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(54) **Title**: METHOD FOR REMOVING PHOSPHATE FROM WATER FRACTIONS

(57) **Abstract**: The invention pertains to a method for removing phosphate from a phosphate-containing water fraction comprising the steps of contacting a phosphate-containing water fraction with an adsorbent, the adsorbent comprising a complex of Fe(III) and starch and withdrawing an effluent water fraction from the adsorbent. It has been found that the use of this specific adsorbent makes it possible to obtain effluent water fractions with very low phosphate contents. Further, it has been found that the adsorbent has a high adsorption capacity, expressed in mg of phosphate per gram of adsorbent. The adsorbent can be regenerated in an efficient manner to allow re-use. It is based on a biobased, degradable material.

Method for removing phosphate from water fractions

The present invention pertains to a method for removing phosphate from water fractions.

Phosphate is present in many water fractions, including waste water and water derived from water cleaning operations. As phosphate is an important nutrient for microorganisms, its presence may contribute to the growth of microorganisms. Therefore, phosphate removal is required to prevent bacterial growth.

A particular problem with bacterial growth is that even minor growth of microorganisms, a process which is sometimes also indicated as biofouling, may interfere with further processing of the water streams. For example, water streams are often subjected to treatment in membrane operations, e.g., membrane filtration or reverse osmosis. The occurrence of even minor amounts of biofouling in apparatus provided with a membrane will severely affect operation thereof. Therefore, there is need in the art for methods for removing phosphate from aqueous water streams to prevent or reduce the occurrence of biofouling, in particular in subsequent membrane operations.

Various methods to effect phosphate removal are known in the art.

WO90/05705 describes a method for the removal of phosphate from water wherein water is treated with an iron(II) compound, e.g., in the form of iron(II) sulphate or iron(II) chloride in the presence of solid particles, which results in the precipitation of iron phosphate onto the particles. The iron phosphate containing particles can then be removed through filtration.

DE10256884 describes a method for processing waste water derived from phosphate treatment of metal surfaces, wherein the waste water is contacted with a precipitation agent which results in the precipitation of heavy metal cations, followed by a nanofiltration step. Phosphate can be removed by adsorption with an ion exchange resin, which can be regenerated using an alkaline solution of, e.g., NaOH or KOH. WO2011/107524 also describes phosphate adsorption using ion exchange resin. The resin can be regenerated using an alkaline solution.

EP1764348 describes the use of thermophilic ferritin in the removal of phosphate from water fractions.

US2014/0138320 describes an agent for removing dissolved phosphorus compounds from water which comprises a biopolymer and at least one metal compound. The biopolymer is selected from a large number of compounds, and so are the metal compounds. In the Examples, the biopolymer is selected from alginate, kappa-carrageenan, xanthan, and gellan. The adsorption capacity of the materials described therein is between 1 and 12 mg P/g adsorbent.

US2014/0141243 describes a method for removing dissolved phosphorus from water comprising the steps of activating a cellulose material, coating the activated cellulose material with a biopolymer with an ionic character, coating the thus obtained materials with a water soluble polyvalent metal, and crosslinking the cellulose biopolymer material and the metal compound. The biopolymer is selected from a large number of compounds, and so are the metal compounds. In the Examples, the biopolymer is selected from alginate, kappa-carrageenan, xanthan, and gellan. The adsorption capacity of the materials described therein is of the order of 1 mg P/g adsorbent.

There are various problems with the methods described in the art. More specifically, it has been found that there is need in the art for a method for removing phosphate from water

fractions which allows phosphate removal to a very low level and which makes use of an adsorbent with attractive properties, including a high adsorption capacity, which can be prepared though a straightforward preparation method. The present invention provides such a method.

The invention pertains to a method for removing phosphate from a phosphate-containing water fraction comprising the steps of contacting a phosphate-containing water fraction with an adsorbent, the adsorbent comprising a complex of Fe(III) and starch, and withdrawing an effluent water fraction from the adsorbent.

It has been found that the use of the specific adsorbent according to the invention has a number of advantages. In the first place, it was found that it makes it possible to obtain effluent water fractions with very low phosphate contents, as will be discussed in more detail below. Further, it has been found that the adsorbent has a high adsorption capacity, expressed in mg of phosphate per gram of adsorbent. This is important as it determines the size of the adsorption unit. Further, it has been found that the adsorbent used in the present invention can be regenerated in an efficient manner to allow re-use. Further, the adsorbent is based on a biobased, degradable material which is attractive from an environmental point of view. Further advantages of the present invention will become clear from the further specification.

