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(54) PROCEDE DE TRAITEMENT DE L'EAU
(54) WATER TREATMENT PROCESS

(57) L'invention concerne un procédé destiné à purifier l'eau des contaminants et à fabriquer de l'eau à faible teneur en substances dissoutes telles que le sel dans l'eau de mer. Le procédé, qui consiste à faire passer l'eau à travers une membrane à zéolites qui a été traitée avec de l'acide silicique ou avec un silicate d'alkyle, permet d'obtenir un flux d'eau très important à très faible teneur en contaminants.

(57) A method for removing contaminants from water and for producing water with a low level of dissolved substances, e.g. salt in sea-water comprises passing the water through a zeolite membrane which has been treated with silicic acid or an alkyl silicate, the method enables a high flux of water with very low level of contaminants.

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(54) Title: WATER TREATMENT PROCESS

(57) Abstract

A method for removing contaminants from water and for producing water with a low level of dissolved substances, e.g. salt in sea–water comprises passing the water through a zeolite membrane which has been treated with silicic acid or an alkyl silicate, the method enables a high flux of water with very low level of contaminants.

Water Treatment Process

The present invention relates to a method for the preparation of purified water; more particularly, it relates to a method for the preparation of purified water by means of a membrane.

Water purification, e.g. preparation of potable water or chemically pure water from water containing dissolved salts or other chemicals, is used in areas where pure water is not available.

Two widely used techniques are distillation and reverse osmosis. These methods are used for desalinisation of water and for purification of brackish water and are widely applied. However, these methods are relatively expensive in use as distillation, even using flash distillation and vacuum distillation techniques require large amounts of energy and large scale plant. Reverse osmosis requires the use of high pressures and membranes capable of withstanding these pressures.

Other polymeric membranes have been suggested but these have suffered defects in practice due to their lack of robustness, a tendency to foul and difficulty to produce in large sizes.

Zeolite membranes are known to be able to remove water from organic fluids and several processes and applications have been disclosed. However, in these previously disclosed applications, relatively small amounts of water are removed from the organic liquid, which is required to be dehydrated. We have found that with previously disclosed zeolite membranes, contact with a liquid mixture which is predominantly water in order to separate water from other compounds is not practicable. This is thought to be due to the defects in the membrane, allowing contaminants to be present in the water and, whereas this is not significant when a dehydrated organic liquid is required, it is not acceptable when pure water is required.

Other defects arise from the nature of the zeolite membrane; these include cracking and ion-exchange. When water containing salts come into contact with the zeolite membrane, the membrane will 'crack' and defects appear which affect the utility of the membrane. With salts and other ionic compounds present in the water, ion-exchange can take place with the zeolite membrane and the membrane loses its effectiveness.

Hitherto with known zeolite membranes it has not proved possible to remove contaminants from water when the contaminants are only present in small amounts as the volume of water which has to pass through the water makes it impractical for use.

However we have found surprisingly that with our membranes it has proved practical to remove contaminants which are present in a small amount and we have devised a method of purifying water using a treated membrane which reduces these problems.

According to the invention there is provided a method for obtaining purified water from water containing contaminants which method comprises passing the contaminated water through a crystalline zeo-type material to separate the contaminants from the water, characterised by the zeolite membrane having been treated by contact with a with a silicic acid and/or polysilicic acid or a mixture of silicic and/or poysilicic acids or with an organic silicate.

Zeo-type materials are also known as molecular sieves which are widely known and used. They comprise an extended network of channels formed from silicon/oxygen tetrahedrons joined through the oxygen atoms. Zeolites and alumino-silicates are the most commonly known form of zeo-type materials and the present invention is applicable to any membrane formed from zeo-type materials and particularly applicable to zeolites and alumino-silicates. In the "Atlas of Zeolite Structure Types", Meier and Ofsen, 1987, Polycrystal Book Service, Pittsburg USA, various types of structure are described and, for example, those described as having LTA, MEL, MFI or TON structure can be used.

In "New Developments in Zeolite Science and Technology Proceedings of the 7th International Conference, Tokyo, 1986, page 103, another class of zeo-type materials are disclosed as crystalline aluminophosphate, silicoalumina phosphates and other metallo-alumino phosphates.

