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(54) Title: ADSORPTION CONTAINER AND IRON OXIDE ADSORBER

(57) **Abrégé/Abstract:**

The invention relates to a filtration unit containing fragments or granulates consisting of fine particle iron oxides and/or iron oxyhydroxides of any modification with a high specific surface, to methods for producing said fragments or granulates and to the use thereof in the filtration units.

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Abstract

The invention relates to a filtration unit containing fragments or granulates consisting of fine particle iron oxides and/or iron oxyhydroxides of any modification with a high specific surface, to methods for producing said fragments or granulates and to the use thereof in the filtration units.

- 1 -

ADSORPTION CONTAINER AND IRON OXIDE ADSORBER

The invention relates to an adsorption container through which can flow a liquid to be treated, in particular a filter adsorption container which, filled with granulated or pulverized, solid, water-insoluble adsorption media, in particular iron (oxy) hydroxide, is used for removing arsenic or heavy metals from drinking water. The apparatus can be attached, for example, in the home to the sanitary and drinking water supply.

10 The invention further relates to a process for synthesizing the iron (oxy)hydroxide adsorber for charging into the inventive filtration units.

Studies of the National Academy of Sciences verified in 1999 that arsenic in drinking water causes bladder, lung and skin cancers.

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Frequently one is faced with the problem, especially in regions where well water, mains water or drinking water in general is contaminated with arsenic or other heavy metals, of not having a suitable drinking water treatment plant in the vicinity, or not having a suitable system to hand which would continuously remove the pollutants.

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Filter cartridges for purifying liquids, preferably contaminated water, which can also contain an adsorption medium, are known in various embodiments.

To remove solids from waters, membrane filter candles, for example, in suitable housings are used.

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The company Brita Wasser-Filter-Systeme GmbH has disclosed cartridges and apparatuses for treating liquids (DE-A 19 905 601; DE-A 19 915 829; DE-A 19 814 008, DE-A 19 615 102, DE-A 4 304 536, US-A 6,099,728). These apparatuses are highly suitable for the complete or partial desalination of drinking water in domestic jugs immediately before use of the drinking water.

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- 2 -

US-A 4,064,876 discloses a filtration unit constructed as a filter cartridge which has a bed of activated carbon particles between a polyester urethane foam layer and a glass fiber layer.

- 5 DE-A 19 816 871 (Sartorius) describes a filtration unit for removing pollutants from fluids.

RU-A 2 027 676 describes a cartridge filter having a sorbent for drinking water purification having a connection to the water tap in the residence.

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HU-A 00 209 500 describes a filter cartridge for removing radioactive material and heavy metals from water which is packed with a mixture of ion-exchange material, activated carbon, filter sand, zeolites, aluminum oxide and red mud.

- 15 Usually these adsorber cartridges are packed with activated carbon or ion-exchange resins. However, activated carbon has the disadvantage that arsenic salts and heavy metal salts, as they occur in aqueous systems, because of the low adsorption capacity of the activated carbon, are not removed to a sufficient extent, which affects the service life of the cartridges.

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Ion-exchange resins have the disadvantage that they bind ions from aqueous solution highly unselectively, and competing reactions frequently occur in the adsorption. A further disadvantage of ion-exchangers is the high dependency of the adsorption capacity of the ion exchanger on the pH of the water, so that large amounts of
25 chemicals are required for pH adjustment of the water, which is not practicable when the adsorber cartridge is used in the home.

Contact granules and adsorber granules, including those based on iron oxides and/or iron oxyhydroxides, have already been described. They are used predominantly in
30 continuous processes, where they are usually found in tower- or column-like apparatuses, through which the medium to be treated flows, and on the external and

- 3 -

internal surface of the granules of which the chemical or physical reaction or adsorption processes take place. For this purpose pulverulent materials cannot be used, because they compact in the direction of flow of the medium and as a result increase the resistance to flow until the apparatus plugs. If an apparatus is cleaned by
5 backwashing (see below), large amounts of the powder are discharged, are lost or lead to an intolerable pollution of the wastewater.

However, the flowing media also exert forces on the granules which can lead to abrasion and/or to movement up to vigorous agitation of the granules. As a result the
10 granules collide with one another and in consequence unwanted abrasion results. This leads to loss of contact or adsorber material and to contamination of the medium to be treated.

In gas cleaning, the medium is used in adsorbers for binding unwanted constituents,
15 such as hydrogen sulfide, mercaptans and prussic acid, and other phosphorus, arsenic, antimony, sulfur, selenium, tellurium compounds and also cyano compounds and heavy metal compounds in exhaust gases. It is also possible to adsorb gases such as HF, HCl, H₂S, SO_x NO_x.

20 A filter cartridge for drying gases is described, for example, in US-A 5,110,330.

It is also possible to remove compounds of phosphorus, arsenic, antimony, selenium and tellurium, and also cyano compounds and heavy metal compounds from waste oils and other contaminated organic solvents.

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Contact granules and adsorber granules based on iron oxides and/or iron oxyhydroxides are also used to catalyze chemical reactions in the gas phase or in the liquid phase.

30 Differing types of process are known to remove trace substances and pollutants from aqueous systems using adsorption media.

- 4 -

To remove pollutants from water, DE-A 3 800 873 describes an adsorption medium based on porous materials, for example hydrophobized chalk having fine to medium particle size.

- 5 DE-A 3 703 169 discloses a process for preparing a granulated filter substance for treating natural water. The adsorbent is prepared by granulating an aqueous suspension of kaolin with addition of pulverulent dolomite in a fluidized bed. The granules are then fired at 900 to 950°C.
- 10 DE-A 40 34 417 discloses a process for preparing and using highly reactive reagents for purifying exhaust gas and wastewater. Descriptions are given here of mixtures of $\text{Ca}(\text{OH})_2$ with additions of clays, stone flours, fly dust and fly ashes which can be prepared so as to be porous and have a surface area of approximately 200 m²/g.
- 15 Said processes and the contacts used for this purpose share the disadvantage that the respective component responsible for the selective adsorption of constituents of the media to be purified, that is to say the actual adsorbent, must have high levels of additives to permit shaping to form granules. As a result, the binding capacity for the water pollutants to be removed is decreased considerably. Furthermore, the later
- 20 workup or further processing of the material is problematic, since the foreign materials used as binder must first be removed again.

DE-A 4 214 487 describes a process and a reactor for removing impurities from water. Flow passes horizontally through a funnel-shaped reactor in which the sorbent

25 used for water impurities is very finely divided iron hydroxide in flock form. A disadvantage of this process is the use of the flock-form iron hydroxide which, owing to the low differences in density between water and iron hydroxide leads to the fact that such a reactor can only be operated at very low flow velocities and there is the risk that the sorbent, possibly already loaded with pollutants, is discharged from the

30 reactor together with the water.

- 5 -

JP-A 55 132 633 describes a granulated red mud as byproduct of aluminum production as adsorbent for arsenic. This is composed of Fe_2O_3 , Al_2O_3 and SiO_2 . The stability of the granules and the granulation process are not reported herein. A further disadvantage of this adsorbent is the lack of constancy in the product composition, the uncertain availability and the possible aluminum pollution of the drinking water. Since aluminum is under suspicion of promoting the development of Alzheimer's disease, contamination with this is in particular to be avoided.

DE-A 19 826 186 describes a process for preparing an iron hydroxide-containing adsorption medium. An aqueous polymer dispersion is mixed into iron hydroxide in water-dispersible form. This mixture is then either dried to achieve a solid state and the solid material then mechanically comminuted into the desired shape and/or size, or the mixture is, if appropriate after predrying, submitted to shaping and then end-dried to achieve a solid state. As a result a material is obtained in which the iron hydroxide is firmly embedded in the polymer and is said to have a high binding capacity for the pollutants usually present in the wastewaters or exhaust gases.

A disadvantage of this process is the use of organic binders which additionally pollute the water to be treated by leaching out and/or abrading organic materials. In addition, stability with relatively long use of the adsorber compound is not ensured. An organic binder can also serve as nutrient medium to bacteria and other microorganisms, so that there is a risk of colonization of the contacts with microorganisms and contamination of the medium by the same.

In principle the presence of different types of aids required for the production of the adsorbents is disadvantageous in the workup, recycling or further processing of used adsorbents, because the utilization of pure substances is less of a problem than is the case with mixtures of substances. Thus, for example, polymeric binders in the further processing of adsorber materials based on iron oxide as pigments for coloring concrete is disadvantageous, since these binders impede the dispersion of the pigment in liquid concrete.

- 6 -

DE-A 4 320 003 describes a process for removing dissolved arsenic from ground-water using colloidal or granulated iron hydroxide. For the use of fine, suspended iron(III) hydroxide products, it is recommended here to introduce the iron hydroxide suspension into fixed-bed filters which are packed with granular material or other supports having a high external or internal porosity. This process is also accompanied by the disadvantage that, based on the adsorbent "substrate + iron hydroxide", only low specific loading capacities are achievable. Furthermore, there is only weak binding between substrate and iron hydroxide, so that in a subsequent treatment with arsenic-containing water, there is the risk of discharge of iron hydroxide or iron arsenate. In this publication, in addition, the use of granulated iron hydroxide as adsorber material for a fixed-bed reactor is mentioned. The granulated iron hydroxide is prepared via a freeze-conditioning (freeze-drying) of iron hydroxide obtained by neutralizing acidic iron(III) salt solutions at temperatures below minus 5°C. This production process is highly energy-consuming and leads to wastewaters with a high salt pollution. In addition, the result of this production process produces only very small grains having low mechanical stability. This leads, in the case of use in a fixed-bed reactor, to the fact that the grain size spectrum is partially decreased by mechanical abrasion of the particles in the course of operations, which in turn leads to the fact that finely dispersed particles of loaded or unloaded adsorption medium are discharged from the reactor. A further disadvantage of these granules is that the adsorption capacity with respect to arsenic compounds is considerably decreased if the granules lose water, for example as a result of relatively long dry idle time.

US-A-5,948,726 has disclosed adsorber/binder systems which are produced by withdrawing a sufficiently large amount of water from a mixture of (a) a cross-linkable binder of colloidal metal oxides or metalloid oxides, (b) oxidic adsorbents such as metal oxides and (c) an acid, in such a manner that the components (a) and (b) crosslink, forming an adsorber/binder system. From the evidence of the illustrative embodiments, the binders used are colloidal clay earths or aluminum oxide.

- 7 -

A disadvantage of these compositions is the use of acid (column 9, line 4) required in their production, and the circumstance that these are not pure substances, but heterogeneous substances, which is undesirable not only for production and regeneration of such adsorbers, but also for their disposal or final deposit, for example in landfill. The scope of the disclosure of this publication is also said to encompass adsorbers which are suitable for adsorbing arsenic; however, specific examples are not presented. It is known that aluminum oxide is considerably inferior to iron oxides with respect to the adsorption capacity for arsenic.

10 For water treatment, preferably, continuously operated adsorbers are used, which are frequently operated in groups arranged in parallel. In order to free, for example drinking water, from organic impurities, such adsorbers are charged with activated carbon. At peak consumption times, the adsorbers present are then operated in parallel in order to prevent the flow velocity from increasing above the design-limit
15 maximum. During times of lower water consumption, individual adsorbers are taken out of operation and during this can be serviced, for example, the adsorber material being exposed to particular stresses, as are described in more detail below.