It is noted that iron-on-starch complexes have been described for phosphate adsorption in body fluids, to reduce hyper-phosphataemia. Reference can be made to US6,174,442, EP2319804, US5,846,426, WO2010/100112, and EP1932808. The adsorption of phosphate from body fluids to reduce hyperphosphataemia cannot be compared to phosphate adsorption

in water treatment. In the first place, in water treatment, phosphate has to be reduced to very low levels, to prevent the growth of microorganisms as has been discussed above. In the human organism, phosphate removal to such low levels is not intended, and even undesirable.

The invention will be discussed in more detail below.

The water stream to be treated with the process according to the invention is a phosphate-containing water stream. In general, the water stream has a phosphate content of at least 10 ppb, in particular at least 20 ppb, more in particular at least 50 ppb, still more in particular at least 100 ppb. The maximum for phosphate content is not critical. A suitable maximum value may be at most 50000 ppb (50 ppm). In one embodiment, the phosphate content may be at most 2000 ppb, specifically at most 1000 ppb, more specifically below 500 ppb.
Within the context of the present specification, the term phosphate encompasses organic and inorganic phosphates, including orthophosphate and polyphosphate. The phosphate content can be determined using the phosphate-molybdenum method, which is well known in the art.

Other parameters of the water fraction to be treated with the process according to the invention are generally not critical.
The water fraction to be treated will generally have a pH around 7, e.g. in the range of 6 to 7.5.
The water fraction to be treated may have a variable salt content. Its conductivity is generally in the range of 20-100 mS/m, in particular in the range of 40-70 mS/m.
The water fraction to be treated may, e.g., have a nitrate content in the range of 0.1 to 50 mg N/l, in particular 1-20 mg N/l.

The water fraction to be treated may originate from various sources. In one embodiment it is derived from a waste water treatment plant. The water fraction can be subjected to conventional pretreatment steps to remove contaminants. Examples of suitable pretreatment steps include filtration and ultrafiltration.

The adsorbent used in the present invention comprises a complex of Fe(III) and starch.
Starch or amylum is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysaccharide is produced by most green plants as an energy store. It is contained in large amounts in plants like potatoes, wheat, maize (corn), rice, and cassava.
The starch industry extracts and refines starches from seeds, roots and tubers, by wet grinding, washing, sieving and drying. Starch can be hydrolyzed into simpler carbohydrates by acids, various enzymes, or a combination of the two. The resulting fragments are known as dextrins. Starch is commercially available form a large number of manufacturers.

In one embodiment of the present invention, oxidised starch is used. It has been found that, as compared to unoxidised starch, oxidised starch may result in an adsorbent with a higher phosphate adsorption capacity in mg/g.
In one embodiment, oxidised starch is used with a carboxylate content of at least 200 µeq/g (microequivalent carboxylate per gram). It is preferred for the carboxylate content to be higher, e.g. at least 300 µeq/g, in particular at least 400 µeq/g, as a higher carboxylate content makes for increased phosphate adsorption. As a maximum for the carboxylate content, a value of at most 2000 µeq/g may be mentioned, more in particular a value of at most 1000 µeq/g.

The carboxylate content may be determined by methods known in the art, e.g., by conductometric titration or FTIR (Fourier Transform Infrared spectroscopy).

Oxidised starch is known in the art, and commercially available. It can be obtained by subjecting a starch, or a starch-containing material to an oxidation step. This can be effected using various types of oxidising agents in various ways, e.g., using oxidising agents like hydrogen peroxide or other peroxide compounds, nitrogen tetroxide, whether gaseous or in solution such as phosphoric acid solution, periodate, leading to the corresponding dialdehyde derivative, followed by oxidation to the dicarboxy starch with sodium chlorite, optionally in the presence of hydrogen peroxide, hypochlorite, hypobromite, or hypoiodite compounds, organic oxidising agents like TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl), or 4-hydroxy-TEMPO, and combinations thereof. Suitable combinations are reaction with hypochlorite, hypobromite, or hypoiodite, or other oxidising compound in the presence of TEMPO. The use of 4-hydroxy-TEMPO, in particular at a pH of 3-4 as such without any further oxidising agent is also possible. Methods for manufacturing oxidised starch require no further elucidation here. JP57-130545 describes oxidising starch with periodate and using the resulting product as urea adsorbing compound in a blood perfusion method.

The oxidised starch, e.g., has a degree of oxidation between 1 and 30%. If the degree of oxidation is below 1 wt.% the advantageous effect of using oxidised starch may not be obtained. If the degree of oxidation is above 30 wt.%, the integrity of the starch may be affected. It may be preferred for the oxidised starch, if used, to have a degree of oxidation in the range of 3-20 wt.%.

The complex of Fe(III) and starch generally has an Fe(III) content of at least 1 wt.%, expressed as metallic iron, per gram of starch. If the Fe(III) content is too low, the adsorption capacity of the adsorbent will be insufficient. It may be preferred for the Fe(III) content to be at least 5 wt.%, expressed as metallic iron per gram of starch, more in particular at least 10 wt.% expressed as metallic iron per gram of starch.

