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(54) **Title:** A FILTER APPARATUS AND A METHOD FOR REMOVING DISSOLVED ORGANIC COMPOUNDS FROM A WATER BASED LIQUID

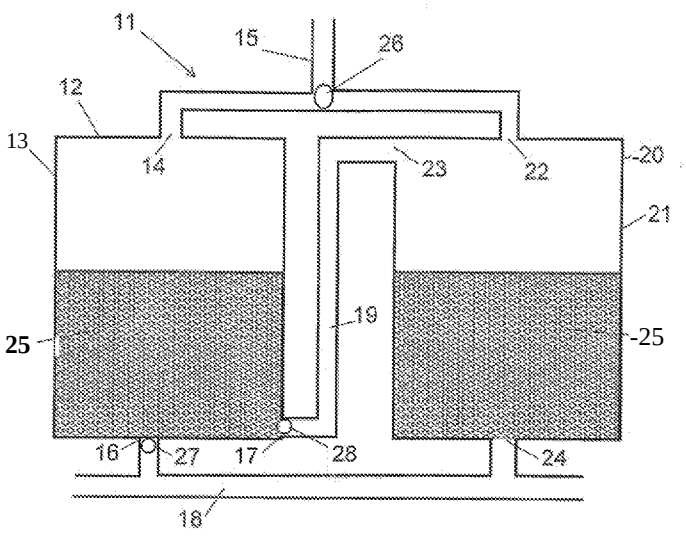


Fig. 6

(57) **Abstract: A** filter apparatus (11) for removing dissolved organic compounds from a water based liquid, comprising at least one filter unit (12, 20) in the form of a container (13, 21) in which an inlet (14, 22, 23) and an outlet (16, 17, 24) is provided, a filter bed (25) being arranged in the at least one container between the inlet and the outlet, the filter bed comprising at least one layer of an adsorbent comprising an amorphous precipitated silica material, wherein the amorphous precipitated silica material has a porosity with an average pore width of less than 10 nm.

WO 2018/143883 A1

A filter apparatus and a method for removing dissolved organic compounds from a water based liquid

TECHNICAL FIELD

The present invention relates to a filter apparatus according to the preamble of claim 1 and to a method for removing dissolved organic compounds from a water based liquid. The invention also relates to use of an amorphous precipitated silica material and to use of a filter apparatus.

By "produced water" is herein intended any water that comes out of an oil or gas reservoir as part of an oil or gas production process. Sources of produced water include connate water present in the reservoir prior to production, condensed water from produced gas, and injected water derived from injection wells.

BACKGROUND AND PRIOR ART

Produced water is the largest by-product generated by oil and gas extraction, hence, there are significant quantities requiring remediation, of which the removal of dissolved organic compounds in low concentrations is the final step.

Produced water, at the refining stage, contains only low concentrations of dissolved oil droplets, mainly pollutants in the form of benzene, toluene, ethylbenzene and xylene (BTEX group). The concentrations of these pollutants are typically well below the solubility limits.

Multilayer filters comprising filtration media in the form of e.g. anthracite, sand, garnet, gravel and rock have commonly been used for removal of such pollutants from produced water. Also walnut shells are commonly used as a filtration media. However, multilayer filters comprising sand are heavy and the abrasive sand particles reduces the lifetime of the filter components. The

fine sand particles may also cause an elevated pressure loss across the filter bed, thus reducing the efficiency of the filter. The expected lifetime of filtration media is relatively low, with replacement required frequently, depending on media type and feed water quality.

Another technique for treatment of produced water is adsorption using a variety of materials including zeolites, organoclays, activated alumina, and activated carbon. However, the adsorption material eventually becomes consumed with contaminants and must be disposed or regenerated using chemicals. Furthermore, activated carbon is associated with relatively slow kinetics and large volumes are needed, thus requiring space consuming vessels. Organoclays, on the other hand, are relatively expensive.

Currently used techniques for removal of dissolved organic compounds in produced water also include use of a porous polymeric bed impregnated with an organic surfactant. However, this method is relatively costly and is therefore less suitable for large scale filtration of produced water.

SUMMARY OF THE INVENTION

It is an objective of the present invention to achieve an in at least some aspect improved technique for removal of dissolved organic compounds from water based liquids such as produced water.

This and other objectives are according to a first aspect of the present invention achieved by means of the initially defined filter apparatus, which is characterised in that the filter bed comprises at least one layer of an adsorbent comprising an amorphous precipitated silica material, wherein the amorphous precipitated silica material has a porosity with an average pore width of less than 10 nm.

According to another aspect of the invention, the above defined objective is achieved by means of use of the proposed filter apparatus for removing dissolved organic compounds from a water based liquid. The dissolved organic compounds may typically be present at a concentration of 200 ppm or less.

According to another aspect of the invention, the above defined objective is achieved by means of a method for removing dissolved organic compounds from a water based liquid, comprising passing the water based liquid through the proposed filter apparatus.

Amorphous precipitated silica material, which is a mesoporous, low density material having a relatively large surface area, has according to the present disclosure been found to be efficient for the removal of dissolved organic compounds from water based liquids at low concentrations, typical for produced water. The filter apparatus according to the invention is therefore suitable for the final step of cleaning of produced water. The adsorption of dissolved organic compounds on amorphous precipitated silica has been found to be a predominantly physical process, in which organic compounds are adsorbed on the surfaces of the adsorbent due to primary adsorption interactions with the surface and thereafter cooperative multilayer formation.

In particular, precipitated silica material with an average pore width of less than 10 nm, as determined using BET (Braunauer-Emmett-Teller) analysis, has been found to be efficient as an adsorbent. The organic compounds which are to be adsorbed can within this size range gain good access to the pores of the adsorbent, while as molecular repulsion that can be observed with large adsorbate clusters can be avoided.

Low cost synthetic routes for producing amorphous precipitated silica using ambient pressure drying are already known to produce suitable amorphous precipitated silica materials from

waterglass, having excellent mechanical properties. The amorphous precipitated silica material can be produced in a cost efficient manner by mixing alkali silicate with a salt solution, e.g. such as previously described in WO2006/071183.

The low density of the adsorbent makes the filter apparatus light-weight.

According to one embodiment, the amorphous precipitated silica material has a porosity with an average pore width within the range of 1-9 nm.

According to one embodiment, the amorphous precipitated silica material has been prepared via the precipitation of sodium silicate with sodium chloride by mixing an aqueous sodium silicate solution with aqueous sodium chloride. Such an adsorbent has proved to exhibit desirable adsorption properties.

According to one embodiment, the amorphous precipitated silica material has a BET surface area of at least 100 m^2/g. The surface area is thereby sufficiently large to achieve efficient adsorption of organic compounds. Preferably, the amorphous precipitated silica material has a BET surface area of at least 300 m^2/g, providing optimum conditions for adsorption. Even more preferably, the BET surface area is at least 500 m^2/g. The BET surface area may be up to 700 m^2/g or larger, depending on the conditions of preparation.

According to one embodiment, the amorphous precipitated silica material has a total pore volume within the range of 0.50-1.2 cm^3/g. The relatively large total pore volume results in enhanced adsorption.

