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METHOD AND SYSTEM FOR PHOSPHATE RECOVERY FROM A STREAM

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The invention relates to a method and system for phosphate recovery from a stream. The method comprises the steps of:

- providing an incoming stream comprising an initial amount of phosphate; and
- dosing iron salt to the stream such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream, and preferably also the steps of:
 - separating the vivianite like structures from the stream; and
 - recovering the phosphates from the separated vivianite like structures.

METHOD AND SYSTEM FOR PHOSPHATE RECOVERY FROM A STREAM

The invention relates to a method for recovery of phosphate from a (wet) stream, such as a waste flow. For example, the method recovers phosphate from sewage or another sludge stream, and/or manure.

It is known from practice to remove phosphorus from waste water to prevent eutrophication in effluent receiving surface waters. Conventional techniques include enhanced biological phosphorus removal (EBPR) and chemical phosphorus removal (CPR).

Conventional phosphorus recovery from waste water involves the production of struvite in EBPR plants and/or phosphorus recovery from sludge ash. It is known that struvite precipitation enables recovery of phosphorus. However, the efficiency to recover phosphorus as struvite is typically only in the range of 10-50% of the total influent phosphorus load. Also, struvite precipitation is limited to plants using EBPR. Incineration involving recovery of phosphorus from sludge ash is relatively expensive. Also, sludge can be applied to agricultural land. However, there are areas with agricultural land that have a surplus of phosphorus due to manure surpluses. Also, the elemental composition of sludge/manure may not match with crop demand.

An objective of the present invention is to provide a method for phosphate/phosphorus recovery from a stream that obviates or at least reduces the aforementioned problems and is more effective and/or more efficient as compared to conventional methods.

This object is achieved with the method for phosphate/phosphorus recovery from a stream according to the present invention, wherein the method comprises the steps of:

- providing an incoming stream comprising an initial amount of phosphate; and
- dosing iron salt to the stream such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream.

Streams may comprise phosphate (PO_4) that is the main molecule in the relevant streams that comprises the element Phosphorus (P). These streams relate to (wet) waste water flows, sewage, manure or other streams.

Dosing iron salt to the stream enables forming of precipitates in the stream. More specifically, dosing iron salts to the stream enables forming of vivianite (which is a Fe(II) phosphate mineral: $\text{Fe}_3(\text{II})[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$) or vivianite like structures. Vivianite like structures includes pure vivianite and also structures including some impurities like magnesium or calcium.

In a presently preferred embodiment of the invention phosphate is removed from waste water in sewage treatment plants. In experiments it is seen that often a mixture of Fe (III) phosphate precipitates and vivianite like structures is formed. After the preferred anaerobic/anoxic digestion step (for example for biogas production during manure/sewage treatment) all Fe(III)

transforms into Fe(II) and vivianite like structures can form. In the mentioned experiments these vivianite like structures are effectively formed when oxygen is absent and bacteria are active. Also without this anaerobic/anoxic step vivianite formation may occur. However, in the mentioned experiments it was shown that in a preferred embodiment of the invention the vivianite formation is favoured during anaerobic/anoxic digestion.

The vivianity like structures may constitute a valuable phosphorus source as such. Optionally, the structures are further treated to recover the phosphates from the structures. In such preferred embodiment the method further comprises the steps of:

- separating the vivianite like structures from the stream; and
- recovering the phosphates from the separated vivianite like structures.

According to the invention the phosphate recovery is achieved effectively as more than 60% (and up to 90%) of the initial amount of phosphate in the incoming stream is incorporated into the vivianite like structures. This enables an effective removal of phosphorus from the stream. In accordance to the method of the invention this removal is achieved by separating the vivianite like structures from the stream. This separation of the vivianite like structures enables removal of the phosphates from the stream. As a further effect this (indirectly) obviates or at least reduces the problem associated with eutrophication of effluent receiving surface waters due to the iron dosing. In other words, the higher Fe dosage (than normal) may also help to lower phosphate concentrations in the effluent of sewage treatment plants

As a next step in the method for phosphate recovery according to the invention the phosphates are recovered from the separated vivianite like structures. This enables recycling of phosphorus. Furthermore, recovery of phosphorus is desired due to the limited availability of phosphorus such that a waste water flow may act as a secondary source of phosphorus, for example. This renders streams such as waste streams, sewage and manure, as an alternative source of phosphorus. This also allows for a circular use of phosphate which is an important component of fertilizers. This improves the sustainability of the global food production that involves phosphorus as an essential nutrient.

Furthermore, by “capturing” more than 60%, preferably up to about 90% or more, of the amount of phosphate into the vivianite like structures an improved removal rate and/or recovery rate is achieved as compared to alternative conventional methods, including struvite precipitation. It is suggested that in the presence of iron vivianite, including its structures, preferably forms over other inorganic phosphate phases. More particularly, in the presence of sufficient iron the forming of vivianite like structures is limited by the organic phosphate and sulphide in the stream. The vivianite like structures that are formed are substantially formed as crystals and/or aggregates with a size substantially in the range of 10-100 μm . Depending on the initial stream and components therein the purity of the vivianite like structures can be relatively high thereby enabling application

of the structures in different processes. In the presently preferred embodiment the phosphates are recovered from the separated vivianite like structures to enable use for a fertilizer production, for example. Optionally, the vivianite like structures can be used as colour pigment, and in the production of lithium iron batteries, for example.

Optionally, in addition or as an alternative, the separated vivianite particles (or synthetically produced vivianite) could also be recycled in the waste stream to allow further growth. In such a way formed (larger) vivianite particles could be separated more easily from the wastewater, for example using a separator such as an (electro)magnetic separator. This “growing” process is also referred to as seeding. In addition, other possibilities could be envisaged, such as the possibility to produce food grade phosphoric acid out of the vivianite.

The improved removal and recovery rates of phosphates from a stream, such as a sewage sludge, obviates or at least reduces the need for incineration of the sludge enabling recovery of phosphates and the capital investments that are associated therewith. Furthermore, the method according to the present invention does not rely on the immense use of chemicals as compared to some of the conventional processes. More particularly, the vivianite like structures are separated from the stream and the resulting concentrated stream can be subjected to a post treatment that may involve a dedicated chemical treatment. This treatment enables circular use of the iron. Also in such case a significant reduction of the use of chemicals is achieved.