In general, the Fe(III) content will be at most 90 wt.%, expressed as metallic iron, per gram of starch. When more iron is present, the accessibility of the additional iron will be limited, and it will therefore only have a limited contribution to the phosphate removal. More specifically, the Fe(III) content may be at most 60 wt.%, more in particular at most 50 wt.%, expressed as iron per gram of starch.

It may be preferred to use lower Fe(III) contents, e.g., at most 50 wt.%, more in particular at most 30 wt.%, in some embodiments at most 20 wt.%. In one embodiment of the invention, where the particle size is at least 100 microns, as discussed in more detail below, it may be particularly preferred for the Fe(III) content to be in the range of 1-30 wt.%, in particular 5-20 wt.

The complex of Fe(III) and starch can be obtained by conventional methods. For example, starch may be contacted with an aqueous solution of an Fe(III) salt, e.g., a sulphate, nitrate, or chloride salt, resulting in adsorption of Fe(III) onto the starch. It may be preferred for this adsorption step to be carried out at acidic pH. When the adsorption step has been completed, the starch onto which iron(III) has been adsorbed can be removed from the aqueous solution, and dried if so desired.

It may be preferred within this embodiment to subject the Fe(III)-containing material to a post-treatment step with a base, in gaseous or dissolved form, to improve the bonding of

the iron to the cellulose substrate. Suitable bases include, e.g., sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, NH3, and NH4OH.

In one embodiment of the present invention, a complex of Fe(III) and starch, optionally oxidised starch is prepared as follows: starch, optionally oxidised starch, is contacted with an aqueous suspension comprising one or more Fe(III)oxide, Fe(III)hydroxide, and Fe(III) oxyhydroxide, followed by removal of water, to form a complex of starch, optionally oxidised starch with iron. The aqueous suspension comprising one or more Fe(III)oxide, Fe(III)hydroxide, and Fe(III) oxyhydroxide, can suitably be obtained by adding a water soluble inorganic base, in solid form, or in the form of an aqueous solution, to a solution of an inorganic Fe(III) salt, e.g., a sulphate, nitrate, or chloride salt. In this way, a suspension will be obtained wherein the Fe(III) (hydr)oxide compounds have a relatively small particle size, which makes for a high dispersion of the Fe(III) (hydr)oxide compounds on the (oxidised) starch. The water soluble inorganic base is, e.g., selected from one or more of sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, NH3, and NH4OH. This method may be particularly suitable for (oxidised) starch with a particle size below 100 microns to ensure a good Fe(III) distribution.

In another embodiment of the present invention, a complex of Fe(III) and starch, optionally oxidised starch, is prepared as follows: (oxidised) starch is contacted simultaneously with an aqueous solution of an inorganic Fe(III) salt, e.g., a sulphate, nitrate, or chloride salt, and an aqueous solution of a water soluble inorganic base, e.g., selected from one or more of sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, and NH4OH, followed by removal of water. In this embodiment, one or more

Fe(III)oxide, Fe(III)hydroxide, and Fe(III) oxyhydroxide, are formed in the presence of the (oxidised) starch. This may lead to an improved distribution of the Fe(III)(hydr)oxide compound on the (oxidised) starch. This method may also be particularly suitable for (oxidised) starch with a particle size below 100 microns to ensure a good Fe(III) distribution.

In a further embodiment of the present invention, a complex of Fe(III) and starch, optionally oxidised starch, is prepared as follows: In a first step, (oxidised) starch is contacted with an aqueous solution of an inorganic Fe(III) salt, e.g., a sulphate, nitrate, or chloride salt. If necessary, excess water is removed, e.g., by filtration. Preferably, the resulting Fe(III)-containing starch is dried. Then, in a second step, the Fe(III)-containing starch is contacted with an aqueous solution of a water soluble inorganic base, e.g., selected from one or more of sodium carbonate, sodium hydroxide, potassium carbonate, and potassium hydroxide, followed by removal of water. In this embodiment, one or more Fe(III)oxide, Fe(III)hydroxide, and Fe(III) oxyhydroxide, are formed after the Fe(III) salt has been adsorbed onto the starch. This may lead to an improved distribution of the Fe(III)(hydr)oxide compound on the starch, especially, where the starch has a particle size of at least 100 microns. It can of course also be applied on starch with a smaller particle size.

Where the use of oxidised starch is aimed for, it is preferred to first prepare the oxidised starch, e.g., by one of the methods discussed above, and then provide the iron(III). Other methods are also possible. For example, it is possible to first add the iron to the starch, and then carry out the oxidation step. This is less preferred, however, as the presence of iron may interfere with the oxidation reaction. It is also possible to carry out the

addition of iron and the oxidation reaction simultaneously, but this is also considered less preferred.

