(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 November 2017 (23.11.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/200467 A1

(51) International Patent Classification:
C05G 1/00 (2006.01) *C05B 15/00* (2006.01)

(21) International Application Number:
PCT/SE2017/050504

(22) International Filing Date:
16 May 2017 (16.05.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1650655-2 16 May 2016 (16.05.2016) SE

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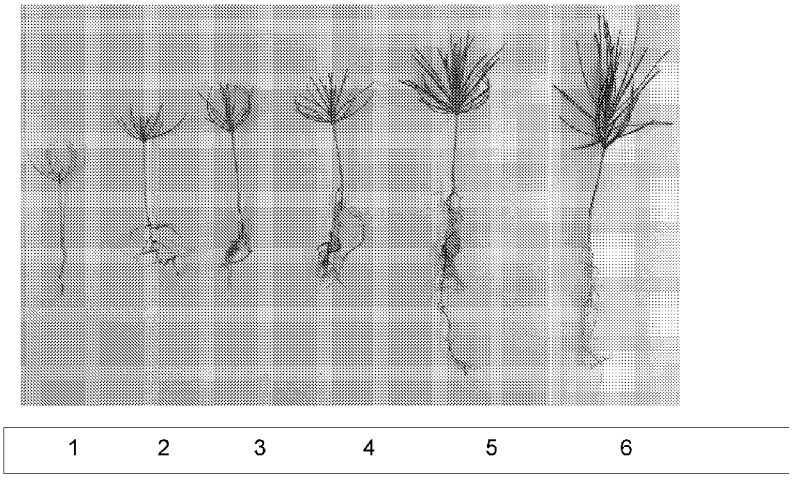
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

WO 2017/200467 A1

(54) Title: SOLID PHASE FERTILIZER COMPOSITION

Fig. 12 C



(57) Abstract: The present invention relates to a fertilizer composition comprising nitrogen and phosphorus, wherein nitrogen is provided by basic L-amino acid(s)complexed to polyphosphate(s). The complex may be precipitated with multivalent metal ion(s) to provide a solid phase fertilizer composition. The basic L-amino acid is advantageously L-arginine and/or L-lysine. The fertilizer composition is capable of providing controlled release of nitrogen during prolonged periods of time.

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Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

SOLID PHASE FERTILIZER COMPOSITION

Technical Field

The present invention relates to a solid phase fertilizer composition and a method for the preparation thereof. More specifically, the fertilizer composition according to the invention comprises at least one basic L-amino acid based complexed to at least one polyphosphate. In addition, the invention relates to the use of a complex of at least one basic amino acid and at least one polyphosphate to provide slow release of nitrogen to plants.

Background

Methods of improving soil and/or growth conditions have in principle been applied since the first days of agriculture and horticulture. Starting with a very limited understanding of mechanisms, it was recognised that the waste from the household animals such as cows improved the growth of crops in the fields. As nitrogen, potassium and phosphorus were identified as the key components required to efficiently fertilize the soil, commercial preparations became widely available and the principle of more is less was generally applied for decades, resulting in the by now well-known over fertilization effects. While preparations including nitrogen, potassium and phosphorus together with various other mineral nutrients still constitute the standard in most plant culture, research is continuously improving with regard to the refinement of fertilizer compositions to provide plants with what is needed for their optimal growth. Specifically designed compositions for certain plants have been developed, and different formats such as liquids and dry preparations are also provided in order to balance a desired growth, feasibility of application and a minimal environmental impact.

One way to decrease the harmful environmental effects of fertilizers, and especially the losses of mineral nutrients to recipient ecosystems, is to develop compositions

which provide a slow or delayed release of active component(s). Such compositions are often referred to as controlled-release preparations.

Coating of mineral nutrient salts has been proposed as one way of slowing down release. However, as a common mechanism, coatings will act to delay the release of the enclosed nutrients – in the early stages, the coating will prevent any release of nutrient, and once 'opened' or consumed, the nutrients will all be available at once. Thus, the released nutrients will then either be utilized by the cultured plant, or, if the amount is more than needed, will leak to the environment. Thus, a general challenge with coating technology is to provide for a release which is extended in time, and with a rate suitable for the needs of the cultured plant.

WO 2015/066691 (University of Florida Research Foundation) relates to such slow-release fertilizer compositions wherein graphene oxide films are utilized to delay release. More specifically, the described fertilizer composition comprises a plurality of fertilizer particles and a reduced-graphene oxide layer disposed on the surface of each particle. The fertilizer particles may comprise one or more of nitrogen, phosphorus, potassium, calcium, magnesium and sulphur, boron, chlorine, cupper, iron, manganese, molybdenum, zinc and nickel, wherein at least one is in salt form and can act to reduce graphene oxide. The described coating technology is stated to provide great promise for environmentally-benign controlled-release fertilizers for crop production.

An alternative way of providing for optimised release is to create complexes including the relevant nutrient(s). WO 2016/035090 (Chaudhry) relates to such a fertilizer composition and a process for its preparation. More specifically, a multifunctional organic bio-complexed composition is described, which comprises nutrient sources, such as nitrogen, phosphorus and potassium, and phosphopeptides, such as phosphopeptides comprising a complexation product of organic acids:biocomplexing agent together with a phosphorous source. The bio-complexing agents may be

peptides, amino acids or hydrolysed proteins. As compared to conventional fertilizers using nitrogen from urea, which is stated to evaporate quickly, the described complexation of nitrogen to cations is proposed to increase the efficiency.

Further, WO 2016/040564 (Sun Chemical Corporation) relates to a micronutrient fertilizer comprising immediate release as well as sustained release components within a hydrated polyelectrolyte solution. The micronutrients may be selected from a large number of elements, and the polyelectrolyte may be a polymer that has an ionic charge repeated along the polymer. In addition, the composition comprises a metal complexing agent, which may be arginine.

US 8,262,765 (Ajinomoto North America) relates to a method of preparing controlled release fertilizers from fermentation by-products. More specifically, the method may comprise obtaining an amino acid fermentation by-product liquor, adding a phosphate to the amino acid by-product fermentation liquor, adjusting the pH of the liquor and adding a source of magnesium according to '765, not only can magnesium ammonium phosphate be formed by converting a fraction of amino acid fermentation by-product liquors, but it can be formed more efficiently and over a wider pH range than possible with pure systems of ammonium such as ammonium sulphate.