The use of granules which can be produced by compacting, for example, pulverulent
20 iron oxide by using high linear forces, has already been mentioned. Such granules have already been described for homogeneously coloring liquid concrete. The use of high linear forces in compacting is greatly energy intensive and costly and the stability of the compacted material is unsatisfactory for relatively long use in adsorbers. Therefore, such materials are not considered for use in, for example,
25 adsorbers, in particular continuously operated adsorbers, in the purification of water. In particular during servicing or cleaning the adsorber systems by backwashing (see below), such granules, as a result of the associated agitation of the same, lose large amounts of substance. The backwash water is made highly turbid due to the abrasion. This is unacceptable for several reasons: firstly, adsorber material is lost which, after
30 a long service time, is highly loaded with impurities and is therefore a toxicological hazard. The wastewater stream is then polluted with the abrasion which can sediment

30916-60

8

and thus lead to impairment of the piping systems, and finally the sewage treatment plant is undesirably physically and toxicologically polluted, just to name some reasons.

The present invention relates to a filtration unit for removing arsenic and heavy
5 metals from drinking water, service water, mineral water, garden pond water, agricultural water, holy water and therapeutic water using iron oxyhydroxide particles or iron oxide particles as contact medium or adsorption/reaction medium, which, owing to the adsorber performance of the packing medium ensure high removal of the dissolved pollutants, which at the same time withstands the mechanical and
10 hydraulic stresses in the adsorber housings and in addition, for safety as a result of the filtration performance of installed filters, to prevent the discharge of suspended impurities or abraded adsorber parts, possibly loaded with pollutants.

In one filtration unit aspect, the invention relates to a filtration unit, comprising: (a) a vessel having a hollow interior, an inlet opening, and an outlet opening, whereby
15 media may pass into and out of said hollow interior by entering said inlet opening and exiting said outlet opening; and (b) an agglomerate of finely divided iron oxyhydroxide of the phase α -FeOOH in piece form having a particle size of 0.2 to 40 mm, wherein the finely divided iron oxyhydroxide has a BET surface area of 50 to 500 m²/g, wherein said agglomerate is housed within the hollow interior of said vessel and
20 positioned so as to allow communication between said agglomerate and any media passing through the hollow interior of the vessel.

In a further filtration unit aspect, the invention relates to a filtration unit, comprising:
(a) a vessel having a hollow interior, an inlet opening, and an outlet opening, whereby media may pass into and out of said hollow interior by entering said inlet opening and
25 exiting said outlet opening; and (b) an adsorbent/catalyst in pellet form consisting essentially of fine-particle α -FeOOH having a particle size of 0.2 to 40 mm, produced from an iron (II) salt suspension using NaOH as an alkaline precipitant followed by oxidation of the iron (II) to iron (III), filtering the suspension, washing the resulting filter cake, completely dehydrating the filter cake, and comminuting the dried filter

30916-60

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cake, wherein the fine-particle α -FeOOH has a BET surface area of 50 to 500 m²/g, and the adsorbent/catalyst in pellet form has a mechanical and hydraulic abrasion resistance of $\leq 12\%$ by weight, wherein said adsorbent/catalyst is housed within the hollow interior of said vessel and positioned so as to allow communication between
5 said adsorbent/catalyst and any media passing through the hollow interior of the vessel.

This is achieved by a filtration unit which consists of a housing of plastic, wood, glass, ceramic, metal or a composite material which is provided with inlet and outlet orifices. Examples of simple types of embodiments are shown in figures 1a and 1b. This
10 housing is described extensively in DE-A 19 816 871. The inlet and outlet orifices are separated from the actual housing space, which comprises a bed of the iron oxyhydroxide adsorption medium by the covering flat filter systems. The fluid to be treated thus passes successively through the first flat filter layer, the adsorber particles, the second flat filter layer and the outlet orifice. The housing space can be
15 completely or partially filled with the adsorber particles. The housing space is preferably conical or pyramidal, but can also be cylindrical, spherical, parallelepipedal or in spiral shape. By means of a tapering of the housing space (see drawing fig. 1b), the filtration can be operated in any desired layer and no bypass can form between the bed of the adsorber particles, which can pass unhindered the fluid

- 9 -

to be filtered without adsorption. By packing the housing space with a bed of adsorber particles which occupies between 97 and 99% of the total housing volume, high flow rate of the fluid to be purified is ensured, since, owing to the stability of the adsorber granules, low resistance is encountered by the influent liquid.

5

In preferred embodiments of the invention the housing space, in the tapering sections, is constructed as a truncated cone or truncated pyramid.

Various materials are shown for the flat filter layers, depending on the field of use,
10 for example in DE-A 19 816 871.

An improved embodiment of an adsorber tank is shown in the diagram fig. 2a and fig. 2b. They show the domestic filter module, in each case in longitudinal section.

15 The adsorber housing (4) containing the iron oxyhydroxide adsorber material (5) having filter plates disposed at the top (3) and bottom (10) ends and a centrally disposed inlet tube (6) can be isolated as a unit via a threaded joint with the lid (13) at the top end and a threaded joint with the bottom support (9) at the bottom end by unscrewing the connections. If the cartridge is loaded, a new one can be inserted and
20 the bottom plate and lid plate can be cleaned. At the top end, the inlet tube (6) is fixed securely via a suitable gasket to the inlet port (2) during use. The inlet tube can be removed from the cartridge housing and inserted into a new fresh cartridge housing. As a result the incoming liquid flows directly onto a sieve basket (7) which prefilters suspended matter, algae and the like, and retains these on entry into the
25 actual adsorber cartridge, so that the adsorber material does not clump or stick together. The screen (7) serves for uniform distribution of the incoming liquid stream into the bottom space, is therefore preferably conical, that is to say truncated cone-shaped and completely encloses the inlet tube and is fixed via loose sealing rings both to this and also to the filter plate (10) enclosing it. The screen cloth can consist
30 of customary fine-meshed filter materials, for example plastic, natural material or metal.

- 10 -

The screwed-on bottom part (9) can in addition contain a suitable filter material or nonwoven filter (8) which can be selected depending on the type and amount of expected suspended matter. In the presence of large amounts of solid foreign matter, the screen (7) and the nonwoven filter (8) can readily be removed and cleaned by unscrewing the bottom part. The filter plate (10) which can consist of fine-porous ceramic, separates the bottom space (9) from the contact space containing the iron oxhydroxide granules (5) so that no adsorber material passes into the bottom space and no prefiltered material passes into the contact space. By passing the water to be purified through the contact space containing the iron oxhydroxide adsorber ascending from bottom to top, the pollutants to be removed are removed by physisorption and/or chemisorption to the adsorber material. An additional filter plate at the top end of the cartridge housing ensures that no adsorber material passes into the outlet (12). As a result of elevated water pressure or long service life of the adsorber tank, fine matter can abrade from the adsorber material, which fine matter passes through the filter plate (3). In order to avoid this fine matter (loaded with pollutants) passing into the outlet, filter material or nonwoven filter (11) is embedded in the interior of the lid (13), which retains the fine matter.

The filter layers (3) and (10) also serve for uniformly distributing the fluid into the adsorber space (5) or uniformly recollecting this after exit. The clean water freed from foreign matter and pollutants leaves the adsorber tank via the outlet port (12).

The lid (13) can additionally have a valve in order to allow escape of gases co-entrained during initial operation during operations (for example air present in the cartridge housing).

Depending on the application, it can be advantageous to operate the above-described adsorber tank in reverse sequence (fig. 2b). This means that the water to be purified now enters from the inlet port (1) directly onto the prefilter (11) which retains suspended matter and foreign bodies, then passes through the filter plate (3), enters into the contact space where the dissolved pollutants adsorb to the adsorber material,

- 11 -

enters, via the cartridge bottom plate (10) into the bottom space (9), where filter material (8) may be embedded, in order to retain abraded adsorber material, the sieve basket (7) additionally performing filtration services, so that the purified water leaves, via the outlet tube (6) and the outlet port, the adsorber tank via the orifice (1).

5 Figure 3 shows the use (cartridge, filter cartridge) alone.

A simpler embodiment which operates, however, according to the same principle as described above, is shown in figure 4. It shows the adsorber tank which contains the inventive adsorber granules, and in which the adsorber cartridge forms a unit.

10

In principle, obviously, further embodiments and designs are possible which are similar to the structures described and which operate according to the manners described, that is to say contain an inlet and outlet orifice for waters and iron oxide and/or iron (oxy)hydroxide as adsorber media.

15

Fig. 5 shows a filter bag which, filled with adsorber granules, can be supplied to a body of water to be purified in order to remove the pollutants present therein by adsorption.

20 Filter bags and extraction envelopes are known, for example in many forms and embodiments for preparing hot infused beverages, in particular tea. DE-A 839 405 describes, for example, such a folded bag as used for preparing tea and the like. By means of a special folding technique which forms a double-chamber system, intensive mixing of the eluent with the substance to be extracted is ensured.

25

However, by the same token, iron oxides and iron (oxy)hydroxides in pulverized, fine-granulated or coarse-granulated form may also be embedded into semipermeable bags having a filtering action (for example the above-described folding bag) and these packages may be supplied to the waters to be purified in order, by this means, 30 after a certain contact time, to remove from the waters the pollutants by adsorption to the adsorber material (see diagram fig. 5). Firstly, the iron oxides and/or iron

- 12 -

(oxy)hydroxides withstand the mechanical and hydraulic stresses in the filter bag and, secondly, owing to the filter action of the filter membrane, exit of any fine material of the adsorption medium produced by abrasion into the waters to be purified is prevented.

5

The various embodiments of the present invention share the fact that iron hydroxide or iron oxhydroxide in fine granulated, coarse granulated or pulverized form is embedded in housings having a filtering action and the liquid to be purified is allowed to flow through the filter housing or the filter packing is supplied to the liquid to be purified and thus ensures adsorption of the pollutants.

10

To prepare the inventive granules, firstly an aqueous suspension of finely divided iron oxhydroxides and/or iron oxides is prepared according to the prior art. From this the water and constituents dissolved therein can be removed in two different ways:

15

Method 1:

For applications in which fewer demands are made of the mechanical strength of the granules/contacts, first only the water is removed, for example by evaporation. A residue is obtained which, in addition to the finely divided iron oxide and/or iron oxhydroxide also contains the entire salt loading. This residue, after drying, is redispersed in water, for which only a relatively small shearing force must be used. This suspension is then filtered and the residue is essentially washed salt-free. The filter cake which is obtained as residue is a solid to semisolid paste which generally has a water content between 10 and 90% by weight.

25

This can then be completely or partially dewatered and the resultant material can then be comminuted into the desired form and/or size. Alternatively, the paste or filter cake, if appropriate after predrying to achieve a sufficiently solid state, can be subjected to shaping and subsequent (further) drying to achieve a particulate state.

The later use of the granules determines the preferred procedure for their production and can be determined by those skilled in the art for the particular field of application

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- 13 -

by simple guideline preliminary experiments. Not only the immediately dried filter cake but also the dried shaped bodies can then be used as contact or adsorber.

Method 2:

- 5 For applications for which greater demands are made of the mechanical strength of the granules/contacts, the suspension is filtered and the residue is washed essentially salt-free. The filter cake which is obtained as residue is a solid to semisolid paste. This can then be completely or partially dewatered and the resultant material can then be comminuted into the desired shape and/or size. Alternatively, the paste or the
10 filter cake, if appropriate after predrying to achieve a sufficiently solid state, can be subjected to shaping and subsequent (further) drying to achieve a particulate state. The later use of the granules determines the preferred procedure in their production and can be determined by those skilled in the art for the respective field of application by simple guideline preliminary experiments. Not only the immediately
15 dried filter cake but also the dried shaped bodies can then be used as contact or adsorber.