It is noted that in the context of the present specification the term “complex of Fe(III) and starch” does not place a limitation on the chemical relationship between the iron(III) and the starch, as long as the iron is chemically or physically bonded with the starch.

The adsorbent used in the present invention may comprise additional components to the complex of Fe(III) and starch. Examples of additional components are bonding agents.

It is preferred for the adsorbent to be made up for at least 50 wt.% of the complex of Fe(III) and starch, in particular for at least 70 wt.%, more in particular for at least 80 wt.%, in some embodiments for at least 90 wt.%. The reason for this preference is that the complex of Fe(III) and starch is responsible for the phosphate adsorption. The presence of other components will increase the volume of the adsorbent without contributing to the phosphate adsorption. Therefore, the amount of other components is preferably limited.

The particle size of the adsorbent used in the present invention can vary within wide ranges, e.g., in the range of 10 microns to 5 mm. In one embodiment, the particle size of the adsorbent is at least 100 microns, in particular at least 200 microns, especially where the material will be used in an adsorption column, as this minimum particle size will result in an improved performance of this embodiment. The maximum particle size preferably is at most 4 mm, in particular at most 2 mm. A particle size range of 0.2-2 mm is considered preferred. Within the context of the present specification, particle size refers to the Dv50, which is the median diameter of the particle size distribution, where 50% of the

volume of particles in a sample has a diameter above the median particle diameter, and where 50% of the volume of particles in a sample has a diameter of at most the median particle diameter.

The adsorbent used in the present invention preferably has a phosphate adsorption capacity of at least 15 mg/g. Higher values, e.g., at least 30 mg/g, in particular at least 40 mg/g are considered preferred. As a general attainable maximum a value of 300 mg/g may be mentioned.

In the process according to the invention, the phosphate containing water fraction is contacted with the adsorbent. This can be done by methods known in the art, including providing the adsorbent in a fixed bed, fluidised bed or moving bed, in a column, in a stirred reactor, or in any other way. The use of a column is preferred.
Contacting conditions are not critical, and encompass a contacting temperature of 0-100°C, in particular 1-50°C, more in particular 1-30°C. The pressure may vary between wide ranges, e.g. from 0.1 to 10 bar. Atmospheric pressure is generally suitable. Where a column is used, a velocity of 0.1-100 m/hour is generally suitable.

An effluent water fraction is withdrawn from the adsorbent. The phosphate content of the effluent water fraction is lower than the phosphate content of the starting phosphate-containing water fraction.
In one embodiment, the phosphate content of the effluent water fraction is less than 50% of the phosphate content of the starting phosphate-containing water fraction, in particular less than 25%, more in particular less than 10%.
In one embodiment, the phosphate content of the effluent water fraction is reduced to a value of less than 100 ppb, in particular less than 50 ppb, more in particular less than 20

ppb, or even less than 10 ppb. A process wherein the phosphate content of the effluent water fraction is below 10 ppb is of particular interest, especially, but not limited to, the situation where the effluent water fraction is to be provided to a reverse osmosis process, as will be discussed in more detail below.

The phosphate content of the effluent water fraction is determined by the phosphate content of the starting water fraction, the carboxylate and iron content of the adsorbent, the space velocity, and the amount of adsorbent. It is within the scope of the skilled person to select these parameters so that an effluent with the desired phosphate content is obtained.

The effluent water fraction can be processed as desired. In one embodiment, the effluent water fraction is provided to a reverse osmosis step, where the effluent water fraction is treated to form a purified effluent water fraction and a contaminant fraction. The reverse osmosis step effects contaminant removal, in particular salt removal.

When the adsorbent has become saturated with phosphate, as can be seen from an increase in phosphate content of the effluent water fraction, the adsorbent can be regenerated if so desired.

Therefore, the present invention also pertains to a method as described above wherein the adsorbent is periodically regenerated by a process comprising the steps of

- stopping the provision of phosphate-containing water fraction to the adsorbent
- contacting the adsorbent with an alkaline aqueous regeneration solution,
- withdrawing the alkaline aqueous regeneration solution from the adsorbent, and

- resuming the provision of phosphate-containing water fraction to the regenerated adsorbent.

The adsorbent can be regenerated by contacting it with an alkaline aqueous regeneration solution, more specifically an aqueous solution with a pH above 11.5. The pH preferably is above 12. In general, the pH will not be above 14.
The nature of the alkaline compound in the aqueous alkaline solution is not critical. Alkali metal hydroxides are generally preferred for reasons of availability, cost, and safety. The use of sodium hydroxide and/or potassium hydroxide is considered preferred.
It may be preferred to use a solution comprising both an alkali metal hydroxide and a dissolved inorganic salt, in particular an alkali metal salt, e.g., NaCl or KCl. The presence of a salt has been found to improve regeneration efficiency. A salt concentration of 0.05 to 1 M/l may be mentioned as suitable.

