

Agent for reducing the phosphate concentration in wastewater

5 The present invention relates to an agent for reducing the concentration of phosphate in wastewater, to a method for reducing the concentration of phosphate in wastewater, as well as to the use of the agent for reducing the concentration of phosphate in wastewater.

10 In order to reduce the concentration of phosphate in wastewater, in principle, chemical phosphate precipitation (P-precipitation) by adding precipitation agents is known, along with biological phosphorus elimination (P-elimination) by metabolization of the phosphates in the biomass of the activated sludge.

15 Chemical P-precipitation is usually divided into simultaneous precipitation, pre-precipitation and post-precipitation.

20 Phosphates dissolved in aqueous systems – in particular orthophosphates – can be converted into undissolved phosphates with the aid of suitable precipitating agents and can be removed from the aqueous system as a solid, together with other solids. The separated phosphates are then components of the sludge.

Common precipitating agents are:

- o iron chlorides (FeCl_2 or FeCl_3)
- o iron chlorosulphate (FeClSO_4)
- 25 o iron(II) sulphate/copperas (FeSO_4)
- o aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$)
- o aluminium chloride (AlCl_3)
- o polyaluminium chloride ($\text{Al}_x(\text{OH})_y\text{Cl}_z$)
- o sodium aluminate ($\text{NaAl}(\text{OH})_4$)
- 30 o milk of lime ($\text{Ca}(\text{OH})_2$),

wherein iron and aluminium salts or solutions of these salts are preferably used as the precipitating agent.

35 If the precipitating agent is added directly to the biological purification step, this is known as simultaneous precipitation. Simultaneous precipitation is a precipitation

reaction in which ions dissolved in the water are transformed into a water-insoluble compound by the addition of a precipitating agent. Furthermore, the addition of the precipitating agent results in an improved sludge structure and better settling properties. Simultaneous precipitation is thus frequently carried out, not only to
5 remove nutrients, but also in order to improve the operation of the plant, because in this manner, the separation of activated sludge and purified wastewater in the secondary sedimentation tank is improved.

“Pre-precipitation” is the term given to the removal of phosphorus from wastewater by
10 the transformation into undissolved metal salts. This precipitation is carried out prior to the biological stage. As an example, the primary sedimentation tank may be used to settle the precipitation products.

The key point with pre-precipitation is not the phosphate precipitation itself, but
15 dispensing with the biological stage. Outdated wastewater treatment plants in particular are frequently overloaded. If renovation is delayed for various reasons, then by using pre-precipitation, regular outflow values can be maintained even with facilities of this type. The disadvantages with this method are a great deal of primary sludge and a very high consumption of precipitating agents, in particular in the form
20 of trivalent metal salts.

In the case of post-precipitation, the precipitation of phosphorus is carried out after the secondary sedimentation. Trivalent metal salts in particular are used. Post-precipitation guarantees very low phosphorus outflow values, however the
25 consumption of precipitating agents is very high. In addition, a downstream separation of the flocculate which is formed is necessary via a separate filtration stage.

In the case of biological phosphorus elimination (abbreviation: bio-P), polyphosphate-accumulating organisms (PAO) in an anoxic environment are forced into a stress
30 situation. When these microorganisms have no oxygen and nitrate available to them, the primary sources of nutrition are absent and the microorganisms could die. In order to prevent this, the microorganisms which are in this situation release the phosphates deposited in their cells, releasing energy which they use to survive. When the microorganisms then encounter an aerobic, oxygen-rich environment, they once more

take up the phosphate which has been released and deposit even more phosphates in their cells, whereupon the total concentration of phosphate in the water is reduced.

In practice, a combination of different methods is used.

5

The application JP 11319411 A discloses a water purification agent with a high solubility which is capable of binding and precipitating rich sources of nutrients, water contamination and bacterial groups. The water purification agent comprises a powder formed from mussel shells, preferably Hokkaido mussel shells, wherein the water

10

purification agent furthermore preferably comprises a precipitating agent, in particular aluminium sulphate. The ratio of mussel shells to precipitating agent should preferably be in the range 8/2 to 6/4. For the purification of water, the water purification agent should be added to the water to be purified, preferably in a concentration of 0.5% by weight or less with respect to the mussel shells. As an alternative, the water

15

purification agent may also be added to the water to be purified in a quantity of 12 to 13 kg per tsubo (3.3 m²). In order to purify water containing heavy metals, a precipitating agent such as iron(III) chloride is proposed, after or together with the water purification agent of JP 11319411 A, in order to precipitate out the heavy metals.