According to one embodiment, the amorphous precipitated silica material has a density within the range of 0.06-0.1 g/cm^3. The

relatively low density makes it possible to provide a light weight filter which can e.g. be transported in an energy efficient manner.

According to one embodiment, the amorphous precipitated silica material has a hydrophilic surface. This generally removes the need for functionalising agents and enables use of cheaper precursors, thereby reducing the cost of synthesis of the adsorbent. The production and waste management of these materials thereby becomes economically suitable for a single adsorption cycle, hence, removing filter regeneration costs and associated issues. This embodiment is particularly suitable for filtering of water based liquid containing organic compounds at very low concentrations, such as at concentrations up to 200 ppm.

According to one embodiment, the adsorbent has been functionalised using at least one type of functional group to obtain a hydrophobic surface. The functionalization, in which for example methyl groups are used to achieve hydrophobicity, improves the affinity to organic adsorbates and can thereby increase adsorption. It also helps to prevent long-term deterioration of the structure due to the absorption of water. Regeneration of the adsorbent thereby becomes possible, enabling reuse of the adsorbent.

According to one embodiment, the adsorbent is in the form of granules having an average particle size within the range of 0.5-2 mm. By using granules within this size range, regeneration of the adsorbent is facilitated in comparison with smaller powder particles. The flow resistance of the filter bed may be adapted by adjusting the size of the granules, and the size may therefore be selected on the basis of the desired flow resistance. Flow resistance is generally inversely proportional to particle size. Too large granules will thereby offer too little flow resistance and the adsorption will be less efficient.

According to one embodiment, the filter apparatus comprises at least two filter units connected in series, so that the water based liquid can be passed through the filter bed of each filter unit successively. The filter apparatus may comprise several filter units connected in series and/or in parallel, depending on the needs. This allows a more efficient large scale filtration .

According to one embodiment, the filter apparatus further comprises bypass means for selectively bypassing at least one of said filter units. Thus, it is possible to bypass one or more of the filter units while it is being regenerated . Bypass conduits as well as pumps and valves may of course be provided in order to achieve an efficient flow of liquid and bypass of filter units that are to be regenerated .

The invention also relates to use of an amorphous precipitated silica material as an adsorbent for removing dissolved organic compounds from a water based liquid , wherein the amorphous precipitated silica material has a porosity with an average pore width of less than 10 nm. Preferred embodiments of such an amorphous precipitated silica material appear from the above description of the adsorbent.

Further advantages as well as advantageous features of the present invention will appear from the following detailed description .

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will in the following be described with reference to the appended drawings, in which:

Fig. 1 schematically shows a cross sectional view of a filter apparatus according to a first embodiment,

Fig. 2a shows absorbance spectra of three different adsorbents,

Fig. 2b shows absorbance spectra of a hydrophilic and a hydrophobic adsorbent,

Fig. 2c shows incremental pore volume as a function of pore width for an adsorbent according to an embodiment of the invention,

Fig. 3a shows kinetic profiles of benzene adsorption on the adsorbents of fig. 2a,

Fig. 3b shows kinetic profiles of toluene adsorption on the adsorbents of fig. 2a,

Fig. 4a shows adsorption isotherms for benzene on the adsorbents of fig. 2a,

Fig. 4b shows adsorption isotherms for toluene on the adsorbents of fig. 2a,

Fig. 5a shows kinetic profiles of benzene adsorption on the adsorbents of fig. 2b,

Fig. 5b shows adsorption isotherms for benzene on the adsorbents of fig. 2b, and

Fig. 6 schematically shows a filter apparatus according to a second embodiment.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

A filter apparatus 1 according to a first embodiment of the invention is schematically shown in fig. 1. The filter apparatus comprises a filter unit 2 in the form of a container 3, in which an inlet 4 and an outlet 5 is provided for passage of water based liquid such as produced water. A filter bed 6 comprising an adsorbent is arranged in the container 3, between the inlet 4 and the outlet 5 so that the liquid may pass through the filter bed. The filter apparatus may of course comprise several filter units 2 arranged in series and/or in parallel, with conduits for passage of liquid, valves and one or more pumps being provided between the filter units. Bypass arrangements may be provided such that one

or some of the filter units can be bypassed during regeneration of the bypassed filter unit/units.

During use, water based liquid containing dissolved organic compounds is introduced into the filter unit 2 via the inlet 4, is passed through the filter bed 6 and is discharged via the outlet 5. Organic compounds within the water based liquid are thereby adsorbed by the adsorbent of the filter bed 6.

A filter apparatus 11 according to a second embodiment is schematically shown in fig. 6. The filter apparatus 11 comprises a first filter unit 12 in the form of a container 13 having an inlet 14 connected to a supply pipe 15. The first filter unit 12 has two outlets 16, 17, of which a first one 16 is connected to a collecting pipe 18 and a second one 17 is connected to a transfer pipe 19 leading to a second filter unit 20 in the form of a container 21. The second filter unit 20 has a first inlet 22 connected to the supply pipe 15 and a second inlet 23 connected to the transfer pipe 19. The second filter unit 20 has an outlet 24 connected to the collecting pipe 18. In both filter units, a filter bed 25 comprising a layer of an adsorbent is provided. A split valve 26 is provided in the supply pipe 15, by means of which a flow of liquid can be controlled to the first filter unit 12 or to the second filter unit 20. A valve 27 is also provided in the first outlet 16 of the first filter unit 12, by means of which the first outlet 16 can be opened or closed. Another valve 28 is provided in the second outlet 17 of the first filter unit 12, for closing and opening of the second outlet 17. A pump (not shown) is provided in the transfer pipe 19 for pumping liquid from the first filter unit 12 to the second filter unit 20.

When the filter apparatus 11 is in use, the split valve 26 is first open so that liquid is passed via the supply pipe 15, the open split valve 26 and the inlet 14 to the first filter unit 12, in which it is passed through the filter bed 25. The valve 27 is initially closed while the valve 28 is open, so the liquid, after passing through the

filter bed 25, is pumped via the transfer pipe 19 to the second filter unit 20, where it passes through the filter bed 25 and into the collecting pipe 18 via the outlet 24. When a need to regenerate the first filter unit 12 arises, i.e. when the adsorbent in the filter bed 25 has reached its full adsorption capacity, the split valve 26 is closed so that liquid is passed directly to the second filter unit 20 via the first inlet 22. Liquid then passes through the filter bed 25 and into the collecting pipe 18 via the outlet 24. Once the first filter unit 12 is regenerated, the split valve 26 is opened again and liquid flows once again into the first filter unit 12. For regeneration of the second filter unit 20, the valve 17 is closed so that the second outlet 17 is blocked, and the valve 27 is opened. Liquid thereby flows via the first outlet 16 to the collecting pipe 18.

Of course, it is also possible to provide a second transfer pipe from the second filter unit to the first filter unit, so that liquid may be passed either via the first filter unit to the second filter unit, or via the second filter unit to the first filter unit. In this way, the filtering process can always be started in the currently more exhausted filter unit.