US 6,776,816 (Ringelberg et al) relates to a process for producing forms of magnesium ammonium phosphate e.g. for slow-release fertilizers from animal manure. More specifically, animal excreta is provided; the nitrogen content thereof is determined; a pre-specified amount of at least one magnesium compound is added to yield a first mix, wherein said pre-specified amount is based on said nitrogen content; the pH of said first mix is adjusted to within a pre-specified range of pH to yield a second mix; a pre-specified amount of at least one enzyme is added to said second mix to yield a third mix having a cell structure, wherein said at least one enzyme is mixed with a phosphate buffer to bring the enzyme into solution; said third mix is maintained at a pre-specified temperature range for a pre-specified time; wherein said ammonium

magnesium phosphate is precipitated.

Despite the many products and publications related to controlled release of nutrients, there is still a need for improved compositions which provides a greater flexibility in terms of adapting to different plants' different growth requirements, especially in terms of their different needs during different growth cycles.

Summary of the invention

One object of the invention is to provide a solid phase fertilizer composition, which provides organic nitrogen to plants during prolonged periods of time.
Another object of the invention is to provide a solid phase fertilizer composition, which provides a low leakage of nitrogen to the environment.
Another object of the invention is to provide a method of preparing a solid phase fertilizer composition from fermentation liquid or a liquidified protein hydrolysate.

These objects and others may be achieved as described in the appended independent claims. Further embodiments, details and advantages of the invention will appear from the dependent claims as well as from the detailed description and experimental part below. All details and embodiments of fertilizer compositions, their preparation and use discussed below are applicable to all of the aspects of the invention.

Definitions

The term "plant" is used herein in a broad sense to denote a species or kind of plant.
The term "amino acid" as used herein includes derivatives or modified forms thereof.
The term "polyphosphate" is used herein in its conventional meaning, i.e. for salts or esters of polymeric oxyanions formed from tetrahedral PO_4 (phosphate) structural units linked together by sharing oxygen atoms. Polyphosphates can adopt linear or a cyclic ring structures.

Brief Description of Drawings

Figure 1 shows the arginine content in precipitated fertilizer compositions according to the invention as a function of the L-arginine/hexametaphosphate molar ratio in solution.

Figure 2 shows the arginine content in precipitated fertilizer compositions according to the invention before and after washing in water.

Figure 3 shows how the arginine content in the precipitates decreases when the arginine concentration in the starting solution is reduced.

Figure 4 shows how the amount of ferrous ion added to the arginine-hexametaphosphate solution affects the arginine content in the precipitate.

Figure 5 illustrates the use of alternative metal ions for precipitation of salts in order to prepare different fertiliser compositions according to the invention.

Figure 6 shows the amino acid content in precipitated fertilizer compositions according to the invention for L-arginine as well as the other basic amino acids as a function of the amino acid/hexametaphosphate molar ratio in solution.

Figure 7 shows a comparison of N/P ratios in different precipitates as determined with XPS.

Figure 8 A-C shows the solubility of arginine complexes including polyphosphates of different chain lengths.

Figure 9A-B shows the solubility of ArgdiPFe(II) and ArgHexaMetaFe(II), respectively.

Figure 10A-B shows the solubility of arginine hexametaphosphate complexes including Fe(II) or Fe(III).

Figure 11 shows how the amount of arginine in the different argP complexes is dependent on phosphate chain length.

Figure 12A-C shows the effect of germination and growth of pine with different types of arginine phosphate complexes, as described in more detail below.

Figure 13A-B shows the effect of different arginine-polyphosphate complexes on the growth of lettuce.

Figure 14A-B illustrate the stability of arginine polyphosphate with a chain length of approximately 10000 phosphorus atoms, prepared as described in Example 9.

Detailed Description of the Invention

As appears from the above, the present invention relates to controlled release fertilizer compositions, the basic composition of which can be tuned to suit the many different needs of different plants in different growth cycles and different climates.

In its broadest aspect, the invention is a fertilizer composition comprising nitrogen and phosphorus, which comprises complexes of at least one basic L-amino acid and at least one polyphosphate. The fertilizer composition may be a liquid or a solid phase fertilizer.

The solid phase fertilizer may comprise at least one basic amino acid complexed to polyphosphate. The complex is conveniently precipitated by the addition of metal ions to a solution comprising at least one complex, resulting in a precipitate of solid phase fertilizer composition which also comprises such metal. The complexing of the organic nitrogen provided by the invention appears to delay its release of nitrogen to a rate corresponding to the need of the fertilized plant, whereby nitrogen leakage to the environment is reduced or even eliminated.

Thus, a first aspect of the invention is a solid phase fertilizer composition comprising nitrogen and phosphorus, wherein nitrogen is provided by at least one basic L-amino acid which has been complexed to polyphosphate in solution and precipitated with multivalent metal ion(s).

The basic L-amino acid may be L-arginine; L-lysine; or L-histidine. In one embodiment, the basic L-amino acid is L-arginine and/or L-lysine. In this context, it is to be understood that the amino acids used in the present invention may include modified forms of basic L-amino acids, provided that they have maintained the herein

discussed properties of complexing with polyphosphates by multivalent metal ions and being released to provide organic nitrogen to soil. Basic L-amino acids are available from commercial sources.

The solid phase fertilizer may include a mixture of basic L-amino acids. As will be discussed in more detail below, the nature and amount of amino acid(s) is one of the parameters that are used according to the invention to optimise the specific contents of a fertilizer composition for a specific plant and/or growth condition.

The multivalent metal ion may be any multivalent metal ion capable of precipitating a complex of at least one basic L-amino acid and polyphosphate. In one embodiment, the multivalent metal ion is an alkaline earth metal, such as calcium; a transition metal, such as iron or manganese; or a post-transition metal, such as Al. In a specific embodiment, the multivalent metal ion is selected from the group consisting of Fe(II), Fe(III) and Ca(II). Suitable multivalent metal ions are available from commercial sources.

In one embodiment of the fertilizer composition according to the invention, the Fe(II) or Fe(III) was used to precipitate the solid phase fertilizer.

The multivalent metal ion(s) is another parameter which may be used according to the invention to optimise the specific contents of a fertilizer composition for a specific plant and/or growth condition.

The polyphosphate present in the fertilizer composition according to the invention may be of any size and structure capable of complexing with a basic L-amino acid. In one embodiment of the fertilizer composition, the number of phosphorous atoms in the polyphosphate is at least or equal to two. In another embodiment, the number of phosphorous atoms in the polyphosphate is at least or equal to about six, such as six. In a further embodiment, the number of phosphorous atoms in the polyphosphate is at

least or equal to about 700, such as 700. In an additional embodiment, the number of phosphorous atoms in the polyphosphate is at least or equal to about 1000 or about 2000, such as 1000 or 2000.