Typical zeolites which can be used in the present invention are Zeolites include but are not limited to, 3A, 4A, 5A, 13X, X, Y, ZSM5, MAPOs, SAPOs, Silicalite, β, θ,etc.

The porous supports on which zeo-type membranes are formed and which can be used in the present invention include those formed of metals, ceramics, glass, mineral, carbon or polymer fibres or cellulosic or organic or inorganic polymers. Suitable metals include titanium, chromium and alloys such as those sold under the Trade Marks "Fecralloy" and "Hastalloy" and stainless steels. The porous supports may be formed of a mesh or from sintered metal particles or a mixture of both. These are commonly sold in the form of filters.

Porous ceramics, glass mineral or carbon materials can be used including porous silicon and other carbides, clays and other silicates and porous silica. If desired, the support can be a zeolite formed by compression or using a binder. The shape of the support is not critical, for example, flat sheet, tubular, wound spiral, etc. can be used. If polymeric materials are used, these can optionally be film coated with metal or metal oxide or a silicic acid as herein defined.

The porous support can be also be a granular solid e.g. formed of particles of a closely packed material such as a pellitised catalyst.

The present invention can be used with porous supports of any suitable size although, for large flux rates through a membrane, large pore sizes are preferred. Preferably pore sizes of 0.01 to 2,000 microns, more preferably of 0.1 to 200 and ideally of 1 to 20 microns are used. Pore sizes up to 300 microns can be determined by bubble point pressure as specified in ISO 4003. Larger pore sizes can be measured by microscopic methods.

The larger the relative amount of the surface which is composed of voids in general the more suitable the porous support.

The membranes which can be treated to be used in the method of the present invention can be formed by any method, for example by crystallisation from a gel or solution, by plasma deposition or by any other method such as electro deposition of crystals on conducting substrates e.g. as described in DE 4109037.

When the membrane comprising a film of zeo-type material is prepared by crystallisation from a synthesis gel, any of the methods described in the prior art can be used.

The synthesis gel used in the process can be any gel which is capable of producing the desired crystalline zeo-type material. Gels for the synthesis of zeo-type materials are well known and are described in the prior art given above or, for example, in EP-A-57049, EP-A- 104800, EP-A-2899 and EP-A-2900. Standard text books by D W Breck ("Zeolites Molecular Sieves, Structure Chemistry and Use") published by John Wiley (1974) and P.A Jacobs and J.A Martens (Studies in Surface Science and Catalysis No. 33, Synthesis of High Silica Alumino silicate Zeolites" published by Elsevier (1987), describe many such synthesis gels. The process which can be used includes conventional syntheses of zeo-type materials, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat.

The treated membrane which is used in the process of the invention can be prepared by a process which comprises deposition or crystallisation from a growth medium. In one embodiment of the invention the growth medium can be used in two different methods.

In the gel method (method 1) for forming the membrane the gel used to form the membrane preferably has a molar composition in the range of

$$(1.5 - 3.0)Na_2O : (1)Al_2O_3 : (2.0)SiO_2 : (50\text{-}200)H_2O$$

and the method used can be used in any of the methods disclosed in the references listed above.

In the liquid solution method (method 2) the liquid solution used to form the membrane preferably has a molar composition in the range of :-

$$(6 - 10.0)Na_2O : (0.2)Al_2O_3 : (1.0)SiO_2 : (150\text{-}250)H_2O$$

The liquid solution preferably contains a maximum amount of the compound capable of crystallising to form a zeo-type material whilst still remaining a liquid solution. By maximum amount is meant the maximum amount which can be maintained in solution so that no precipitation occurs before zeolite formation.

Methods (1) and (2) can be used under the conditions listed below and method (1) and method (2) can be used either on their own or with method (1) followed by method (2) or vice versa.