Contacting the adsorbent with the aqueous alkaline regeneration solution can be carried out using methods known in the art. Regeneration will be complete when the phosphate content of the regeneration solution does not further increase.

If so desired, it is possible to neutralise the adsorbent between the regeneration step and the restart of the phosphate removal step. In this case, the adsorbent is contacted with a neutralizing solution between the step of withdrawing the alkaline aqueous regeneration solution from the adsorbent, and the step of resuming the provision of phosphate-containing water fraction to the regenerated adsorbent, the adsorbent is contacted with a neutralizing solution.

A suitable neutralising solution is, e.g., a slightly acidic solution with a pH in the range of 4-6.

Various embodiments and preferences described herein can be combined, as will be evident to the skilled person, except where they are mutually exclusive.

The invention will be elucidated by the following examples, without being limited thereto or thereby.

Example 1 preparation of starch samples

The following starting materials were used:
- potato starch (commercially available from Honig)
- wheat starch (commercially available from Sigma Aldrich)
- dextrin I (commercially available from Sigma Aldrich, derived from corn starch)
- dextrin II (commercially available from Sigma Aldrich, derived from corn starch)
- corn starch (commercially available from Sigma Aldrich)

The following oxidation methods were applied:

Method 1: Oxidation with hypochlorite/bromide

A sample of 4.0 grams of starch was suspended in 500 ml water. After adjusting the pH to 11, 100mg sodium bromide was added. Subsequently, sodium hypochlorite (15 % active chlorine) was added at once, the amount adjusted to obtain the desired degree of oxidation. The pH was maintained at pH 10 by addition of 0.5 M NaOH. When no further pH drop was observed, 100 mg $NaBH_4$ was added. After 60 minutes, 110 ml ethanol absolute was added and the pH was adjusted to 7 by addition of 4 M sulphuric acid. The solid was isolated by centrifugation and washed repeatedly with ethanol (70%). The isolated material was dried in air.

Method 2: Oxidation with hypochlorite/bromide/TEMPO

A sample of 4.0 grams of starch was suspended in 500 ml water. After adjusting the pH to 11, 100mg sodium bromide and 20 mg TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) were added. Subsequently, sodium hypochlorite (15 % active chlorine) was added all at once, the amount adjusted to obtain the desired degree of oxidation. The pH was kept at 11 during reaction by adding 0.5 M NaOH. After 60 minutes 1 ml ethanol was added to quench the residual hypochlorite, followed by 100 mg $NaBH_4$. After 60 minutes 110 ml ethanol absolute was added and the pH was adjusted to 7 by addition of 4 M sulphuric acid. The solid was isolated by centrifugation and washed repeatedly with ethanol (70%). The isolated material was dried in air.

Example 2: preparation of adsorbent using iron(III)chloride and sodium carbonate

The samples obtained in Example 1 were loaded with Iron (III) to form adsorbents in accordance with the following procedure.

A solution of 3.61 g iron (III) chloride hexahydrate (13 mmol) in 7 ml water, and a solution of 2.87 g Na2CO3 (27 mmol) were added simultaneously to 1.0 g of starch sample (non-oxidized and oxidized samples), suspended in 5ml water in the course of 5 minutes while stirring continuously. After stirring during 1 hour, the suspension was centrifuged. The pellet was washed several times with water and finally with ethanol (96%). Then the solid was dried in vacuum at 70 °C (1mmHg).

The resulting material had an iron(III) content of 35 wt.%, expressed as metallic iron per gram of starch.

Example 3: Preparation of adsorbent using iron(III) chloride and ammonium hydroxide

Various samples were prepared in accordance with the following general procedure: A solution of FeCl3 (40% wt; amounts in Table 1) was neutralized to pH 7-8 by addition of NH4OH (27% NH3 diluted with demiwater to desired concentration; amounts in Table 1). The suspension was allowed to cool to room temperature, after which potato starch (Sigma; amounts in Table 1) was added in dry form while stirring vigorously. After settling for 1 hour, the supernatant was decanted. The material was centrifuged at 10000 rpm for 10 minutes. The supernatant was decanted and the pellet resuspended in 40ml demiwater. The suspension was centrifuged at 10000rpm for 10 minutes and the supernatant was decanted. The final weight of the adsorbent was 0.5g. The resulting material had an iron(III) content, expressed as metallic iron per gram of starch as specified in Table 1.

Table 1: Specification of the samples prepared for Example 3.