Thus, the number of phosphorous atoms in the polyphosphate may be in a range of 2-700, such as about 2-6; 6-50; 50-500 or 50-700, e.g. 500-700.
Larger phosphates may alternatively or additionally be used, in which case the number of phosphorous atoms in the polyphosphate is in the range of 500-2000, such as 700-2000, 700-1000 or 700-10000, e.g. 1000-10000.
As the skilled person will appreciate, the endpoints of the herein given intervals may vary with one or a small number of P atoms, and should not be interpreted as exact unless specifically expressed so. It would appear that the longer the polyphosphates are, the larger the variation of the endpoint may result in similar growth results.

Alternatively, the fertilizer composition according to the invention may be described by its ratio between nitrogen originating from basic L-amino acid(s) and phosphorous. Thus, the N:P ratio may be at least about 2:1; such as about 4:1. In one embodiment, the N:P ratio is about 8:1.

It should be noted that the number of L-arginine molecules are likely to be the same number as the number of phosphorous atoms in the polyphosphate. For example L-arginine-diP have two molecules L-arginine and two phosphorous atoms and L-arginine hexametaP have six molecules L-arginine and six phosphorous atoms in the phosphate complex. Thus an arginine polyphosphate molecule with 10000 phosphates may comprise 10000 arginine molecules.

As the skilled person will appreciate, the contents of a solid phase fertilizer composition according to the invention may be analysed using routine methods. Thus, elemental analysis may be used to convert the ratios given above to percentages, and

commonly used standard methods for total nitrogen and phosphorous determination may be applied to a fertilizer composition to define its contents.

As mentioned above, the structure of the polyphosphate may be one of many, such as linear or cyclic forms, or a mixture of linear and cyclic forms. Polyphosphates useful in the fertilizer compositions according to the invention may include substituents or additional groups, as long as their capability of complexing a basic L-amino acid which can be precipitated with a multivalent metal ion is not impaired.

The size and structure of the polyphosphate is an additional parameter which may be used according to the invention to optimise the specific contents of a fertilizer composition for a specific plant and/or growth condition.

Thus, the solid phase fertilizer composition according to the invention may be tuned to be particularly suitable for a slowly growing plant, such as a tree e.g. pine, or a fast growing plant, such as lettuce. As the skilled person will appreciate, other factors to consider when optimising the availability of nutrient from a fertilizer composition will be the desired growth rate, light and soil, etc.

The present inventors have surprisingly found that by providing organic nitrogen to plants via a precipitated phosphorous complex, the rate of nitrogen uptake can be extended in time or delayed by adjusting the chemical structure and contents of the complex. For example, by using a longer or larger polyphosphate, the availability of nitrogen to a certain plant may be delayed and/or prolonged in action, as a slower release may be provided. This is an advantageous difference from many prior art coated fertilizer composition, the action of which is delayed until the coating is consumed or removed, at which point the full nutrient content is made available at once, often resulting in substantial leakage of nitrogen to the environment.

As is well known, additional nutrients to phosphorous and nitrogen are required for growth of a plant. Thus, the first aspect of the invention also includes a fertilizer

preparation, which comprises a solid phase fertilizer composition as described above together with other macronutrient(s) such as potassium and/or micronutrient(s) in addition to the basic L-amino acid polyphosphate metal precipitate.

In one embodiment, the fertilizer preparation comprises a combination of two or more differently composed fertilizer compositions according to the invention.

A fertiliser preparation according to the invention may be presented in any conventional fertilizer format. Thus, in one embodiment, the fertilizer preparation is in particulate or granular form.

A second aspect of the invention is a method of preparing a solid phase fertilizer composition, which method allows for the design of controlled-release fertilizer compositions specifically for desired conditions of nitrogen release. In one embodiment, the method is for the preparation of a solid phase fertilizer composition as discussed above, in any one of its embodiments.

The liquid may be any aqueous liquid capable of dissolving the below-discussed amino acids, such as water. Preparation of solid phase fertilizer compositions from water solutions will be described in detail in the experimental part below.

In one embodiment, the liquid is comprises fermentation liquid. Such liquid may for example be a by-product of fermentation, in which case the present invention provides an advantageous use of otherwise discarded products thereby avoiding uncontrolled release of nitrogen to the environment.

In an alternative embodiment, the liquid is a liquidified protein hydrolysate. Suitable protein hydrolysates are commercially available and commonly used as undefined growth media.

In one embodiment of the present method, the basic L-amino acid is L-arginine and/or L-lysine. As discussed above in relation to the first aspect of the invention, such amino acids may be in modified and/or substituted forms, provided they are capable of providing the herein discussed effects. Amino acids are available from commercial sources.

As the skilled person will appreciate, pH adjustment may be required before addition of the phosphate source, depending on the nature of the liquid and other parameters.

In one embodiment of the method, the polyphosphate source is a phosphate powder dissolved in water, wherein the pH suitably is close to that of the liquid comprising at least one basic L-amino acid. The skilled person will be able to define a suitable phosphate starting material which together with the appropriate tuning of the other components, amounts and conditions will provide a fertiliser composition with desired properties of nitrogen release. As the skilled person will appreciate, the actual growth properties of candidate compositions are suitably confirmed by routine experimentation.

The phosphate solution may be added to the amino acid solution under stirring, and the resulting solution is conveniently left to settle, for example at room temperature.

At least one multivalent metal ion is then added in order to precipitate the complex formed between amino acid and phosphate. The multivalent metal ion may be any multivalent metal ion capable of precipitating a complex of at least one basic L-amino acid and polyphosphate. In one embodiment, the multivalent metal ion is an alkaline earth metal, such as calcium; a transition metal, such as iron or manganese; or a post-transition metal, such as Al. In a specific embodiment, the multivalent metal ion is selected from the group consisting of Fe(II), Fe(III) and Ca(II). Suitable multivalent metal ions are available from commercial sources.

After completed precipitation, the supernatant may be decanted and the remaining slurry centrifuged. The resulting solid material may be collected and dried before any further, optional steps to make a preparation including combination with further components and/or specific formatting such as granulation.

A third aspect of the invention is the use of a complex formed of at least one polyphosphate and at least one basic L-amino acid to supply nitrogen to plants. Thus, this aspect is a method of using a complex formed of at least one polyphosphate and at least one basic L-amino acid for the supply of nitrogen to plants. One embodiment of this aspect uses of a solid phase fertilizer composition as discussed above, in any one of its embodiments.

In one embodiment, the period of time for supply of nitrogen from the complex is prolonged as compared to the supply of the same amount of non-complexed nitrogen and phosphorous under otherwise equivalent conditions.