In both embodiments shown, the filter bed 6, 25 comprises a layer of adsorbent in the form of an amorphous precipitated silica material with an average pore width of less than 10 nm. The adsorbent can be prepared by preparing two solutions, solution A and solution B. Solution A is a dilute aqueous alkali silicate solution, comprising silica ($S1O2$) and an alkali metal oxide, e.g. sodium oxide ($Na2O$) or potassium oxide ($K2O$). Solution B is a concentrated or even saturated salt solution, such as a sodium chloride (NaCI) solution. Solution B may also comprise metal salts, such as magnesium or calcium salts. Also salts based on other metals may be used. An activation level of the silica source can be selected such as to obtain desired properties in terms of surface area, pore size distribution, density, total pore volume, etc.

Solutions A and B are mixed under rapid stirring and coagulates immediately. The resulting precipitate is rinsed, before dewatering using e.g. vacuum filtration or centrifugal filtration until a paste is obtained. The paste is dried via spray drying or via other techniques, such as in a rotary drier, or using pressure gradients such as described in WO2015/104317.

WO2006/071183 discloses a method for preparing an amorphous precipitated silica material which has, within the frame of the present disclosure, been found to be useful as an adsorbent for removing dissolved organic compounds from a water based liquid, such as produced water. The material is formed as a precipitate by mixing alkali silicate with a salt solution. The precipitate is thereafter processed in various ways to obtain an end product having desired properties in terms of pore size, particle size, surface area, density, etc.

The filter bed may also comprise several layers, e.g. of different types of amorphous precipitated silica materials, different particle sizes, different functionalization, etc.

EXAMPLES

Four different types of amorphous precipitated silica materials were prepared, wherein one of the materials, ND type, is according to an embodiment of the invention, and wherein the other materials, namely Z1, Z1HPO and CMS types, are included as comparative examples. The silica materials are sold under the trade name Quartzene®.

ND type silica was prepared via the precipitation of sodium silicate with sodium chloride at ambient temperature. A defined amount of dilute active aqueous sodium silicate solution (Si02: Na20 = 3.35) was prepared, representing solution A, while solution B was composed of aqueous sodium chloride (NaCl).

Solutions A and B were mixed under rapid stirring and the resulting precipitate was mixed with a defined amount of tap water, before vacuum filtration through a filter paper until a paste, comprising up to 85% water, was obtained and dried via spray drying.

Z1 type silica samples were prepared using a method analogous to that for ND, but with a different level of activation of the silica source.

A methylated version of Z1, herein called Z1HPO, was also prepared, i.e. a Z1 type silica functionalised using methyl groups to obtain a hydrophobic surface.

CMS type silica was prepared by adding calcium and magnesium sources at concentrations of 1:2 to the silica source (waterglass SiO_2:Na_2O = 3.35). A 500 ml salt solution, consisting of $MgCl_2$ hexahydrate and $CaCl_2$ dihydrate was prepared at a ratio of 68 mol% Mg and 32 mol% Ca; 500 ml salt solution, was poured onto 1.5 M (with respect to S1O2) sodium silicate solution (500 ml), and the resulting mixture agitated at room temperature. Subsequent coagulation occurred, and the obtained gel was washed, filtered and dried in the same manner as ND.

The ND and CMS type samples were powders, with particle sizes within the range of 2-150 μm. The Dv90 of the ND and CMS type silica materials, i.e. the 90th percentile of the particle size distribution by volume, was determined to be 46 and 75 μm, respectively. The Z1 and Z1HPO samples were in the form of granules with particle sizes between 1 and 1.5 mm.

Surface chemical functionalities of adsorbent materials are known to determine the hydrophilic or hydrophobic nature of a material. FT-IR analysis was used to determine surface functionalities of the samples (dried at 248 K for 2 h) prepared as hydrophilic. The obtained spectra shown in fig. 2a show the presence of silanol

polar groups (Si-OH), in the range of 2700-3650 cm^{-1}, for all materials studied, with Z1 and ND showing similar surface chemistries, while CMS exhibits more refined Si-OH bond peaks; consequently, the ND, CMS and Z1 type materials can be categorised as hydrophilic in nature. Fig. 2b shows a comparison between the hydrophilic Z1 and the hydrophobic Z1HPO materials.

Nitrogen sorption measurements were performed at 77 K using a Micromeritics ASAP 2420, on samples accurately weighed between 0.15 and 0.5 g and degassed at 393 K. 40 adsorption points and 30 desorption points were collected per isotherm, spanning the relative pressure range 0 - 0.99. Degassing at low temperatures requires longer treatment times but has the benefit that the structure of the material is preserved. Brunauer-Emmett-Teller (BET) analysis was used to interpret the data obtained.

Surface areas and pore volumes were also estimated using a-plot analysis of a nitrogen adsorption isotherm obtained at 77 K. Such a-plot analysis is for small pore sizes generally considered more reliable.

The surface areas obtained for the four samples show good agreement between the two methods (BET and a-plot), except in the case of ND, which exhibits small mesopores (Table I), thereby suggesting that the value obtained using the a-plot method would be more accurate. Pore sizes determined using BET analysis are for the comparative examples CMS, Z1 and Z1HPO widely distributed between 2 and 80 nm, while ND exhibits a discrete pore size distribution centred on 3.3 nm (Table I). Consequently, ND is the only material with a small mesopore contribution but it is notable that all samples exhibit significant total pore volume.

Sample name	S_{BET} [m^2/g]	S_α [m^2/g]	Average pore width [nm]	Total pore volume [cm^3/g]	Small mesopore volume [cm^3/g]	Meso- and macro-pore volume [cm^3/g]
Z1 (comp.)	325	331	20.3	1.03	-	1.03
Z1HPO (comp.)	186	186	17.4	0.97	-	0.97
CMS (comp.)	158	161	14.6	0.50	-	0.50
ND (inv.)	597	546	3.3	0.54	0.40	0.14

Table 1

A pore size distribution of an ND sample is shown in fig. 2c, in which incremental pore volume is plotted as a function of pore width. The surface area was analysed by nitrogen adsorption measurements, performed at 77K using a Micromeritics Tristar 3200, on samples accurately weighed between 0.15 and 0.5 g and degassed at 150°C, for 24h. The adsorption desorption points were collected for isotherm and spanning the relative pressure range of 0-0.99. BET theory was used to interpret the data obtained. The pore width was calculated according to the density functional theory (DFT) pore size method, and it was observed that the ND sample had an average pore width of less than 10 nm. Based on the definition of IUPAC (International Union of Pure and Applied Chemistry), the ND sample therefore contains microporous material (pore size under 2.0 nm) and mesoporous material (pore size between 2.0 nm and 50 nm). The calculated data were also confirmed by resulting physisorption isotherms, which were of the type IV isotherm known for mesoporous materials (Sing *et al.*, 1985, *Pure Appl. Chem.* 57, pp. 603-619).