20

That specification indicates that the mussel shells primarily consist of calcium carbonate which, however, has a significantly higher solubility in water than commercially available calcium carbonate which is obtained from limestone by purification. More precisely, the solubility of this calcium carbonate should be 40.59 mg/100 mg.

25

In the single example of the specification, for the purification of seawater, a water purification agent consisting of 70% by weight Hokkaido mussel shells and 30% by weight of aluminium sulphate powder was tested in a concentration of 0.1% by weight with respect to the water to be purified, and a reduction in the total phosphorus concentration from an original 1.4 mg/L to 0.1 mg/L or less was determined.

30

The application JP 09-038414 A concerns a precipitating agent with a high sedimentation speed which forms large flocculates when added to wastewater and facilitates the treatment of the wastewater sludge. The coagulation sedimentation agent contains two types of calcium carbonate: coarse-grained particles with a mean

particle diameter of 50-500 μm and fine particles with a mean particle diameter of 1-30 μm . The weight ratio of the coarse particles to the fine particles is preferably in the range from 2:1 to 40:1. The quantity of calcium carbonate is preferably at least 60% by weight. Furthermore, the coagulation sedimentation agent preferably contains a soluble

5 aluminium salt, a soluble iron salt or a polymeric precipitating agent of an organic system. In that connection, aluminium sulphate, polyaluminium chloride, iron (II) sulphate and iron (III) sulphate are mentioned by way of example.

10 In the examples of that specification, a precipitating agent consisting of coarse-grained calcium carbonate particles with a mean particle diameter of 100 μm , fine calcium carbonate particles with a mean particle diameter of 3.1 μm , aluminium sulphate, calcium hydroxide and polyacrylamide was tested for the purification of sewage water. An improvement in the filterability, the flocculate size, the sedimentation rate, the transparency as well as the pH of the purified water compared with the untreated sewage

15 water were observed. However, statements regarding the concentration of phosphorus in the sewage water and/or the purified water were not found in the specification.

The article "Nutrient removal and sludge production in the coagulation-flocculation process" by Aguilar, M.I., Sacz, J., Llorens, M., Soler, A. and Ortuno, J.F. in Water

20 Research (2002), 36 (11), pages 2910-2919 concerns the treatment of wastewater from an abattoir. $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ and polyaluminium chloride were used as the coagulation agent. Activated silica, activated carbon, precipitated calcium carbonate (PCC), cationic polyacrylamide, polyacrylic acid, anionic polyacrylamide and polyvinyl alcohol were used as coagulation auxiliaries, wherein calcium carbonate was only used in combination with

25 $\text{Al}_2(\text{SO}_4)_3$ or polyaluminium chloride. For $\text{Fe}_2(\text{SO}_4)_3$, independently of the coagulation auxiliary, a 100% removal of orthophosphate and a removal of total phosphorus of at least 99.53% was reported. For $\text{Al}_2(\text{SO}_4)_3$ independently of the coagulation auxiliary, a 100% removal of orthophosphate and a removal of total phosphorus of at least 98.88% was reported, whereas the use of PCC as the coagulation agent produced the worst

30 results. For polyaluminium chloride, independently of the coagulation auxiliary, a 100% removal of orthophosphate and a removal of total phosphorus of at least 99.70% was reported, whereas the use of PCC as the coagulation agent produced worse results than the use of polyaluminium chloride without further coagulation agents.

The publication “Stickstoff und Phosphor in Fließgewässern”, [Nitrogen and Phosphorus in Watercourses] Arbeitsbericht des ATV-Ausschusses 2.1, Korrespondenz Abwasser 11/87 [ATV Work Report, Committee 2.1, Wastewater Correspondence] deals with the necessity for substantial nitrogen oxidation in wastewater treatment plants, a substantial
5 nitrogen elimination in wastewater treatment plants and the need to eliminate phosphorus in watercourses. Regarding the origin of phosphorus loads in the watercourses, it was assumed that the vast majority originates from punctiform wastewater pipework. It is stated that:

“Phosphorus loads entering watercourses in the German Republic could be
10 almost halved if phosphorus were to be eliminated from all wastewater treatment plants with connection sizes of over 20000 PE. This would mean that the risk of extreme overfertilization would be alleviated. From the point of view of expediency and economy, elimination percentages should be graduated, as a function of the respective connection size, to between approximately 70% and
15 95% and in particular the efficiency of chloride- and sulphate-free precipitation processes as well as biological processes for phosphorus elimination should be fully exploited. The positive side effects associated with the elimination of phosphorus would also play an instrumental role in the control of water
pollution”.

