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Adsorbent containing titanium and iron compounds

The present invention concerns a method of producing an adsorbent containing titanium and iron compounds, adsorbent the adsorbent prepared thereby and its use in a method of removing toxic substances and pollutants from
5 a fluid using said adsorbent.

Arsenic is a constituent part of our environment, which is disseminated predominantly from natural sources and is subject to a perpetual biogeochemical cycle. Thus the greatest occurrence of arsenic in the earth occurs bound in sulphide form in the earth's crust. Arsenic has many interesting properties. Thus
10 the toxic element occurs in many different forms, both organic and also inorganic. On a worldwide basis around 200 millions of people are exposed to arsenic-contaminated water. Tumour diseases such as for example skin and lung cancer can be the consequence of increased absorption of arsenic. Arsenic exhibits its carcinogenic action in particular after chronic absorption of small amounts over
15 many years.

Earlier arsenic was used as a fertiliser so that many areas of ground are still contaminated. Arsenic is a problem in particular in Asiatic countries. The main nutrients there include rice which grows in water. If that water is heavily arsenic-bearing then the plant accumulates the toxic substance. Whereas on average only
20 25 grams of rice per day are consumed in Europe where the arsenic content in drinking water is limited to ten micrograms per litre, in Asia the consumption is 300 grams. Here levels of concentration of 800 micrograms of arsenic per kilo have already been found in rice. In algae for example the arsenic is increased in content by the factor of 100000 compared to sea water. Thus 180 milligrams of organic
25 arsenic per kilogram of algae (dry weight) have already been found. The plants which are extolled as a miracle health cure from the sea can also contain up to 40 milligrams of inorganic arsenic per kilo of algae dry weight. Unlike the situation for drinking water there is no limit value in Germany for foodstuffs so that those algae may be freely sold.

30 One possible way of reducing the introduction of arsenic into the food chain involves eliminating the arsenic from drinking water or water which is used for agriculture or livestock breeding or at least reducing the concentration thereof.

Iron oxides and hydroxides have a high affinity for arsenic and are therefore used as adsorbents. For example Schlegel et al. describe a granular material comprising iron oxide and hydroxide with a high specific surface area (50 to >200 m²/g) which is highly suitable for the adsorption of heavy metals from fluid flows
5 (A. Schlegel et al., European patent EP 1582505 B1). Adsorbents produced specifically for that application are offered for example by Lanxess under the name Bayoxide E33 (with BET surface areas in the range of between 120 and 250 m²/g) and Evers under the name Everzit As (with a BET surface area of >300 m²/g).

US patent No 2006/0144793 describes titanium dioxide nanoparticles (<100
10 Å), whose surface is occupied by hydroxyl groups, and describes that the adsorption of heavy metals takes place on hydroxyl groups and therefore the hydroxyl groups are absolutely necessary for adsorption.

Furthermore, WO2006087432 discloses titanitic acid-containing products and methods for removing substances from aqueous solution. In particular, the
15 present invention relates to the purification of water and the removal of arsenic.

US06923917 relates to a process for removing bioavailable phosphorus from animal waste and soil using an industrial by-product from a metal manufacturing process.

Generally a large effective surface area is an aspect of significant
20 advantage for adsorption processes. It is for example possible to produce an effective TiO₂-based adsorbent with a large surface area from titanium compounds (for example chlorides or sulphates) by means of hydrolysis in the presence of a porous substrate (US No 2003/068683).

In addition a finely divided titanium dioxide from Dow Chemicals (Adsorbsia
25 GTO with a BET surface area in the range of between 200 and 300 m²/g) was proposed for the adsorption of arsenic.

Graver Technologies offers a granulated adsorbent (granule size 250 –
1190 µm) which for the main part contains titanium dioxide but also titanium hydroxide, but no foreign elements in proportions worth mentioning. That product
30 is used for adsorption of heavy metals. According Graver Technologies both the good adsorption kinetics and also the adsorption capacity are advantages of titanium-based adsorbents.