Benzene and toluene were used as representative components of dissolved oils in produced water. The organics were purchased from Sigma Aldrich as chromatography grade reagents (HPLC, ≥

99.9%). Benzene is more representative of dissolved oil, as it is the most difficult organic compound from the BTEX group to adsorb from solution , due to the fact that the adsorption potential of the solute in the liquid carrier decreases with increasing solubility of the adsorbate. Since the solubility of the monoaromatics in the BTEX group decreases with molecular weight, their adsorption potential increases with the molecular weight, hence, the lowest molecular weight species (benzene) is the most difficult to adsorb.

Borosilicate glass bottles were used for all adsorption studies, and bottle volumes were selected in order to reduce headspace within the vessel. Mixtures of water and benzene were stirred in filled bottles for 1 h using a magnetic stirrer to solubilize the organic, before samples were extracted with a micropipette, then mixed with methanol and internal standard before injection , using a microsyringe, into the port of a gas chromatograph equipped with FID detectors to determine the concentration present. Pre-determined amounts of adsorbent were added to prepared bottles of aqueous phase organics to study adsorption characteristics; kinetic tests were conducted at pre-determined intervals, over 24 h, to determine times for maximum equilibria to be achieved for each sample. All measurements were conducted at 293 K.

Adsorption tests involved the addition of benzene, at concentrations in the range 0-1 100 ppm, to 110 ml of distilled water mixed with 100-500 mg of adsorbent, equilibrated for 24 h before analysis. An analogous procedure was used for toluene but using aqueous concentrations in the range of 0-400 ppm. However, the adsorption behaviour of hydrophobic Z1HPO was only tested using aqueous benzene, agitated using a rotary shaker to guarantee sorbent contact with the aqueous phase since the Z1HPO material floats in water.

All procedures were performed at 293 K using sealed cups with minimal headspace, as outlined above, to reduce volatilisation

losses. Blank tests, conducted without sorbent, demonstrated that volatilisation rates were negligible for both kinetic and adsorption measurements. The stirring rates used were constant, 200 rpm for magnetic stirring and 20 rpm for rotary stirring. Sampling was performed at various depths within a selected test vessel to verify the absence of concentration gradients within the bulk.

Gas chromatography was used to measure the concentrations of organic species in the aqueous systems studied.

Kinetic profiles of benzene and toluene adsorption on Z1, ND and CMS samples are shown in figs. 3a and 3b, respectively, showing equilibrium uptake q (mg adsorbate per g adsorbent) as a function of time. 84-90% of adsorption takes place on CMS and ND samples within the first six hours, with a full equilibrium time of less than 24 hours. For Z1, less than 80% of toluene and less than 70% of benzene is adsorbed after 24 hours.

The Freundlich adsorption model was used to determine adsorption capacities of the samples. According to this model,

$$q = k\text{-}Ce^{1/n},$$

wherein C_e is the equilibrium concentration of the solute (mg/l), k is the unitless constant of adsorption, indicating capacity, and 1/n is a unitless constant related to the intensity of adsorption.

Adsorption isotherms for benzene and toluene adsorption on Z1, ND and CMS samples are shown in figs. 4a and 4b, respectively.

Table 2 shows maximum uptakes of the samples Z1, ND and CMS type as calculated using data obtained for adsorption of benzene and toluene, determined from extrapolative interpolation to a benzene solubility of 1.763 g/l or a toluene solubility of 0.57 g/l.

The maximum uptake is shown in terms of mg adsorbate per gram adsorbent.

Sample	Adsorbate	Max. uptake [mg/g]
Z1 (comp.)	Benzene	53.25
	Toluene	46.91
CMS (comp.)	Benzene	110.48
	Toluene	51.36
ND (inv.)	Benzene	264.03
	Toluene	78.82

Table II

It can be seen from Table II that the ND sample performs significantly better than the comparative CMS and Z1 samples from the three sorbents studied in the range of concentrations used, with maximum adsorption capacities for ND estimated as close to the adsorbate solubility limits. The higher adsorption of ND is ascribed not only to the comparatively high surface area of this material, but also to its discrete pore size distribution centred around 3.3 nm, which provides good access for the organic molecules of interest while also being sufficiently narrow to prevent the molecular repulsion that can be observed with large adsorbate clusters. Z1, which was the only original material used in granular form, however underwent mechanical degradation during stirred reaction experiments.

Aqueous benzene concentrations below 0.25 ppm were explored in the comparison of adsorption characteristics of the hydrophilic Z1 and the hydrophobic Z1HPO. Adsorption was faster and a higher quantity of benzene was adsorbed for Z1HPO as shown in figs. 5a and 5b, showing kinetic profiles and isotherms, respectively. Furthermore, Z1HPO showed no significant mechanical degradation even after five days of rotary stirring at 20 rpm. Equilibrium was reached in less than three hours for Z1HPO.

The comparison of adsorption behaviour for hydrophilic Z1 and hydrophobic Z1HPO indicates that hydrophobicity is advantageous if multiple cycle use of the adsorbent is desired. At concentrations of approximately 200 ppm, benzene adsorption on Z1HPO is four times higher than for Z1, but the difference in terms of uptake between the two adsorbents is reduced with decreasing organic concentration. Hence, at very low aqueous concentrations of organics, functionalization to achieve hydrophobicity may have negligible effect on the organic compound's access to the internal porosity of the material. According to an embodiment of the invention, hydrophobized ND material may be used as the adsorbent.

The invention is of course not in any way restricted to the embodiments described above. On the contrary, many possibilities to modifications thereof will be apparent to a person with ordinary skill in the art without departing from the basic idea of the invention such as defined in the appended claims.

CLAIMS

1. A filter apparatus (1, 11) for removing dissolved organic compounds from a water based liquid, the filter apparatus (1, 11) comprising at least one filter unit (2, 12, 20) in the form of a container (3, 13, 21) in which at least one inlet (4, 14, 22, 23) and at least one outlet (5, 16, 17, 24) are provided, a filter bed (6, 25) being arranged in the at least one container (3, 13, 21) between the at least one inlet (4, 14, 22, 23) and the at least one outlet (5, 16, 17, 24), so that water based liquid can pass into the container (3, 13, 21) via the at least one inlet (4, 14, 22, 23), through the filter bed (6, 25), and out via the at least one outlet (5, 16, 17, 24),

characterised in

that the filter bed (6, 25) comprises at least one layer of an adsorbent comprising an amorphous precipitated silica material, wherein the amorphous precipitated silica material has a porosity with an average pore width of less than 10 nm.

2. The filter apparatus according to claim 1, wherein the amorphous precipitated silica material has a porosity with an average pore width within the range of 1-9 nm.

3. The filter apparatus according to claim 1 or 2, wherein the amorphous precipitated silica material has been prepared via the precipitation of sodium silicate with sodium chloride by mixing an aqueous sodium silicate solution with aqueous sodium chloride.

4. The filter apparatus according to any one of the preceding claims, wherein the amorphous precipitated silica material has a BET surface area of at least 100 m^2/g, preferably at least of 300 m^2/g.

5. The filter apparatus according to any one of the preceding claims, wherein the amorphous precipitated silica material has a total pore volume within the range of 0.50-1.2 cm^3/g.

