

Via Mauro Macchi 26, 20124 Milan, Italy

(72) Inventors
Franco Ciallie
Guido Vaccaro

(74) Agent and/or Address for Service
Mewburn Ellis
2 Cursitor Street, London, EC4A 1BQ, United Kingdom

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(54) **Process for removing nitrates from drinkable water by using membrane systems**

(57) Process for removing nitrates and other ions, such as chlorides, sulphates and others, from drinking water, which consists in subjecting the crude water to be purified to a plurality of membrane purification means, particularly within electrodialysis units of the polarity-reversal type, arranged in series so as to allow the units to progressively purify the water until the concentration of nitrates and other ions is reduced at least below the limits prescribed by statutory provisions for drinking water, in then concentrating in a single flow "C" all the waste water in output from the electrodialysis units and in then subjecting the concentrated discharge flow "C" to a biological denitrification treatment, so as to obtain waste water with a content of nitrates and other ions which is within the limits set by the rules for waste water.

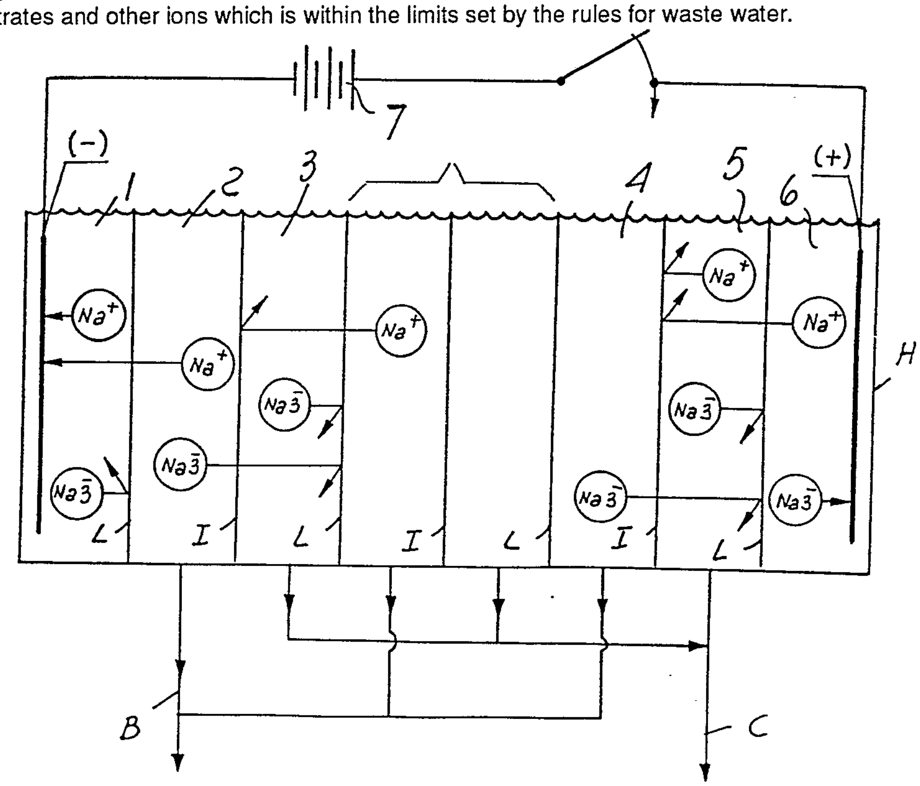

FIG.2

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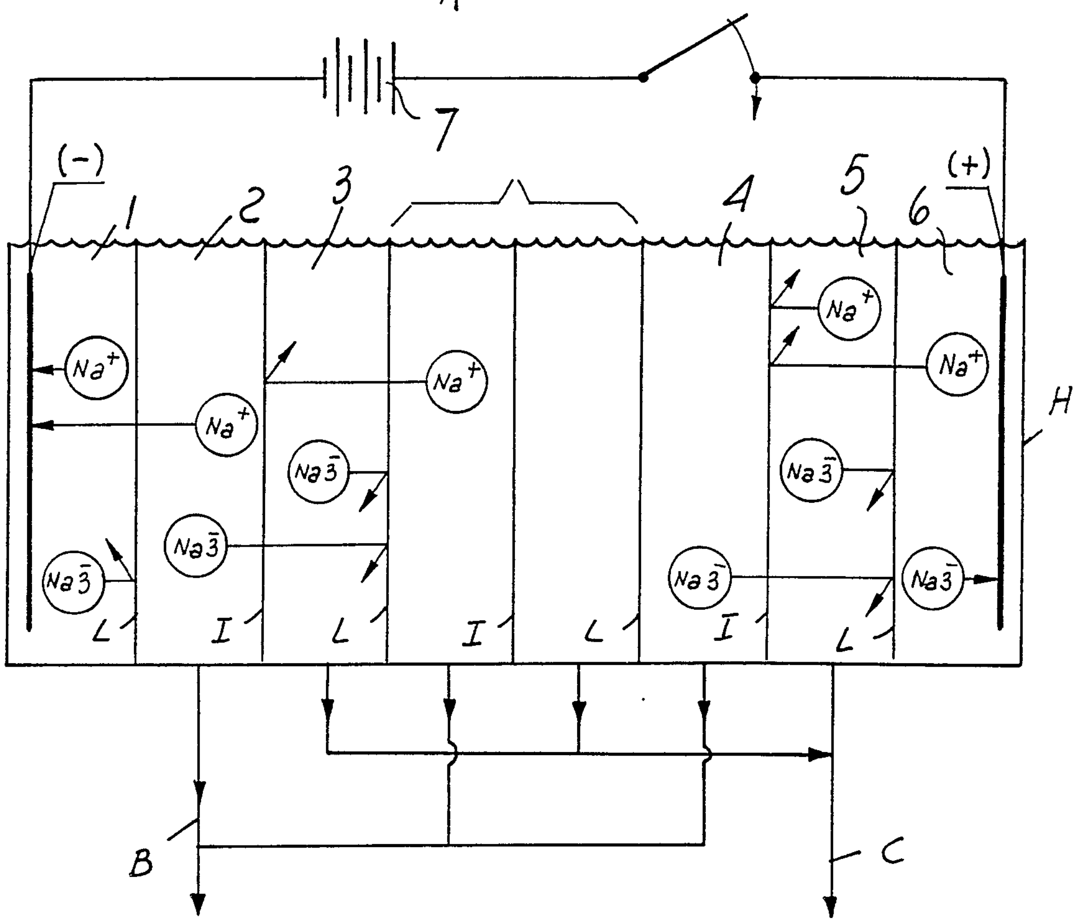

Fig.2

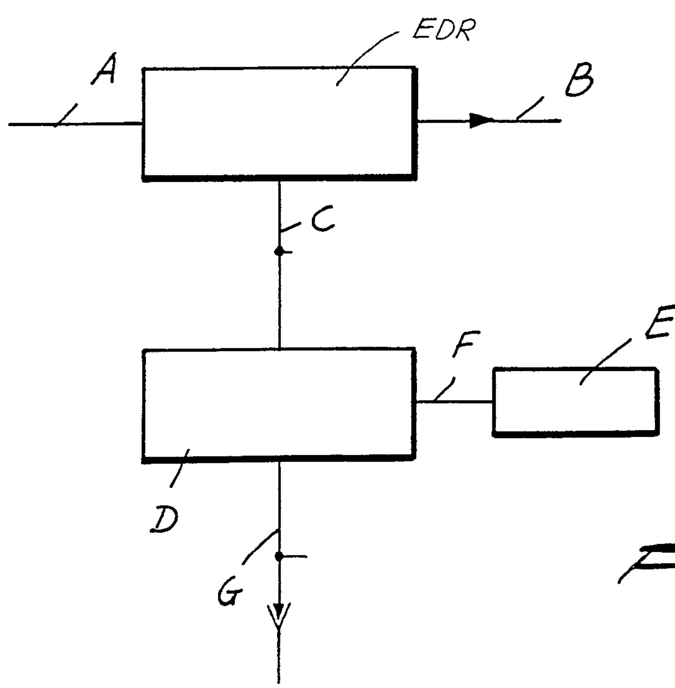

Fig.1

PROCESS FOR REMOVING NITRATES FROM DRINKABLE WATER BY USING MEMBRANE SYSTEMS AND THE LIKE

The present invention relates to a process for removing nitrates and other ionic components exceeding the statutory provisions from water intended for drinking, by using membrane systems, particularly a polarity-reversal electrodialysis battery which uses membranes which are alternately permeable to cations and to anions, in combination with a system for the denitrification of the discharge flow alone, capable of eliminating from the discharge brine the nitrates exceeding the statutory provisions.