Basically it is assumed on the part of the persons skilled in the art that the adsorption action is correspondingly better, in proportion to the adsorbent being more finely divided or the BET surface area being larger or the concentration of hydroxyl groups being higher.

5 A disadvantage with the existing adsorbents is the complicated production procedure and the high costs linked thereto for the adsorbent, especially as in practice very large amounts of adsorbent are frequently required, for example for purifying ground water.

Therefore the object of the present invention is to find an alternative,
10 inexpensive and highly effective adsorbent which can replace the known adsorbents and which overcomes the existing disadvantages.

According to the invention, this task is solved by providing a process for preparing an adsorbent containing titanium and iron compounds, wherein the process comprises:

15 (i) digesting a titanium- and iron- containing starting material, preferably ilmenite and/or titanium slag, with sulphuric acid to obtain a solids containing digestion solution;

(ii) separating the solids contained in the digestion solution to obtain a digestion residue and a digestion solution substantially free of solids;

20 (iii) adding compounds containing iron ions to the digestion residue;

(iv) completing or partial neutralising the digestion residue;

(v) washing the neutralised digestion residue to remove sulphate salts; and

(vi) drying and/or granulating the digestion residue to obtain an adsorbent,

25 wherein the iron ion containing compounds are added to the digestion residue prior to the neutralisation step, and

wherein the adsorbent contains at least 10 wt.% Ti and at least 3.5 wt.% Fe, preferably 30 wt.% Ti and at least 5 wt.% Fe based on the total weight of the adsorbent.

30 From investigations on the part of the inventors it has surprisingly turned out that, in particular for the adsorption of metals on the adsorbent, it is particularly advantageous if the adsorbent used is digestion residue which occurs as a by-product in the production of titanium dioxide using the sulphate process and which is prepared according to the inventive process. The inventors assume, without

being tied down to this hypothesis, that the use of digestion residue is particularly advantageous as it is a chemically heterogeneous material which contains both titanium (Ti) and also iron (Fe) in oxide forms.

The heavy metal-bearing compounds can involve in particular lead,
5 mercury, cadmium, uranium, nickel, chromium, copper, zinc and/or tin-bearing compounds.

In various embodiments of the invention the compound to be adsorbed is an arsenic- or lead-bearing compound, preferably an arsenic-bearing compound.

In connection with the present invention the expression “-bearing
10 compound” relates to a compound which contains the aforementioned element in elementary, bound, ionic and/or complexed form. The expression includes salts, complexes, crystals and all other forms of the corresponding element, that is to say also the elementary form. The corresponding compound can occur in the form of a solid, in fluid form, including a dissolved form, or as a gas.

15 According to the invention, the adsorbent used contains at least 10 wt.% Ti and at least 3.5 wt.% Fe, preferably at least 30 wt.% Ti and at least 5 wt.% Fe with respect to the total weight of the adsorbent.

In an embodiment the adsorbent can contain titanium dioxide (TiO_2) and/or iron oxide at least 16 wt.% TiO_2 and/or at least 5 wt.% Fe_2O_3 .

20 According to the invention the adsorbent contains digestion residue which occurs as an insoluble residue in the production of titanium dioxide using the sulphate process for the production or manufacture of titanium dioxide in accordance with the state of the art (see for example Industrial Inorganic Pigments (editor G. Buxbaum, Wiley-VCH, Weinheim, 3rd edition 2005, pages 59 to 61) or
25 Ullmann's Enzyklopädie der Technischen Chemie, 4th edition, volume 15 (1979)) and is separated from the so-called black solution and produced according to the process of the invention.

In the production of titanium dioxide using the sulphate process firstly the titanium-bearing ore, for example ilmenite or titanium slag, is crushed and then
30 decomposed with sulphuric acid. That results in a solids-bearing solution or suspension, the so-called solids-bearing black solution, in which the titanium is present in dissolved form as titanyl sulphate.