20 Calcium carbonate is not mentioned in the publication.

The utility model CN 205328829 U discloses a device for wastewater treatment for restaurants, comprising a zone for removing phosphorus which comprises a mixture of
25 limestone and aluminium filler. Iron salts are not mentioned in that utility model, however.

WO 2013/040716 A1 describes a method for the treatment of phosphate-containing wastewater, in which:

- 30 a) a first cation is added to the wastewater in order to precipitate fluorosilicate from the wastewater;
b) a second cation is added to the wastewater in order to precipitate fluoride from the wastewater;

- c) the pH of the wastewater is raised in order to precipitate the second cation from the wastewater;
- d) the remaining silica is removed from the wastewater, and
- e) phosphate precipitates out from the wastewater.

5

Step a) is stated to preferably include raising the pH of the wastewater to about 2.0 in order to precipitate out the fluorosilicate.

Adding the second cation is stated to preferably include the addition of limestone.

10

Step e) is stated to preferably include the addition of a third cation and/or a fourth cation in order to precipitate out the phosphate as struvite analogues, which preferably should include iron ammonium phosphate.

15 There are no other indications regarding iron salts in that patent application.

Thus, the objective of the present invention is to propose better possibilities for reducing the concentration of phosphate in wastewater, in particular in municipal and industrial wastewater. In particular, more effective possibilities for the removal of

20 phosphates from wastewater should be provided. In this regard, the properties of the wastewater should be compromised as little as possible, and instead be improved as far as possible. Furthermore, the properties of the activated sludge, in particular its settling behaviour, should be compromised as little as possible, and instead be

25 improved as far as possible. Furthermore, the phosphate load in running water into which the wastewater to be purified is fed should be reduced and overfertilization of the running water should be avoided as far as possible. Furthermore, a highly cost-effective solution to these objectives is sought which can be carried out in the simplest possible manner.

30 These objectives are achieved by the provision of an agent for reducing the concentration of phosphate in wastewater with all of the features of the independent claim 1. The claims which are dependent on claim 1 describe preferred embodiments of the agent in accordance with the invention. The remaining claims protect a particularly advantageous method for reducing the concentration of phosphate in

wastewater as well as a particularly advantageous use of the agent in accordance with the invention.

Because an agent is provided which, respectively with respect to its total weight, comprises > 50.0% by weight of calcium carbonate and at least 1.0% by weight of an iron salt, wherein the calcium carbonate has a solubility in water of less than 20 mg/1000 mL of water at 25°C, surprisingly, an agent for reducing the concentration of phosphate in wastewater, in particular in municipal and industrial wastewater, can be accessed which enables phosphates to be removed from wastewater more effectively.

In this regard, the properties of the wastewater are not compromised, but in particular are significantly improved because of the pH-buffering action of the agent.

Furthermore, the properties of the activated sludge, in particular its settling behaviour, are not compromised, but are significantly improved. Furthermore, the phosphate load of watercourses into which the purified wastewater is introduced is significantly

reduced by the invention and overfertilization of the running water is avoided to the maximum extent. Furthermore, an extremely efficient solution to the objective of the invention has been found which can be implemented in a particularly simple manner.

By using the agent in accordance with the invention, more phosphate which is dissolved in wastewater is removed than with the prior art use of iron or aluminium salts alone. In addition, the agent in accordance with the invention prevents a reduction of the pH at the dosing point, whereupon more phosphate can be precipitated out.

Furthermore, the use of corrosive substances can be reduced as far as possible or avoided altogether using the agent in accordance with the invention.

A further advantage of a particularly preferred embodiment of the agent in accordance with the invention lies in the fact that it does not constitute dangerous goods within the meaning of the European Convention on the Transportation of Dangerous Goods By Road (ECE), and therefore can be handled and used easily.