As is known, the content of nitrates in drinking water has progressively increased, forcing legislative bodies to intervene in order to set a maximum safety limit for human consumption. At the same time, the statutory provisions have set parameters for all the other ionic components of drinking water, making obsolete many conventional treatments which solve the problem partially (lime softening, ion-exchange softening, selective nitrate removal on ion-exchange resins, biological aerobic or anaerobic denitrification) or fully, to the extent of requiring the remineralization of the product (reverse osmosis, evaporation systems).

The most recent statutory provisions, for example the EEC Directive No. 80/778 of July 15, 1980, the Decree of the President of the Italian Cabinet dated February 8, 1985, have established, for nitrates, maximum acceptability limits for drinking water, which must not be exceeded, and guideline values to be observed for other chemical parameters, including the hardness of the water, chlorides, sulphates, sodium and total dissolved solids (TDS), as well as acceptability limits for nitrates present in discharge water; said limits, according to the most recent provisions, are specified as 20 ppm as nitrogen or as 88.5 ppm as NO_3.

The technology used so far tends to cope with one problem at a time in order to improve the drinkability characteristics of the water, i.e.:

- lime softening or ion-exchange resin softening to reduce hardness;

- selective ion-exchange resins or biological treatments for nitrate removal;

- electrodialysis or reverse osmosis for reducing the total dissolved salts (TDS), chlorides and sulphates, particularly in the treatment of salt water.

The new statutory provisions instead require the treatment of the problem of drinking water in a global sense, since very often the available water is not drinkable due to several parameters and not only due to its nitrate content or to its chloride content.

Among the various known processes, only the one which uses electrodialysis units, and especially units for polarity-reversal electrodialysis (EDR), allows removal of nitrates from water while simultaneously reducing other polluting agents within the maximum acceptability threshold of the new provisions, furthermore allowing to approximate or reach the indicated guideline values in an economical and energy-wise optimum manner.

Furthermore, since this process is constituted by successive stages, it allows stopping the treatment at the actual requirements of the available water source.

It should in any case be noted that the known systems, such as reverse osmosis and evaporation, by producing an excessive demineralization, require remineralization, either with chemical products or by mixing with crude water, in order to provide drinkability.

It should also be noted, as will become apparent hereinafter, that the use of EDR units allows quantitatively equivalent removals both for chloride and for nitrates, allowing the nitrates to drop below the maximum allowed threshold and the chlorides to approximate or improve the guideline value of the statutory provisions.

All the known nitrate removal processes, including electrodialysis and with the only exception of those which perform the biological nitrate removal treatment directly on the drinking water, have the disadvantage of collecting the removed nitrates in the discharge flows, so that the content of said flows can exceed the acceptable values established by the statutory provisions for waste water. A further treatment is therefore necessary in order to include the discharge flow, too, within the limits set by the law.

Biological treatment performed directly on the drinking water instead leads to another severe disadvantage, which is due to the fact that the direct contact and permanence of bacteria in the drinking water, which is technically possible, can cause damage to the human body. It is in particular this possibility of the presence of bacteria which the present invention has the purpose of eliminating completely.

The aim of the present invention is therefore to provide a process for removing nitrates (and other harmful ions) from drinking water, which allows, by means of a particular combined process of water treatment by means of membrane systems and of denitrification of the waste water separately from the drinking water, achievement of the values prescribed by the statutory provisions both for the drinking water and for the waste water.