In one embodiment of the present use, the nitrogen is supplied to a plant selected from the group consisting of trees, grasses, vegetables and crops.

In one embodiment of the present use, the basic L-amino acid is L-arginine and/or L-lysine.

In one embodiment of the present use, the metal ion(s) are selected from the group consisting of Fe(II), Fe(III), and Ca(II).

In one embodiment of the present use, the number of phosphorous atoms in the polyphosphate is at least or equal to two phosphates.

In one embodiment of the present use, the number of phosphorous atoms in the polyphosphate is at least or equal to six phosphates.

In one embodiment of the present use, the number of phosphorous atoms in the polyphosphate is at least or equal to 700 phosphates.

Detailed Description of Drawings

Figure 1 shows the arginine content in precipitated fertilizer compositions according to the invention as a function of the L-arginine/hexametaphosphate molar ratio in solution. In Figure 1, HMP is abbreviation for hexametaphosphate. The compositions were prepared as described in the Example 2 below. As appears from the figure, the L-arginine content in the composition increases linearly when the relative amount of arginine in the solution from which complexes are formed and precipitated increases. Thus, a large excess of arginine compared to hexametaphosphate in the solution results in higher arginine content in the final precipitated complex.

Figure 2 shows the arginine content in precipitated fertilizer compositions according to the invention before and after washing in water. As appears from this figure, the arginine content is slightly lower after washing. This suggests that during precipitation, some of the free arginine in solution will adsorb to the surface of the precipitate particles. The major part of the arginine is however retained in the precipitate and not released during washing in water.

Figure 3 shows how the arginine content in the precipitates decreases when the arginine concentration in the starting solution is reduced. The relative ratio of arginine to hexametaphosphate was constant throughout all experiments (Example 3). However, the amount of recovered precipitate remains relatively constant regardless of the starting arginine concentration.

Figure 4 shows how the amount of ferrous ion added to the arginine-hexametaphosphate solution affects the arginine content in the precipitate (Example 4). When the molar amount of ferrous ions is equal to the amount of phosphorous atoms present, approximately 50 mg/g arginine is present in the precipitate. When the amount of ferrous ions is reduced, the arginine content increases significantly. The association between arginine and hexametaphosphate most probably occurs through a combination of ionic association and hydrogen bonding, and metal cations added as a

precipitant will compete with arginine for the binding sites on the hexametaphosphate molecules. By reducing the amount of ferrous ions in the precipitation step, a more arginine rich precipitate was obtained with only a slight decrease in precipitate recovery.

Figure 5 illustrates the use of alternative metal ions for precipitation of salts in order to prepare different fertiliser compositions according to the invention (Example 5). Examples of formation and appearance of arginine-hexametaphosphate precipitate using different metal salt solutions as the precipitating agent are shown. Precipitates have been obtained for several di- and trivalent cations. Monovalent metal ions are not expected to form insoluble species and no precipitation was observed when potassium sulphate was added as the precipitating agent.

Figure 6 shows similar to Figure 1 the amino acid content in precipitated fertilizer compositions according to the invention for L-arginine as well as the other basic amino acids L-lysine and L-histidine as a function of the amino acid/hexametaphosphate molar ratio in solution. All experiments were carried out according to the example 6 below. As appears from this figure, all three basic amino acids are capable of forming amino acid-hexametaphosphate complexes. The complex including histidine has an amino acid content comparable to that of the arginine complex, while lysine results in a lower arginine content in the precipitate. The difference in amino acid content is likely related to the interaction strength between the individual amino acid and the hexametaphosphate molecule.

Figure 7 shows a comparison of N/P ratios in different precipitates prepared according to Example 2-6 above as determined with XPS. The N/P ratio in the starting solution is shown for comparison. Depending on the choice of the experimental variables, the final N/P ratio in the fertilizer composition can be controlled. By exploiting the findings from the different examples, a broader range of N/P ratios of the precipitates can be obtained.

Figure 8 shows the solubility of arginine complexes. To 100 mg complex 10 mL dH_2O was added and left to rotate in a rotator mixer at 15 rpm. The supernatant was collected. This was repeated seven times. Extracted supernatants were analysed by UPLC and the concentration of arginine plotted as wt% of total complex.
The results appear from Figures 8A-C, wherein Figure 8A is ArgP extracted with H_2O at 1 min intervals; Figure 8B is ArgPP extracted with H_2O at 1 min intervals; and Figure 8C is ArgHexaMetaP extracted with H_2O at 10 min intervals.
Thus, these figures show that an increased phosphate chain length also leads to decreased solubility of the complexes. For ArgP the complex was dissolved completely after 7 minutes compared to the ArgHexaMetaP complex which was dissolved after 70 minutes.

Figure 9 shows the solubility of arginine complexes with bound Fe(II). To 100 mg complex 10 mL dH_2O was added and left to rotate in a rotator mixer at 15 rpm. The supernatant was collected. This was repeated seven times for the ArgdiPFe(II) and eight times for the ArgHexaMetaFe(II) complex. At the last time point 4M HCl was added to dissolve the remaining complex. Extracted supernatants were analysed by UPLC and the concentration of arginine plotted as wt% of total complex. The results appear from Figures 9A-B, wherein Figure 9A is ArgdiPFe(II) extracted with H_2O with 3 days intervals and Figure 9B is ArgHexaMetaFe(II) extracted with H_2O with 3 days intervals. Thus, with the addition of Fe(II) there is a drastic reduction in the solubility of the complexes from minutes to weeks. At the last time point 4M HCl was added to dissolve the remaining complex ArgHexaMetaP contained more than 50% of arginine still bound in the complex at the last time point at 24 days compered to ArgdiP where only 10% of the arginine remained after 21 days. Depending on the type of polyphosphate chain there is an effect on solubility of the complex.

Figure 10 shows the solubility of arginine complexes with bound Fe(II) or Fe(III). To 100 mg complex 10 mL dH_2O was added and left to rotate in a rotator mixer at 15

rpm. The supernatant was collected. This was repeated five times for the Fe(III) complex and nine times for the Fe(II) complex. At the last time point 4M HCl was added to the Fe(II) complex to dissolve the remaining complex. Extracted supernatants were analysed by UPLC and the concentration of arginine plotted as wt% of total complex. The results appear from Figures 10A-B, wherein Figure 10A shows ArgHexaMetaPFe(II) extracted with H_2O with 3 days intervals; and Figure 10B shows ArgHexaMetaPFe(III) extracted with H_2O with 3 days intervals.
Thus, the form of Fe (II or III) has a marked effect on the solubility of the complex. The Fe(III) complex was completely dissolved after 6 days compared to the Fe(II) complex that had more than 50 % arginine left after 27 days.