Furthermore, the agent in accordance with the invention is particularly environmentally-friendly. The salification in the purified water is significantly lower with the invention than with conventional methods for the purification of wastewater.

- 5 Thus, the subject matter of the present invention is an agent for the reduction of the concentration of phosphate in wastewater, in particular the concentration of orthophosphate.

10 In this context, the term “wastewater” is a general term for types of water from various sources which are supplied via structural installations and in particular includes rainwater, in particular water from precipitation flowing off the surface of fixtures; sewage water, in particular water which has been contaminated by consumption (“with changed properties or composition”) which may in particular include grey water (according to EN 12056-1, faeces-free, slightly contaminated wastewater such as that
15 which arises from showering, bathing or handwashing, but also that which comes from the washing machine and which can be used for the preparation of process water or industrial water. Rainwater flowing from a roof or balcony is included here); black water (according to ISO 6107-7:1997, domestic wastewater with urine and/or faecal solids, in particular including yellow water (urine with flushing water) and brown
20 water (faeces, flushing water and toilet paper, without urine)); external water, which enters the pipework through structural damage.

During wastewater removal, wastewater is collected in the pipework and transported; in central Europe, it is usually treated in wastewater treatment plants and then fed into
25 bodies of water which act as preflooders or into the groundwater by seepage, broad irrigation or sprinkler irrigation.

In the context of the present invention, the wastewater to be purified usually has a pH, measured at 25°C, in the range from 5.0 to 10.0, in particular in the range from 6.0 to
30 9.0. After the wastewater treatment in accordance with the invention, the pH of the purified water, measured at 25°C, is preferably in the range from 5.0 to 10.0, in particular in the range from 6.0 to 9.0.

Phosphates are the salts and esters of orthophosphoric acid (H_3PO_4). In a broader sense, condensates (polymers) of orthophosphoric acid and their esters are also known as phosphates. In all of these compounds, the phosphorus is in the oxidation state (V).

- 5 The determination of the concentration of phosphate in wastewater, in particular of the concentration of orthophosphate, can be carried out in a manner which is known per se. A determination of the concentration of phosphate in wastewater, in particular of the concentration of orthophosphate, by means of commercially available photometric tests has been shown to be particularly effective. As an alternative, the phosphorus
10 concentration may also be determined by means of ICP-OES.

The agent in accordance with the invention for reducing the concentration of phosphate in wastewater comprises, respectively with respect to its total weight:
>50.0% by weight, preferably >60.0% by weight to 99.0% by weight, particularly
15 preferably >60.0% by weight to 80.0% by weight, in particular 65.0% by weight to 75.0% by weight, of calcium carbonate and
at least 1.0% by weight, preferably at least 10.0% by weight, particularly preferably 20.0% by weight to <40.0% by weight, in particular 25.0% by weight to 35.0% by weight, of an
iron salt.

20

Particularly preferably, the proportion by weight of calcium carbonate and iron salt together in the agent in accordance with the invention is >51.0% by weight, preferably >60.0% by weight, advantageously >70.0% by weight, yet more preferably at least 80.0% by weight, more particularly preferably at least 90.0% by weight, in particular at least
25 99.0% by weight. In the context of a more particularly preferred embodiment of the present invention, the agent in accordance with the invention exclusively consists of calcium carbonate and at least one iron salt.

The solubility in water of the calcium carbonate at 25°C is less than 20 mg/1000 mL of
30 water, preferably less than 16 mg/1000 mL of water, particularly preferably less than 15 mg/1000 mL of water, more particularly preferably less than 14 mg/1000 mL of water, advantageously less than 12 mg/1000 mL of water, preferably less than 10 mg/1000 mL of water, yet more preferably less than 8 mg/1000 mL of water, in particular less than 7 mg/1000 mL of water.

The solubility in water of the calcium carbonate can be determined in a manner which is known by stirring the calcium carbonate in CO₂-free distilled water at 25°C for at least 1 h and subsequent determination of the dissolved quantity of calcium carbonate, preferably by means of a photometric method.