The conditions which can be used for forming the membrane are with a temperature of the growth solution preferably in the range of 50 to 100°C and the pH can be adjusted e.g. to pH of 12.5 to 14 by addition of sodium hydroxide or ammonia. If desired the sodium ion concentration can be increased without increasing the pH by the addition of a sodium salt such as sodium chloride. The growth solution can be seeded with zeolite crystals of the desired zeolite to be synthesised. The membrane can be washed to pH neutral after membrane formation prior to any post-treatment.

The porous support can be contacted with the growth medium by immersion or by pouring the growth medium over the support with the support held substantially horizontal, either face up at the bottom of a container, or face down at the surface of the growth medium, or it can be passed over one or both sides of the support, with the support held substantially horizontal, or it can be passed over one or both sides of the support with the support held substantially vertical or the support can be in any intermediate position.

The growth medium can be kept static, stirred, tumbled or passed over or around the support, alternatively the growth medium can be passed over both sides of the support with the support held substantially horizontal or at any intermediate position.

Pressure may also be applied but it is usually convenient to conduct the crystallisation under autogenous pressure. Preferably the porous support is completely immersed in the growth medium; alternatively, if desired, only one surface of the support may be in contact with the growth medium. This may be useful, for example, if it is desired to produce a membrane in the form of a tube, where only the inside or outside of the tube need be in contact with the growth medium.

It may be useful if it is desired to produce a membrane containing two different zeolites, one on each side of the support. Use of such a bi-functional membrane would be equivalent to using two separate membranes, each carrying a different zeolite.

If desired, the treatment with the gel or liquid solution can be repeated one or more times to obtain thicker membrane coatings.

Preferably the porous support is pre-treated with a zeolite initiating agent. The zeolite initiating agent is preferably a cobalt, molybdenum or nickel oxide or it can be particles of a zeolite, e.g. the zeolite which it is intended to deposit on the porous support, or any combination of these. Another example of an initiating agent is a compound which can deposit a zeo-type pre-cursor material e.g. a silicic acid or polysilicic acid.

The zeolite initiation agent can be contacted with the porous support by a wet or dry process. If a dry process is used, the particles of the zeolite initiation agent can be rubbed into the surface of the porous material, or the porous material surface can be rubbed in the particles.

Alternatively the particles of the zeolite initiation agent can be caused to flow over and/or through the porous support, or pulled into the support by means of a vacuum.

If a wet process is used, a liquid suspension of powder of the zeolite initiation agent is formed and the liquid suspension contacted with the porous support to deposit the zeolite initiation agent on the support.

Before contacting the surface of the porous support with the zeolite initiation agent the surface is preferably wetted with wetting agent such as an alcohol, water or a mixture of these.

When a silicic acid is used as an initiating agent it can be a silicic acid as herein defined.

In the present specification by silicic acid is meant monosilicic, low, medium and high molecular weight polysilicic acids and mixtures thereof.

As well as treatment with silicic acids the zeo-type materials can be treated with alkylorthosilicates such as tetra ethyl ortho silicate (TEOS) and tetra isopropyl ortho silicate (TIPOT) akoxyorthosilicates such as tetramethoxyortho silicate which form a polysilicic acid when applied to the zeo-type material. These alkylorthosilicates and alkoxyorthosilicates form mesoporous silica compounds which consist essentially of a series of polysilicic acid units linked together, each unit comprising a polysilicic acid molecule as described in GB Patent Application 9316350.9 and comprising a plurality of three dimensional species linked together with each species either having silicon atom bridges with an oxygen atom between each silicon atom or hydroxyl groups on the silicon atoms.

The treatment of zeo-type materials by silicic acids is described in WO 96/09110.

Methods of making silicic acids are described in GB Patent Application 2269377 and a preferred method is by acidification of a sodium silicate solution followed by separation of the silicic acid by phase separation using an organic solvent such as tetrahydrofuran. The organic phase can then be dried and anhydrous silicic acid separated e.g. by addition of n-butanol to obtain a substantially anhydrous solution of silicic acid. The degree of polymerisation of the silicic acid depends on the actual conditions used e.g. the time the sodium silicate solution is in contact with the acid before addition of the organic solvent, temperature etc.

The silicic acid used in the present invention preferably has an average molecular weight in the range of 96 to 10,000 and more preferably of 96 to 3220.