6. The filter apparatus according to any one of the preceding claims, wherein the amorphous precipitated silica material has a density within the range of 0.06-0. 1 g/cm^3.

7. The filter apparatus according to any one of the preceding claims, wherein the amorphous precipitated silica material has a hydrophilic surface.

8. The filter apparatus according to any one of claims 1-6, wherein the adsorbent has been functionalised using at least one type of functional group to obtain a hydrophobic surface.

9. The filter apparatus according to any one of the preceding claims, wherein the adsorbent is in the form of granules having an average particle size within the range of 0.5-2 mm.

10. The filter apparatus according to any one of the preceding claims, comprising at least two filter units (12, 20) connected in series, so that the water based liquid can be passed through the filter bed (25) of each filter unit (12, 20) successively.

11. The filter apparatus according to claim 10, further comprising bypass means for selectively bypassing at least one of said filter units (12, 20).

12. Use of an amorphous precipitated silica material as an adsorbent for removing dissolved organic compounds from a water based liquid, wherein the amorphous precipitated silica material has a porosity with an average pore width of less than 10 nm.

13. Use of a filter apparatus according to any one of claims 1-11 for removing dissolved organic compounds from a water based liquid.

14. A method for removing dissolved organic compounds from a water based liquid, comprising passing the water based liquid through a filter apparatus (1) according to any one of claims 1-11.

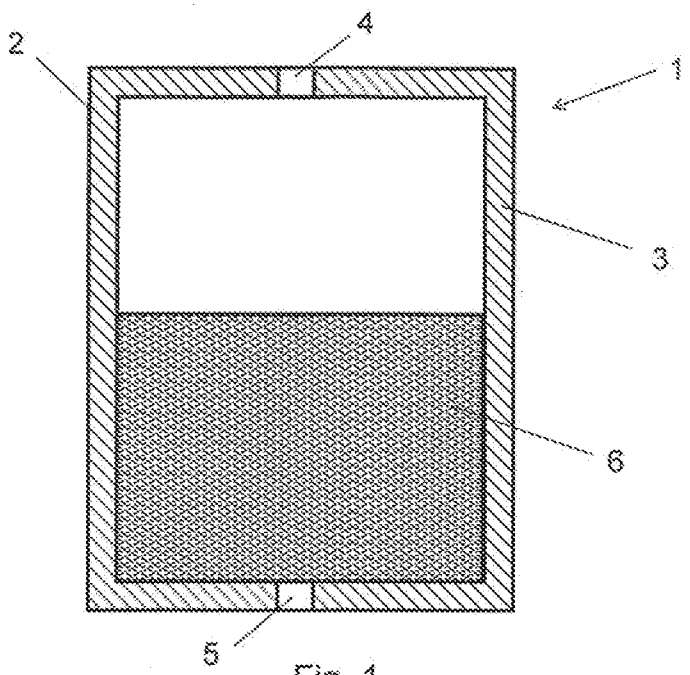


Fig. 1

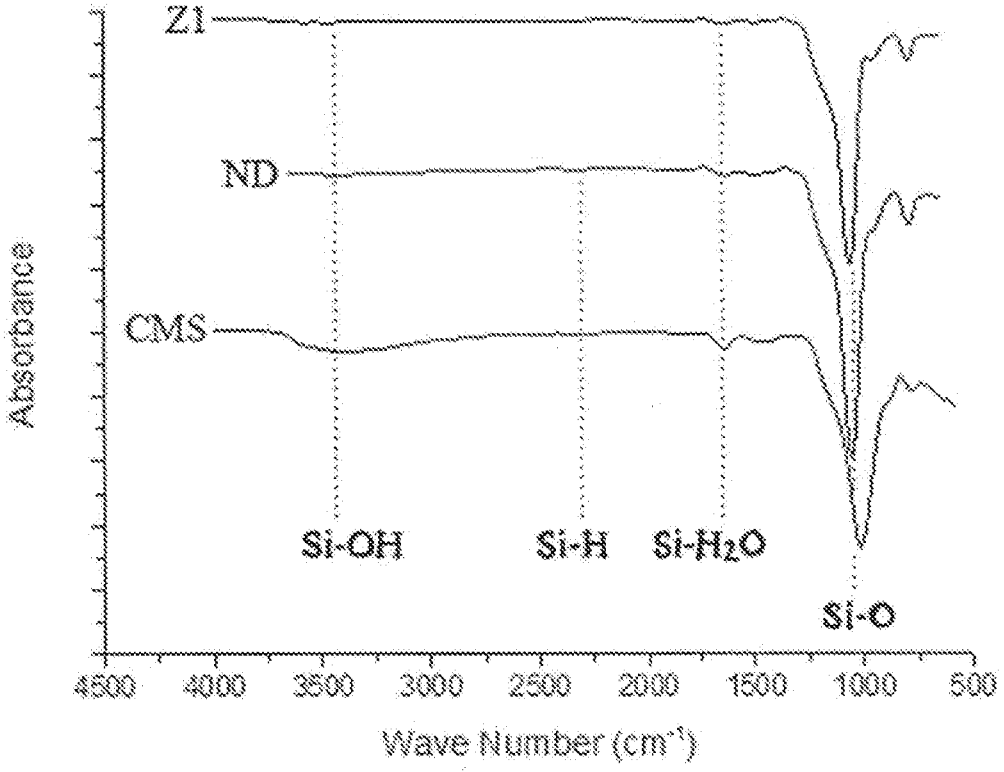

Z1
ND
CMS
Absorbance
Si-OH
Si-H
Si-H2O
Si-O
4500
4000
3500
3000
2500
2000
1500
1000
500
Wave Number (cm-1)