- 5 The agent in accordance with the invention comprises at least one iron salt, preferably an iron (II) salt or an iron (III) salt. Preferred iron salts are FeSO₄, FeSO₄·H₂O, FeSO₄·4H₂O, FeSO₄·5H₂O, FeSO₄·6H₂O, FeSO₄·7H₂O, FeCl₃, FeCl₃·6H₂O, FeCl₂, FeCl₂·4H₂O, Fe₂(SO₄)₃, Fe₂(SO₄)₃·1H₂O and FeCl(SO₄). For the purposes of the present invention, iron(II) salts, in particular iron(II) sulphates, are more particularly suitable.

10

In principle, there are no further constraints as regards the calcium carbonate and it can in general be freely selected. For the purposes of the present invention, however, the use of calcium carbonates with a mean particle size in the range from 5 µm to 30 µm has been shown to be particularly suitable. Furthermore, the calcium carbonate preferably has a BET specific surface area in the range from 0.4 m²/g to 10.0 m²/g, preferably in the range from 0.6 m²/g to 6.0 m²/g, in particular in the range from 0.8 m²/g to 2.0 m²/g.

15

Furthermore, in the context of the present invention, a ground calcium carbonate is preferably used. "Ground calcium carbonate" (GCC) in the context of the present invention is a calcium carbonate which has been obtained from natural sources such as marble, chalk, limestone or dolomite. GCC is normally obtained by grinding, screening, sizing and/or wet and/or dry fractionation. Because of its natural origin, GCC may contain a certain amount of magnesium such as, for example, in the case of GCC produced from dolomitic limestone.

25

GCC is different from PCC ("precipitated calcium carbonate"), which is a synthetic material usually obtained by precipitation following the reaction of carbon dioxide with calcium hydroxide in an aqueous environment, by precipitation of a calcium and a carbonate source in water or by precipitation of calcium and carbonate ions, for example CaCl₂ and Na₂CO₃, from solution.

30

For the purposes of the present invention, particularly suitable GCC is obtained from limestone, preferably from corallian limestone, particularly preferably from Devonian massive limestone, in particular from Lahn marble.

- 5 Sedimentary rocks which mainly consist of the chemical substance calcium carbonate (CaCO_3) in the form of the minerals calcite and aragonite are known as limestone.

Corallian limestones are limestones which originate from the bulk aggregation of corals, sponges and other sessile marine organisms. They occur primarily in coastal or
 10 other flat marine regions. In contrast to shell limestone, the limestone skeletons are not washed together by the ocean waves, but are transformed in the original living space of the organism, often in the position when alive.

Particularly massive and extensive corallian limestone deposits are often known as
 15 massive limestone. Examples in Germany are known in the Rhine Massif. Here, extensive deposits can be found in the Eifel, Bergische Land and Sauerland regions as well as in the Lahn-Dill regions; they are obtained from many sites for cement manufacture and as sources of natural stone. Significant proportions of these corallian limestones are formed from stromatopores (extinct sponge-like organisms) and extinct
 20 types of coral. Typical index fossils of this massive limestone are the brachiopods *Stringocephalus burtini* and *Uncites gryphus*.

Limestones which can be polished and are from the Middle Devonian period in the south eastern region of the Rhine Massif are collectively known as Lahn marble (formerly
 25 Nassauer marble). The production centres were in Balduinstein, Hahnstätten, Diez (Rhein-Lahn district, Rheinland-Pfalz), Villmar and Schupbach (both in the Limburg-Weilburg district, Hessen).

The agent in accordance with the invention may be manufactured in a manner which is
 30 known per se, by mixing the components. Comminution of the agent, for example by grinding, is not usually necessary.

Reduction of the concentration of phosphate in wastewater can be carried out by means of a method in which the agent in accordance with the invention is added to the

wastewater to be purified, preferably in a quantity in the range from 1 ppm to <1000 ppm, preferably in the range from 5 ppm to 500 ppm, particularly preferably in the range from 10 ppm to 400 ppm, advantageously in the range from 15 ppm to 250 ppm, in particular in the range from 20 ppm to 100 ppm, with respect to the total weight of the

5 wastewater to be purified.

The dosing point for the agent in accordance with the invention for reducing the concentration of phosphate may in principle be freely selected.

10 In the context of a first preferred embodiment of the present invention, the agent in accordance with the invention is added directly to a biological purification stage of the wastewater purification in order to obtain simultaneous precipitation, in which phosphate ions dissolved in water are converted into phosphate salts which are insoluble in water by adding the agent in accordance with the invention.