The silicic acids are known compounds and are usually prepared as a mixture of acids with a range of different molecular weights and this mixture is suitable for use in the present invention.

The silicic acids are combination of silicon, oxygen and hydrogen, linked together in the case of polysilicic acids through an oxygen bridge, with terminal -OH groups.

They have a generic formula of $Si_nO_p(OH)_r$ where n, p and r can vary from n=1, p=0, r=4 in the case of monosilicic acid through to n=8-12, p=12-20, r=8-12 in the case of medium molecular weight silicic acids through to n=20-32, p=36-60 and r=8-20 in the case of a higher molecular weight polymers.

The membrane can be treated with anhydrous silicic acid and a preferred method is to contact the membrane with an anhydrous solution of the silicic acid e.g. by dipping, pulling through with vacuum, forming with pressure etc. Preferably the solution containing the silicic acid is removed e.g. by evaporation at room temperature and/or by heating.

Alternatively cross-linking can be accomplished by treating with an acid or base or with acidified or basified water e.g. of pH 2 to 12 preferably of 4 to 10.
The silicic acids used in the present invention can be used in "narrow" molecular weight distribution as formed or in a combination of different molecular weight ranges.

Greater flexibility can be introduced into the final membranes by treating them with a flexibilising agent by adding e.g. a hydroxy terminated polysiloxane into the silicic acid solution before treatment of the membrane.

When the membrane is treated by a alkylorthosilicate the membrane is preferably treated as above using the alkylorthosilicate in place of the silicic acids.

The membranes treated by this process are improved in terms of their performance and membrane strength compared with untreated membranes.

The method of the invention can be used to produce water with very low levels of contaminants e.g. below 10ppm from contaminated water..

The degree of purification of the water, i.e. the level of contaminants still present in the purified water will depend on the thickness and nature of the zeolite membrane, the pressure applied to the water, the time of contact of the contaminated water with the zeolite membrane, temperature, etc. At the very low levels of contaminants obtained, particularly when the exact nature of the contaminants is unknown it is convenient to measure the conductivity of the water. De-ionised water typically has a conductivity of about 0.1 to 30µS/cm and distilled water has a conductivity of about

1 to 2 µS/cm. The method of the present invention can produce water with a conductivity of below these values which shows that there is a very low level of contaminants.

The water can be purified by being passed through the membrane by applying a reduced pressure or vacuum to one side of the membrane and this reduction in pressure causing the water to pass through the membrane and be separated from the impurities.

Owing to the action of the treated membrane, a wide range of contaminated water can be purified, e.g. sea water, brackish water, water contaminated with industrial chemicals such as hydrocarbons, organic chlorine compounds, metals, detergents etc., biological materials such as urines etc. and water contaminated by human or animal use e.g. the so-called "grey" water obtained for example from washing, showers, bathwater etc. If desired, by increasing the severity of the treatment conditions, substantially pure water or de-ionised water can be obtained.

Even with sea-water which has a relatively high conductivity levels of conductivity (~30,000 µS/cm) below 30 µS/cm can be achieved indicating a very low level of salt in the water.

It is surprising that by treating a zeolite membrane as described above enables the membrane to be used to purify contaminated water in a way not possible with the untreated zeolite membrane and to obtain such very low levels of conductivity.

The method can be used in a pervaporation process or as a reverse osmosis process. In general reverse osmosis processes have a higher flux.

The invention is described in the following Examples in which Example 1 is an example of the preparation of a membrane using a known method, Example 2 is an example of preparation of a post-treatment solution, Example 3 is an example of the test procedure, Example 4 is an example of the post-treatment procedure and Examples 5 to 11 are examples of production and testing of treated membranes.

Example 1 Membrane Growth

The substrate used was a Bekipor (Trade Mark) ST 5BL3 filter. This consists of very fine 316 stainless steel fibres brought together in a 3-dimensional labyrinthic structure. The fibres are arranged randomly in a homogeneous web. This web is further compacted and sintered to give a very strong metallic bond at each fibre crossing. The average pore size is approximately 5.3 microns and the diameter of the wire on the surface is 6.5 microns.