The products obtained according to method 1, although they are less mechanically stable, filtration can be carried out more readily and more rapidly. In addition, the
20 finely divided pigments thus isolated can very readily be incorporated into paints and polymers, for example, because considerably less shear force needs to be used for this than is required for incorporating the finely divided pigments obtained according to method 2.

- 25 The finely divided iron oxide and/or iron oxhydroxide used has a particle size of up to 500 nm, preferably up to 100 nm, particularly preferably 4 to 50 nm, and a BET surface area of 50 to 500 m²/g, preferably 80 to 200 m²/g.

The primary particle size was determined by scanning electron microscopy, for
30 example at an enlargement of 60 000:1 by measurement (instrument: XL30 ESEM FEG, Philips). If the primary particles are needle-shaped, as, for example, in the

- 14 -

phase of α -FeOOH, the needle width may be reported as a measure of the particle size. In the case of nanoparticulate α -FeOOH particles, needle widths of up to 100 nm are found, but chiefly between 4 and 50 nm. α -FeOOH primary particles customarily have a length:width ratio of 5:1 to 50:1 typically from 5:1 to 20:1. By
5 doping or special reaction procedures, the needle shapes, however, may be varied in their length:width ratio. If the primary particles are isometric, as, for example, in the phases α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄, the particulate diameters can equally well be less than 20 nm.

10 By mixing nanoparticulate iron oxides or iron oxhydroxides with pigments and/or Fe(OH)₃, on the scanning electron micrographs, the presence of the added pigment or seed particles is recognized in their known particle morphology, which are held together or stuck to one another by the nanoparticulate seed particles or the amorphous Fe(OH)₃ polymer.

15

Products obtainable by the methods 1) or 2) can then be further comminuted, for example by shredding or grinding. Since the products, on their first contact with water, for example during the first filling of a freshly charged adsorber apparatus with water, autogenously decrease in size, however, this is not generally necessary.

20

Another method of producing granules which has proven itself in practice is pelletizing a semimoist paste. In this process pellets or rods are formed from a semi-solid paste, for example, by means of a simple perforated plate, a roller press or an extruder, and this is either dried straight away or the extrudates are additionally
25 brought into a spherical or granular form by means of a spheronizer. The still-moist beads or granules can subsequently be dried to a desired moisture content. In order that the granules do not clump together, a residual moisture content of < 50% is advisable. Such a spherical form can be advantageous for the use in fixed-bed adsorbers because of the improved bed in the absorber container compared with
30 shredded granules or pellets in rod form.

- 15 -

In general it is possible, for improving the filtration behavior of the suspensions, to employ customary measures enhancing filtration, such as are described, for example, in Solid-Liquid Filtration and Separation Technology, A. Rushton, A.S., Ward R.G., Holdich, 2nd edition 2000, Wiley-VCH, Weinheim, and Handbuch der Industriellen
5 Fest/Flüssig-Filtration [Handbook of industrial solid/liquid filtration], H. Gasper, D. Öchsle, E. Pongratz, 2nd edition 2000, Wiley-VCH Weinheim. Thus, for example, flocculents can be added to the suspensions.

In addition to, or in place of, the iron oxhydroxides, iron carbonates can also be used.
10

The inventive products can be subjected to drying in air and/or in vacuo, and/or in a drying cabinet and/or on belt dryers or by spray-drying, preferably at temperatures of -25 to 250°C, particularly preferably at 60 to 120°C.

15 The inventive products preferably have a residual water content of less than 20% by weight.

It has been found that the resultant pieces or granules have a high binding capacity for pollutants present in waters, liquids or gases, and, in addition, they have a
20 sufficiently high stability with respect to mechanical or hydraulic stress due to flowing media.

In particular, it is surprising that finely divided iron oxhydroxides or iron oxides having high specific surface areas solidify on drying into very hard agglomerates
25 which have, without addition of binder, a very high mechanical abrasion strength and very high hydraulic stability with respect to contact with flowing water, and which have a high binding capacity for the pollutants and trace substances present in the water.

30 For the inventive use of finely divided iron oxhydroxides, for example transparent iron oxhydroxide pigments having specific surface areas of greater than 80 m² are

- 16 -

suitable. However, correspondingly finely divided iron oxide pigments can also be used, preferably hematites, magnetites or maghemites.

The production of yellow finely divided iron oxhydroxide pigments (for example goethite) in the acidic or alkaline pH range, what are termed acidic or alkaline seeds, is prior art. The production of other finely divided iron oxide or iron oxhydroxide pigments is also prior art. Such pigments can contain structures based on α -, β -, γ -, δ -, δ' -, ϵ -phases and/or $\text{Fe}(\text{OH})_2$ and mixed and interphases of the same. Finely divided yellow iron oxhydroxides can be ignited to form finely divided red iron oxides.

The preparation of transparent iron oxides and iron oxhydroxides is disclosed, for example, according to DE-A 2 603 050 by BIOS 1144, pp. 29 to 33, or by FIAT 814, pp. 1 to 26.

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Finely divided yellow iron oxhydroxide pigments are generally synthesized by precipitating iron(II) hydroxides or carbonates from corresponding iron(II) salt solutions, for example FeSO_4 , FeCl_2 in pure form, or as pickling solutions in the acidic or alkaline pH range and subsequent oxidation to form iron(III) oxide hydroxides (see, inter alia, G. Buxbaum, Industrial Inorganic Pigments, VCH Weinheim, 2nd edition, 1998, pp. 231 ff). Oxidation of divalent to trivalent iron is preferably performed with air, with intensive gas introduction being advantageous. Oxidation with H_2O_2 also leads to finely divided iron oxhydroxides. The temperature in the precipitation and in the oxidation should be selected to be as low as possible in order to achieve very finely divided yellow pigments. It is preferably between 15°C and 45°C . Preferably, NaOH is used as alkaline precipitant. However, other precipitants can be used, such as KOH , Na_2CO_3 , K_2CO_3 , CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , NH_3 , NH_4OH , MgO and/or MgCO_3 .

30 In order to direct the precipitated pigments in the direction towards the necessary high finely divided character, the precipitations, for example of yellow α - FeOOH , as

- 17 -

described in US patents US-A 2 558 303 and US-A 2 558 304, are carried out in the alkaline pH range using alkali metal carbonates as precipitants and generally adding modifiers, for example SiO_2 , salts of zinc, aluminum or magnesium, hydroxy-carboxylic acids, phosphates, metaphosphates. Products thus produced are described
5 in US-A 2 558 302. Such seed modifiers do not interfere [lacuna] prevent later workup, recycling or other type of use of the inventive adsorbents. In the case of the precipitation processes in the aqueous medium, according to previous knowledge, precipitation in the alkaline environment leads to less firmly agglomerated powders than those in the acidic environment.

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DE-A 4 235 945 reports on the synthesis of finely divided iron oxides by a precipitation process in the acidic pH range and without modifiers.

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DE-A 4 434 669 describes a process by which highly transparent yellow, chemically pure iron oxide pigments can be prepared by post-treatment of the same with sodium hydroxide solution.

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DE-A 4 434 972 reports on highly transparent, yellow iron oxide pigments of the α -FeOOH modification having a specific surface area of more than $100 \text{ m}^2/\text{g}$ with high temperature stability.

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DE-A 4 434 973 describes highly transparent yellow iron oxide pigments which are produced via the process steps seed precipitation in the acidic pH range, seed oxidation, seed ripening and pigment build up.

Red, transparent iron oxide pigments which are formed by ignition from yellow, transparent iron oxide pigments are disclosed by DE-A 4 434 668 and DE-A 4 235 946.

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By means of the fact that iron oxhydroxides of the most varied phases each in pure form or in any mixture are prepared by the known precipitation and oxidation

- 18 -

reactions from iron(II) salt solutions, the resultant iron oxhydroxides, if appropriate after a post-treatment, are separated off from the suspension by filtration from the salt solution and washed substantially salt-free, preferably up to a residual conductivity of < 5 mS/cm, the solid or semisolid filter cake is subjected as it is, or if
5 appropriate after a mechanical shaping, subsequently to drying to achieve a solid state, a high mechanical strength material is obtained which has a high binding capacity for the pollutants usually present in wastewaters or exhaust gases.

The drying is expediently performed at temperatures up to 250°C . Vacuum-drying or
10 freeze-drying of the material is also possible. The particle size of the material is optional, it is preferably between 0.2 and 40 mm, particularly preferably between 0.2 to 20 mm. This can be achieved by mechanical shaping of the semisolid pasty filter cake before drying by a granulation or pelletizing system or in an extrusion press to give shaped bodies having a size in the range from 0.2 to 20 mm, and subsequent
15 drying in air, on a belt dryer or in a drying cabinet, and/or by mechanical comminution to the desired particle size after drying.

Compared with the prior art, the products described, the process for their production and their use are an improvement. The inventive granules based on finely divided
20 iron (oxy)hydroxides and/or iron oxides, in contrast to those made of coarse particulate iron oxhydroxides and/or iron oxides can bear considerably greater loads and thus have a much greater abrasion stability toward mechanical and hydraulic stress. They can be used directly as such. Even the comminution or shredding of the initially obtained crude dry substance from filter cake or extrusion presses can be
25 dispensed with, for example when used in adsorber systems for water purification, since the coarse pieces reduce themselves in size on contact with water. In this case a random particle size distribution occurs, but no particles of a size which are discharged from the adsorber by the flowing medium to a significant extent.

- 19 -

A separate granulation, as would be necessary when conventional iron oxhydroxides are used in the form of (flowable) powder, either with the aid of foreign binders or very high linear forces in compacting, can be dispensed with completely.

- 5 According to the invention, the suspensions of the finely divided iron oxhydroxides or iron oxides can also be admixed with conventional pulverulent iron oxhydroxides or iron oxides. The respective amounts are determined by the properties of these pulverulent iron oxhydroxides or iron oxides and the requirements made of the inventive product with respect to its mechanical stability and abrasion strength.
- 10 Although the addition of pulverulent pigments will generally decrease the mechanical strength of the inventive products, filtration of the finely divided suspensions is facilitated. Those skilled in the art active in the respective field of application will be able to determine by means of a few preliminary experiments the optimum mixing ratio for the respective use.

15

- The suspensions of the alkaline finely divided seeds can also be additionally admixed with an amount corresponding to the NaOH excess of aqueous salts of Fe^{3+} , Al^{3+} , Mg^{2+} , Ti^{4+} or mixtures thereof so that sufficiently slightly soluble precipitates of $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{TiO}(\text{OH})_2$, or products of aging and secondary
- 20 dehydrated products thereof precipitate onto the suspended iron oxide particles and/or iron(oxy)hydroxide particles. Vice versa, the slightly soluble precipitates $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{TiO}(\text{OH})_2$ or their products of aging and secondary products can be precipitated onto the iron oxide or iron (oxy)hydroxide particles suspended in Fe^{3+} , Al^{3+} , Mg^{2+} , Ti^{4+} by adding alkalis, for example NaOH, $\text{Ca}(\text{OH})_2$,
- 25 KOH, CaCO_3 , Na_2CO_3 , K_2CO_3 , NH_4OH . The aluminum oxide or aluminum (oxy)hydroxide can also be precipitated from an aluminate suspension (for example NaAlO_2) onto the iron oxide particles and/or iron (oxy)hydroxide particles.