15

In the context of a further preferred embodiment of the present invention, the agent in accordance with the invention is added prior to a biological stage for wastewater purification in order to obtain pre-precipitation of the phosphates from the wastewater by transformation into insoluble metal salts.

20

In the context of yet another preferred embodiment of the present invention, the agent in accordance with the invention is added after a biological stage for wastewater purification in order to obtain post-precipitation of phosphates after the secondary sedimentation.

25

The following dosing points have been shown to be particularly suitable for wastewater treatment plants:

- into the preliminary sedimentation outflow,
- into the inflow or outflow from bio-P tanks, denitrification tanks, nitrification tanks,
- 30 combined denitrification and nitrification tanks, as well as
- into the secondary sedimentation inflow.

The agent may preferably be dosed directly into the activated sludge at a turbulent site.

Particularly preferably, in accordance with the invention, the agent in accordance with the invention is added directly to a biological purification stage of the wastewater purification, and also, the agent in accordance with the invention is added prior to a biological stage of the wastewater purification, wherein the best results are obtained when the agent in accordance with the invention is added directly to a biological purification stage of the wastewater purification.

At best, the agent is dosed directly into the activated sludge at a site which is as turbulent as possible, advantageously between two activated sludge tanks at the edge of an overflow before or after a pump or lifting means.

Preferably, the agent in accordance with the invention is added to the wastewater as an advantageously dried powdered composition by means of a dosing device, preferably by means of an auger which is connected to a storage device, preferably a silo. A further preferred form of administration is the direct dosing of the agent into the wastewater purification plant, in particular a wastewater treatment plant, by adding the agent, preferably from sacks or Big Bags, advantageously specifically to the activated sludge.

Dosing of the agent in accordance with the invention may be carried out in batches or continuously, wherein in principle, in continuous processes, dosing quantities which are as uniform as possible are preferred. Particularly preferably, dosing is carried out several times a week, or daily. Ideally, in the case of larger wastewater treatment plants, the agent is distributed in small portions over a day using a silo unit with a discharge system. Because of the buffering action of the agent in accordance with the invention, however, it does not necessarily have to be dosed continuously and uniformly round the clock.

By using the agent in accordance with the invention, a reduction in the concentration of phosphate in wastewater, in particular in the concentration of orthophosphate in wastewater, may be obtained which significantly exceeds the reducing action of aluminium salts or iron salts alone. In addition, because no comparable reducing action can be achieved with calcium carbonate alone, the synergistic effect observed

when using the agent in accordance with the invention in the present invention is particularly surprising.

The invention will now be illustrated with the aid of examples and comparative
5 examples, without in any way limiting the scope of the invention.

Determination of solubility of calcium carbonate in water

The determination of the solubility of calcium carbonate in water was carried out in
10 ultra-pure, CO₂-free water at 25°C by stirring the calcium carbonate for one hour and by photometric determination.

Calcium carbonate

For the examples in accordance with the invention, ground Devonian limestone (Lahn marble; GCC) with the following properties was used:

- 15
- mean particle size d_{50} : 15.5 μm ;
 - BET: 1.2 m^2/g ;
 - solubility in water: 6 mg/L .

Example 1

- 20 An aqueous K₂HPO₄ solution (concentration of phosphate: 5.8 ppm; pH: 7.7) was supplemented with
- a) 70 mg CaCO_3
 - b) 70 mg CaCO_3 and 30 $\text{mg FeSO}_4 \cdot \text{H}_2\text{O}$
 - c) 30 $\text{mg FeSO}_4 \cdot \text{H}_2\text{O}$
- 25 and stirred for 5 h.