Fig. 2a

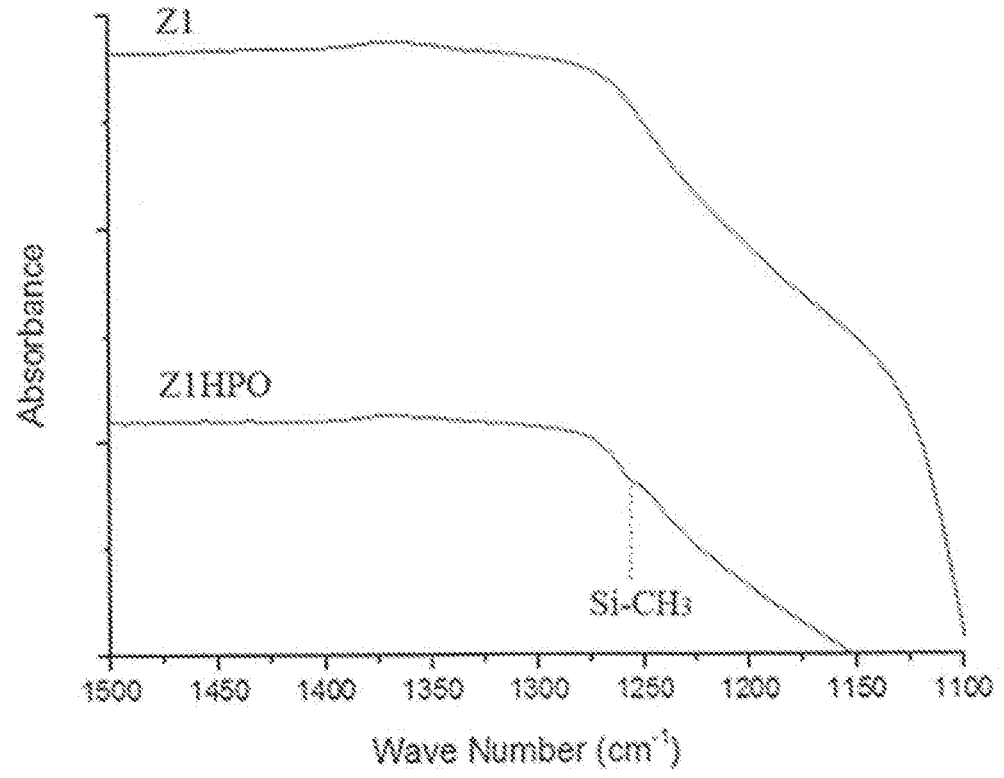

Z1
Z1HPO
Absorbance
Si-CH3
1500
1450
1400
1350
1300
1250
1200
1150
1100
Wave Number (cm-1)