A 7cm. disc of the metal mesh was placed in a 100ml flat bottomed petri dish which had previously been cleaned by washing with de-ionised water, acetone, toluene and finally acetone before being dried in an oven at 90 degrees C. for 3 hours.

(a) Cobalt pre-treatment:

The mesh was placed in a beaker to which was added 50ml of 0.1 M cobalt nitrate solution, the beaker was placed in an oven at 90°C to dry, then the mesh was removed from the beaker and fired at 250°C for 4 hours. The mesh was removed from the furnace and allowed to cool. This procedure was repeated 2 more times to obtain a good cobalt oxide coating.

(b) Zeolite Pre-treatment

Zeolite 4A powder was rubbed into the active side of the substrate, which had already been cobalt coated as above, using a gloved finger, until no more zeolite will rub into the surface, any excess zeolite was tapped off.

Two solutions A and B were prepared separately
in two 500 ml glass bottles as follows:-

Solution A

24.49g Sodium Aluminate, 3.75g Sodium Hydroxide and 148.60g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48% Al_2O_3, 35.24% Na_2O, and 2.28% H_2O.

Solution B

50.57g Sodium Silicate of composition 14.21% Na_2O, 35.59% SiO_2 and 50.20% H_2O was dissolved in 148.60g de-ionised water.

Solution A was added slowly to solution B with both stirring and shaking by hand to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). This resulted in a hydrogel having a molar composition

$$2.01\ Na_2O : Al_2O_3 : 2.0\ SiO_2 : 120.0\ H_20$$

100 ml of the hydrogel was slowly poured into a growth vessel containing the cobalt oxide treated and zeolite rubbed mesh in a vertical position. The growth vessel was placed in a domestic pressure cooker together with a beaker containing the remaining hydrogel solution. The pressure cooker was placed in an oven preheated to 100 degrees C. for 5 hours. Subsequently it was removed from the oven and allowed to cool for 30 minutes. The growth vessel was removed and the solution poured away.

The metal mesh was carefully removed with a long flat rod ensuring that the mesh was not bent or damaged in any way. The mesh was placed in a glass beaker and washed three times with 100ml aliquots of de-ionised water, swirling the solution each time to ensure complete removal of residues. The membrane was allowed to air dry overnight.

The surface of the dried coated mesh was subsequently wiped clean with a clean lens tissue in order to remove any loose powdery deposits which may have formed on the surface. The mesh was inverted and the process repeated

The mesh was reinverted and the top surface cleaned again. It was then washed with de-ionised water and left to air dry.

X-ray Analysis showed this to be a Zeolite 4A

Example 2 Preparation of TEOS For Post Treatment of Membrane

The post treatment solution was prepared by placing 40ml of (TEOS) into a clean, dry beaker, adding 180 ml of deionised water and 180ml of ethanol. The mixture was then stirred at 300r.p.m. for a period of 5 mins.

Example 3 Membrane Test Procedure

A membrane is loaded into a pervaporated test cell in an apparatus as shown in the accompanying drawing. The apparatus consists of a stainless steel test cell (1) fitted with a pressure gauge (2) relief valve (3) magnetic stirrer (4) and thermocouple (5). The membrane prepared as in Example 1 was placed on a porous stainless steel disc (6) and was sealed into the cell with O ring (7).

The cell could be simultaneously heated and stirred by a heater /stirrer (8). Vacuum could be applied through line (9). Vapour removed from the test cell was condensed out in cold trap (10). Line (9) had a pressure gauge (11) and relief valve (12).

The test cell was filled with an isopropanol/water (IPA/H_2O) mixture (90/10 wt. % respectively). The membrane was tested at approximately 70^{0}C.

The pressure on the side of the membrane remote from the liquid was reduced to 4 mbar (0.4 kN). Permeate was collected over periods of 8 hours and weighed, and small aliquots were analysed, feed water concentration was monitored throughout.

Example 4 Post-treatment Procedure of Membrane

After the initial test of the untreated membrane in the apparatus of Example 3 with IPA/Water, the cell was emptied, rinsed with 2 x 50 ml aliquots of ethanol and then another 50ml aliquot of ethanol was placed into the cell which was then placed under vacuum for 30 mins.