In a presently preferred embodiment of the invention the vivianite like structures comprise more than 70%, preferably more than 80%, and most preferably about 90% or even more, of the initial amount of phosphate of the incoming stream. This further improves the efficiency of the removal and/or recovery of phosphate from a stream. Measurements with the method according to the invention even show that more than 80%, such as about 90%, of the total amount of phosphate in a sewage sludge is bound in vivianite. This significantly improves the recovery efficiencies of phosphate as compared to traditional struvite technologies, for example.

Iron salts are also referred to as Fe (II)/Fe (III) salts. Preferably, the iron salts that are added to the stream comprise one or more of iron chloride and iron sulphate. Experiments showed that the use of these specific iron salts achieves an efficient removal and/or recovery by effectively forming of the desired precipitates in the stream.

In a presently preferred embodiment of the invention the step of dosing iron salt to the stream comprises adding an amount of iron with a molar ratio of iron to phosphorus of at least 1.3, preferably at least 1.5.

By dosing iron salt in accordance to the preferred molar ratio the phosphate in the incoming stream is effectively included in the vivianite like structures. The iron chloride may include ferric and/or ferrous chloride. The presently preferred range is from 1.3 to 1.9, with the actual value more preferably being about 1.5.

Optionally, some additional iron salt is added to the stream to bind sulphide in the incoming stream before actually binding the phosphate in the stream. Preferably, the amount of sulphide and/or phosphate is known to improve the effective dosing of iron salts and to prevent underdosing and/or overdosing. This may further improve the efficiency of the phosphate removal and/or phosphate recovery. Especially the relatively high amount of dosed iron salts as compared to conventional treatment plants enables not only removal of phosphate it also enables effective recovery of phosphate.

More specifically, in a presently preferred embodiment, the dosing of iron salt is controlled by a (dosing) controller in response to a measurement of the initial amount of phosphate in the incoming stream. As already mentioned, by measuring the amount of phosphate in the incoming stream a dedicated dosing of the iron salt to the stream can be achieved. This prevents underdosing and/or overdosing thereby improving the overall efficiency. It will be understood that, in addition or as an alternative, also other measurements could be envisaged, such as measuring after an anaerobic stage.

As an example, after a presently preferred anaerobic stage, total iron (Fe) and total phosphorus (P) can be measured. Then, in response to the measurement(s), the iron dosing is adjusted to reach the desired Fe:P ratio in the sludge that was mentioned earlier for optimal P recovery. This optimal ratio is preferably somewhere between 1.3 and 1.9. In (commercial) applications this could be monitored about once /week or other time intervals. In practice, it could be that the amount of organic phosphorus is for some reason extraordinary high. This may limit vivianite formation, because organic phosphorus is not available for vivianite formation and/or that sulphide is occurring in high concentrations (which would require further iron overdosing because after substantially all sulphide has reacted to iron sulphide the formation of vivianite starts at an effective rate). Therefore, under these circumstances an evaluation/measurement of the presence of organic phosphorus and sulphide during the anaerobic stage may further improve the removal/recovery.

In a presently preferred embodiment of the invention separating the vivianite like structures from the stream comprises magnetic separating of the structures with a magnetic and/or electromagnetic separator.

The use of a magnetic and/or electromagnetic separator achieves an efficient and effective separation of the vivianite like structures from the stream. Such separator may involve a channel around which the magnets or electromagnets are provided that attract the vivianite like structures, while other non-magnetic material continues to travel through the channel such that the magnetically separated material is separated from the non-magnetic material. Optionally, this may include the use of profiled plates, walls or surfaces, as are known components of high-gradient

magnetic separators, such as the Jones separator, for example. This enables an effective and efficient separation of the magnetic vivianite like structures from the stream.

Alternatively, or in addition thereto, vivianite like structures are separated from the stream with a gravity separator that separates heavy materials with a high density from light materials with a low density.

Using the density difference between the vivianite like structures and the other components in the stream enables an effective separation of vivianite like structures. Such gravity separator may relate to a (hydro)cyclone, for example.

In a further preferred embodiment of the invention, the step of recovering the phosphates, and possibly the iron, from the separated vivianite like structures comprises treating the vivianite like structures to produce iron oxide precipitates.

In a further preferred embodiment of the invention, the vivianite-like particles are concentrated from the stream by magnetic separation and/or gravity separation following a process step that frees (liberates) the vivianite-like particles from organic particles, such as fibers, that stick to the vivianite-like particles or entangle them. In general, intense shear of the liquid phase by high-speed rotors or jets will promote liberation of particles of different types that are embedded in the liquid. Liberation of the vivianite-like particles from organic particles, in turn, will promote the effectiveness of subsequent magnetic and/or gravity separation.

By forming iron oxide precipitates from the vivianite like structures the phosphates can be recovered effectively. Preferably, treating the vivianite like structures involves performing an alkaline treatment. This alkaline treatment may involve the use of sodium hydroxide (caustic soda, potassium hydroxide (caustic potash).

In a presently preferred embodiment the alkaline treatment involves adding potassium hydroxide that enables production of a potassium phosphate solution. Such recovery of phosphate involving the alkaline treatment enables an effective recovery that enables effective re-use of the phosphate and potassium in the potassium phosphate solution that can be applied as a fertilizer, for example.

In a further preferred embodiment of the invention the method further comprises the step of treating the iron oxide with hydrochloric acid to produce iron chloride.

By performing a further treatment step the produced iron oxide may react with the hydrochloric acid to produce the iron chloride. Preferably, this production of iron chloride enables a recycling step of the resulting iron chloride to the dosing step of iron salt to the stream. This improves the overall efficiency of the method for phosphate recovery by recycling the iron in the method. Also, the iron oxide can be used as such in other (existing) processes, for instance as an alternative to iron ore.

In a presently preferred embodiment the incoming stream is a flow to an anaerobic treatment system, such as a digester. Such combination of process steps improves the overall process efficiency.