To be able to further process the solids-bearing black solution it is necessary for that black solution to be prepared by solids separation to afford a solids-free solution or digestion solution, the so-called solids-free black solution. In that case the solid particles in the black solution, which usually involve residues of the titanium-bearing starting material, that is to say non-decomposed ore, are removed. That is necessary to obtain titanium dioxide in an adequate state of purity in the subsequent further method steps and stages.

Solids separation can be effected for example by centrifuging, sedimentation or by filtration. In general this solids separation operation is effected by vacuum filtering or filter pressing, for example by means of a vacuum rotary filter or a chamber or diaphragm filter press. The solid matter in the solids-bearing black solution is frequently pre-concentrated prior to filtration in a thickener.

Further steps which possibly serve for processing the digestion residue obtained by solids separation are one or more washing steps which can be implemented with water or dilute sulphuric acid, one or more neutralisation steps (for example by means of NaOH, CaCO₃, CaO, cement or NH₃), one or more drying steps or one or more grinding steps.

The digestion residue occurring in titanium dioxide production by means of the sulphate process is present in a constant quality on a large-scale basis and is inexpensively available as it usually has to be disposed of.

The product obtained in that way is referred to hereinafter as the "digestion residue" or "titanium concentrate".

The adsorbent contains 1 to 20 % by weight of silicon, preferably 5 to 15 % by weight of silicon, relative to the total weight of adsorbent.

The adsorbent can have a BET surface area of between 1 and 350 m²/g, preferably between 4 and 150 m²/g, particularly preferably between 6 and 40 m²/g.

The adsorbent can have a crystallite size, measured at the rutile reflex, of more than 10 nm, preferably >20 nm.

The digestion residue which substantially contains non-decomposed ore, filter additives and possibly other residues, can have a high content of titanium dioxide of from 10 to 80 % by weight, preferably from 25 to 70 % by weight, still more preferably from 40 to 60 % by weight, relative to the solids proportion. In that case the titanium dioxide can be present predominantly, that is to say >50 %,

preferably >75 %, in the form of the rutile modification or as iron titanate. In such embodiments the proportion of anatase can be less than 50 %, preferably less than 25 %. For example, the ratio of the intensities, determined by powder diffractometry, of the (101)-reflection line of anatase (at approximately $25.28^\circ 2\theta$) and the (110)-reflection line of rutile (at approximately $27.45^\circ 2\theta$) can be less than 1, preferably less than 0.40.

The digestion residue can be washed with dilute sulphuric acid and/or water prior to use as a component of the adsorbent. According to the invention, the digestion residue can be entirely or partially neutralised prior to use with a base or by further washing with water.

According to the invention it may be advantageous to dry the digestion residue, for example by blowing dry with air or heated air.

In addition, the drying operation can also be implemented with any method and assembly known to the man skilled in the art, for example in a drying compartment, with a belt drier, a spray drier or a spinflash drier.

The dried digestion residue can be deagglomerated or ground to a fine powder to improve processability, for example by means of a pinned disc mill, a rolling mill, a Bauermeister mill or other assemblies known to the man skilled in the art.

The titanium-bearing starting material, from which the digestion residue remains after the digestion operation in the form of a solids component, is usually ilmenite or titanium slag or a mixture thereof.

Further steps which optionally serve to process the digestion residue obtained by the solids separation operation are one or more washing steps which can be carried out with water or dilute sulphuric acid, one or more drying steps, one or more neutralisation steps which can optionally include the addition of neutralisation agent, and one or more grinding and/or granulation steps.

In the context of the invention the adsorbent can be used at a pH-value of <7, for example <5.5 or <4. A low pH-value can improve in particular the adsorption of arsenic-bearing compounds, for example As^{5+} , from aqueous solutions.