- The resultant initially amorphous $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ age with time, for example to
- 30 give the FeOOH or AlOOH phase. This ensures complete consumption of the sodium hydroxide solution which was used in excess for preparing the alkaline seed. The

- 20 -

resultant materials also have high specific surface areas. The material, just like the above-described nanoparticulate iron oxyhydroxides, is outstandingly suitable for use in adsorbers, since, in addition to a high adsorption capacity, it also has high stability toward mechanical stress.

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Particularly preferably, the inventive granules are used in the purification of liquids, in particular for removing heavy metals. A preferred use in this technical field is decontaminating water, in particular drinking water. Very recently, particular attention has been paid to removing arsenic from drinking water. The inventive
10 granules are outstandingly suitable for this purpose, since using the inventive granules achieves concentrations which not only comply with the low limiting values specified by the US EPA, but can also be lower than these.

For this purpose the granules can be used in customary adsorber apparatuses as are
15 currently used, for example charged with activated carbon, for removing other types of pollutants. A batchwise operation, for example in cisterns or similar containers, which may be equipped with stirrers, is also possible. However, use in continuous systems, such as continuous-flow adsorbers, is preferred.

20 Since untreated water to be treated to produce drinking water customarily also contains organic impurities such as algae and similar organisms, the surface of adsorbers, in particular the outer surface of a granule-type adsorbent, becomes coated during use with generally slimy deposits which impede or even prevent the ingress of water and thus the adsorption of the constituents to be removed. For this reason, the
25 adsorber apparatuses are backwashed with water from time to time, which is preferably carried out during times of low water consumption (see above) on apparatuses which are individually taken out of operation. In this case the adsorbent is swirled up and, as a result of the associated mechanical stressing of the surface, the unwanted coating is removed and discharged in counterflow to the direction of flow
30 during operation in service. The washing water is customarily fed to a sewage treatment plant. In this case the inventive adsorbents prove themselves particularly

- 21 -

well in service, since their high strength makes possible cleaning in a short time, without significant losses of adsorber material being encountered or the backwashing water fed to the wastewater being highly polluted with discharged adsorber material, or possibly even highly polluted with heavy metals.

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A suitable prefilter and postfilter retain the impurities which can plug the adsorber cartridge.

As a result of the inventive stability of the granules and owing to suitable packing of the adsorber granules, material abrasion is minimized.

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Sprayed granules of the iron oxyhydroxide adsorbers having a particle size $< 250 \mu$ have proven particularly expedient, because these lead to a particularly good packing density.

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Since the inventive granules are free from foreign binders, the material is relatively simple to dispose of after use. Thus the adsorbed arsenic can be removed thermally or chemically, for example in special apparatuses, and an iron oxide pigment is obtained as a pure substance, which can be either recycled for the same use, or can be fed to customary pigment applications. Depending on the application and legal provisions, the adsorber content can also be used without the prior removal of heavy metals, for example as pigment for pigmenting permanent construction materials such as concrete, since the heavy metals removed from the drinking water are permanently immobilized in this manner and are removed from the water cycle.

20

Therefore, water treatment plants or waterworks in which apparatuses charged with the inventive granules are operated are also subject-matter of the present invention, as are processes for decontaminating water using such apparatuses, and apparatuses of this type themselves.

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- 22 -

For many applications, in particular those in which a maximum mechanical strength of the granules is not required, the addition of pulverulent pigments in the production of the inventive granules is a preferred embodiment.

- 5 Thus, for example, a seed suspension in accordance with example 2 of the present application can be admixed with up to 40% by weight of commercially customary goethite (for example Bayferrox[®] 920, Bayer AG, Leverkusen DE), if the resultant inventive granules are to be used for removing arsenic from drinking water in adsorbers through which water flows.

10

The specific surface area of the inventive products is determined in accordance with BET via the carrier gas method (He:N₂ = 90:10) using the one point method as specified by DIN 66131 (1993). Before measurement, the sample is heated for 1 h at 140°C in a stream of dry nitrogen.

15

- To measure the adsorption of arsenic(III) and arsenic(V), 3 l of an aqueous solution of NaAsO₂ or Na₂HAsO₄ having a concentration in each case of approximately 2 - 3 mg/l of arsenic is treated with 3 g of the sample under test in a 5 l PE flask over a defined period, and the flask is agitated in the course of this on rotating rollers. The
20 adsorption rate of As ions on iron hydroxide over this defined period, for example one hour, is reported as $\text{mg}(\text{As}^{3+/5+})/\text{g}(\text{FeOOH}) \cdot \text{h}$ from the difference from the $\text{As}^{3+/5+}$ ions remaining in solution.

- To measure the adsorption of Sb³⁺, Sb⁵⁺, Pb²⁺, Hg²⁺, Cr⁶⁺, Cd²⁺ ions, the same pattern
25 is followed, more precisely the desired concentrations are prepared by dissolving appropriate amounts of Sb₂O₃, KSb(OH)₆, PbCl₂, NaCrO₄, CdCl₂ in H₂O and the pH is set to 7-9.

- The As, Sb, Cd, Cr, Hg and Pb contents of the loaded iron oxyhydroxide or of the
30 solutions is determined using mass spectrometry (ICP-MS) as specified in DIN 38406-29 (1999) or via optical emission spectroscopy (ICP-OES) as specified by

30916-60

- 23 -

EN-ISO 11885 (1998), in each case using inductively coupled plasma as the excitation unit.

Mechanical and hydraulic abrasion strength was evaluated according to the following method: 10 g of the granules under test having particle sizes < 0.1 mm were admixed with 150 ml of deionized water in a 500 ml conical flask and rotated at 250 rotations/minute for a period of 30 minutes in a LabShaker shaking machine (Kühner model, from Braun). The fraction < 0.1 mm was then isolated from the suspension using a screen, dried and weighed. The weight ratio between final weight and initial weight gives the abrasion value in %.

The invention will now be described in more detail below with reference to examples. The examples are intended to illustrate the process and do not represent a limitation.

Examples**Example 1:**

- 5 237 l of an aqueous iron sulfate solution having a concentration of 150 g/l of FeSO_4 were charged at 24°C. 113 l of an aqueous NaOH solution (227 g/l) were then added rapidly and the light blue suspension was then oxidized for 1.5 hours with 40 l of air per hour and mole of iron.
- 10 The resultant yellow suspension was filtered off via a filter press and the solids were washed to a residual filtrate conductivity of 1 mS/cm. The filter cake was produced as a spreadable and kneadable paste, which was dried on sheets in a circulated-air drying cabinet at 75°C to a residual moisture content of 3% by weight. The dried material was then brought to particle sizes between 0.5 and 2 mm by coarse grinding.
- 15 The resultant hard pieces were used directly in an adsorber tank.

The product consisted 100% of $\alpha\text{-FeOOH}$ having an extreme short-needled habit, the needles having aggregated to form solid macroscopic agglomerates. From the scanning electron micrograph, for example at a magnification of 60 000:1, the needle

20 widths were determined by measurement between 15 and 35 nm, and the needle lengths between 150 and 350 nm. The needles were highly agglomerated.

The specific BET surface area was 122 m²/g. The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.3 mg (As^{3+})/l was 2.14 mg of (As^{3+})/g(FeOOH)·h, and with respect to Na_2HAsO_4 at a starting concentration of

25 2.7 mg of (As^{5+})/l was 2.29 mg of (As^{5+})/g(FeOOH)·h.

Example 2:

- 30 800 l of an aqueous iron sulfate solution having a concentration of 150 g/l of FeSO_4 were charged at 29°C and were admixed with stirring with 147 l of an aqueous

WO 02/26633

PCT/EP01/10930

- 25 -

NaOH solution (300 g/l) in 20 minutes. The resultant grayish-blue suspension was then admixed with 2.16 kg of a 57% strength aqueous glycolic acid solution and oxidized for 7 hours with 38 l of air per hour and mole of iron.

- 5 The dark-brown suspension was filtered off via a filter press and the solids were washed to a residual filtrate conductivity of 1 mS/cm. The filter cake was dried to a residual moisture of 5% at 70°C in a circulating air drying cabinet and the very hard blackish-brown dried material was coarsely ground to particle sizes up to 2 mm via a roller crusher. The fines content < 0.2 mm was separated off via a screen.

10

- The product consisted, according to an x-ray diffractogram, 100% of α -FeOOH. From the scanning electron micrograph, for example at a magnification of 60 000:1, the needle widths were determined by measurement between 15 and 20 nm, and the needle lengths were determined between 50 and 80 nm. The particles were highly agglomerated. The specific BET surface area was 202 m²/g. The resultant granules
15 were packed into an adsorber tank directly without further treatment.

- The granules exhibited an excellent adsorption behavior for the pollutants present in the water flowing through and exhibited a high adbrastion strength, in particular
20 while the adsorber tank is being backwashed and as a result the granules are highly vortexed. The abrasion value, after 30 minutes, was only 1%.

- Adsorption behavior: The adsorption rate with respect to NaAsO₂, at a starting concentration of 2.4 mg of (As³⁺)/l was 1.0 mg of (As³⁺)/g(FeOOH)·h, and with
25 respect to Na₂HAsO₄ at a starting concentration of 2.8 mg of (As⁵⁺)/l was 2.07 mg of (As³⁺)/g(FeOOH)·h.

Example 3:

- 30 An α -FeOOH suspension obtained in accordance with example 2, after being aged for two hours at 30°C, was admixed with stirring with 1.3 l of an aqueous 300 g/l

- 26 -

NaOH solution and simultaneously reoxidized for one hour with 190 l of air. The product was worked up as described in example 2. Finely divided needles of pure α -FeOOH resulted which had a specific BET surface area of 130 m²/g. From the scanning electron micrograph, for example at a magnification of 60 000:1, the needle widths were determined by measurement between 15 and 20 nm, and the needle lengths between 50 and 90 nm. The needles were highly agglomerated. The granules proved to be very mechanically and hydraulically stable, and the abrasion value was only 3.9%.

- 10 Adsorption behavior: The adsorption rate with respect to NaAsO₂, at a starting concentration of 2.3 mg of (As³⁺)/l was 1.1 mg of (As³⁺)/g(FeOOH)·h, and with respect to Na₂HAsO₄ at a starting concentration of 2.8 mg of (As⁵⁺)/l was 1.7 mg of (As³⁺)/g(FeOOH)·h.

15 **Example 4:**

306 l of an aqueous NaOH solution (45 g/l) were charged at 31°C and, with stirring, were rapidly admixed with 43 l of an aqueous FeCl₂ solution (344 g/l) and then oxidized with 60 l of air per hour and mole of Fe. The resultant dark-yellow suspension was worked up as described in example 1.

According to the x-ray diffractogram, the product consisted 100% of α -FeOOH. From the scanning electron microgram, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 15 and 50 nm, and the needle lengths between 100 and 200 nm. The needles were highly agglomerated. The specific BET surface area was 132 m²/g.

The resultant granules were packed without further treatment into an adsorber tank. The granules displayed an excellent adsorption behavior for the pollutants present in the water and displayed a high abrasion strength, in particular while the adsorber

- 27 -

tank is being backwashed and as a result the granules are highly vortexed. The abrasion value after 30 minutes was only 12% by weight.