An object of the invention is to provide a nitrate removal process which is conceived so as to allow stopping the nitrate removal treatment at the values set by the statutory provisions for drinking water, so as to allow the simultaneous removal, together with the nitrates, also of the chlorides, sulphates, of the hardness and total dissolved solids, as well as to ensure the constant quality of the produced water when the chemical characteristics of the crude fed water are correspondingly constant.

A further object of the invention is to provide a process of the above specified type which can provide a high yield in drinking water and also does not require any particular mixing, homogenations and remineralizations of the water produced, with evident economical and practical advantages, and is also highly advantageous, with respect to the nitrate removal processes currently in use, in terms of area occupation, of facility cost and operating cost.

This aim, these objects and others which will become apparent from the following description are achieved by a process for removing nitrates from drinking water, which consists, according to the present invention, in subjecting the crude feed water to a treatment for the removal of nitrates and other ions present in said water within a plurality of membrane purifying elements, particularly a plurality of units for electrodialysis of the polarity-reversal type, arranged in series so as to allow each membrane unit to progressively purify the water, until a removal of the nitrates and of other ions, such as chlorides, sulphates and the like, such as to ensure the degree of drinkability prescribed by the statutory provisions for drinking water is obtained; in then subjecting said nitrates and other ions, removed by said units, to a biological denitrification treatment by means of known technologies, so as to comply with the limit nitrate content set by the applicable statutory provisions for the waste water as well.

Further characteristics and advantages of the process according to the invention will become apparent from the following detailed description of a preferred but not exclusive practical embodiment thereof, which is given with reference to the accompanying drawings, provided only by way of non-limitative example and wherein:

figure 1 is a block diagram of the individually known apparatuses which can be used to carry out the operating steps of the nitrate removal process according to the invention, and

figure 2 is a schematic view of a series of electrodialysis units with reverse-polarity membranes, used to separate, according to the invention, the nitrates and other ions from the drinking water and to remove the nitrate-enriched discharge flows emitted by said electrodialysis units, for a successive and separate overall denitrification treatment.

With reference to figure 1, the crude water to be treated, appropriately filtered in order to remove any foreign solid matter, is conveyed, by means of a pipe A, into a plurality of units or cells for electrodialysis with reverse-polarity membranes which are arranged mutually in series and in a number suitable for obtaining the removal of the nitrates, chlorides and the like, until their concentration in the water is reduced below the limits of the statutory provisions for drinking water. The water purified by the various units, as will become apparent hereinafter, is conveyed by means of a pipe B to the user facilities, whereas the discharge flows from the units are combined and, by means of a pipe C, are conveyed to a biological denitrification unit D where, after treatment with the addition of organic nutrient substances E fed by means of a pipe F, the nitrate-free discharge flow is conveyed to landfills by means of a pipe G.

More particularly, the operating steps for the removal of the nitrates by means of a membrane system constituted by electrodialysis units with reverse-polarity membranes can be summarized as follows.

With reference to said figure 2, an electrodialysis system is substantially constituted by a parallelepipedal container H inside which a plurality of equally spaced vertical membranes is arranged; said membranes define compartments or cells indicated by the numerals 1 to 6.

The membranes are of the anionic type and of the cationic type and are arranged alternatively inside the container 4; the end compartments 1 and 6 contain the electrodes, and specifically the cathode in the compartment

1 and the anode in the compartment 6. Said electrodes are connected to a direct-current electric power source 7. By means of this arrangement, the electrodialysis system is capable of maintaining a constant quality of the purified water by reversing the polarities of the electric current fed by the source 7. The crude water is in fact fed continuously into the compartments comprised between the first one and the last one of the series, and the membranes separate the dissolved ionized impurities (nitrates, chlorides, etc.).

More precisely, in figure 2 the membranes are indicated in pairs, i.e. with the letters I and L for each contiguous pair.

The membranes indicated by "I" are of the anionic type, are impermeable to water and allow the passage of negatively charged ions (anions).

The membranes indicated by "L" are of the cationic type, are impermeable to water and allow the passage of positively charged ions (cations). As regards the cells or compartments, the compartments 1 and 6 are special compartments, since they contain the electrodes, whereas the others respectively perform the following functions:

- compartment 2 - NO_3 and other negatively charged ions cannot pass through the membrane "L" and remain in compartment 2.