The invention also relates to a system for phosphate recovery from a stream, the system being capable of performing the method in one or more of the embodiments according to the invention, wherein the system comprising:

- a reactor comprising:
 - an inlet for an incoming stream comprising an initial amount of phosphate;
 - an iron salt dosing device configured for dosing iron salt in the reactor such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream; and
 - an outlet.

The system provides the same effects and advantages as those described for the method.

Preferably the system further comprises:

- a separator for separating the vivianite like structures from the stream; and
- a treatment system for treating the vivianite like structures to produce iron oxide precipitates.

More specifically, the system enables an efficient and effective phosphate recovery from a stream involving a separator, such as a magnetic/electromagnetic separator and/or a gravity separator. The treatment system may enable performing different treatment steps, preferably including the alkaline treatment.

In a presently preferred embodiment the system further comprises a dosing controller and a phosphate measurement system that are configured to control dosing of iron salt in response to a measurement of the initial amount of phosphate in the incoming stream, for example. This further improves the overall efficiency of the iron salt dosing preventing underdosing and/or overdosing of iron into the stream. Optionally, in addition or as an alternative, also the amount of sulphide can be measured to further improve the dosing. As mentioned earlier, also other measurements can be envisaged in accordance with the present invention.

As was mentioned earlier, alternatively and/or in addition to the sulphide measurement, total iron (Fe) and total phosphorus (P) can be measured.

Further advantages, features and details of the invention are elucidated on the basis of preferred embodiments thereof, wherein reference is made to the accompanying drawings, in which:

- Figure 1 shows the method according to the present invention;

- Figure 2 shows an embodiment of the system capable of performing the method of figure 1; and
- Figure 3 shows a magnetic separator that can be used in the system of figure 2.

Process 2 (figure 1) starts with supply of stream 4 that comprises an amount of phosphate. In the illustrated embodiment measurement step 6 measures the amount of phosphate and/or sulphide. Calculation step 8 determines the optimal amount of iron or iron salt to be dosed into the stream. In dosing step 10 iron is added to the stream to enable forming 12 of precipitates comprising vivianite like structures. In separation step 14 the vivianite like structure is separated and removed from the stream. The vivianite like structures undergo a post treatment to recover the phosphorus components, such as an alkaline treatment 16. For example, this treatment may provide a potassium phosphate solution that can be used 18 as fertilizer. The iron oxide precipitates can be treated 20 with hydrochloric acid resulting in recycle iron stream 22 that can be used in dosing step 10. Recycle stream 22 may even obviate the need for external iron or at least significantly reduce this need.

Recovery system 24 (figure 2) comprises reactor 26 that receives incoming stream 4. In the illustrated embodiment in reactor 26 anaerobic/anoxic conditions are maintained. From reactor 26 flow 28 is directed towards separator 30. Sludge/waste 32 leaves system 24.

In the illustrated embodiment the resulting vivianite like structures 34 are provided to alkaline reactor 36 to enable posttreatment, or vivianite like structures 34 are directly applied. The recovered phosphate, for example in the form of potassium phosphate, leaves reactor 36 in flow 38 and can be used as fertilizer, for example. The iron oxide leaves reactor 36 as flow 40 and can be treated in acid reactor 42, or can be used as such. This treatment enables a recycling flow 22 of iron salt that provides iron to dosing device 44 enabling dosing stream 46 to reactor 26. Therefore, dosing device 44 receives iron or iron salts from recycle flow 22 and from external incoming flow 48.

In the illustrated embodiment sensor 50 measures the composition of the stream in reactor 26, for example the amount of phosphate. Measurement signal 52 is provided to controller 54 that determines control setting(s) 56 of dosing device 44. This may involve periodic sampling of the sludge, for example weekly, and analysing the sample. It will be understood that also other components can be measured with one or more of sensors 50, such as the amount of sulphide that is preferably measured in a digester. Preferably, controller 54 also provides control settings 58 to acid dosing device 60 that provides acid, such as hydrochloric acid, to acid reactor 42.

In a sewage treatment plant reactor 26 comprises a receiving reactor (a sewage treatment plant, a waste water treatment plant) that receives the phosphate rich influent. Preferably, phosphate poor effluent leaves the system through an exit (not shown). The phosphate rich effluent

28 is provided to an anaerobic digester that in the illustrated embodiment is part of reactor 26. Iron is optionally added to the receiving reactor and/or the anaerobic digester.

It will be understood that other configurations implementing the present invention could also be envisaged in accordance to the invention. For example, as mentioned, iron may be added before the anaerobic stage to reach the preferred Fe:P range to further reduce the downflow Phosphorus level(s).

Separator 30 (figure 3) comprises frame or housing 62 that is preferable made of steel or another magnetisable material for guiding the magnetic flux, first magnet 64 and, advantageously, second magnet 66. Magnets 64, 66, are provided at a distance wherein assembly 68 is provided. Assembly 68 comprises first (magnetisable) plate 70 and second plate 72 that in the illustrated embodiment are provided with profile 74. In the illustrated embodiment the serrated profile 74 has a height H of about 1-2 mm and a width W of about 3-4 mm. Plates 70, 72 are provided at distance D in the range of 0.1-1 mm, preferably in the range of 0.2-0.4 mm. It will be understood that another configuration for separator 30 and/or other separator techniques can be applied in accordance with the invention.

The method according to the invention is applied to difference incoming streams with different characteristics/composition. In the experiments the sludge remains under anaerobic or anoxic conditions for several days, for example for about 20-30 days. The amount of vivianite like structures has been determined by Mössbauer Spectroscopy and semi quantitative XRD measurements. The table illustrates that the vivianite bound phosphorus increases with the molar Fe:P in the sludge. For example, a molar ratio of about 1.11 results in more than 60% of the incoming phosphorus being bound in vivianite, while higher percentages of above 80% are measured at higher ratio's. This indicates an effective and efficient removal/recovery of phosphorus from a stream.

Table 1: Percentage of phosphorus bound in vivianite or its structures

Sample reference	Sample location	Molar ratio Fe:P	XRD-measurement	Mössbauer-measurement
Sludge sample 1	A	0.14	0	
Sludge sample 2	L	0.50	15.3	13
Sludge sample 3	N	0.82	49.7	30
Sludge sample 4	D	1.11	63.7	
Sludge sample 5	B	1.62	82.1	
Sludge sample 6	C	1.57	83.6	61
Sludge sample 7	F	2.36	102.3	89

The table indicates that according to Mössbauer (at 300 K), for the highest Fe:P ratio of 2.36, a significant amount of P is bound in vivianite.