Sample	Fe (%wt)	$FeCl_3$ (ml)	m_{starch} (g)	NH_4OH (ml)	Final weight (g)
A	10	0.248	0.43	0.17	0.50
B	20	0.438	0.38	0.31	0.50
C	50	0.807	0.28	0.56	0.50
D	100	1.095	0.19	0.76	0.50

Example 4: Preparation of adsorbent using iron(III) chloride and sodium hydroxide

5.76ml $FeCl_3$ (40% wt_3, d: 1.26 g/ml) was diluted to 12.5ml using demiwater. While stirring, the solution was adjusted to pH 7.0 by dropwise addition of NaOH (5M). To this solution, 10g of starch sample was added while stirring. The suspension

was allowed to rest for 1 hour and the supernatant was decanted. The slurry was centrifuged at 10000rpm for 10 minutes, after which the supernatant was decanted. The material was washed with demiwater and centrifuged again. The final supernatant is decanted.
The resulting material had an iron(III) content of 10% wt.%, expressed as metallic iron per gram of starch.

Example 5: Performance of samples in phosphate removal from phosphate-containing water fractions - static conditions

The phosphate adsorption capacity for the various samples described in Example 2 was determined as follows: 1 g of the iron(III) on starch material obtained as described in Example 2 was brought in a 30 ml column. Through the column 250 ml of a phosphate solution (0.47 g/L) was recirculated (5 ml/min) for a period of 18 hours at room temperature.
The adsorption capacity of Lewatit® FO 36 (Lanxess) was also determined. Lewatit® FO 36 is a weakly basic macroporous monodisperse polystyrene-based ion exchange resin for the selective adsorption of oxoanions, which is doped with a nano-scaled film of iron oxide covering the inner surfaces of the pores of the polymer bead.
The results are summarized in Table 2.

In Table 2, the indication -1 refers to the unoxidised sample. The indications -2 and -3 refer to oxidized versions of the corresponding -1 version.

Table 2: Phosphate adsorbing capacity of iron(III) starch complexes

Starch type	Oxidation method	Degree of oxidation (%)	carboxylate content (microeq/g)	phosphate adsorption capacity (mg/g)
potato-1	-	0	<200	22
potato-2a	2	5	300	40
potato-2b	2	10	580	58
potato-2c	2	20	1150	55
potato-3a	1	10	1200	81
wheat-1	-	0	<200	67
wheat-2	1	10	1200	75
corn-1	-	0	<200	23
dextrin A-1	-	0	<200	36
dextrin A-2	1	10	1200	37
dextrin B	-	-	<200	16
Lewatit® FO 36				41

From the data in table 2, the following conclusions can be drawn:

All samples show at least an acceptable phosphate adsorption, wherein acceptable is defined as an adsorption capacity of at least 15 mg/g.

From a comparison between potato-1 and potato-2a through 2c it can be seen that oxidized starch shows a higher phosphate adsorption capacity as compared to the unoxidised starting material. A comparison between potato-1 and potato-3 shows the same trend to a larger extent. Also for wheat starch, oxidized starch has an adsorption capacity which is higher than that of the unoxidised starting material. For dextrin this effect is not shown.

Example 6: Phosphate uptake by starch and Lewatit® FO36 - dynamic conditions

Kinetic experiments were performed as follow: 1.0 g of the sample to be tested was added to a solution containing 1.04 mg/L phosphate while stirring mechanically. From this suspension samples were taken at 2, 5, 15, 30, 60, 90, and

120 minutes. Immediately after sampling, the sample was filtrated over a 0.2 mm cellulose acetate filter to remove present adsorbent. The phosphate concentration was determined using the phosphate molybdenum test. The rate of phosphate adsorption onto the adsorbent is calculated from the decrease in phosphate concentration in the solution.

The results are provided in Table 3 below.

Table 3: Rate of phosphate adsorption of iron(III) loaded starch and Lewatit FO 36. Initial phosphate concentration is 1.04 mg/L.

Sample/time (minutes)	0	2	5	15	30	60	90
Lewatit FO 36	1.04	0.93	0.79	0.44	0.20	0.03	0.01
Potato-2c	1.04	0.81	0.67	0.41	0.18	0.04	0.04

As can be seen from Table 3, the material according to the invention shows the same kinetic profile as the standard Lewatit® FO 36, showing that the material according to the invention is suitable for commercial operation. It should be noted in this context that the adsorbent of the present invention is derived from a renewable resource, and is biodegradable, both of which do not apply to Lewatit® FO 36. Additionally the adsorbent of the present invention is more attractive from a commercial point of view than Lewatit® FO 36.

Example 7: Performance of samples in phosphate removal from phosphate-containing water fractions - batch equilibrium test

The dynamic phosphate adsorption capacity for the samples obtained with Example 3 was determined as follows: 0.5g of iron(III) on starch material obtained as described in Example 3 was brought in 2-7L of a phosphate solution (10.08 g/L).