Adsorption behavior: The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.4 mg of $(\text{As}^{3+})/\text{l}$ was 2.11 mg of $(\text{As}^{3+})/\text{g}(\text{FeOOH})\cdot\text{h}$, and with respect to Na_2HAsO_4 at a starting concentration of 2.7 mg of $(\text{As}^{5+})/\text{l}$ was 2.03 mg of $(\text{As}^{5+})/\text{g}(\text{FeOOH})\cdot\text{h}$.

Example 5:

10

124 l of an aqueous NaOH solution (114 g/l) were charged at 24°C and, with stirring, were rapidly mixed with 171 l of an aqueous solution of FeSO_4 (100 g/l) and then oxidized with 10 l of air per hour and mole of Fe. Immediately after oxidation was complete, 56 l of an aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ (100 g/l) were added and the mixture was stirred for 30 minutes. The resultant yellowish-brown suspension was worked up as in example 1.

According to the x-ray diffractogram, the product consisted 100% of $\alpha\text{-FeOOH}$. From the scanning electron microgram, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 15 and 35 nm, and the needle lengths between 70 and 180 nm. The needles were highly agglomerated. The specific BET surface area was 131 m^2/g . The abrasion value after 30 minutes was only 7% by weight.

25 Adsorption behavior: The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.3 mg of $(\text{As}^{3+})/\text{l}$ was 1.7 mg of $(\text{As}^{3+})/\text{g}(\text{FeOOH})\cdot\text{h}$, and with respect to Na_2HAsO_4 at a starting concentration of 2.7 mg of $(\text{As}^{5+})/\text{l}$ was 1.2 mg of $(\text{As}^{5+})/\text{g}(\text{FeOOH})\cdot\text{h}$.

Example 6:

7905 kg of FeSO_4 were charged, dissolved with water to a volume of 53.3 m^3 , the solution was cooled to 14°C and this solution admixed with 1000 kg of
5 $\text{MgSO}_4 \cdot 7 \text{ H}_2\text{O}$. This charge was then diluted at 14°C with 5056 kg of NaOH as a solution of approximately 300 g/l; and then oxidized with $4000 \text{ m}^3/\text{h}$ of air up to a degree of precipitation $> 99.5\%$. The batch was washed on a filter press to a residual filtrate conductivity of $< 1000 \mu\text{S}/\text{cm}$ and the paste was forced through a perforated plate having hole diameters of 7 mm and thus formed into rods. The rods were dried
10 on a belt dryer to a residual moisture content of approximately 3%. The product, according to the x-ray diffractogram, consisted 100% of $\alpha\text{-FeOOH}$ of very short needles. From the scanning electron micrograph, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 30 and 50 nm. The needle lengths could not be determined clearly, since the needles were
15 too highly agglomerated. The specific BET surface area was $145 \text{ m}^2/\text{g}$. The abrasion value after 30 minutes was only 6%.

Adsorption behavior: The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.5 mg of $(\text{As}^{3+})/\text{l}$ was 1.8 mg of $(\text{As}^{3+})/\text{g}(\text{FeOOH}) \cdot \text{h}$, and with
20 respect to Na_2HAsO_4 at a starting concentration of 2.9 mg of $(\text{As}^{5+})/\text{l}$ was 1.5 mg of $(\text{As}^{5+})/\text{g}(\text{FeOOH}) \cdot \text{h}$.

Example 7

25 4096 kg of NaOH were charged (as a solution of approximately 300 g/l) and diluted with water to 40 m^3 . 4950 kg of FeSO_4 are diluted with water to give a solution of 48.5 m^3 , cooled to 15°C and then pumped in 1 h to the NaOH charge. The suspension was then oxidized with $1500 \text{ m}^3/\text{h}$ of air in approximately 2 h. Approximately 2 m^3 of the seed suspension was washed on a filter press to a filtrate
30 conductivity of $< 1000 \mu\text{S}/\text{cm}$, the filter cake was dried at 75°C in a drying cabinet and the dry material was coarsely ground to particle sizes $< 1.5 \text{ mm}$. The fines

- 29 -

fraction < 0.5 mm was separated off via a screen. The resultant material had a specific BET surface area of $153 \text{ m}^2/\text{g}$ and consisted 100% of $\alpha\text{-FeOOH}$. From the scanning electron micrograph, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 15 and 35 nm, and the needle
5 lengths between 50 and 100 nm. The needles were highly agglomerated.

Adsorption behavior: The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.7 mg of $(\text{As}^{3+})/\text{l}$ was 1.7 mg of $(\text{As}^{3+})/\text{g(FeOOH)}\cdot\text{h}$, and with respect to Na_2HAsO_4 at a starting concentration of 2.8 mg of $(\text{As}^{5+})/\text{l}$ was 1.4 mg of
10 $(\text{As}^{5+})/\text{g(FeOOH)}\cdot\text{h}$.

Example 8

1600 g of the alkaline seed suspension synthesized as in example 7 (2.7% FeOOH)
15 were admixed at room temperature with stirring with an aqueous solution of FeSO_4 (100 g/l) with simultaneous aeration with 130 l/h of air to pH 8. The resultant seed suspension was filtered and washed, and the filter cake was dried at 75°C and coarsely ground as in example 7 to particle sizes between 0.5 and 2 mm. The resultant material had a specific BET surface area of $163 \text{ m}^2/\text{g}$ and, according to the
20 x-ray diffractogram, consisted 100% of $\alpha\text{-FeOOH}$. From the scanning electron micrograph, for example at an enlargement of 60 000:1, it could be seen that the needles were highly agglomerated. Adsorption behavior: The adsorption rate with respect to NaAsO_2 at a starting concentration of 2.7 mg of $(\text{As}^{3+})/\text{l}$ was 2.0 mg of $(\text{As}^{3+})/\text{g(FeOOH)}\cdot\text{h}$, and with respect to Na_2HAsO_4 at a starting concentration of
25 2.7 mg of $(\text{As}^{5+})/\text{l}$ was 1.9 mg of $(\text{As}^{5+})/\text{g(FeOOH)}\cdot\text{h}$, in the case of KSb(OH)_6 (starting concentration 3.0 mg of $(\text{Sb}^{5+})/\text{l}$), the adsorption was 2.5 mg of $(\text{Sb}^{5+})/\text{g(FeOOH)}\cdot\text{h}$, and with respect to Na_2CrO_4 (starting concentration $47 \mu\text{g}$ of $(\text{Cr}^{6+})/\text{l}$), $42 \mu\text{g}$ of $(\text{Cr}^{6+})/\text{g(FeOOH)}\cdot\text{h}$ were adsorbed, and in the case of PbCl_2 (starting concentration 0.94 mg of $(\text{Pb}^{2+})/\text{l}$), 0.46 mg of $(\text{Pb}^{2+})/\text{g(FeOOH)}\cdot\text{h}$ were
30 adsorbed.

- 30 -

Example 9

6.4 l of an aqueous solution of NaOH (100 g/l) were charged at 29°C with stirring and were admixed with simultaneous feed of air with 12.2 l of an aqueous iron(II) sulfate solution (100 g/l) to pH 9. The resultant suspension was worked up as in example 1. The material had a specific BET surface area of 251 m²/g and consisted, according to the x-ray diffractogram, 100% of α -FeOOH. In the scanning electron micrograph short stumpy needles may be observed which are highly agglomerated. Abrasion behavior: 5%.

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Adsorption behavior: The adsorption rate with respect to NaAsO₂ at a starting concentration of 2.7 mg of (As³⁺)/l was 1.1 mg of (As³⁺)/g(FeOOH)·h, and with respect to Na₂HAsO₄ at a starting concentration of 2.7 mg of (As³⁺)/l was 1.0 mg of (As⁵⁺)/g(FeOOH)·h.

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Example 10

4096 kg of NaOH (as a solution containing approximately 300 g/l) were charged and diluted with water to 40 m³. 4950 kg of FeSO₄ are dissolved with water to give a solution of 48.5 m³, cooled to 15°C and then pumped in 1 h to the NaOH charge. The suspension was then oxidized in approximately 2 h with 1500 m³/h of air. Approximately 87 m³ of this suspension were admixed with stirring with 14.4 m³ of FeClSO₄ solution (113.4 g/l) and stirred for a further 30 min. The batch was washed on a filter press to a residual filtrate conductivity of < 1000 μ S/cm and the paste was formed through a perforated plate having hole diameters of 7 mm and formed into rods. The rods are dried on a belt dryer to a residual moisture of approximately 5%. The dry pellets were coarsely ground to a particle size of 2 mm. The resultant material had a specific BET surface area of 142 m²/g and consisted of 100% α -FeOOH. From the scanning electron micrograph, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 15 and

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- 31 -

50 nm, and the needle lengths between 10 and 150 nm. The needles were highly agglomerated.

Adsorption behavior: The adsorption rate with respect to NaAsO₂ at a starting
5 concentration of 2.7 mg of (As³⁺)/l was 2.1 mg of (As³⁺)/g(FeOOH)·h, and with
respect to Na₂HAsO₄ at a starting concentration of 2.8 mg of (As⁵⁺)/l was 2.0 mg of
(As⁵⁺)/g(FeOOH)·h, with respect to CdCl₂ (starting concentration 2.7 mg of (Cd²⁺)/l)
the adsorption was 1.1 mg of (Cd²⁺)/g(FeOOH)·h, with respect to KSb(OH)₆ (starting
10 concentration 2.6 mg of (Sb⁵⁺)/l), it was 1.9 mg of (Sb⁵⁺)/g(FeOOH)·h, with respect
to Sb₂O₃ (starting concentration 2.3 mg of (Sb³⁺)/l) it was 2.0 mg of
(Sb³⁺)/g(FeOOH)·h, with respect to Na₂CrO₄ (starting concentration 2.6 mg of
(Cr⁶⁺)/l) it was 1.1 mg of (Cr⁶⁺), with respect to PbCl₂ (starting concentration 1.6 mg
of (Pb²⁺)/l it was 1.57 mg of (Pb²⁺)/g(FeOOH)·h.

15 Example 11

1 l of a suspension of Bayferrox[®] 920 having a solids content of 50 g/l of FeOOH
was admixed with 569 ml of an MgSO₄ solution (100 g/l), then admixed with stirring
with 173 g of a 24% strength NaOH solution and stirred for a further 15 min.

20

The yellow suspension was washed on a vacuum filter to a residual filtrate
conductivity of 1 mS/cm, and the filter cake was dried at 75°C in a drying cabinet
with a residual moisture of < 2%. The product was granulated to particle sizes
between 0.5 and 2 mm and the granules were used for adsorption of arsenic.

25

The product, according to the x-ray diffractogram, consists of α-FeOOH and
Mg(OH)₂. From the scanning electron micrograph, for example at a magnification of
60 000:1, it may be seen that the needles of the α-FeOOH type of amorphous layers
are stuck to one another or agglomerated. The specific BET surface area was 43 m²/g
30 and has thus more than doubled, compared with Bayferrox[®] 920 (BET approximately
15 m²/g). The abrasion value after 30 minutes was only 11%.

- 32 -

The adsorption rate with respect to an aqueous NaAsO_2 solution at a starting concentration of 2.6 mg of $(\text{As}^{3+})/\text{l}$ was 1.2 mg of $(\text{As}^{3+})/\text{g}(\text{FeOOH})\cdot\text{h}$, and with respect to an Na_2HAsO_4 solution at a starting concentration of 2.7 mg of $(\text{As}^{5+})/\text{l}$ was 1.5 mg of $(\text{As}^{5+})/\text{g}(\text{FeOOH})\cdot\text{h}$.