The amount of the adsorbent can be so selected that the mass ratio of adsorbent to the substance to be adsorbed is from 10 to 10000, preferably from 20 to 500, particularly preferably from 40 to 100.

In the use according to the process of the invention, the inorganic and/or
5 organic compounds can be removed from a fluid, for example a gas or a liquid, such as for example water, in particular waste water or sewage or ground water. In that case the substances to be removed can be present in dissolved form, for example in aqueous solution.

In a further aspect, the invention therefore also concerns a method of
10 removing inorganic and/or organic compounds, in particular pollutants and/or toxic substances, from a fluid, wherein the method includes bringing the fluid into contact with an adsorbent as defined in claim 3.

In an embodiment of the method the fluid is a gas, for example a waste gas, or a liquid, such as for example water, in particular waste water or ground water.
15 The waste gases can be for example waste gases from combustion processes or waste gases occurring in chemical processes. The waste waters can involve industrial waste waters or domestic waste waters.

In an embodiment of the method the fluid is the starting material (also referred to in English as the feed) for so-called fluid catalytic cracking (FCC). That
20 method is used for example to convert heavy petroleum fractions into valuable olefins (ethene, propene, butene), cat cracker benzene, light cycle oil (LCO) and heavy cycle oil components (heavy cycle oil, HCO, and slurry). In that process impurities of in particular nickel and vanadium but also for example copper or other metallic impurities are particularly damaging to the catalyst used. The adsorbent
25 can be used to remove those impurities directly from the feed. A further possible option is the addition of adsorbent to the reaction mixture. As a third possible option the adsorbent can be added to the catalyst, as a catalyst component. In that case the fluid is for example petroleum or petroleum fractions.

The pollutants and/or toxic substances which are adsorbed from the fluid by
30 the method according to the invention can be phosphates or compounds containing arsenic, antimony, sulphur, selenium, tellurium, cyano and heavy metal. Heavy metals by way of example are those mentioned hereinbefore. Preferably the adsorbed substances are arsenic-bearing and/or lead-bearing compounds.

The operation of bringing the adsorbent into contact with the fluid can be effected in known manner. In particular the adsorbent can be brought into contact with the fluid in the form of a solid, for example in granulate form. In that case the adsorbent can be applied to a carrier or can be used in the form of a cartridge or cassette through which the fluid flows.

The titanium- and iron-bearing starting material may be titanium-bearing ores such as for example ilmenite or titanium slag.

The digestion- and/or separation step can be carried out similarly to the corresponding steps in the known sulphate method for the production of titanium dioxide.

The digestion residue is entirely or partially neutralised in the course of the process according to claim 1. All neutralisation agents with which the man skilled in the art is familiar are suitable for that purpose, but particularly preferably use is made of those neutralisation agents which either form sulphates which can be well washed out (for example alkali, ammonia, Mg) or difficultly soluble sulphates (for example Ba). In that way the adsorbent according to the invention contains little salts which in use pass into the medium to be purified. The latter is the case in particular when using Ca-bearing neutralisation agents.

According to the invention, compounds containing iron ions are added to the digestion residue prior to the neutralisation step. In that way finely divided iron hydroxides which boost the adsorption action are formed in the neutralisation step. Preferably iron salts are added in dissolved form, particularly preferably in the form of iron(II)sulphate and/or iron(III)sulphate.

The proportion of soluble iron in the adsorbent with the addition of iron(II)sulphate or iron(III)sulphate is preferably >0.5 % by weight, more preferably >1.0 % by weight, particularly preferably >2 % by weight, in each case relative to the amount of adsorbent.

The proportion of soluble iron in the adsorbent can also be related to the amount of dissolved titanium: the mass ratio of soluble iron to soluble titanium in the adsorbent to which iron(II)sulphate or iron(III)sulphate is added is >0.8, preferably >1.5 particularly preferably >3.