The ethanol was removed from the cell and the TEOS post-treatment solution prepared as in Example 2 was poured into the cell. The cell was then treated to 70^{0}C for a period of 24 hours, with the downstream side under vacuum. After this period, the mix was removed, the heat switched off, vacuum removed and then compressed air was passed over the membrane for a period of one hour.

Example 5

A membrane produced by the method of Example 1 was treated under pervaporation conditions described on Example 3 and the results shown in Table 1 below

Table 1

Isopropanol/water mixture at 70°C

Time on Stream (hours)	Feed Water % weight	Permeate Water % weight	Permeate Water Flux (J) $kg/m^2/day$
1	11.10	90.11	147.75
1.5	6.00	96.47	88.00
2.0	4.36	94.81	72.87
4.0	2.94	81.14	29.74
5.5	0.47	30.57	4.91

The membrane was then post treated as in Example 4, the membrane was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 2.

Table 2

Isopropanol/water mixture at 70°C

Time on Stream (hours)	Feed Water % weight	Permeate Water % weight	Permeate Water Flux (J) kg/m^2/day
0.5	7.36	98.62	102.82
0.8	5.27	100.00	99.40
1.3	4.01	99.69	63.05
1.8	2.60	98.28	30.96
3.2	0.75	89.06	10.51
3.5	0.63	85.00	1.13

Example 6

A membrane produced by the method as described in Example 1 was treated under pervaporation conditions described in example 3 and the results shown in Table 3

Table 3

Isopropanol/water mixture at 70°C

Time on Stream (hours)	Feed Water % weight	Permeate Water % weight	Permeate Water Flux (J) kg/m^2/day
1.0	9.42	87.46	156.34
1.5	3.33	86.31	65.84
2.0	2.10	76.84	45.81
4.0	1.15	46.30	12.65
5.5	0.37	18.88	1.36

The membrane was then post treated as in Example 4, the membrane was re-tested under pervaporation conditions as in example 3 and the results shown in Table 4.

Table 4

Isopropanol/water mixture at 70°C

Time on Stream (hours)	Feed Water % weight	Permeate Water % weight	Permeate Water Flux (J) kg/m^2/day
0.5	10.16	98.83	103.04
0.83	6.86	100.00	99.40
1.33	4.91	99.53	62.95
1.83	3.39	97.43	30.69
3.17	0.40	88.48	10.44
3.5	0.28	85.00	1.13

Examples 7-11 Various different water samples were purified using the membrane of the invention.

Example 7

The membrane used was prepared as in Example 6 and after post treatment was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 5.

Table 5

Tap Water at 70°C

Time on Stream (hours)	Permeate Water Flux (J) kg/m^2/day
1	269.6
2	270.2
3	274.1
4	274.7
5	279.2
6	280.2

Conductivity

Tap Water	660 µS/cm
Tap Water Permeate	2.2 µS/cm

Example 8

The membrane used was prepared as in Example 6 and after post treatment was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 6.

Table 6

De-ionised Water at 70°C

Time on Stream (hours)	Permeate Water Flux (J) kg/m^2/day
1	394.9
2	368.1
3	346.3
4	339.4

Conductivity

De-ionised Water	1.8 µS/cm
De-ionised Water Permeate	0.8 µS/cm

Example 9

The membrane used was prepared as in Example 5 and after post treatment was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 7

Table 7

Soapy Water at 70°C

Time on Stream (hours)	Permeate Water Flux (J) kg/m^2/day
1	129.1
2	154.1
3	172.4
4	182.1
5	183.9
6	182.2
7	180.7

Conductivity

Soapy Water	771 µS/cm
Soapy Water Permeate	24.8 µS/cm

Example 10

The membrane used was prepared as in Example 5 and after post treatment was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 8.

Table 8

Urine at 70°C

Time on Stream (hours)	Permeate Water Flux (J) kg/m^2/day
1	91.9
2	77.1
3	77.2
4	71.9
5	72.3
6	70.1

Conductivity

Urine	12,600 µs/cm
Urine Permeate	25.6 µs/cm

Example 11

The membrane used in Example 6 and after post treatment was re-tested under pervaporation conditions as in Example 3 and the results shown in Table 9.