Figure 11 shows that the amount of arginine in the different argP complexes is dependent on phosphate chain length. 100 mg ArgHexaMetaP and ArgdiP was dissolved in 5 mL 4M HCl and the arginine content was analysed by UPLC. The arginine content was plotted as wt% of total complex. A longer polyphosphate chain length leads to increased arginine content in the complex.

Figure 12 shows the effect of germination and growth with different types of arginine phosphate complexes. 20 mg nitrogen in the form of different arginine phosphate complexes was incorporated in to peat and the effect on germination and growth was studied. The results appear from Figures 12A-C, where 12A shows the germination of pine seedlings fertilized with 20 mg of N in different types of ArgP complexes (%); 12B shows the dry weight of pine seedlings fertilized with 20 mg of N in different types of ArgP complexes; and 12C shows pine seedlings fertilized with 20 mg of N in different types of ArgP complexes. More specifically, in Figure 12C: 1 is Arg-HCl; 2 is ArgP; 3 is ArgPP; 4 is ArgHexaMetaP; 5 is ArgHexaMetaPFe(II); and 6 is Arg-P10000. Thus, Figure 12 illustrates how the solubility of the different argP complexes affects growth and germination of pine seedlings. More rapidly dissolving forms of argP complexes lead to reduced germination and decreased growth of the seedlings, probably as a result of nitrogen toxicity.

Figure 13A-B show the effect of different arginine-polyphosphate complexes on the growth of lettuce. Lettuce is a relatively fast growing plant, which would explain why no difference is noted in the results from differently sized polyphosphates.

Figure 14A-B illustrate the stability of arginine polyphosphate with a chain length of approximately 10000 phosphorus atoms, prepared as described in Example 9. More specifically, Figure 14A shows the release of arginine with time; while Figure 14B shows the release of phosphorous with time, both figures illustrating how a slow release with time may be obtained from fertilizer compositions according to the invention wherein the phosphate chain is long. Thus, the results shows the advantage of versatility of the present invention, enabling the preparation of a fertilizer composition which is adapted for specific growth needs depending e.g. on the plant and/or the contents of the soil in which it is cultured.

EXPERIMENTAL PART

The present examples are provided for illustrative purposes only, and should not be perceived as limiting the invention as defined by the appended claims. All references cited below and elsewhere in the present application are hereby included herein via reference.

Example 1: General method for preparing arginine-hexametaphosphate-iron complex.

An arginine solution was prepared by dissolving arginine base (Sigma) in purified water to a concentration of 0.5 M. The pH of the solution was adjusted to 8.3 with concentrated hydrochloric acid. A 0.5 M solution of sodium hexametaphosphate was prepared by dissolving the phosphate powder in purified water and adjusting the pH of the solution to 8.3 with a 50 % (w/w) sodium hydroxide solution. The sodium hexametaphosphate solution was slowly added to the arginine solution under continuous stirring. The resulting solution was stirred at room temperature for 4 hours.

To precipitate the arginine-phosphate complex, a solution containing either ferrous or ferric ions was prepared ($FeSO_4$ or $FeCl_3$). The iron salt solution was slowly added to the arginine-phosphate solution which resulted in precipitation of a solid material. The precipitate was left overnight to allow for the precipitate to settle. The supernatant was decanted and the remaining slurry was centrifuged. The resulting solid material was collected and dried in a furnace at 60 °C.

Example 2

According to the general method described in example 1, compositions with different molar ratio of arginine and hexametaphosphate were prepared. The concentrations of the solutions were kept constant and the amount of HMP was reduced to obtain the chosen arginine /HMP molar ratio according to table 1 below.

Table 1:

Experiment	Arginine/HMP (molar ratio)	Arginine (mL)	HMP (mL)	0.6 M $FeSO_4$ (mL)
E1	1.5	30	20	100
E2	3	36	12	60
E3	6	42	7	35
E4	12	48	4	20

Example 3

According to the general method described in example 1, arginine solutions with different concentrations were used according to table 2 below.

Table 2:

Experiment	Arginine/HMP (molar ratio)	Arginine conc. (g/L)	Arginine (mL)	HMP (mL)	0.5 M $FeSO_4$ (mL)
S1	6	104	50	10.0	60
S2	6	69	50	6.67	40
S3	6	35	50	3.33	20
S4	6	17	50	1.67	10
S5	6	8.7	50	0.83	5
S6	6	4.3	50	0.42	2.5

Example 4

According to the general method described in example 1, different amounts of $FeSO_4$ solution was added to the arginine-hexametaphosphate complex solutions according to table 3 below.

Table 3:

Experiment	Arginine/H (MP molar ratio)	HMP (ml)	Arginine (mL)	0.5 M $FeSO_4$ (mL)	Fe/P (molar ratio)
F1	6	8.3	50	50	1
F2	6	8.3	50	40	0.8
F3	6	8.3	50	30	0.6
F4	6	8.3	50	20	0.4

Example 5

According to the general method described in example 1, different metal salt solutions were used to precipitate the arginine-hexametaphosphate complex according to table 4 below.

Table 4:

Exp.	Metal salt	Arginine/H (MP molar ratio)	Amino acid (M)	Amino acid (mL)	HMP (mL)	Metal salt (M)	Metal salt (mL)
ref	$FeSO_4$	0	-	0	8.3	0.5	50
E2	$FeSO_4$	3	0.5	36	12	0.6	60
E4	$FeSO_4$	12	0.5	48	4	0.6	20
E4:2	$FeCl_3$	12	0.5	48	4	1	12
M3	$MnSO_4$	6	0.5	50	8.3	1	50
M4	$CaCl_2$	6	0.5	50	8.3	1	50
M6	$Al_2(SO_4)_3$ + $FeSO_4$	6	0.5	50	8.3	0.5 + 0.5	20 + 40

Example 6

According to the general method described in example 1, different basic L-amino acids were used to form L-amino acid-hexametaphosphate complexes which were then precipitated with $FeSO_4$ according to table 5 below.