The operation of determining the soluble iron and titanium is effected in such a way that, upon suspension of the adsorbent in ten times the amount of a 30

% sulphuric acid, after agitation for one hour and then separation of the undissolved components, the iron and titanium concentration in the fluid phase is determined.

5 Drying of the digestion residue can be effected for example by blowing dry with air or heated air. In addition the drying operation can also be effected with any method and assembly known to the man skilled in the art, for example in a drying compartment, with a belt drier, a spray drier or a spinflash drier.

10 The dried digestion residue can be deagglomerated or ground to a fine powder, for example by means of a pinned disc mill, a rolling mill, a Bauermeister mill or other assemblies known to the man skilled in the art.

 The dried digestion residue can be pressed to form granules of any suitable dimensions, for example by means of a dual rolling press, a tablet press, a screw press or other assemblies known to the man skilled in the art.

15 For granulation of the digestion residue the latter can also be mixed with suitable inorganic additives such as for example SiO_2 , hydraulically reacting Ca-compounds like cement or CaO , polyphosphates and so forth and/or organic additives like polyvinyl acetate, cellulose and so forth, optionally with the addition of water. Thereafter the material obtained can be dried and for example made into pieces by passing through a sieve of suitable mesh width.

20 Granulation of the digestion residue can be effected chemically (by means of additives) or physically (by means of pressing force) or by a combination of the two procedures (by means of additives and by means of pressing force).

 Thus, the invention concerns an adsorbent which can be obtained by the method according to the invention. The adsorbent is present in granulated form.

25 The adsorbent can be applied to a suitable substance, for example polyethylene, or alkyd resins, or PTFE and so forth. That carrier material can be applied to a metal surface, depending on the respective application involved, so that the carrier material operates as a binding layer between that metal surface and the adsorbent. On the other hand it is also possible to produce granulates
30 comprising carrier substance and adsorbent.

 Finally the invention also concerns an apparatus which contains the adsorbent according to the invention. This can involve for example a solid carrier to which the adsorbent is applied or in which the adsorbent is enclosed. An

example of such apparatus is a container such as for example a cartridge or cassette which contains the adsorbent but also an apparatus having plates or sheets to which the adsorbent is applied.

The adsorbent according to the invention can possibly be regenerated after use. For example regeneration of the charged adsorbent can be effected by washing with alkaline or acid solutions. Alternatively the adsorbent can be disposed of after use. For example the charged adsorbent can be vitrified, fixedly bound into a cement-bearing matrix or provided with a water-tight, inorganic or organic coating and thus prepared for disposal.

Further embodiments of the invention are contained in the claims. The following examples concern embodiments of an adsorbent not according to the invention and serve to illustrate a corresponding procedure.

Examples

15 Example 1

The solids-bearing digestion solution obtained upon digestion of a titanium-bearing slag with sulphuric acid was transferred into a thickener. From the underflow of the thickener the digestion residue was separated off in a filter press, neutralised with sodium hydroxide, filtered again and then spray-dried.

20 The product obtained was of the following composition:

Spray-dried digestion residue

Residual moisture IR Tr.30' 105°C	[%]	0.45
Residual moisture IR Tr.2d 30" 160°C	[%]	0.51
TGV MS-S 2' US-sonotrode	D[v,0.1]	1.4
200W [μm]	D[v,0.5]	16.3
	D[v,0.9]	56.6
	D[v,0.98]	89.6
	D[4.3]	23.5
DIN-pH		8.5
Bulk weight	[g/cm ³]	0.96
BET	[m ² /g]	10.6

RFA [%]	Ti	28.9
	Si	12.3
	Fe	5.4
	Ca	2.6
	Na	2.5
	Al	1.7
	Mg	1.4
	S	1.2
	Mn	0.8
	K	0.3
	Zr	0.2
	Nb	0.1

Example 2:

100 ml of heavy metal solution produced by dissolving a heavy metal salt in water was set to the desired pH-value with nitric acid or caustic soda. That solution was provided in a glass beaker and the adsorbent added with agitation. The pH-value was set to the desired pH-value with nitric acid or caustic soda and possibly corrected after 5 minutes. After a total agitation time of 30 minutes at room temperature (20 – 25°C) the solution was allowed to sediment for a short time and the supernatant solution was filtered clear by way of a 0.45 µm membrane filter. The starting solution and the filtrate were analysed.