Table 9

Synthetic Sea Water at 70°C

Time on Stream (hours)	Permeate Water Flux (J) kg/m^2/day
1	96.1
2	97.0
3	96.0
4	103.7
5	104.6
6	91.9

Conductivity

Sea Water	31,000 µS/cm
Sea Water Permeate	25.2 µS/cm

Claims

1. A method for obtaining purified water from water containing contaminants which method comprises passing the contaminated water through a crystalline zeo-type material to separate the contaminants from the water, characterised in that the zeolite membrane has been treated by contact with a with a silicon compound selected from silicic acid and/or polysilicic acid or a mixture of silicic and/or polysilicic acids and organic silicates.

2. A method as claimed in claim 1 characterised in that the membrane is formed by the deposition of a film of zeo-type material on a porous support.

3. A method as claimed in claim 1 or 2 characterised in that the membrane is formed by crystallisation of a film of a zeo-type material from a synthesis gel by immersing a porous support in a synthesis gel comprising a gel of a zeo-type material and the zeo-type material deposited onto the porous support by the application of pressure and/or heat.

4. A method as claimed in any one of the preceding claims characterised in that the zeo-type material is zeolite 3A, 4A, 5A, 13X, X, Y, ZSM5, MPOs, SAPOs, Silicalite, β, or θ.

5. A method as claimed in any one of claims 1 to 4 characterised in that the porous support is pre-treated with a zeolite initiating agent selected from cobalt oxide, nickel oxide or molybdenum oxide, a zeolite or a silicic acid.

6. A method as claimed in any one of claims 1 to 5 characterised in that the crystalline zeo-type membrane is produced by a process which comprises immersing at least one surface of a porous support in a synthesis gel or solution which is capable of crystallising to produce a crystalline zeo-type material, inducing crystallisation of said gel so that zeo-type material crystallises on the support, removing the support from the mix and then contacting the porous support with a liquid solution containing a dissolved compound capable of crystallising from the solution to produce a crystallisation from the said solution so that a second coating of a zeo-type material crystallises on the support.

7. A method as claimed in any one of the preceding cliaims in which the silicic acid has an average molecular weight in the range of 96 to 10,000 and in that the silicic acid is cross-linked in the pores of the membrane.

8. A method as claimed in claim 7 characterised in that the silicic acid has an average molecular weight in the range of 96 to 3220.

9. A method as claimed in any one of claims 1 to 8 characterised in that the silicic acid has a generic formula of $Si_nO_p(OH)_r$ where n, p and r can vary from n=1, p=0, r=4 through to n=8-12, p=12-20, r=8-12.

10. A method as claimed in any one of claims 1 to 9 characterised in that the silicic acid has a generic formula of $Si_nO_p(OH)_r$ where n, p and r are from n=20-32, p=36-60 and r=8-20.

11. A method as claimed in any one of claims 1 to 10 characterised in that the membrane is treated with anhydrous silicic acid.

12. A method as claimed in claim 11 characterised in that the silicic acid is cross-linked by treating with an acid or base.

13. A method as claimed in any one of claims 1 to 6 characterised in that the organic silicate is an alkylorthosilicate or an alkoxyorthosilicates.

14. A method as claimed in claim 13 characterised in that the organic silicate is tetra ethyl ortho silicate, or tetra isopropyl ortho silicate or tetramethoxyortho silicate.

15. A process as claimed in any one of claims 1 to 14 characterised in that a flexibilising agent is added to the silicic acid or organic silicate solution before treatment of the membrane.