Fig. 2b

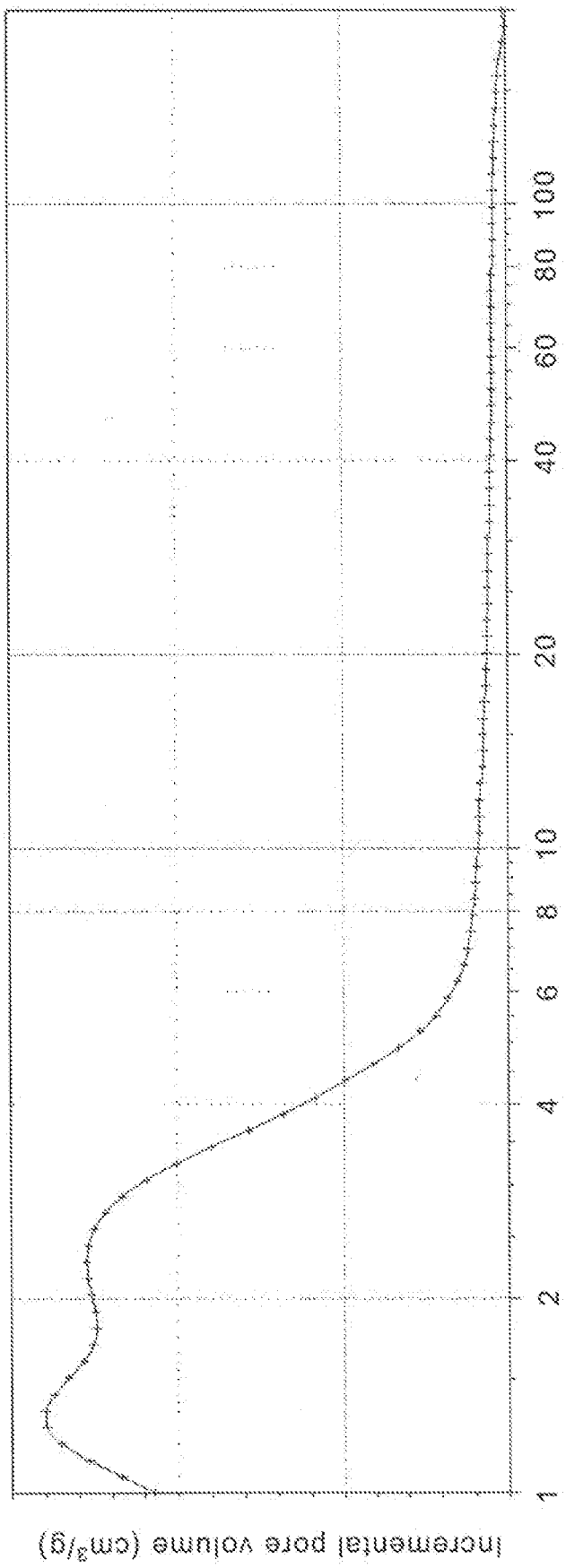

Incremental pore volume (cm³/g)
Pore width (nm)
1
2
4
6
8
10
20
40
60
80
100

Fig. 2c

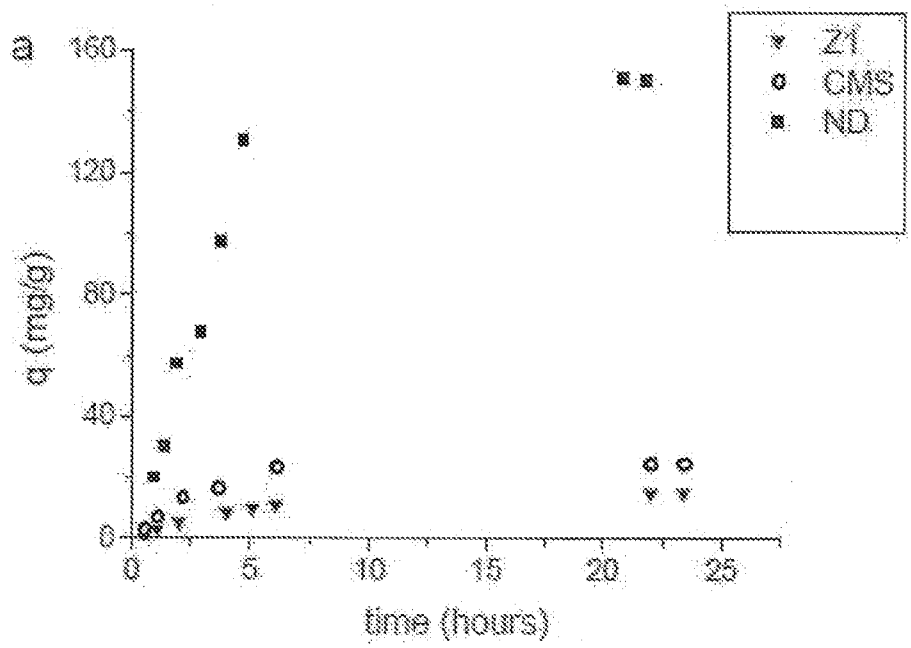

a
160
120
80
40
0
q (mg/g)
0
5
10
15
20
25
time (hours)
Z1
CMS
ND

Fig. 3a

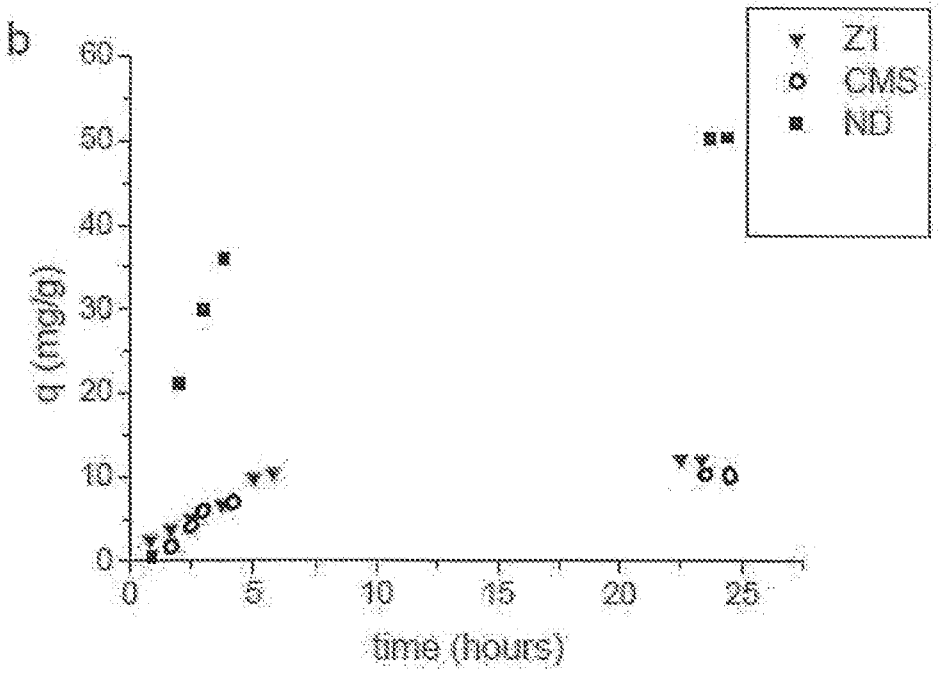

b
60
50
40
30
20
10
0
q (mg/g)
0
5
10
15
20
25
time (hours)
Z1
CMS
ND

Fig. 3b

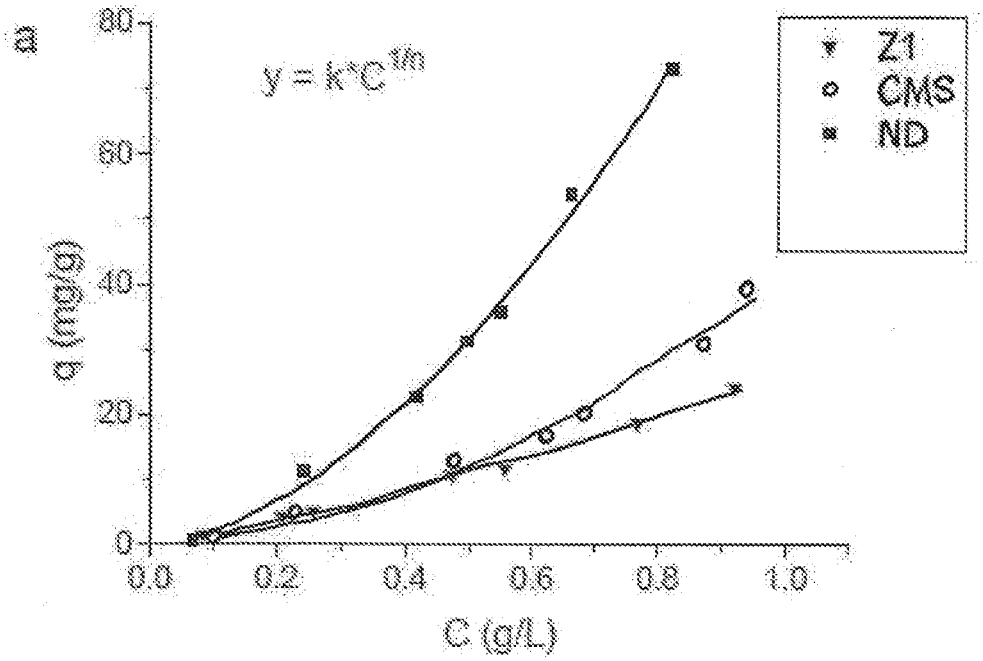

a
y = k*C^1/n
Z1
CMS
ND
q (mg/g)
C (g/L)
0
20
40
60
80
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 4a