The following heavy metals, levels of concentration, pH-values and adsorbent were used:

A: Lead (Pb²⁺) 13 mg/l, pH 2, adsorbent: A-K-1 (finely divided anatase from crenox GmbH with a BET surface area of about 90 m²/g), ratio: 13 mg lead to 1 g adsorber mass;

B: Lead (Pb²⁺) 13 mg/l, pH 2, adsorbent: digestion residue according to Example 1, ratio: 13 mg lead to 1 g adsorber mass;

C: Lead (Pb²⁺) 13 mg/l, pH 3, adsorbent: A-K-1 (finely divided anatase from crenox GmbH with a BET surface area of about 90 m²/g), ratio: 13 mg lead to 1 g adsorber mass;

D: Lead (Pb^{2+}) 13 mg/l, pH 3, adsorbent: digestion residue according to Example 1, ratio: 13 mg lead to 1 g adsorber mass;

E: Arsenic (As^{5+}) 0.058 mg/l, pH 3.2, adsorbent: A-K-1 (finely divided anatase from crenox GmbH with a BET surface area of about 90 m²/g), ratio:
5 0.058 mg arsenic to 1 g adsorber mass;

F: Arsenic (As^{5+}) 0.058 mg/l, pH 3.2, adsorbent: digestion residue according to Example 1, ratio: 0.058 mg arsenic to 1 g adsorber mass;

G: Arsenic (As^{5+}) 0.058 mg/l, pH 3.2, adsorbent: TH 8600 (= commercially available product from crenox GmbH), ratio: 0.058 mg arsenic to 1 g adsorber
10 mass;

H: Arsenic (As^{5+}) 0.058 mg/l, pH 3.2, adsorbent: Bayferrox 920 (= commercially available product from Lanxess Deutschland GmbH), ratio: 0.058 mg arsenic to 1 g adsorber mass;

I: Arsenic (As^{5+}) 11 mg/l, pH 3.2, adsorbent: digestion residue according to
15 Example 5, ratio: 11 mg arsenic to 1 g adsorber mass;

J: Arsenic (As^{5+}) 11 mg/l, pH 3.2, adsorbent: TH 8600 (= commercially available product from crenox GmbH), ratio: 11 mg arsenic to 1 g adsorber mass.

The products obtained are shown in Table 1:

20 (Mass % relates to Pb and As respectively. Charge means: amount of metal in mg relative to the amount of adsorbent in g).

Table 1:

Example	After adsorption:		
	Mass % in sol.	Mass % adsorbed	Charge mg/g
A	92	8	0.9
B	92	8	1
C	72	28	3.5
D	68	32	4.2
E	57	43	0.025
F	12	88	0.051

G	2	98	0.057
H	28	72	0.042
I	72	28	3.1
J	1	99	10.9

Example 3:

Production of a granulate **1** from digestion residue:

143 g of filter cake of an acid-washed titanium concentrate (= filter cake,
 5 washed with 10 % sulphuric acid, of the digestion residue from process step ii) as
 described on page 9) was kneaded in a mixer, mixed with 6 g of calcium oxide and
 69.5 g of distilled water and homogenised so that a paste-like material was the
 result. That was dried at a temperature of 120°C and the drying residue made into
 pieces by passing it by way of a sieve involving a mesh width of 3 mm. The fine
 10 grain proportion <0.5 mm was discarded.