Results:

- 30
- a) concentration of phosphate after treatment: 5.8 ppm; pH: 7.5
 - b) concentration of phosphate after treatment: 2.8 ppm; pH: 7.2
 - c) concentration of phosphate after treatment: 3.6 ppm; pH: 6.4

Example 2

An aqueous K₂HPO₄ solution (concentration of phosphate: 5 ppm; pH: 7.7) was supplemented with

- a) 70 mg CaCO_3
- b) 30 mg $\text{FeSO}_4 \cdot \text{H}_2\text{O}$
- c) 70 mg CaCO_3 and 30 mg $\text{FeSO}_4 \cdot \text{H}_2\text{O}$
- d) 120 mg CaCO_3 and 30 mg $\text{FeSO}_4 \cdot \text{H}_2\text{O}$
- 5 e) 270 mg CaCO_3 and 30 mg $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

Results:

After standing for 30 h, the following results were obtained:

- a) concentration of phosphate after treatment: 5 ppm; pH: 7.5
- 10 b) concentration of phosphate after treatment: 3.1 ppm; pH: 6.1
- c) concentration of phosphate after treatment: 2.9 ppm; pH: 7.3
- d) concentration of phosphate after treatment: 2.8 ppm; pH: 7.5
- e) concentration of phosphate after treatment: 2.6 ppm; pH: 7.2

15 Example 3

The following precipitating agents were added to a municipal wastewater treatment plant (pH of water: 6-9) in three phases:

Phase 1: $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (2.1 kg/100 m³)

Phase 2: $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (2.1 kg/100 m³) + CaCO_3 (4.9 kg/100 m³)

- 20 Phase 3: CaCO_3 (4.9 kg/100 m³)

The initial phosphate concentration value was 2.2 ppm in the outflow from the wastewater treatment plant; the quantities of the individual components were kept constant.

- 25 The concentration of phosphates in the outflow from the wastewater treatment plant in Phase 1 fell to 1.2 ppm.

The concentration of phosphates in the outflow from the wastewater treatment plant in Phase 2 fell to 0.5 ppm.

- 30 The concentration of phosphates in the outflow from the wastewater treatment plant in Phase 3 were almost back up to the initial concentration of phosphate.

Patent claims:

1. An agent for reducing the concentration of phosphate in wastewater comprising,
 5 respectively with respect to its total weight, > 50.0% by weight of calcium carbonate and at least 1.0% by weight of an iron salt, characterized in that the calcium carbonate has a solubility in water of less than 20 mg/1000 mL of water at 25°C.
2. The agent as claimed in claim 1, characterized in that the iron salt is selected from the
 10 group consisting of FeSO_4 , $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FeCl_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, FeCl_2 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 1\text{H}_2\text{O}$ and $\text{FeCl}(\text{SO}_4)$.
3. The agent as claimed in claim 1 or claim 2, characterized in that the iron salt is an iron(II) salt, in particular iron(II) sulphate.
4. The agent as claimed in at least one of the preceding claims, characterized in that the
 15 agent comprises, respectively with respect to its total weight, >60.0% by weight of calcium carbonate and at least 10.0% by weight of an iron salt.
5. The agent as claimed in at least one of the preceding claims, characterized in that the calcium carbonate has a mean particle size in the range from 5 μm to 30 μm .
6. The agent as claimed in at least one of the preceding claims, characterized in that the
 20 calcium carbonate has a BET specific surface area in the range from 0.4 m^2/g to 10.0 m^2/g .
7. The agent as claimed in at least one of the preceding claims, characterized in that the calcium carbonate comprises ground calcium carbonate.
8. The agent as claimed in at least one of the preceding claims, characterized in that the
 25 calcium carbonate originates from Lahn marble.
9. A method for reducing the concentration of phosphate in wastewater, in which an agent as claimed in at least one of claims 1 to 8 is added to wastewater.

10. The method as claimed in claim 9, characterized in that, with respect to its total weight, 1 ppm to <1000 ppm of the agent is added to the wastewater.
11. The method as claimed in claim 9 or 10, characterized in that rainwater, sewage water and/or external water is used as the wastewater.
- 5 12. The method as claimed in claim 9, 10 or 11, characterized in that the agent is added to a wastewater treatment plant at at least one of the following dosing points:
 - into the preliminary sedimentation outflow,
 - into the inflow or outflow from bio-P tanks, denitrification tanks, nitrification tanks, combined denitrification and nitrification tanks, and/or
 - 10 - into the secondary sedimentation inflow.
13. Use of an agent as claimed in at least one of claims 1 to 8 for reducing the concentration of phosphate in wastewater.
14. Use as claimed in claim 13, for reducing the concentration of orthophosphate in
15 wastewater.
15. Use as claimed in claim 13 or claim 14, for reducing the concentration of phosphate in rainwater, sewage water and/or external water.