Table 5:

Exp.	Amino acid	aa/HMP (molar ratio)	N/P (molar ratio)	HMP (ml)	Amino acid (M)	Amino acid (mL)	0.5 M $FeSO_4$ (mL)
A1	lysine	6	2	10	0.5	60	60
A2	lysine	12	4	10	0.5	120	60
A3	histidine	6	3	2	0.17	35	12
A4	histidine	12	6	2	0.17	70	12

Example 7

This example relates to the germination and growth of pine with different types of arginine phosphate complexes. Five different arginine phosphate complexes arginine-monophosphate (2), arginine-diphosphate (3), arginine-hexametaphosphate, (4) and arginine-hexametaphosphate-Fe(II) (5), and finally (6) arginine-P10000, prepared according to Example 9, were tested in peat. Arginine-HCl was used as reference (1). A set of 40 pots were filled with 50 ml of peat mixed with one of the five different arginine complexes, such that each pot got 20 mg N, measured by the number of nitrogen atoms in the arginine complexes. Scots Pine seeds were sown in the pots and grown in greenhouse 16/8h day/night and 23°C, with the pots watered 2 times a day with a total growth period of 8 weeks. The seedlings were harvested, the peat was washed away and the seedlings were dried and dry weight was recorded, see Fig.12.

Thus, the results of this example show that the solubility of the different arginine phosphate complexes affects growth and germination of pine seedlings. It may be that too rapidly dissolving forms of arginine phosphate complexes may lead to a reduced germination and decreased growth of the seedlings. This may be due to nitrogen toxicity, and may be tested by the skilled person to fine-tune the preparation of a

fertilizer according to the invention to suit desired needs of germination and other factors.

Example 8

This example relates t othe germination and growth of a fast growing plant, such as lettuce with different types of arginine phosphate complexes. Five different arginine phosphate complexes, as described in Example 7, were mixed with peat, and forty pots filled with 20 mg N of the different arginine complexes were mixed with unfertilized peat with a total volume of 100 ml per pot for each treatment. A set of 40 pots was filled with 100 ml of peat mixed with one of the five different arginine complexes, i.e. 40 pots with each treatment, such that each pot got 40 mg N, measured by the number of nitrogen atoms in the arginine complexes. Lettuce (*Lactuca sativa*) seeds were sown in the pots and grown in greenhouse 16/8h day/night, 23° C. The pots were watered two times a day with a total growth period of 5 weeks. The lettuce seedlings were harvested, the soil was washed away and the seedlings were dried and dry weight was recorded. The results are shown in Figure 13, where 13A illustrates the biomass of dried plants in mg dry weight fertilized with five different arginine complexes and 13B shows a photo the lettuce plants.

As lettuce is a relatively fast growing plant, the size of the different polyphosphates used may have less impact on growth than what has been observed for more slowly growing plants. However, as these results show, the present invention will still work as a fertilizer for the fast growingplants as well, for the period of time required, and the skilled person may based on this knowledge fine-tune the chemical composition of a fertilizer according to the invention especially in view of the length of the P chain of the complex to include the required amount of nutrients. Such optimization will benefit the environment, as it will enable fertilizers to comprise the amount of nutrients required for growth, whereby unneccessary amounts which may leak to the environment are reduced or even avoided by the present invention.

Example 9

This examplerelates to the preparation of arginine polyphosphate with a chain length of approximately 10000 phosphorus atoms. Arg-P10000 was done by adding 100 g polyphosphate crystals, normally used as a cation exchange resin, to 500 ml of 0.5 M arginine solution with stirring for 24h. Crystals were washed with 500 ml H_2O three times and dried. These crystals were also used in the germination tests discussed in example 7.

One hundred milligram of the Arg-P10000 crystals were treated with either 5 ml of dH_2O, 0.5 mM $CaCl_2$, or 0.5 mM oxalacetic acid in a 15 ml Falcon tube. The Falcon tubes were left on a rolling table (15 rpm) for two week at room temperature, at which time the solution was analysed for arginine (UPLC) and phosphate (ion chromatography). New solutions were added and the process was repeated over a period of 12 weeks. The results are shown in Figure 14. The release of arginine (Figure 14A) and phosphate (Figure 14B) over time is very low, creating a long-lasting fertilizer. Thus, an arginine polyphosphate fertilizer according to the invention with longer chains may be used for long periods of time as a really slow releasing fertilizer.

CLAIMS

1. A fertilizer composition comprising nitrogen and phosphorus, which comprises complexes of at least one basic L-amino acid and at least one polyphosphate.
2. A fertilizer composition according to claim 1, which is a solid phase fertilizer composition which also comprises at least one metal.
3. A fertilizer composition according to claim 1 or 2, wherein nitrogen is provided by at least one basic L-amino acid which has been complexed to polyphosphate in solution and precipitated with multivalent metal ion(s).
4. A fertilizer composition according to any one of the preceding claims, wherein the basic L-amino acid is L-arginine and/or L-lysine.
5. A fertilizer composition according to any one of the preceding claims, wherein the metal ion(s) are selected from the group consisting of Fe(II), Fe(III), and Ca(II).
6. A fertilizer composition according to any one of the preceding claims, wherein the number of phosphorous atoms in the polyphosphate is at least or equal to two.
7. A fertilizer composition according to claim 6, wherein the number of phosphorous atoms in the polyphosphate is at least or equal to six.
8. A fertilizer composition according to claim 7, wherein the number of phosphorous atoms in the polyphosphate is at least or equal to 10000.
9. A fertilizer composition according to any one of the preceding claims, which comprises one or more additional macronutrient(s) and/or micronutrients.
10. A fertilizer preparation which comprises a fertilizer composition according to any one of the preceding claims in particulate or granular form.
11. A fertilizer preparation which comprises a combination of two or more differently composed fertilizer compositions according to any one of the preceding claims.
12. A method of preparing a fertilizer composition, which method comprises to provide a liquid comprising at least one basic L-amino acid; adding a phosphate

source; adding a source of multivalent metal ions; and increasing the pH to precipitate a solid phase fertilizer composition.

13. A method according to claim 12, wherein the liquid comprises fermentation liquid, such as a fermentation by-product.
14. A method according to claim 12, wherein the liquid is a liquidized protein hydrolysate, optionally subjected to one or more steps of pre-treatment.
15. A method according to any one of claims 12-14, wherein the basic L-amino acid is L-arginine and/or L-lysine.
16. A method according to any one of claims 12-15, wherein the polyphosphate source is a phosphate powder dissolved in water.
17. A method according to claim 16, wherein the pH of the dissolved phosphate powder is close to that of the liquid comprising at least one basic L-amino acid.
18. A method according to any one of claims 12-17, wherein the multivalent metal ion(s) are selected from the group consisting of Fe(II), Fe(III), and Ca(II).
19. Use of a complex formed of at least one polyphosphate and at least one basic L-amino acid for to supply nitrogen to plants.
20. Use according to claim 19, wherein the complex includes at least one multivalent metal ion.
21. Use according to claim 19 or 20, wherein the period of time for supply of nitrogen from the complex is prolonged as compared to the supply of the same amount of non-complexed nitrogen and phosphorous under otherwise equivalent conditions
22. Use according to any one of claims 19-21 for the supply of nitrogen to a plant selected from the group consisting of trees, grasses, vegetables and crops.
23. Use according to any one of claims 19-22, wherein the basic L-amino acid is L-arginine and/or L-lysine.
24. Use according to any one of claims 19-23, wherein the metal ion(s) are selected from the group consisting of Fe(II), Fe(III), and Ca(II).
25. Use according to any one of claims 19-24,wherein the number of phosphorous atoms in the polyphosphate is at least or equal to two phosphates.