- compartment 3 - Na+ and other positively charged ions cannot pass through the membrane "I" and remain in compartment 3.

- compartment 4 - NO_3 and other negatively charged ions pass through the membrane "I" into compartment 5. Na+ and other positively charged ions pass through the membrane "L" into compartment 3.

- compartment 5 - NO_3 and other negatively charged ions cannot pass through the membrane "L" and remain in compartment 5.

Na+ and other positively charged ions cannot pass through the membrane "I" and remain in the compartment 5.

The overall result is that the water of compartments 2 and 4 has been depleted of the nitrates and other ions and as such can be collected and distributed for drinking. The water of compartments 3 and 5 has enriched in nitrates and other ions and constitutes the discharge flow.

The overall treatment, exemplified in the diagram of figure 2, collects the discharge flows and combines them in a single discharge flow "C" which can thus be subjected to a biological denitrification treatment in a reactor (or in a fluid bed) D (figure 1) separately from the drinking water.

The removal of the nitrates from the discharge flow of the electrodialysis unit is performed biologically according to the present invention by means of bacterial populations.

Conceptually, it is possible to use both heterotrophic and autotrophic strains.

The greater complexity of the use of autotrophic bacteria (including the need to use hydrogen as a nutrient) limits their advantages to some hypotheses of very particular installations which are not considered herein.

Heterotrophic bacteria instead require an addition of organic substances. Among these, mention can be made of the following: methyl alcohol, acetic acid and ethyl alcohol, as well as numerous by-products of industry, such as for example:

- tailings from the production of alcohol and distilled spirits,
- waste sugary concentrates,
- antifreeze mixtures of cooling circuits.

Due to the low acquisition cost of these substances, the advantage of the proposed process is evident.

The consumption of organic substances is in fact proportional to the mass of nitrates which must be removed from the water to be purified, and is instead not proportional to the entire nitrate content of said water, as occurs for example for processes based on the direct biological denitrification of the water to be purified.

The biochemical denitrification reaction is extensively described by the literature in its biological, equilibrium, kinetic and technological aspects.

Said biological process can be performed by adopting one of the following three technologies, which are already known and described by the literature:

- submerged adhered biomass in a fixed or fluidized bed,
- non-submerged adhered biomass,
- suspended biomass.

In the first hypothesis, the waste water of the electrodialysis, to which methyl alcohol or another suitable source of carbon is conveniently added, flows through a bed of inert material to which the bacterial colonies which perform denitrification adhere. The inert material can be fixed or fluidized by the flow speed.

The second process differs from the preceding one since the flow to be subjected to denitrification does not entirely occupy the empty spaces between the inert material. The residual empty space is thus occupied by a gaseous phase which must not contain oxygen.

In the third process, the biological denitrification mass is kept suspended in the liquid phase in a reactor to which both the fluid to be subjected to denitrification and the carbon source are fed.

The mixture of biomass/denitrified fluid which leaves the reactor is separated in a gravity sedimentation unit and the biomass is continuously returned to the reactor.

In industrial application, the above-mentioned processes differ markedly from one another in terms of area occupation, facility cost and operating costs.

The choice must therefore be performed on a case-by-case basis, taking into account both the operating conditions (flow-rate to be subjected to denitrification, load of nitrates to be removed, temperature) and the external conditions (availability of space, environmental impact, technological level of the area, availability of the nutrient, etc.).

For a greater clarification and for a confirmation of the above, two examples of practical execution of the combined process of electrodialysis and subsequent separate denitrification of the discharge flow, executed according to the invention, are reported hereinafter.

Example 1

The following results were obtained for a three-month period in a pilot plant using electrodialysis units manufactured by the IONICS Inc. company, of the Aquamite XX 4/2 type, capable of producing 50 m^3/h of drinking water, with 4 m^3/h of discharge flow, i.e. with a 92% recovery.