In a further experimental setup, the vivianite like structures are separated by a separator (figure 3). This separator has six channels with a radius of about 1.3 mm and a length of 40 mm with a cavity volume of about 0.41 cm^3 . The stream has a viscosity of about 0.003 Pa.s , an estimated vivianite susceptibility of $1.0 \cdot 10^{-7} \text{ m}^3/\text{kg}$, and a vivianite density of about 2300 kg/m^3 .

During the separation the magnetic field intensity in the cavity was about $1 \cdot 10^{+06} \text{ A/m}$ with a field gradient of about 500 T/m . Particles are subjected to two competing forces, a friction force as a result of the magnetic force that pushes/attracts the vivianite like structure towards the wall of the channel, and a drag force produced by the stream. Non-magnetic particles will only feel the drag force and are flushed out of the cavity. On the other hand, vivianite-like particles, which are magnetic, will resist the drag and stick to the walls. The vivianite-like particles that are thus collected are flushed from the cavity at a later stage. A number of measurements and calculations were performed for different settings. Results are shown in table 2.

Table 2: Relation between pressure drop (liquid head) and flow through the cavity

Liquid head [mm]	Pressure [Pa]	Flowspeed in channel		Re [-]	Total flow [cm ³ /s]	Drag + gravity force on particles near wall			Magnetic stick force on wall			Ratio of drag and stick		
		Central [mm/s]	Average [mm/s]			At 10 micron [N]	At 20 micron [N]	At 30 micron [N]	At 10 micron [N]	At 20 micron [N]	At 30 micron [N]	At 10 micron [N]	At 20 micron [N]	At 30 micron [N]
0.5	5	18	9	3.81	0.09	4.50 E-11	2.07E-10	5.25E-10	3.01 E-11	2.41E-10	8.13E-10	1.49	0.86	0.65
1	10	35	18	7.63	0.18	8.33 E-11	3.60E-10	8.69E-10	3.01 E-11	2.41E-10	8.13E-10	2.77	1.49	1.07
1.5	15	53	26	11.44	0.27	1.22 E-10	5.13E-10	1.21E-09	3.01 E-11	2.41E-10	8.13E-10	4.04	2.13	1.49
2	20	70	35	15.26	0.36	1.60 E-10	6.66E-10	1.56E-09	3.01 E-11	2.41E-10	8.13E-10	5.31	2.77	1.92
2.5	25	88	44	19.07	0.45	1.98 E-10	8.19E-10	1.90E-09	3.01 E-11	2.41E-10	8.13E-10	6.58	3.40	2.34
3	30	106	53	22.89	0.54	2.36 E-10	9.72E-10	2.25E-09	3.01 E-11	2.41E-10	8.13E-10	7.85	4.04	2.77

Experiments with the separator show that it is possible to separate vivianite and vivianite like structures from a flow with a magnetic separator. This separation is effectively possible due to the vivianite like structures being present relatively pure and as “free” particles. Non-optimised experiments already indicate that more than 60% (expressed as % of P bound in vivianite) of the vivianite and vivianite like structures can be separated. It will be understood that this separation would also be possible with an electromagnetic separator or gravity separator. The separation enables an effective removal and enabling an effective recovery of phosphate/phosphorus from a stream.

Furthermore, the experiments show the effect of the molar Fe:P ratio on the efficiency of the removal/recovery of phosphate from the stream. Furthermore, the experiments show that an effective recovery is possible by effective separation of the vivianite like structures from the stream.

The present invention is by no means limited to the above described preferred embodiments thereof. The rights sought are described by the following claims, within the scope of which many modifications can be envisaged.

Clauses

1. Method for phosphate recovery from a stream, the method comprising the steps of:

- providing an incoming stream comprising an initial amount of phosphate; and
- 5 - dosing iron salt to the stream such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream.

2. Method according to clause 1, further comprising the steps of:

- 10 - separating the vivianite like structures from the stream; and
- recovering the phosphates from the separated vivianite like structures.

3. Method according to clause 1 or 2, wherein the vivianite like structures comprise more than 70%, preferably more than 80%, of the initial amount of phosphate in the incoming stream.

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4. Method according to clause 1, 2 or 3, wherein the iron salts comprise one or more of iron chloride and iron sulphate.

5. Method according to one of the foregoing clauses, wherein dosing iron salt comprises

20 adding an amount of iron with a molar ratio iron:phosphorus of at least 1.25, preferably at least 1.5.

6. Method according to one of the foregoing clauses, further comprising the step of controlling the dosing of iron salt in response to a measurement of the initial amount of phosphate in the incoming stream.

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7. Method according to one of the foregoing clauses, wherein separating the vivianite like structures from the stream comprises magnetic separating the structures with a magnetic and/or electromagnetic separator.

8. Method according to one of the foregoing clauses, wherein separating the vivianite like structures from the stream comprises separating the structures with a gravity separator.

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9. Method according to one of the foregoing clauses, wherein the step of recovering the phosphates comprises treating the vivianite like structures to produce iron oxide precipitates.

10. Method according to clause 9, wherein treating the vivianite like structures comprises performing an alkaline treatment to produce a potassium phosphate solution.

5 11. Method according to clause 9 or 10, further comprising the step of treating the iron oxide with hydrochloric acid to produce iron chloride.

12. Method according to clause 11, further comprising the step of recycling the iron chloride in the step of dosing iron salt.

10 13. Method according to one of the foregoing clauses, wherein the stream is a flow to an anaerobic treatment system, such as a digester.

14. System for phosphate recovery from a stream, the system comprising:

- a reactor comprising:

15 - an inlet for an incoming stream comprising an initial amount of phosphate;

 - an iron salt dosing device configured for dosing iron salt in the reactor such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream; and
- 20 - an outlet.

15. System according to clause 14, further comprising:

- a separator for separating the vivianite like structures from the stream; and
- 25 - a treatment system for treating the separated vivianite like structures to produce iron oxide precipitates.