Production of a granulate **2** from digestion residue:

143 g of filter cake of an acid-washed titanium concentrate (= filter cake,
 washed with 10 % sulphuric acid, of the digestion residue from process step ii) as
 described on page 9) was kneaded in a mixer, mixed with 50 g of dilute acid and
 15 11.5 g of a 50 % sodium polyphosphate solution and homogenised so that a
 paste-like material was the result. That was dried at a temperature of 120°C and
 the drying residue made into pieces by passing it by way of a sieve involving a
 mesh width of 3 mm. The fine grain proportion <0.5 mm was discarded.

The results obtained with granulated adsorbent are shown in Table 2.

Table 2

Example	BET	Pollutant	Ratio: mg As/g adsorb er mass	Parameters			Charge : mg As/g adsorbe nt	Masse s % adsorbe d	
				pH	c [mg/l] before adsorpti on	c [mg/l] after adsorpti on			
Granulate 1	14m ² / g	As 5+	104	3.0	104	100	4	4	
		As 5+	10.4	3.0	104	44	6	58	
		As 5+	107	8.0	107	100	7	7	
		As 5+	10.7	8.0	107	42	7	61	
Granulate 2	6 m ² /g	As 5+	104	3.0	104	93	11	11	
		As 5+	10.4	3.0	104	1.0	10	99	
		As 5+	107	8.0	107	83	22	22	
		As 5+	10.7	8.0	107	0.3	11	100	

Example 4:

Various adsorbents were compared in regard to their effectiveness. The results are shown in Table 3.1 (high concentration of dissolved arsenic) and 3.2 (low concentration of dissolved arsenic).

Column 3 (masses % adsorbed) describes in that respect the proportion of the initially dissolved metals which were held fast on the adsorbent.

Table 3.1 (high concentration of dissolved arsenic)

Adsorbent:	Element	Mass % adsorbed	Parameters		
			pH	c [mg/l] before adsorption	c [mg/l] after adsorption
Titanium concentrate	As 5+	28	3	11	7.9
TH	As 5+	99	3	11	0.10
Titanium concentrate	As 5+	6	5	10	9.4
TH	As 5+	> 99	5	10	< 0.10
Titanium concentrate	As 5+	9	7	11	10
TH	As 5+	96	7	11	0.45
Titanium concentrate	As 5+	0	8	11	11
TH	As 5+	91	8	11	1.0

In that respect it is shown that the effectiveness (column 3) of titanium concentrate is correspondingly better, the lower the pH-value of the solution. For titanium hydrate (TH) in contrast the effectiveness in the entire pH-range investigated is approximately equally good.

Table 3.2 (low concentration of dissolved arsenic)

Adsorbent:	Element	Mass % adsorbed	Parameters		
			pH	c [mg/l] before adsorption	c [mg/l] after adsorption
A-K-1	As 5+	43	3	0.058	0.033
Titanium concentrate	As 5+	88	3	0.058	0.007
TH	As 5+	98	3	0.058	0.001
Lanxess iron oxide Bayferrox 920	As 5+	72	3	0.058	0.016
A-K-1	As 5+	94	8	0.017	0.001
Titanium concentrate	As 5+	18	8	0.017	0.014
TH	As 5+	> 94	8	0.017	< 0.001
Lanxess iron oxide Bayferrox 920	As 5+	88	8	0.017	0.002

In that respect it is shown that the effectiveness (column 3) of the titanium concentrate according to the invention is very good at a pH-value of 3 and comparable to the partially substantially finer comparative products (BET surface areas of titanium concentrate = about 10 m²/g, A-K-1 = about 90 m²/g, titanium hydrate 8600 = >300 m²/g, Bayferrox 920 = about 15 m²/g).

Example 5:

Production of a granulate **3** from digestion residue:

The digestion residue is mixed with a binding agent and homogenised to a paste in a kneading machine (Krupps-3-Mix), dried and made into pieces.