TDS	Feed	Output 1st stage ppm	Removal %	Output 2nd stage ppm	Removal %	Discharge flow ppm
Na	12.6	11.8	6.4	10.4	17.5	38
Ca	92	66	28	44	52	790
Cl	30	20	34	12	60	250
SO_4	67	97	45	19	72	760
NO_3	52	37.9	27	23	56	474
TDS	422	312	26	215	49	3238

Since the acceptability limit for nitrates in discharge water is 20 ppm as nitrogen or 88.5 ppm as NO_3, it is necessary to subject the discharge flow to denitrification. Said denitrification was achieved with a biological system which easily obtains a reduction which is far greater than the 88.5% prescribed by the statutory provisions.

Example 2

The following results were obtained, after approximately three months, in a second pilot plant which also used an Aquamite XX 4/2 electrodialysis unit, preset for producing 50 m^3/h of drinking water with a concentrated discharge flow of 8.8 m^3/h and therefore with an 85% recovery.

	Feed ppm	Output 2nd stage ppm	Removal %	Discharge flow ppm
Na	35	22	20	113
Ca	140	70	50	467
HCO_3	450	292.5	35	1052
Cl	54	23.8	56	202
SO_4	80	24	70	374
NO_3	71.7	32	55	265
TDS	870.7	484	45	2606

In this case also, the NO_3 concentration in the discharge flow exceeds by 177 ppm (265-88) the concentration limit (88.5) prescribed by the statutory provisions.

Since electrodialysis requires in practice only the use of electric power and since the consumption of said electric power is proportional to the amount of salts removed, it is evident that the staged system is the one which entails the lowest energy consumption.

In the electrodialysis system, the water fed to the system is always more than the water produced:

the ratio between the produced water (Qp) and the fed water (Qa) is termed Recovery (R) of the system

$$R = \frac{Qp}{Qa} = \frac{Qp}{Qp+S}$$

where S is the concentrated discharge of the system. It is evident that the energy consumption is smaller as S decreases, i.e. as R approaches 1. Systems for electrodialysis and for electrodialysis with polarity reversal are, among the known ones, those which allow maximum recovery.

Bearing in mind that the removed nitrates are all concentrated in the discharge flow and that therefore the content thereof can be higher than the values accepted by the applicable statutory provisions for waste water, the need arises for a further treatment in order to make the discharge flow also comply with the statutory limits. It is noted that this need is also shared by other treatment systems, such as reverse osmosis and selective ion exchange.

Two important aspects must furthermore be taken into account:

- the denitrification kinetics decreases rapidly as the temperature decreases. Since in the electrodialysis process the temperature at which the discharge flow is released is higher than the temperature of the water to be purified, the process according to the present invention allows operation in more favorable kinetic conditions with respect to the process of direct denitrification of the crude water;

- the biological denitrification process is hindered by a high salinity of the stream to be subjected to denitrification. The advantage of the process according to the invention with respect to ion-exchange systems, in which the salinity of the stream to be subjected to denitrification is increased considerably by the sodium chloride used to regenerate the ion exchanger, is therefore obvious.

The denitrification system applied to the concentrated flow obtained from the polarity-reversal electrodialysis unit can be applied to any other membrane system which concentrates the nitrates in a single discharge flow.

After the above description, in order to better point out the differences of the present process with respect to the latest and most efficient nitrate removal processes applied on an industrial scale, the following is noted:

a) <u>Selective ion-exchange process</u>

Treatments with varying degrees of sophistication have been adopted by using selective ion-exchange resins, i.e. resins which have a particularly high affinity for nitrates.

The nitrates are always exchanged by replacement with other anions, and the nitrate reduction is always equivalent to the increase in other anions. The systems are cyclic and cannot ensure a constant quality of the product without having storage volumes for homogenizing the drinking water produced in the cycle.

The discharge brine arriving from the regeneration of the resins introduces other salts which, by altering the overall mass balance, produce a negative environmental impact and do not cope with the problems of nitrates in the waste water and of the increase in salts in the waste water.

A particularly original system entails the biological denitrification of the regeneration eluate, while reducing but not eliminating the external addition of salts.