16. System according to clause 14 or 15, further comprising a dosing controller and a phosphate measurement system that are configured to control dosing of iron salt in response to a measurement of the initial amount of phosphate in the incoming stream.

CONCLUSIES

1. Werkwijze voor fosfaatwinning uit een stroom, werkwijze omvattende de stappen:

- het voorzien van een inkomende stroom omvattende een initiële hoeveelheid fosfaat;
5 en
- het doseren van ijzerzout aan de stroom zodanig dat precipitaat wordt gevormd in de stroom, waarin het precipitaat omvattende vivianiet-achtige structuren omvattende meer dan 60% van de initiële hoeveelheid fosfaat in de inkomende stroom.

10 2. Werkwijze volgens conclusie 1, verder omvattende de stappen:

- het scheiden van de vivianiet-achtige structuren van de stroom; en
- het terugwinnen van de fosfaten uit de gescheiden vivianiet-achtige structuren.

15 3. Werkwijze volgens conclusie 1 of 2, waarin de vivianiet-achtige structuren omvattende meer dan 70%, bij voorkeur meer dan 80% van de hoeveelheid fosfaat in de inkomende stroom.

4. Werkwijze volgens conclusie 1, 2 of 3, waarin de ijzerzouten omvattende één of meer van ijzerchloride en ijzersulfaat.

20 5. Werkwijze volgens één van de voorgaande conclusies, waarin het doseren van ijzerzout omvat het toevoegen van een hoeveelheid ijzer met een molair ratio ijzer:fosfor van ten minste 1,25, bij voorkeur ten minste 1,5.

25 6. Werkwijze volgens één van de voorgaande conclusies, verder omvattende de stap van het regelen van het doseren van ijzerzout in antwoord op een meting van de initiële hoeveelheid fosfaat in de inkomende stroom.

30 7. Werkwijze volgens één van de voorgaande conclusies, waarin het scheiden van de vivianiet-achtige structuren uit de stroom omvat het magnetisch scheiden van de structuren met een magnetische en/of elektromagnetische scheider.

8. Werkwijze volgens één van de voorgaande conclusies, waarin het scheiden van de vivianiet-achtige structuren uit de stroom omvat het scheiden van de structuren met een dichtheidsscheider.

9. Werkwijze volgens één van de voorgaande conclusies, waarin de stap van het terugwinnen van de fosfaten omvattende het behandelen van een vivianiet-achtige structuur voor het produceren van ijzeroxideprecipitaten.

5 10. Werkwijze volgens conclusie 9, waarin het behandelen van de vivianiet-achtige structuren omvattende het uitvoeren van een basische behandeling voor het produceren van een potassiumfosfaatoplossing.

10 11. Werkwijze volgens conclusie 9 of 10, verder omvattende de stap van het behandelen van ijzeroxide met zoutzuur voor het produceren van ijzerchloride.

12. Werkwijze volgens conclusie 11, verder omvattende de stap van het herbruiken van ijzerchloride in de stap van het doseren van ijzerzout.

15 13. Werkwijze volgens één van de voorgaande conclusies, waarin de stroom een stroom is naar een anaerobisch behandelingssysteem, zoals een vergister.

14. Systeem voor fosfaatterugwinning uit een stroom, het systeem omvattende:

- een reactor omvattende:
- 20 - een inlaat voor een inkomende stroom omvattende een initiële hoeveelheid fosfaat;
- een ijzerzout-doseerinrichting geconfigureerd voor het doseren van ijzerzout in de reactor zodanig dat precipitaten worden gevormd in de stroom, waarin de precipitaten omvattende vivianiet-achtige structuren omvattende meer dan 60% van de initiële hoeveelheid fosfaten in de inkomende stroom; en
- 25 - een uitlaat;

15. Systeem volgens conclusie 14, verder omvattende:

- een scheider voor het scheiden van de vivianiet-achtige structuren uit de stroom; en
- en behandelingssysteem voor het behandelen van de gescheiden vivianiet-achtige
- 30 structuren voor het produceren van ijzeroxideprecipitaten.

16. Systeem volgens conclusie 14 of 15, verder omvattende een doseerregelaar en een fosfaatmeetsysteem die zijn geconfigureerd voor het regelen van de dosering van ijzerzout in antwoord op een meting van de initiële hoeveelheid fosfaten in de inkomende stroom.