5

Example 12

950 g of a suspension of an alkaline nanoparticulate seed of $\alpha\text{-FeOOH}$ (solids content: 5.26 g/l of FeOOH , 1.14% NaOH) were admixed with stirring with 46 ml of
10 an $\text{Al}_2(\text{SO}_4)_3$ solution (100 g/l of Al_2O_3) and stirred for a further 15 minutes. The brown suspension was washed on a vacuum filter to a residual filtrate conductivity of 1 mS/cm, and the filter cake was dried at 75°C in a drying cabinet to a residual moisture of $<2\%$. The product was granulated to particle sizes between 0.5 and 2 mm and the granules were used for adsorbing arsenic.

15

In the x-ray diffractogram of the product, only $\alpha\text{-FeOOH}$ was detected, which, as may be seen from the scanning electron micrograph, is present as very short and highly agglomerated needles. The specific BET surface area was $102\text{ m}^2/\text{g}$. The abrasion value after 30 minutes was only 5%.

20

The adsorption rate with respect to an aqueous NaAsO_2 solution at a starting concentration of 2.6 mg of $(\text{As}^{3+})/\text{l}$ was 2.0 mg of $(\text{As}^{3+})/\text{g}(\text{FeOOH})\cdot\text{h}$, and with respect to an Na_2HAsO_4 solution at a starting concentration of 2.1 mg of $(\text{As}^{5+})/\text{l}$ was 1.5 mg of $(\text{As}^{5+})/\text{g}(\text{FeOOH})\cdot\text{h}$.

25

Example 13

3100 kg of NaOH (as a solution of 100 g/l) were charged into a stirred tank and diluted with cold water to 31 m^3 . The temperature of this NaOH solution was 26°C .

- 33 -

3800 kg of FeSO_4 are dissolved with water to give 38 m^3 of solution, cooled to 13-14°C and then, with stirring, pumped in 40 min to the NaOH charge. The resultant suspension was then oxidized with stirring with $2500 \text{ m}^3/\text{h}$ of air in 75 min.

- 5 Then, 18.2 m^3 of an FeSO_4 solution (100 g/l) are added at 150 l/min with aeration with $1300 \text{ m}^3/\text{h}$ of air with stirring.

The seed suspension was washed on a filter press to a filtrate conductivity of $< 1 \text{ mS/cm}$, and the filter paste was forced through a perforated plate and dried on a
10 belt dryer to a residual moisture of $< 20\%$ by weight. The material thus dried was coarsely ground to particle sizes of $< 2 \text{ mm}$. The fines fraction $< 0.5 \text{ mm}$ was separated off via a screen.

The product, according to the x-ray diffractogram, consisted of 100% $\alpha\text{-FeOOH}$.
15 From the scanning electron micrograph, for example at an enlargement of 60 000:1, the needle widths were determined by measurement between 15 and 35 nm, and the needle lengths were between 50 and 300 nm. The particles were highly agglomerated. The specific BET surface area was $145 \text{ m}^2/\text{g}$. The abrasion value after 30 min was only 5.1% by weight.

20

Illustrative embodiment 14

Adsorber granules synthesized according to examples 1-13, typically between 0.5 and 2 mm, or in comminuted form, are introduced into a contact chamber shown
25 according to fig. 1 or 2. The filtration unit has a flow rate for air as fluid of 2000 ml per minute at a pressure difference of 0.1 bar.

CLAIMS:

1. A filtration unit, comprising:

(a) a vessel having a hollow interior, an inlet opening, and an outlet opening, whereby media may pass into and out of said hollow interior by entering
5 said inlet opening and exiting said outlet opening; and

(b) an agglomerate of finely divided iron oxyhydroxide of the phase α -FeOOH in piece form having a particle size of 0.2 to 40 mm, wherein the finely divided iron oxyhydroxide has a BET surface area of 50 to 500 m²/g,

wherein said agglomerate is housed within the hollow interior of said
10 vessel and positioned so as to allow communication between said agglomerate and any media passing through the hollow interior of the vessel.

2. A filtration unit, comprising:

(a) a vessel having a hollow interior, an inlet opening, and an outlet opening, whereby media may pass into and out of said hollow interior by entering
15 said inlet opening and exiting said outlet opening; and

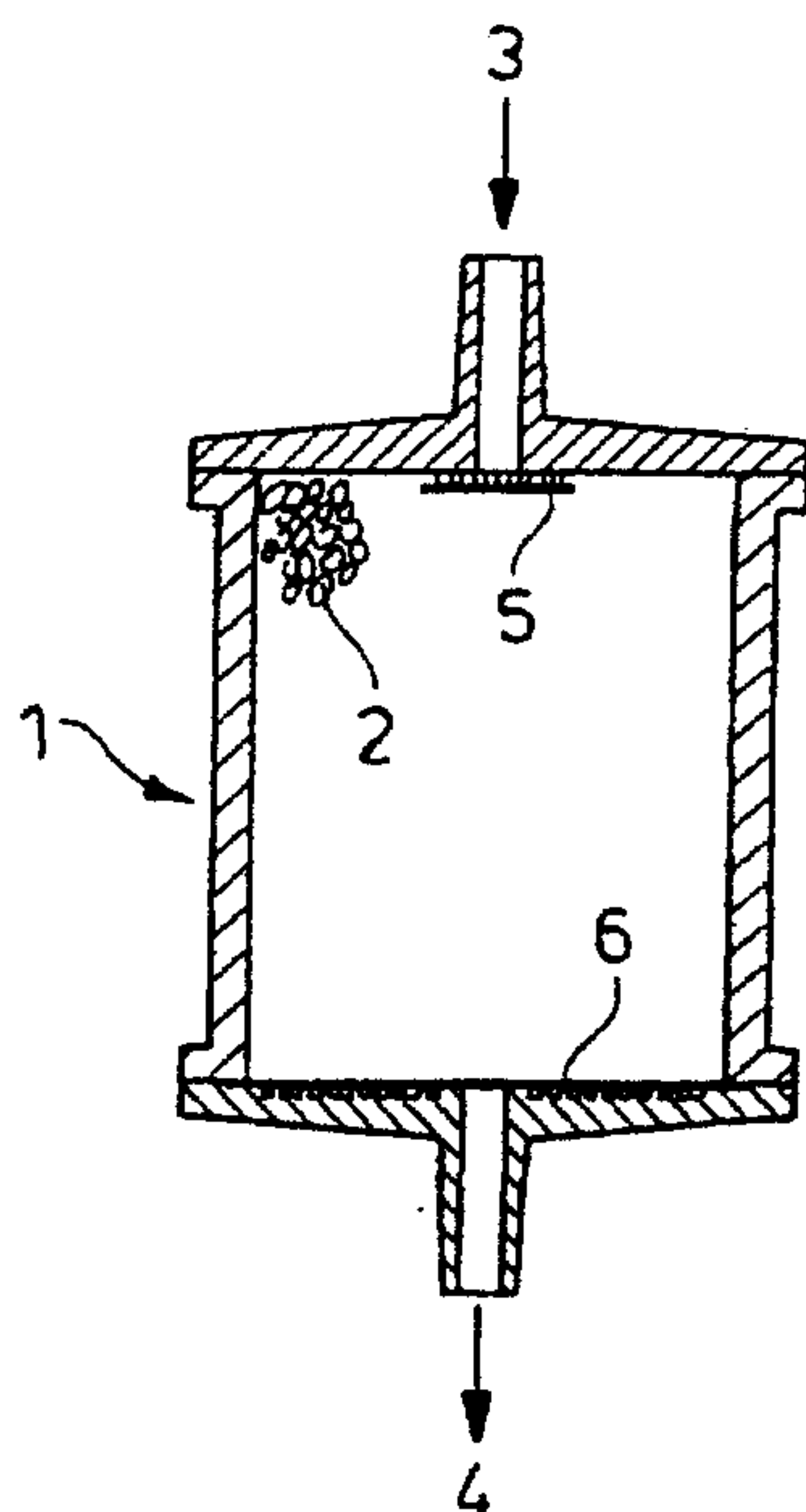
(b) an adsorbent/catalyst in pellet form consisting essentially of fine-particle α -FeOOH having a particle size of 0.2 to 40 mm, produced from an iron (II) salt suspension using NaOH as an alkaline precipitant followed by oxidation of the iron (II) to iron (III), filtering the suspension, washing the resulting filter cake,
20 completely dehydrating the filter cake, and comminuting the dried filter cake, wherein the fine-particle α -FeOOH has a BET surface area of 50 to 500 m²/g, and the adsorbent/catalyst in pellet form has a mechanical and hydraulic abrasion resistance of $\leq 12\%$ by weight,

wherein said adsorbent/catalyst is housed within the hollow interior of
25 said vessel and positioned so as to allow communication between said adsorbent/catalyst and any media passing through the hollow interior of the vessel.

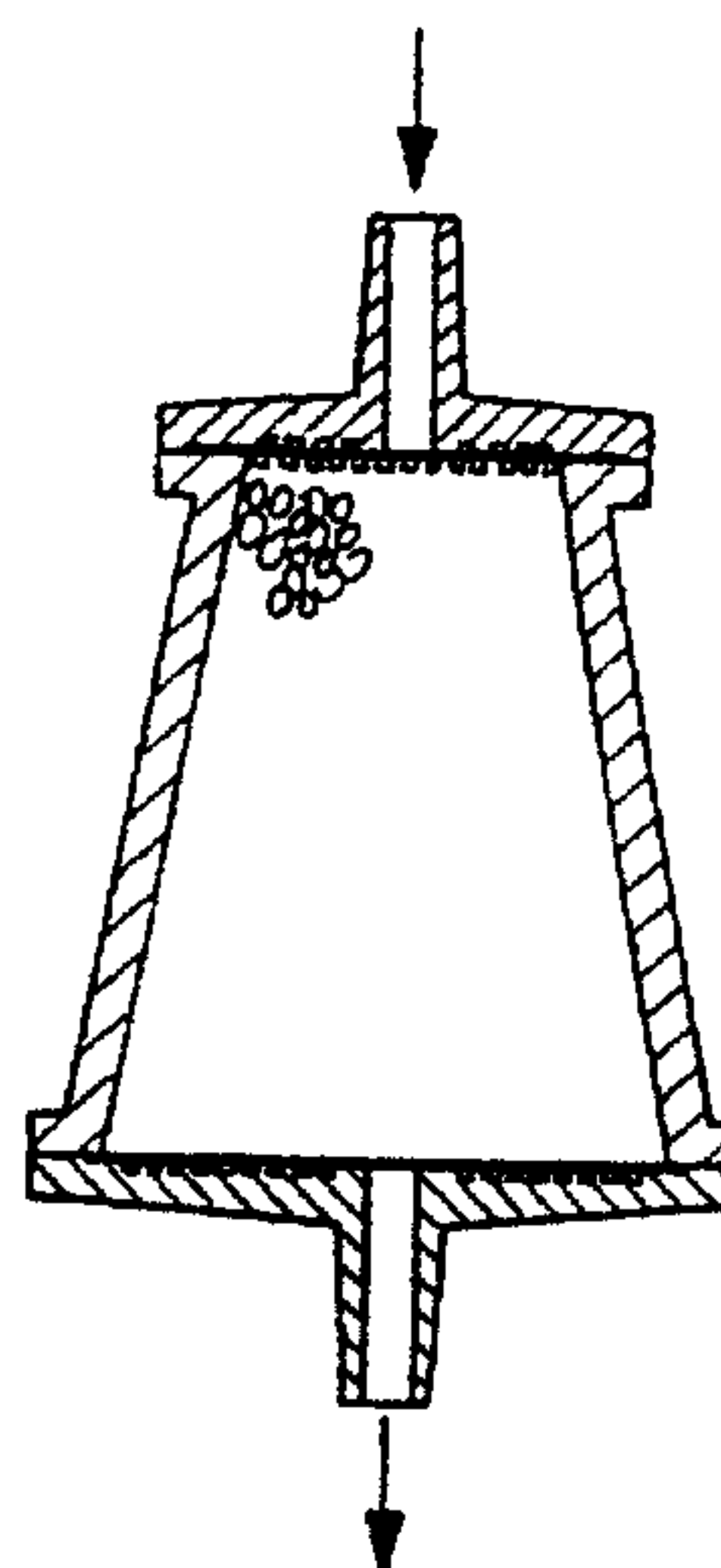
3. The filtration unit according to claim 1 or 2, wherein the α -FeOOH has a needle width of 4 nm to 50 nm.
4. The filtration unit according to any one of claims 1 to 3, wherein the media is a gas.
- 5 5. The filtration unit according to any one of claims 1 to 4, wherein the media is a liquid.
6. The filtration unit according to claim 5, wherein the liquid is water.
7. The filtration unit according to any one of claims 1 to 6, wherein the BET surface area is 80 to 200 m²/g.
- 10 8. The filtration unit according to any one of claims 1 to 7, wherein the agglomerate or adsorbent/catalyst has a residual moisture of less than 50%.
9. The filtration unit according to any one of claims 1 to 8, wherein the agglomerate or adsorbent/catalyst has an arsenic (V) adsorption of greater than 37.0%.
- 15 10. The filtration unit according to any one of claims 1 to 8, wherein the agglomerate or adsorbent/catalyst has an arsenic (III) adsorption of greater than 40.7%.
11. The filtration unit according to any one of claims 1 to 10, wherein the particle size is from 0.2 to 2 mm.