The phosphate solution was stirred continuously for a period of 24 hours at room temperature.

The adsorption capacity of Lewatit® FO 36 (Lanxess) was also determined. As indicated above, Lewatit® FO 36 is a weakly basic macroporous monodisperse polystyrene-based ion exchange resin for the selective adsorption of oxoanions, which is doped with a nanoscaled film of iron oxide covering the inner surfaces of the pores of the polymer. The conditions of the batch equilibrium test are further specified in table 4. The results are presented in figure 1.

Table 4: Specification for the conditions of the batch equilibrium test described in Example 3.

Sample	V_{PO4} (L)	C_{PO4} (ppm)	Total available PO_4 (mg)
A	2	10.08	20.16
B	3		30.24
C	5		50.40
D	7		70.68
Lewatit® FO 36	2		20.16

As can be seen from Figure 1, all samples according to the invention show a higher adsorption capacity than Lewatit® FO 36, with higher iron contents resulting in a higher phosphate adsorption capacity. The phosphate adsorbents tested here have a phosphate adsorption capacity which is significantly higher than that of the adsorbents described in US2014/0138320 and US2014/0141243. The adsorbent used according to the invention is also more environmentally attractive than the comparative Lewatit product as it is based on a biodegradable and renewable material. It is further more attractive from an economic point of view as it is less expensive.

Claims

1. Method for removing phosphate from a phosphate-containing water fraction comprising the steps of contacting a phosphate-containing water fraction with an adsorbent, the adsorbent comprising a complex of Fe(III) and starch, and withdrawing an effluent water fraction from the adsorbent.

2. Method according to claim 1, wherein the phosphate-containing water fraction has a phosphate content of at least 20 ppb, in particular at least 50 ppb, more in particular at least 100 ppb, and/or a phosphate content below 1000 ppb, more specifically below 500 ppb.

3. Method according to any one of the preceding claims, wherein the starch is oxidised starch, in particular oxidised starch which has a carboxylate content of at least 200 µeq/g, in particular at least 300 µeq/g, more in particular at least 400 µeq/g and/or at most 2000 µeq/g, in particular at most 1000 µeq/g.

4. Method according to any one of the preceding claims, wherein the complex of Fe(III) and starch has an Fe(III) content of at least 1 wt.%, expressed as metallic iron, per gram of starch, in particular at least 5 wt.%, more in particular at least 10 wt.%, and/or an Fe(III) content of at most 90 wt.%, expressed as metallic iron, per gram of starch, in particular at most 60 wt.%, more in particular at most 50 wt.%.

5. Method according to any one of the preceding claims, wherein the phosphate containing water fraction is contacted with the adsorbent in a fixed bed, fluidised bed or moving bed, in a column, or in a stirred reactor, preferably a column.

6. Method according to any one of the preceding claims, wherein the phosphate content of the effluent water fraction is less than 50% of the phosphate content of the starting phosphate-containing water fraction, in particular less than 25%, more in particular less than 10%.

7. Method according to any one of the preceding claims, wherein the phosphate content of the effluent water fraction is reduced to a value of less than 100 ppb, in particular less than 50 ppb, more in particular less than 20 ppb, or even less than 10 ppb, in particular less than 10 ppb.

8. Method according to any one of the preceding claims, wherein the effluent water fraction is provided to a reverse osmosis step.

9. Method according to any one of the preceding claims wherein the adsorbent is periodically regenerated by a process comprising the steps of
- stopping the provision of phosphate-containing water fraction to the adsorbent
- contacting the adsorbent with an alkaline aqueous regeneration solution,
- withdrawing the alkaline aqueous regeneration solution from the adsorbent, and
- resuming the provision of phosphate-containing water fraction to the regenerated adsorbent.

10. Method according to claim 9, wherein the alkaline aqueous regeneration solution has a pH of at least 11.5.

11. Method according to claim 9 or 10, wherein between the step of withdrawing the alkaline aqueous regeneration solution from the adsorbent, and the step of resuming the provision of phosphate-containing water fraction to the

regenerated adsorbent, the adsorbent is contacted with a neutralizing solution.

12. Method according to any one of claims 9-11, wherein the regeneration solution comprises alkali metal hydroxide, in particular sodium hydroxide and/or potassium hydroxide.

13. Method according to any one of claims 9-12, wherein the regeneration solution comprises both an alkali metal hydroxide and a dissolved inorganic salt, in particular an alkali metal salt, e.g., NaCl or KCl.