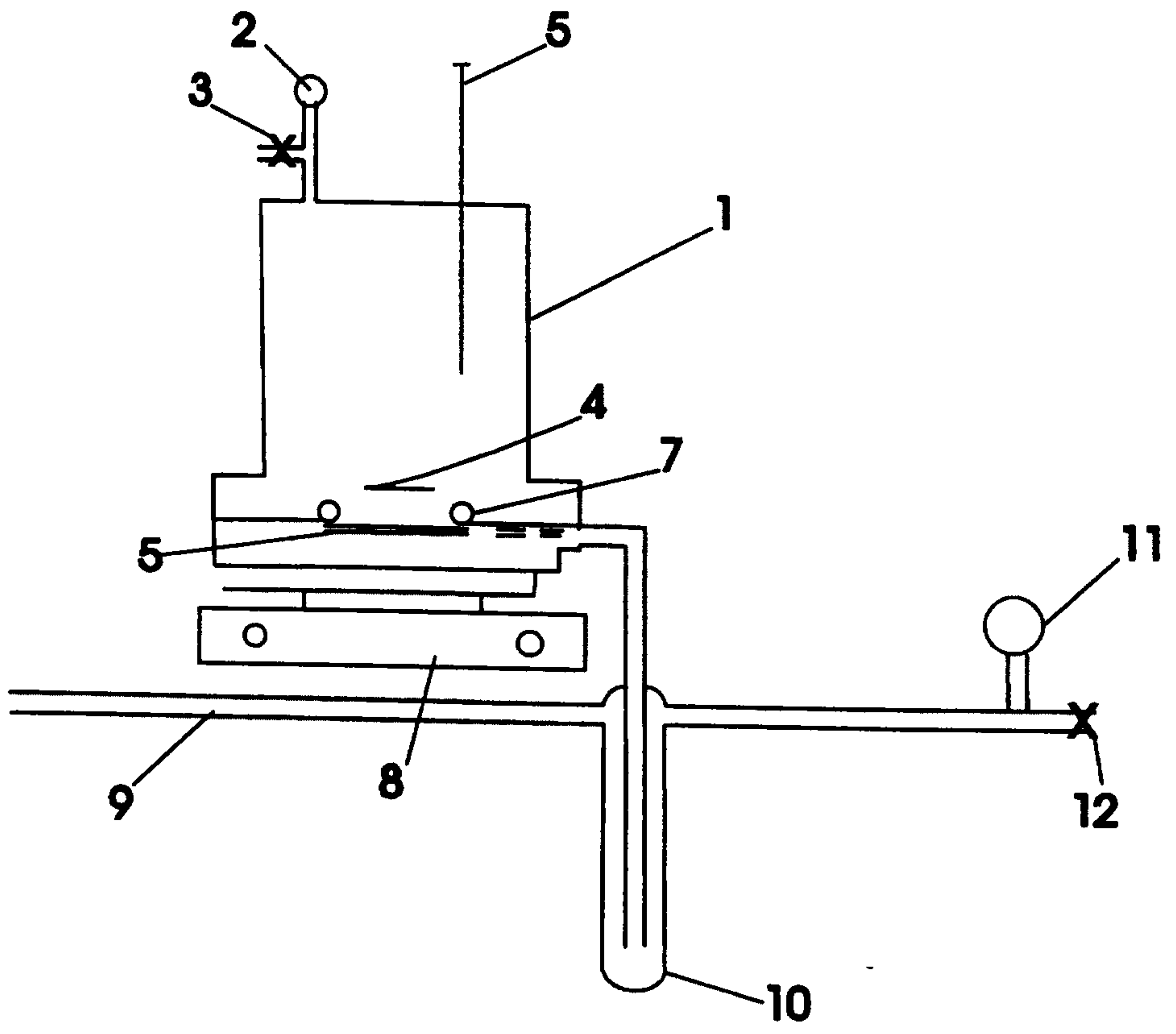
16. A process as claimed in claim 15 characterised in that the flexibilising agent is a hydroxy terminated polysiloxane.

17. A process as claimed in any one of the preceding claims characterised in that the porous support is formed from a metal mesh and/or sintered metal particles.

18. A method as claimed in any one of claims 1 to 17 characterised in that the water containing the contaminants is passed through the membrane so that at least some of the contaminants do not pass through the membrane.

19. A method as claimed in claim 18 characterised in that reduced pressure is applied on the side of the membrane remote from the water containing contaminants.

20. A method as claimed in any one of claims 18 or 19 characterised in that the decontaminated water has a conductivity of less than 30.0 μs/cm.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