Fig. 1a

Adsorber tank containing iron
hydroxide adsorber

**Fig. 1b**

Tapered adsorber tank containing iron
hydroxide adsorber

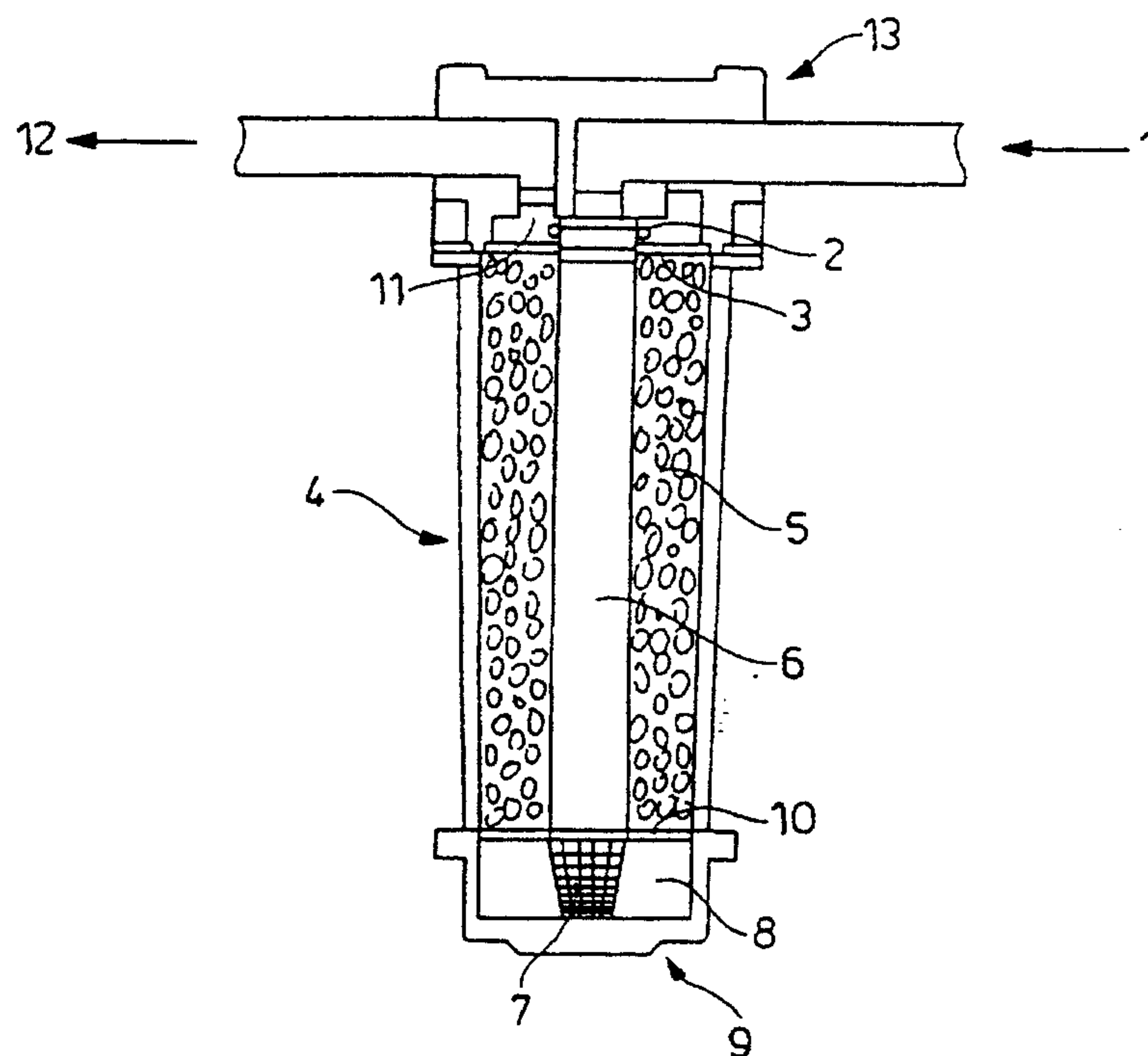


Legend for Figs. 1a and 1b

- 1) Adsorber housing
- 2) Adsorber particles
- 3) Inlet port
- 4) Outlet port
- 5) First flat filter layer together with fluid distribution channels
- 6) Second flat filter layer together with fluid collection channels

Fig. 2a

Adsorber tank having iron (oxy)hydroxide-containing adsorber cartridge and housing



Legend to Figs. 2a, 2b, 3:

- 1) Inlet or outlet tube
- 2) Gasket
- 3) Filter plate
- 4) Adsorber cartridge housing
- 5) Contact chamber containing iron (oxy)hydroxide granules
- 6) Inlet tube
- 7) Sieve basket
- 8) Prefilter or postfilter
- 9) Bottom part
- 10) Filter plate
- 11) Postfilter or prefilter
- 12) Outlet or inlet tube

Fig. 2b

Operating the adsorber tank in the opposite direction (cf. Fig. 2a)