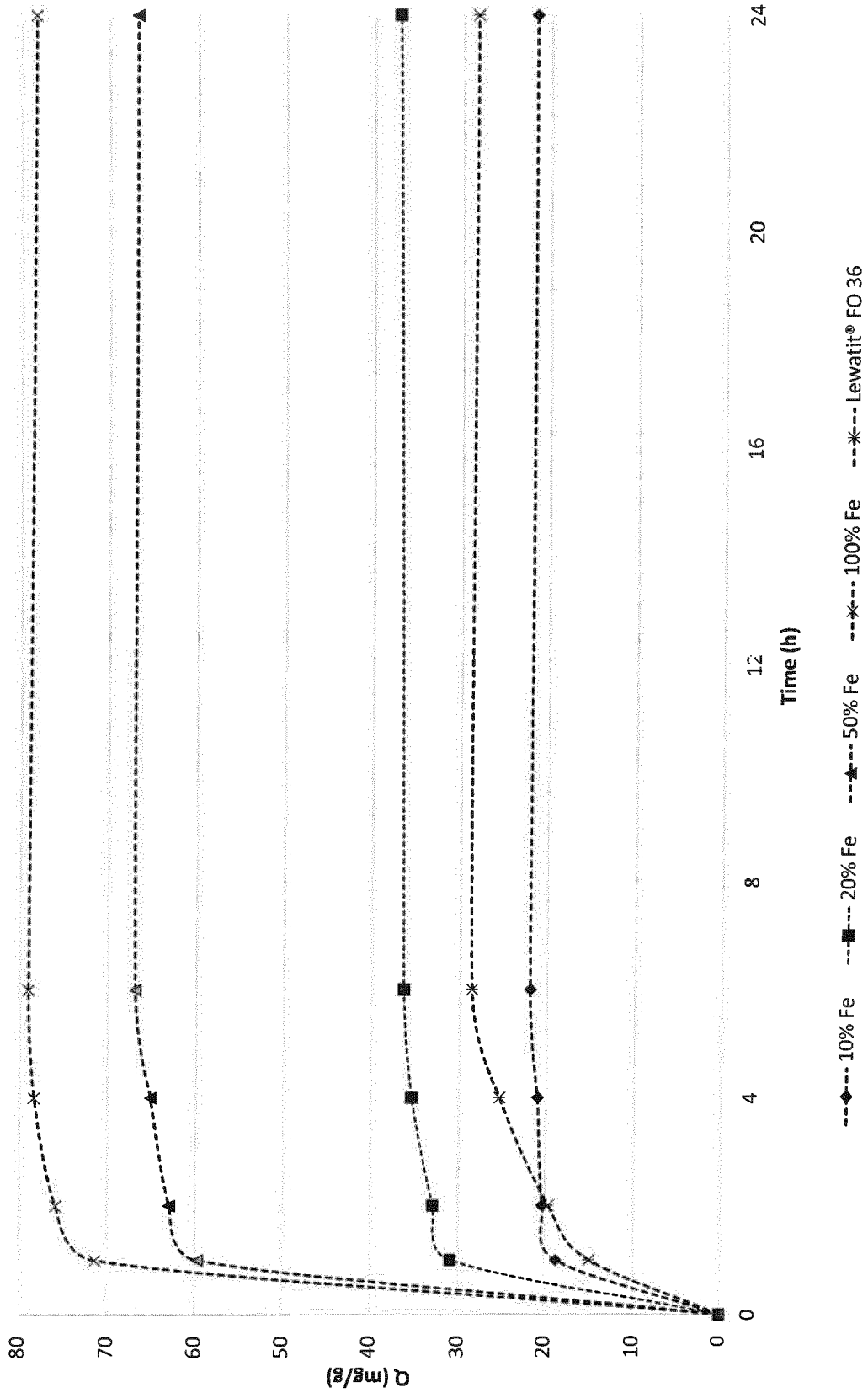

Phosphate capacity (Q, mg/g) vs. Time
Q (mg/g)
0
10
20
30
40
50
60
70
80
Time (h)
0
4
8
12
16
20
24
10% Fe
20% Fe
50% Fe
100% Fe
Lewatit® FO 36

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/061647

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/28 B01J20/24 C01G49/00 B01J20/02 C08B31/18
C02F1/44
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F B01J C01G C08B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/138320 A1 (SIWEK HANNA [PL] ET AL) 22 May 2014 (2014-05-22) cited in the application	1,6,7
Y	paragraphs [0007], [0008], [0010], [0014], [0017], [0018], [0020]	2-5,8-13

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Y	paragraphs [0013] - [0015], [0023] - [0032]	2-5,8-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2015	04/09/2015

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/061647

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 2011/107524 A1 (O'BRIEN PHILIP PATRICK PETER [IE]) 9 September 2011 (2011-09-09) cited in the application page 25, line 4 - page 26, line 12 page 27, line 23 - page 28, line 2 -----	5,9-13
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP2015/061647

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