Abrasion test:

10 10 g of the granulate to be investigated of the grain size fraction 0.5 – 4.0 mm is weighed into a cylindrical 250 ml glass flask, mixed with 150 ml of DI-water and rotated at about 250 rpm at room temperature on a shaker machine over a period of 30 minutes.

The fine component <0.1 mm of the suspension was then isolated by means of a sieve, dried and weighed.

Abrasion value x(%) = [100 x weighing-out fine component(g)/weighing-in granulate(g)]

20 Table 3.3 (Abrasion values with various binding agents)

Binding agent		Proportion	Abrasion value
Binding agent	Trade name	% by wt	%
Polyvinyl acetate	Mowilith	20	8.22
Portland cement	ISTRA 40	20	10.7
Portland blast furnace cement	CEMII/A	20	3.95
Calcium oxide		20	9.72
Calcium oxide + Portland cement		7.3 + 10	5.99

Example 6:

Production of a granulate **4** from digestion residue:

25 8.8 g of the digestion residue is compressed to a homogenous pressing of 3 cm in diameter with a laboratory pressing tool under a pressing pressure of 7.4 kN/cm². The pressing is mixed with 150 ml of DI-water in a cylindrical 250 ml glass

flask and caused to rotate at about 250 rpm at room temperature on a shaker machine over a period of 30 minutes.

The fine component <0.1 mm of the suspension was then isolated by means of a sieve, dried and weighed.

5 Abrasion value $x(\%) = [100 \times \text{weighing-out fine component(g)}/\text{weighing-in pressing(g)}]$

A value of 1.4 % by weight was found.

Patentkrav

1. fremgangsmåde til fremstilling af et adsorptionsmiddel, der indeholder titan- og jernforbindelser, hvor fremgangsmåden omfatter:

5 (i) nedbrydning af et titan- og jernholdigt udgangsstof, fortrinsvis ilmenit og/eller titanslagge, med svovlsyre for at opnå en faststofholdig nedbrydningsopløsning;

10 (ii) separering af faststofferne, der er indeholdt i nedbrydningsopløsningen, for at opnå en nedbrydningsrest og en i det væsentlige faststoffri nedbrydningsopløsning;

(iii) tilsætning af forbindelser, der indeholder jernioner, til nedbrydningsresten;

(iv) fuldstændig eller delvis neutralisering af nedbrydningsresten;

(v) vask af den neutraliserede nedbrydningsrest til fjernelse af sulfatsalte; og

15 (vi) tørring og/eller granulering af nedbrydningsresten, hvor der opnås et adsorptionsmiddel,

hvor forbindelserne, der indeholder jernioner, tilsættes til nedbrydningsresten før neutraliseringstrinnet, og

20 hvor adsorptionsmidlet indeholder mindst 10 vægtprocent Ti og mindst 3,5 vægtprocent Fe, fortrinsvis mindst 30 vægtprocent Ti og mindst 5 vægtprocent Fe baseret på adsorptionsmidlets samlede vægt.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** der som forbindelser, der indeholder jernioner, tilsættes jernsalte i opløst form, fortrinsvis i form af jern(II)sulfat og/eller jern(III)sulfat.

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3. Adsorptionsmiddel, opnået ifølge krav 1 eller 2, indeholdende mindst 10 vægtprocent Ti og mindst 3,5 vægtprocent Fe, fortrinsvis mindst 30 vægtprocent Ti og mindst 5 vægtprocent Fe baseret på adsorptionsmidlets samlede vægt.

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4. Indretning indeholdende adsorptionsmidlet ifølge krav 3, **kendetegnet ved, at** adsorptionsmidlet er fikseret på en bærer eller er indelukket i en beholder i form af en patron eller kartouche.

5. Fremgangsmåde til fjernelse af uorganiske og/eller organiske forbindelser, især af skade- og/eller giftstoffer, af en fluid, hvor fremgangsmåden omfatter at bringe fluiden i kontakt med et adsorptionsmiddel ifølge krav 3.