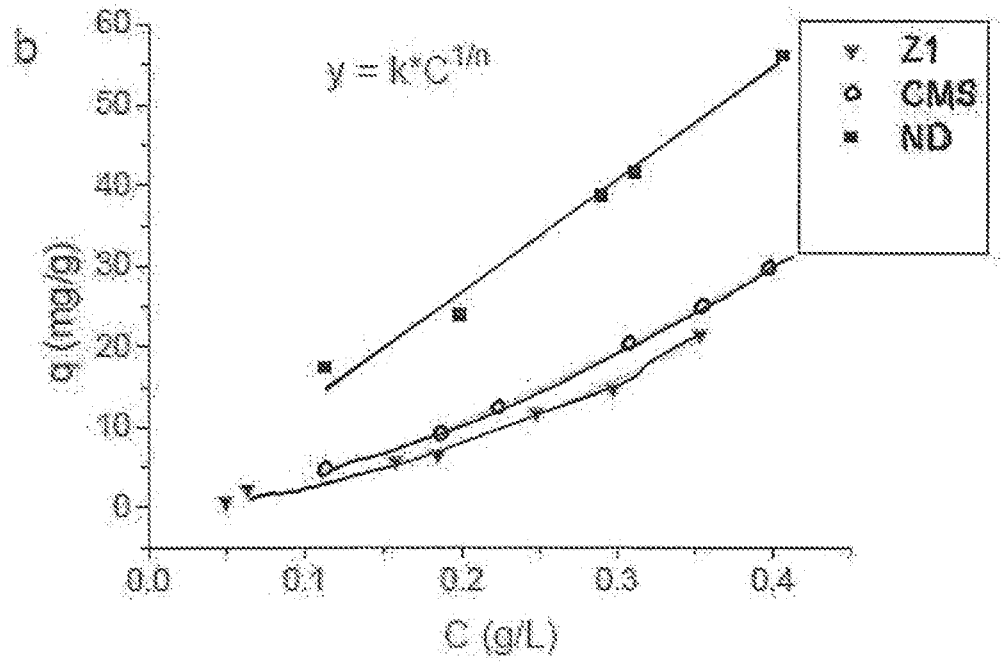

b
y = k*C^1/n
Z1
CMS
ND
q (mg/g)
C (g/L)
0
10
20
30
40
50
60
0.0
0.1
0.2
0.3
0.4

Fig. 4b

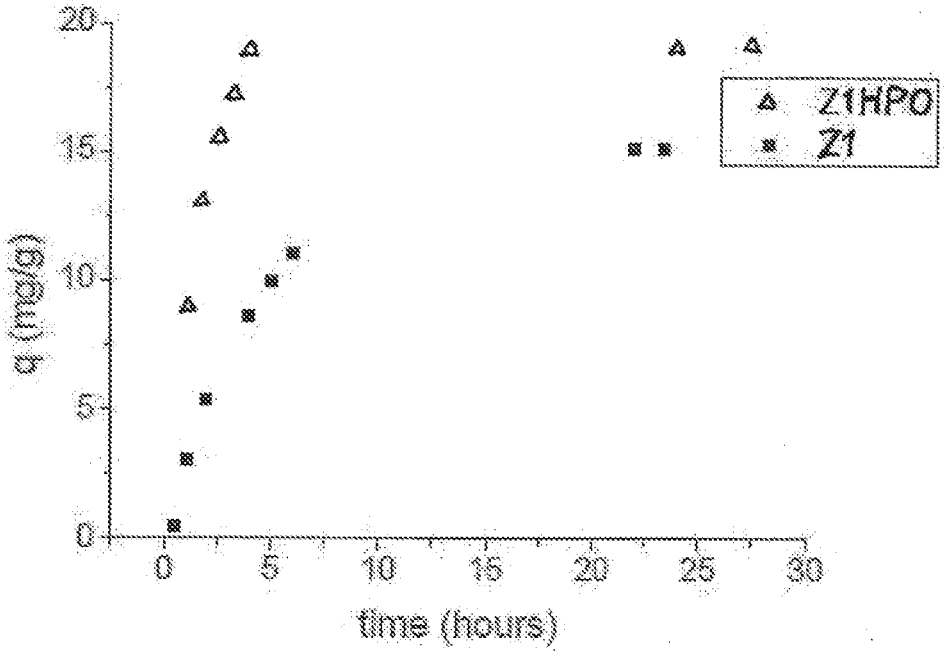

20
15
10
5
0
q (mg/g)
0
5
10
15
20
25
30
time (hours)
Z1HPO
Z1

Fig. 5a

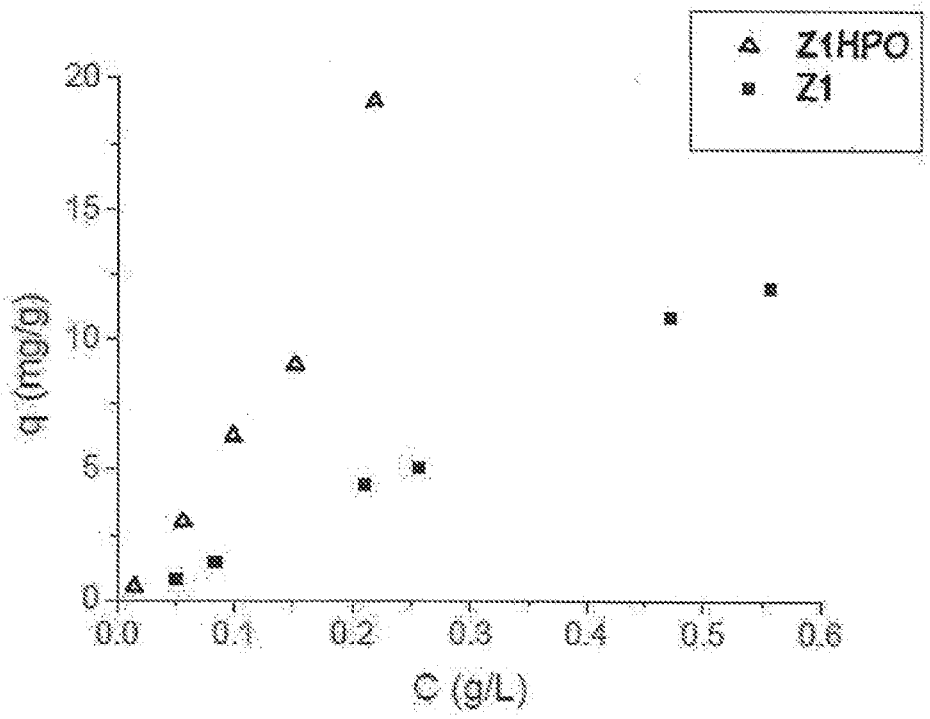

20
15
10
5
0
q (mg/g)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
C (g/L)
Z1HPO
Z1

Fig. 5b

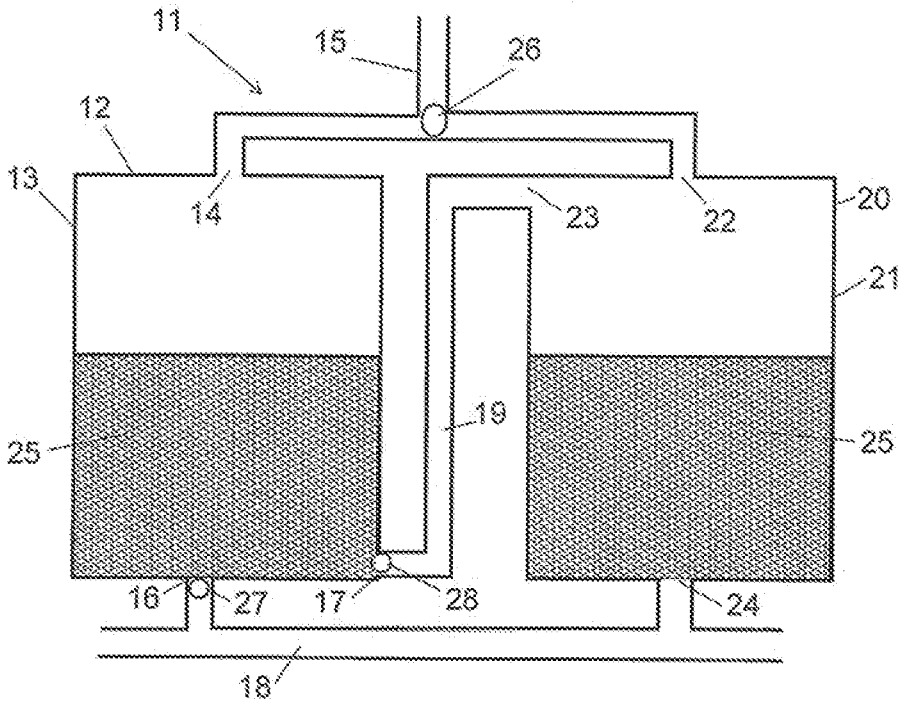


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE201 8/050086

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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: B01J, C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, BIOSIS, COMPENDEX, EMBASE, INSPEC, MEDLINE, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 20090001 021 A 1 (WITHIAM MICHAEL C ET AL), 1 January 2009 (2009-01 -01); page 2; paragraphs [0009], [0021], [0050]	1-14
A	"Precipitation of amorphous SiO2 particles and their properties" Brazilian Journal of Engineering 0 1(28) 201 1 p. 89-94; page 90, paragraph [0001]	3

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"&" document member of the same patent family	

Date of the actual completion of the international search	Date of mailing of the international search report
23-03-201 8	23-03-201 8
Name and mailing address of the ISA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Markus Willgert Telephone No. +46 8 782 28 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE201 8/050086

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 169825 A (OKUBO AKIRA ET AL), 8 December 1992 (1992-12-08); whole document --	1-14
A	US 3755183 A (FAHN R ET AL), 28 August 1973 (1973-08-28); whole document -- --------	1-14

Continuation of: second sheet

International Patent Classification (IPC)

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B01J 20/10 (2006.01)

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