26. Use according to claim 25, wherein the number of phosphorous atoms in the polyphosphate is at least or equal to six phosphates.

27. Use according to claim 26, wherein the number of phosphorous atoms in the polyphosphate is at least or equal to 700 phosphates, such as 10000.

5

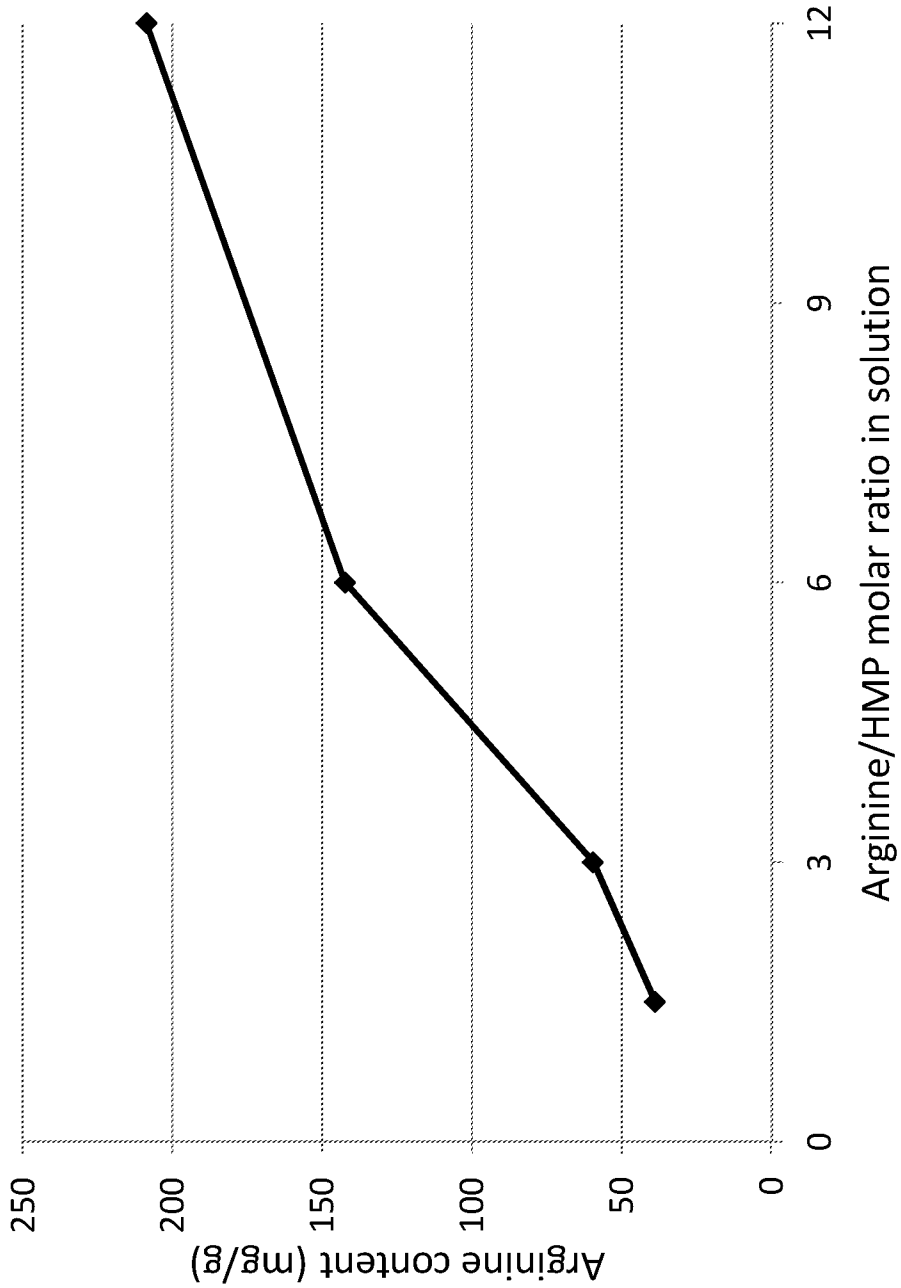

Arginine content (mg/g)
250
200
150
100
50
0
0
3
6
9
12
Arginine/HMP molar ratio in solution