1/3

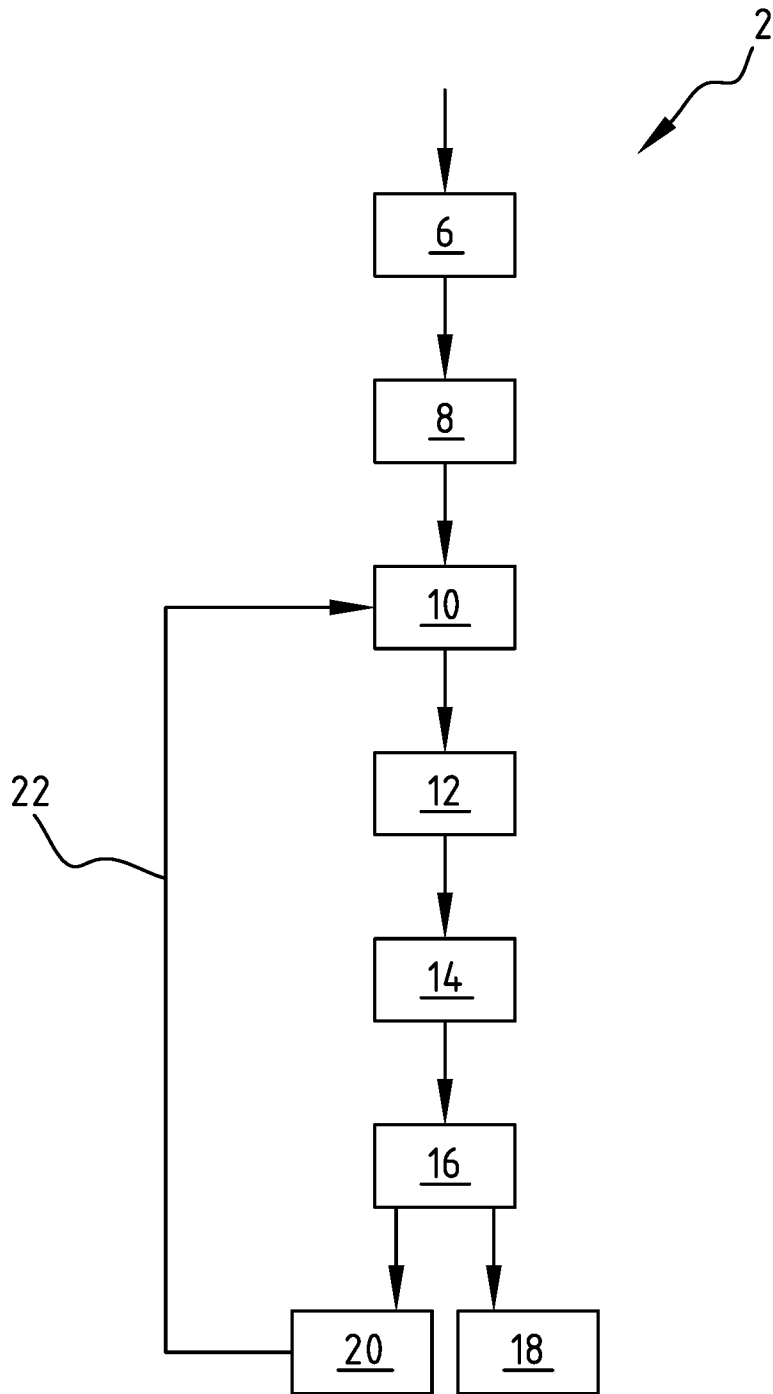
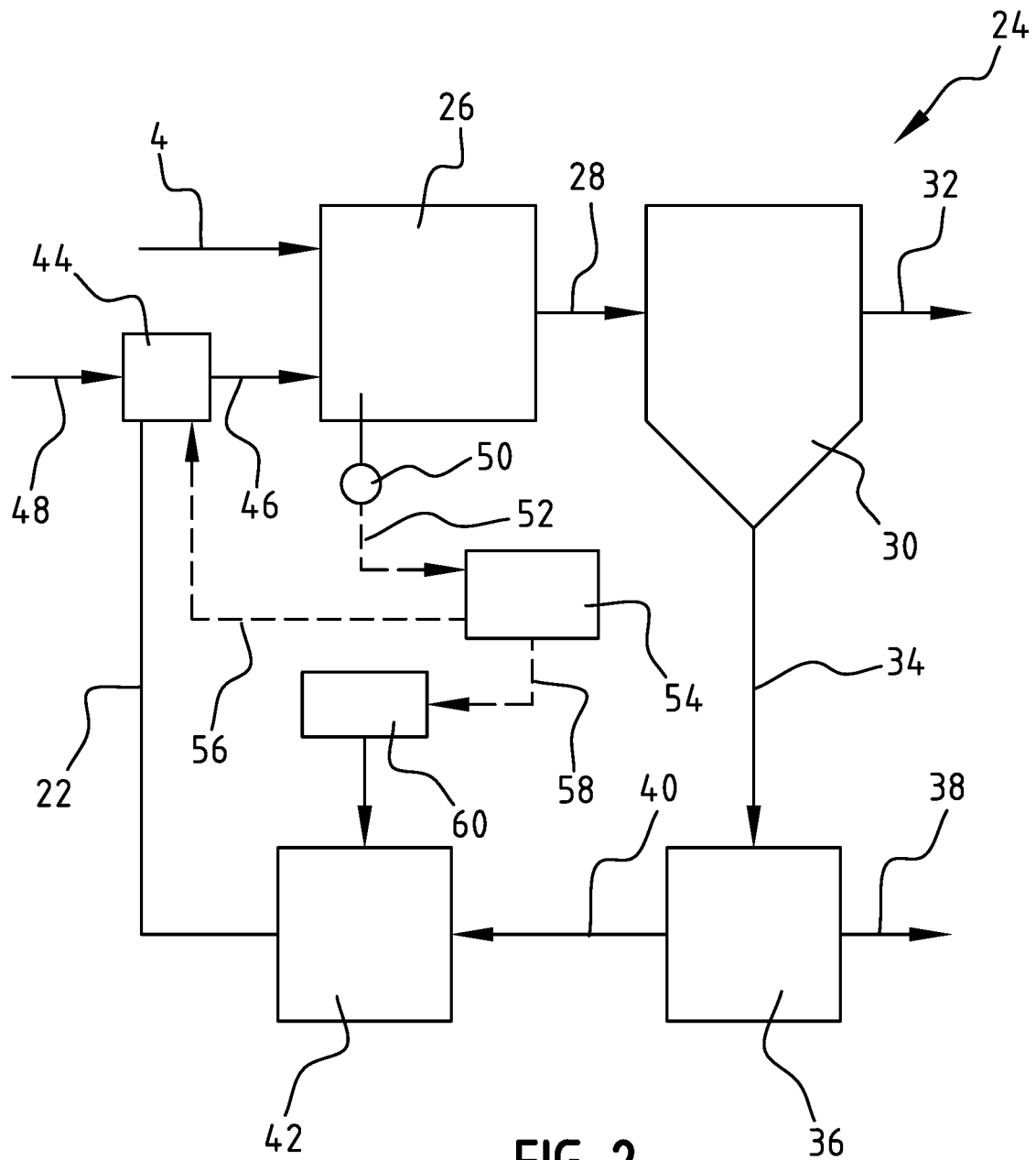