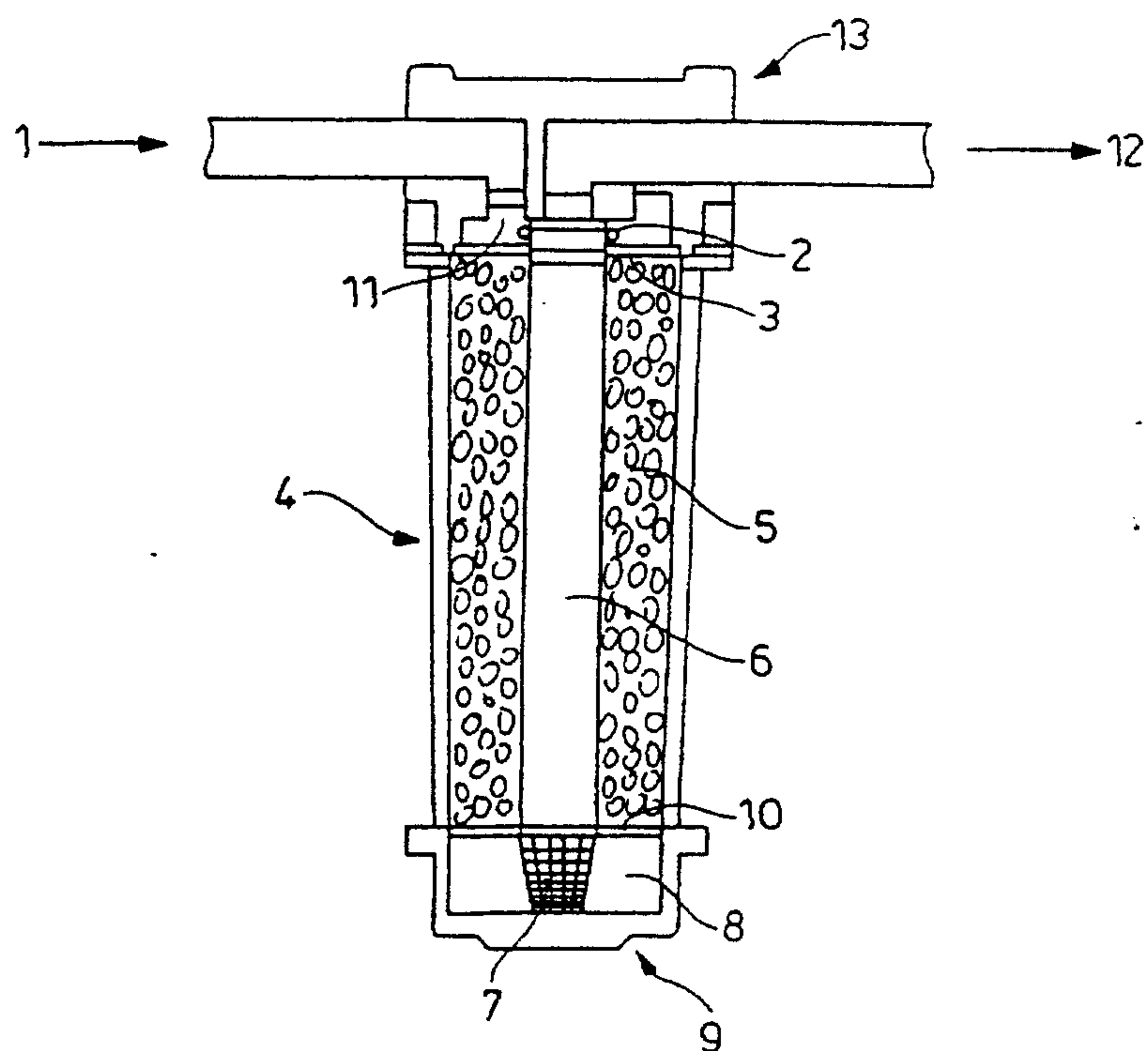


Fig. 3

Filter cartridge housing containing iron (oxy)hydroxide adsorbers

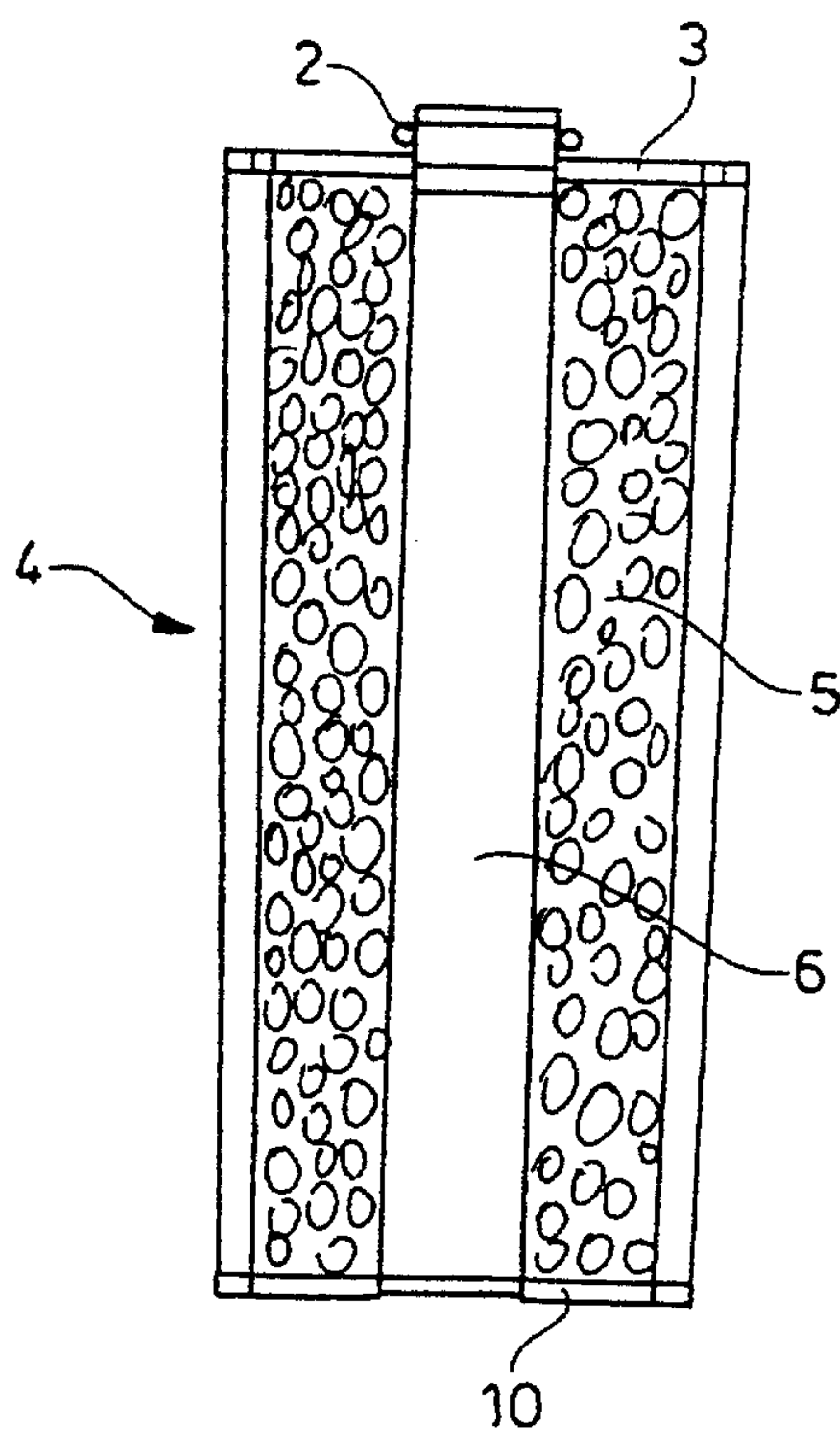


Fig. 4

Adsorber tank containing iron oxide or (oxy)hydroxide adsorber granules

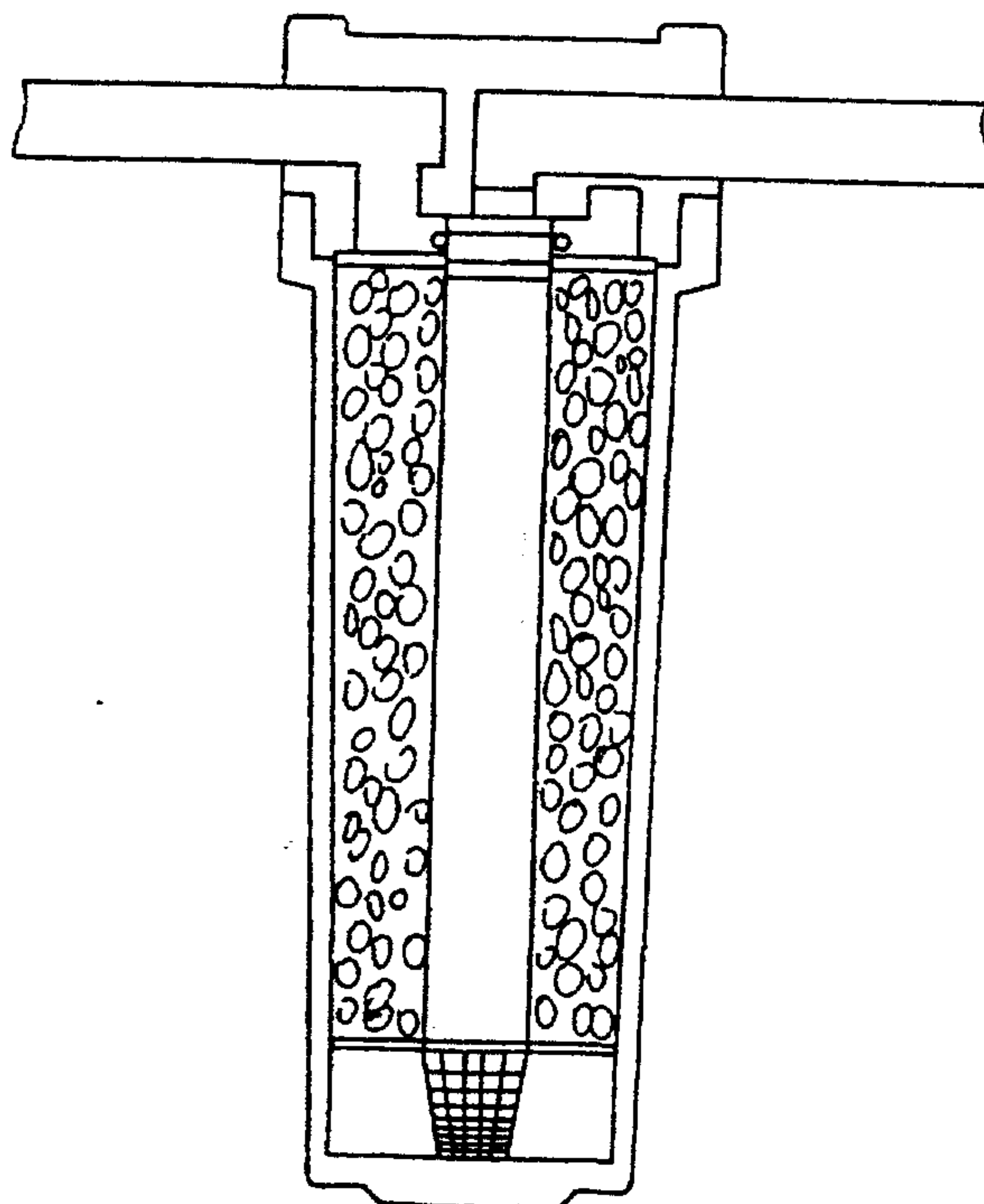
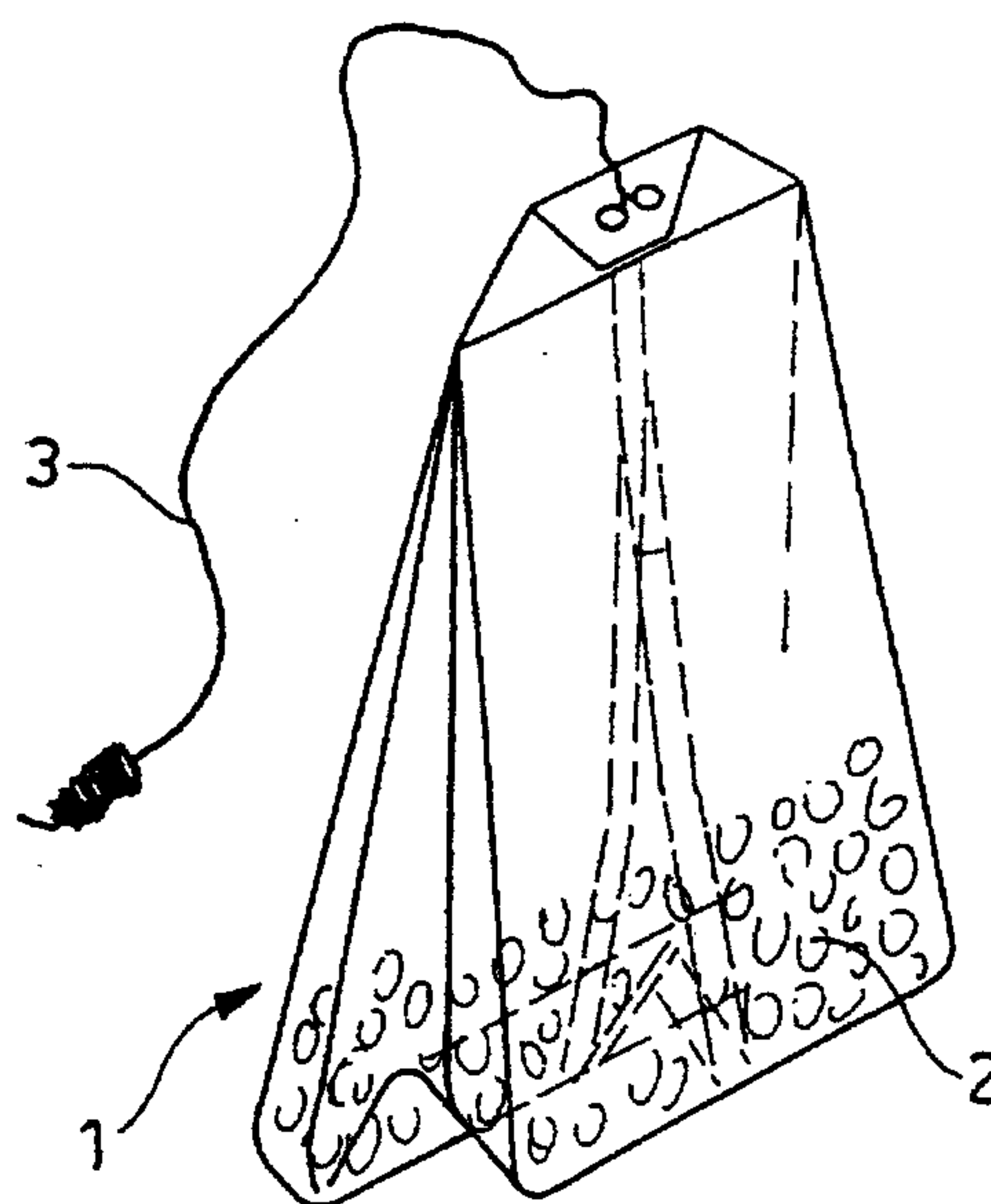


Fig. 5

Bag filter containing iron hydroxide granules



Legend to Fig. 5:

- 1) Filter bag
- 2) Iron oxide or (oxy)hydroxide adsorber
- 3) Suspension