However, the denitrified concentrate is placed in contact with the ion-exchange column intended for the subsequent service, and therefore the potential risk of bacterial contamination of the drinking water remains.

b) Biological processes

Various biological systems, both autotrophic and heterotrophic, by now extensively known in the literature, have been used.

- All the above-mentioned systems entail the direct action of the bacterial activity on the drinking water, and all the systems force the total removal of the nitrates with an addition of organic carbon in excess of the actual requirements.

Finally, the economic, practical and energy advantages obtained with the process according to the invention can be summarized as follows.

- Possibility of stopping the nitrate removal treatment at the actual requirements determined by the statutory provisions or by the requirements of the local Health Authorities.

- Simultaneous removal of nitrates, chlorides, sulphates, hardness and TDS, with the possibility of obtaining, with a single treatment, the adaptation of the chemical characteristics of the drinking water to the statutory provisions or in general of improving the characteristics of said water.

- Constant quality of the produced water, with variations related exclusively to the variations in the composition of the feed source.

- No need for remineralizations, mixings, storage for homogenation.

- The purifying system is absolutely independent of the biological denitrification system, with the absolute exclusion of the possibility of a bacterial contamination of the drinking water induced by the biological process.

- Energy consumption exactly equivalent to the amount of salts or nitrates removed.

- The overall mass balance remains absolutely unchanged, since no addition of reactive agents or regeneration agents, intended to increase the overall saline content of the fed water, is provided.

The nitrates are removed from the feed water without being replaced with other salts as in the typical case of ion exchange, which replaces the nitrate ion with the chloride ion.

CLAIMS

1. Process for removing nitrates from drinking water, characterized in that it consists in subjecting the crude water to be purified to a plurality of membrane purifying elements, particularly within electrodialysis units preferably of the polarity-reversal type, arranged in series so as to allow each of said units to progressively purify the water until the concentration of nitrates and other ions is reduced at least within the limits prescribed by the statutory provisions for drinking water, in then concentrating in a single flow all the waste water flowing out of said electrodialysis units and in then subjecting said concentrated discharge flow to a biological denitrification treatment, so as to obtain waste water with a content of nitrates and other ions which is within the limits set by the rules for waste water.

2. Process according to claim 1, characterized in that said drinking water is obtained with the drinkability characteristics required by the statutory provisions in a direct and continuous manner and with constant quality, without requiring operations for mixing, homogenizing and remineralizing the produced water.

3. Process according to claim 1, characterized in that said biological denitrification is applied only to the concentrated flow of a nitrate removal membrane system, in order to prevent even the merely potential contact between the biological denitrification process and the process for removing the nitrates from the drinking water.

4. Process according to claims 1 and 3, characterized

in that said process for the denitrification of the concentrated discharge flow is obtained by means of a conventional biological process which is constituted by an oxygen-free reactor with suspended biomass, by a clarification unit for separating the biomasses from the denitrified flow, by devices for recirculating the biomass to the reactor, and by devices for the dosage of the organic nutrient.

5. Process according to claims 1 and 4, characterized in that said process for the denitrification of the concentrated discharge flow is constituted by oxygen-free adhered-biomass reactors chosen among:

- adhered biomass introduced on a fixed support, wherein said support is constituted by inorganic material or by structures made of plastic material,
- fluidized adhered biomass, the support of the biomass being constituted by sand or other material suitable for providing a fluidized bed.
- adhered biomass on a non-immersed fixed support, which comprises devices for separating the excess biomass from the denitrified flow, devices for the dosage of the organic nutrient, and auxiliary devices.

6. Process for removing nitrates and other ions from drinking water substantially as described with reference to the accompanying drawings.

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Patents Act 1977
E--aminer's report to the Comptroller under ;ection 17 (The Search Report)

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Relevant Technical fields

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(ii) Int Cl (Edition 5) C02F

Search Examiner

R C SQUIRE

Databases (see over)

(i) UK Patent Office

(ii) WPI

Date of Search

20 DECEMBER 1991

Documents considered relevant following a search in respect of claims 1 TO 6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	DE 3505651 A (METALLGESELLSCHAFT)	1 TO 3

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

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