FIG. 1

**FIG. 2**

3/3

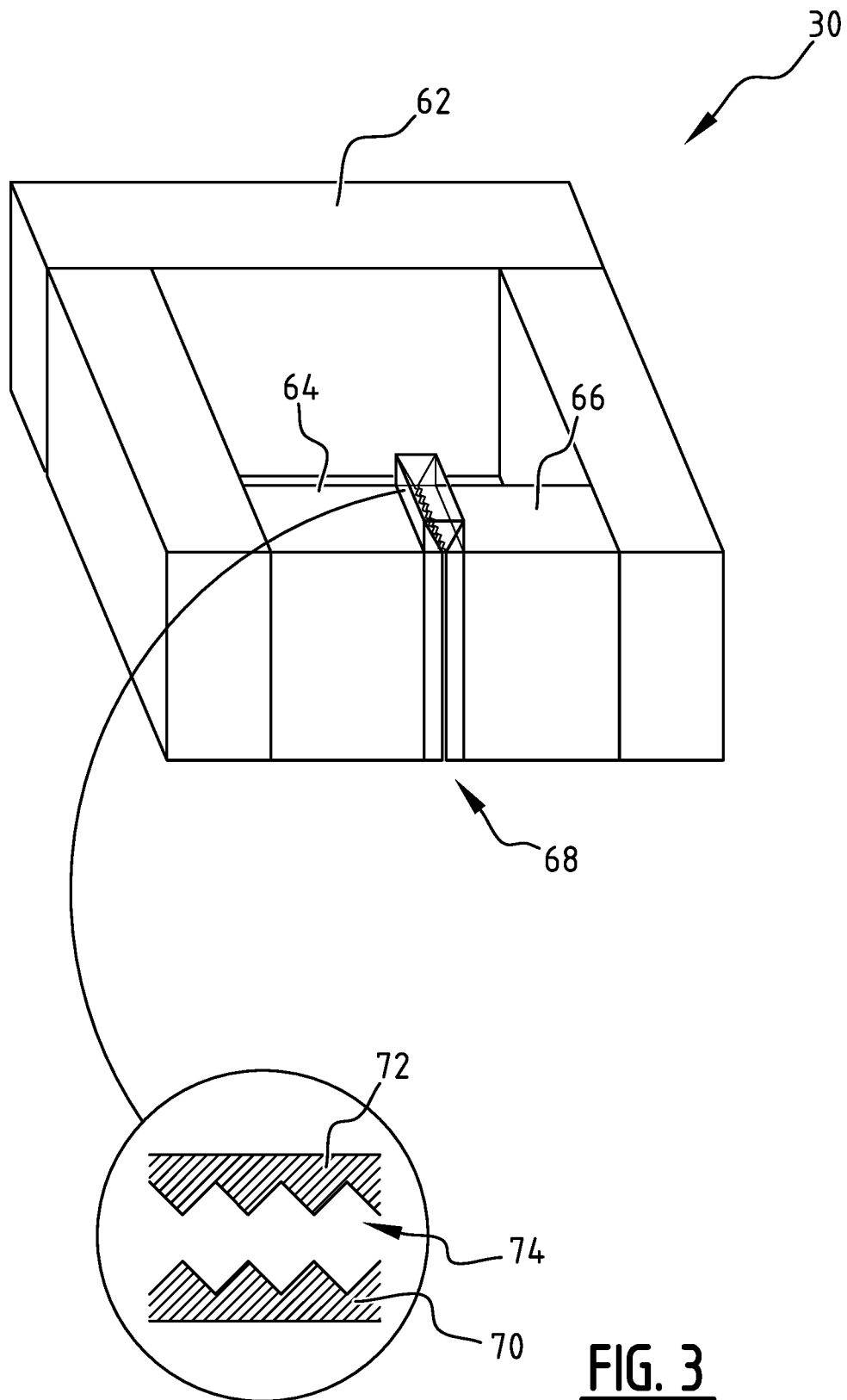


FIG. 3

ABSTRACT

The invention relates to a method and system for phosphate recovery from a stream. The method comprises the steps of:

- 5 - providing an incoming stream comprising an initial amount of phosphate; and
- dosing iron salt to the stream such that precipitates are formed in the stream, wherein the precipitates comprise vivianite like structures comprising more than 60% of the initial amount of phosphate in the incoming stream, and preferably also the steps of:
- separating the vivianite like structures from the stream; and
- 10 - recovering the phosphates from the separated vivianite like structures.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE 	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE 2L/2UP45/MvD-78
Nederlands aanvraag nr. 2018525	Indieningsdatum 15-03-2017
	Ingeroepen voorrangsdatum
Aanvrager (Naam) Stichting Wetsus, European Centre of Excellence for Sustainable Water Technology	
Datum van het verzoek voor een onderzoek van internationaal type 08-04-2017	Door de instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. SN68721
I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven) Volgens de internationale classificatie (IPC) C02F1/52;C02F3/28;C01B25/37;C02F101/10	
II. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK Onderzochte minimumdocumentatie	
Classificatiesysteem IPC	Classificatiesymbolen C02F;C01B
Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen 	
III. ☐	GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES (opmerkingen op aanvullingsblad)
IV. ☐	GEBREK AAN EENHEID VAN UITVINDING (opmerkingen op aanvullingsblad)

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar
de stand van de techniek

NL 2018525

A. CLASSIFICATIE VAN HET ONDERWERP
INV. C02F1/52 C02F3/28 C01B25/37
ADD. C02F101/10

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimum documentatie (classificatie gevolgd door classificatiesymbolen)

C02F C01B

Onderzochte andere documentatie dan de minimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geïsoleerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	EP 2 666 759 A1 (FERTIBERIA S A [ES]) 27 november 2013 (2013-11-27) * alineas [0001], [0002] * * alineas [0006], [0013], [0015], [0018], [0019] * * alineas [0023] - [0036]; voorbeelden 1-2.3 *	1-16
X	CN 104 445 555 A (AU OPTRONICS CORP; NCKU RES & DEV FOUNDATION) 25 maart 2015 (2015-03-25) * samenvatting * * alineas [0039] - [0048] * ----- -/-	1-16



Verdere documenten worden vermeld in het vervolg van vak C.



Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

* Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvraag vermeld

"E" eerdere octrooi(aanvraag), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvraag, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geïsoleerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"Z" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

24 oktober 2017

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

Naam en adres van de instantie

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

De bevoegde ambtenaar

Vaz, Miguel

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar
de stand van de techniek

NL 2018525

C. (Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	US 5 888 404 A (JOKINEN SIMO [FI]) 30 maart 1999 (1999-03-30) * kolom 1, regels 6-13 * * kolom 3, regels 7-11 * * kolom 3, regel 48 - kolom 4, regel 2 * * kolom 4, regels 20-22 * * kolom 5, regels 31-54; figuur 3 * -----	1-16
A	CA 2 252 656 A1 (UNIV WATERLOO [CA]) 5 mei 1999 (1999-05-05) * bladzijde 2, regels 22-24 * * bladzijde 3, regels 6-9 * * bladzijde 5, regels 27-29 * -----	1-16

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar
de stand van de techniek

NL 2018525

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
EP 2666759	A1	27-11-2013	GEEN
CN 104445555	A	25-03-2015	CN 104445555 A 25-03-2015 TW 201536691 A 01-10-2015
US 5888404	A	30-03-1999	AT 193874 T 15-06-2000 AU 4306296 A 24-07-1996 CA 2208970 A1 11-07-1996 CZ 9702032 A3 12-11-1997 DE 69517538 D1 20-07-2000 DE 69517538 T2 19-10-2000 DK 0800483 T3 06-11-2000 EP 0800483 A1 15-10-1997 ES 2148586 T3 16-10-2000 JP 3284275 B2 20-05-2002 JP H10511601 A 10-11-1998 NO 972992 A 26-06-1997 PL 321541 A1 08-12-1997 US 5888404 A 30-03-1999 WO 9620894 A1 11-07-1996
CA 2252656	A1	05-05-1999	CA 2252656 A1 05-05-1999 US 6214229 B1 10-04-2001

WRITTEN OPINION

File No. SN68721	Filing date (day/month/year) 15.03.2017	Priority date (day/month/year)	Application No. NL2018525
International Patent Classification (IPC) INV. C02F1/52 C02F3/28 C01B25/37 ADD. C02F101/10			
Applicant Stichting Wetsus, European Centre of Excellence for Sustainable Water Technology			

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

	Examiner Vaz, Miguel
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WRITTEN OPINION

Application number

NL2018525

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material:
 - ☐ on paper
 - ☐ in electronic form
 - c. time of filing/furnishing:
 - ☐ contained in the application as filed.
 - ☐ filed together with the application in electronic form.
 - ☐ furnished subsequently for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes: Claims	
	No: Claims	1-16
Inventive step	Yes: Claims	
	No: Claims	1-16
Industrial applicability	Yes: Claims	1-16
	No: Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Application number
NL2018525

Box No. VIII Certain observations on the application

see separate sheet

1 **Re Item V**

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1.1 Reference is made to the following documents:

- D1 EP 2 666 759 A1 (FERTIBERIA S A [ES]) 27 november 2013 (2013-11-27)
- D2 CN 104 445 555 A (AU OPTRONICS CORP; NCKU RES & DEV FOUNDATION) 25 maart 2015 (2015-03-25)
- D3 US 5 888 404 A (JOKINEN SIMO [FI]) 30 maart 1999 (1999-03-30)
- D4 CA 2 252 656 A1 (UNIV WATERLOO [CA]) 5 mei 1999 (1999-05-05)

1.2 The present application does not meet the criteria of patentability, because the subject-matter of claim 1 is not new.

1.3 D1 discloses a method for obtaining a vivianite like compound by the addition of an iron salt (ferrous sulphate) to a wastewater containing phosphates (alineas [0001], [0002], [0013] en [0015]). Notwithstanding the lack of clarity (see item VIII below), the amount of vivianite obtained corresponds to the majority of the reaction product, which means that most of the initial phosphates are comprised in said vivianite (alineas [0019]).

1.4 D2 discloses an identical method (samenvatting) wherein the iron salt can be ferrous chloride (alineas [0041], [0042]). The conversion percentage of phosphorous to vivianite is between 91.7 and 97.7% (alineas [0045]-[0048]).

1.5 In view of D1 and D2, the novelty objection made above to the method of claim 1 can be done *mutatis mutandis* to the corresponding system of claim 14, considering that to add an iron salt to a phosphate containing stream, a reactor with an inlet and an outlet is implicit. The subject-matter of claim 14 is therefore not new.

1.6 Dependent claims 2-13, 15, 16 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of novelty and/or inventive step:

- 1.6.1 The features of claims 3-5 are also disclosed in D1 and D2 (cf. passages cited in the search report). The subject-matter of claims 3-5 is therefore not new.
- 1.6.2 D1 and D2 (cf. passages cited in the search report) further disclose the separation of the precipitated vivianite. D3 discloses a method to recover phosphates and iron chloride to be (re)used as a coagulant from a ferrous phosphate product (kolom 1, regels 6-13; kolom 3, regels 7-11), comprising raising the pH with an alkali hydroxide to precipitate iron hydroxides and recover an alkali phosphate salt, and further adding hydrochloric acid to the obtained iron hydroxides to produce iron chloride that can be used as a coagulant (kolom 3, regel 48 - kolom 4, regel 2; kolom 4, regels 20-22; kolom 5, regels 31-54; figuur 3). The subject-matter of claims 2, 9-12 and 15 does not therefore involve an inventive step.
- 1.6.3 D4 discloses that a wastewater from an anaerobic treatment system can be suitably treated with a similar method to obtain vivianite (bladzijde 2, regels 22-24; bladzijde 3, regels 6-9; bladzijde 5, regels 27-29). The subject-matter of claim 13 does not therefore involve an inventive step.
- 1.6.4 The features of claims 6-8 and 16 are obvious possibilities that come within the scope of the customary practice followed by persons skilled in the art, especially as the advantages thus achieved can readily be foreseen. Consequently, the subject-matter of claims 6-8 and 16 also lacks an inventive step.

2 Re Item VIII

Certain observations on the application

- 2.1 Claims 1 and 14 are not clear:
- 2.1.1 Claims 1 and 14 do not meet the requirement of clarity because the matter for which protection is sought is not clearly defined. Stating the desired product characteristics, i.e., the amount of initial phosphate in the vivianite precipitate, without providing the technical features necessary for achieving this result, is an attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem.
- 2.1.2 Furthermore, the feature "configured for dosing (...) such that precipitates are formed (...) comprising more than (...)" in the apparatus claim 14 relate to a method of using the apparatus rather than clearly defining the apparatus in terms of its technical features, i.e., it's a process feature. The intended

limitations are therefore not clear from this claim.