Figure 1

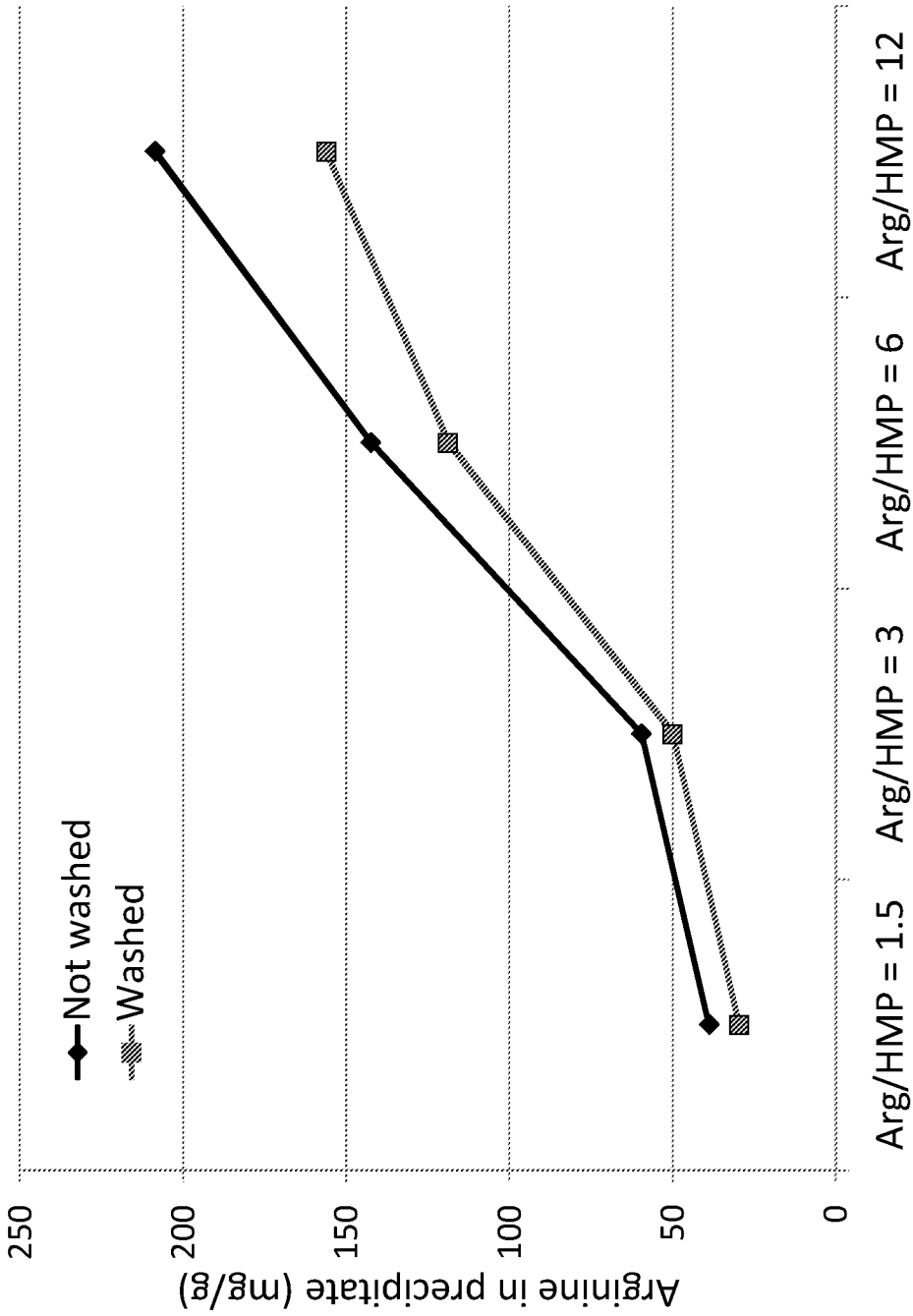

Arginine in precipitate (mg/g)
250
200
150
100
50
0
Not washed
Washed
Arg/HMP = 1.5
Arg/HMP = 3
Arg/HMP = 6
Arg/HMP = 12

Figure 2

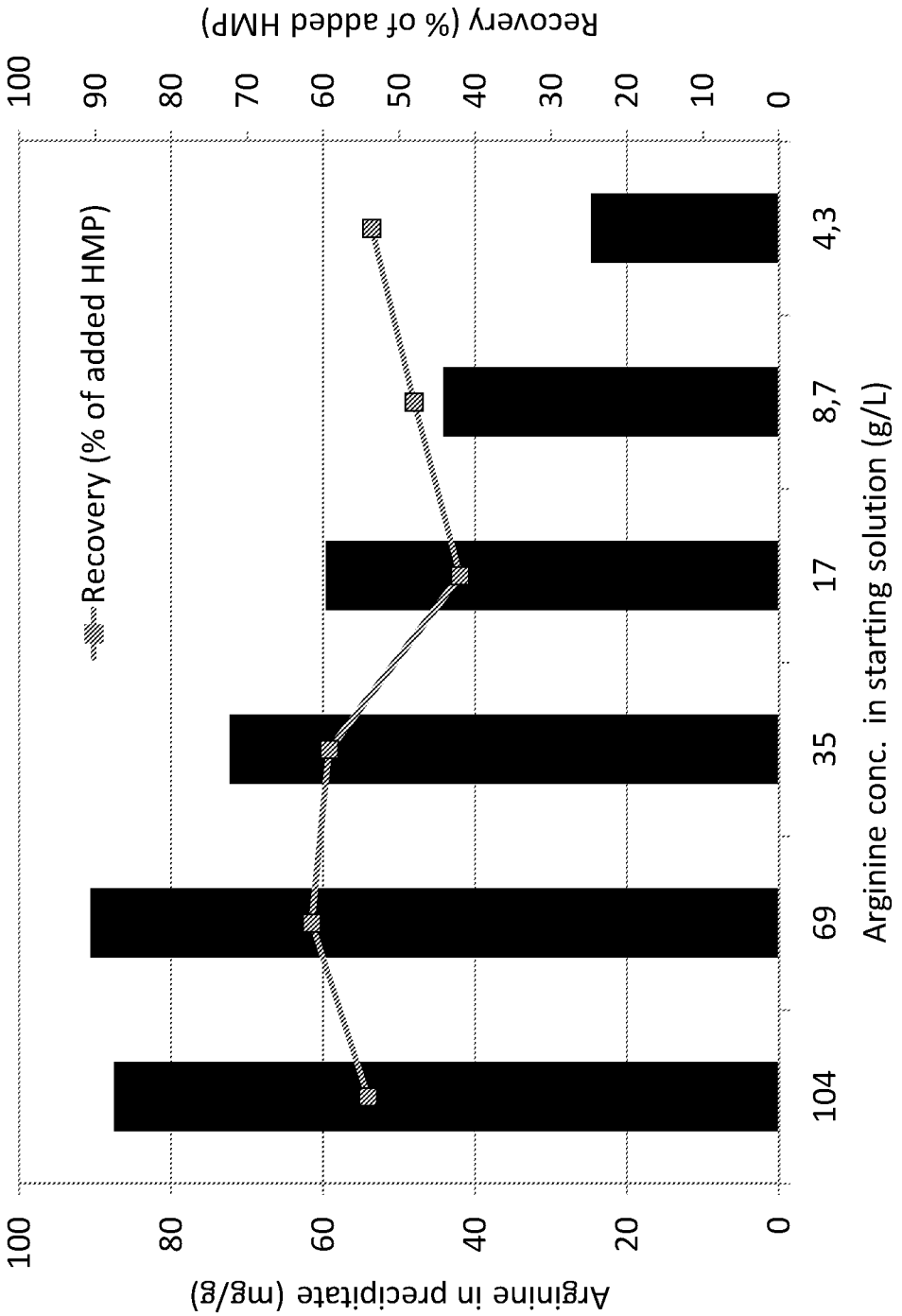

Recovery (% of added HMP)
100
90
80
70
60
50
40
30
20
10
0
Recovery (% of added HMP)
Arginine in precipitate (mg/g)
100
80
60
40
20
0
104
69
35
17
8,7
4,3
Arginine conc. in starting solution (g/L)

Figure 3

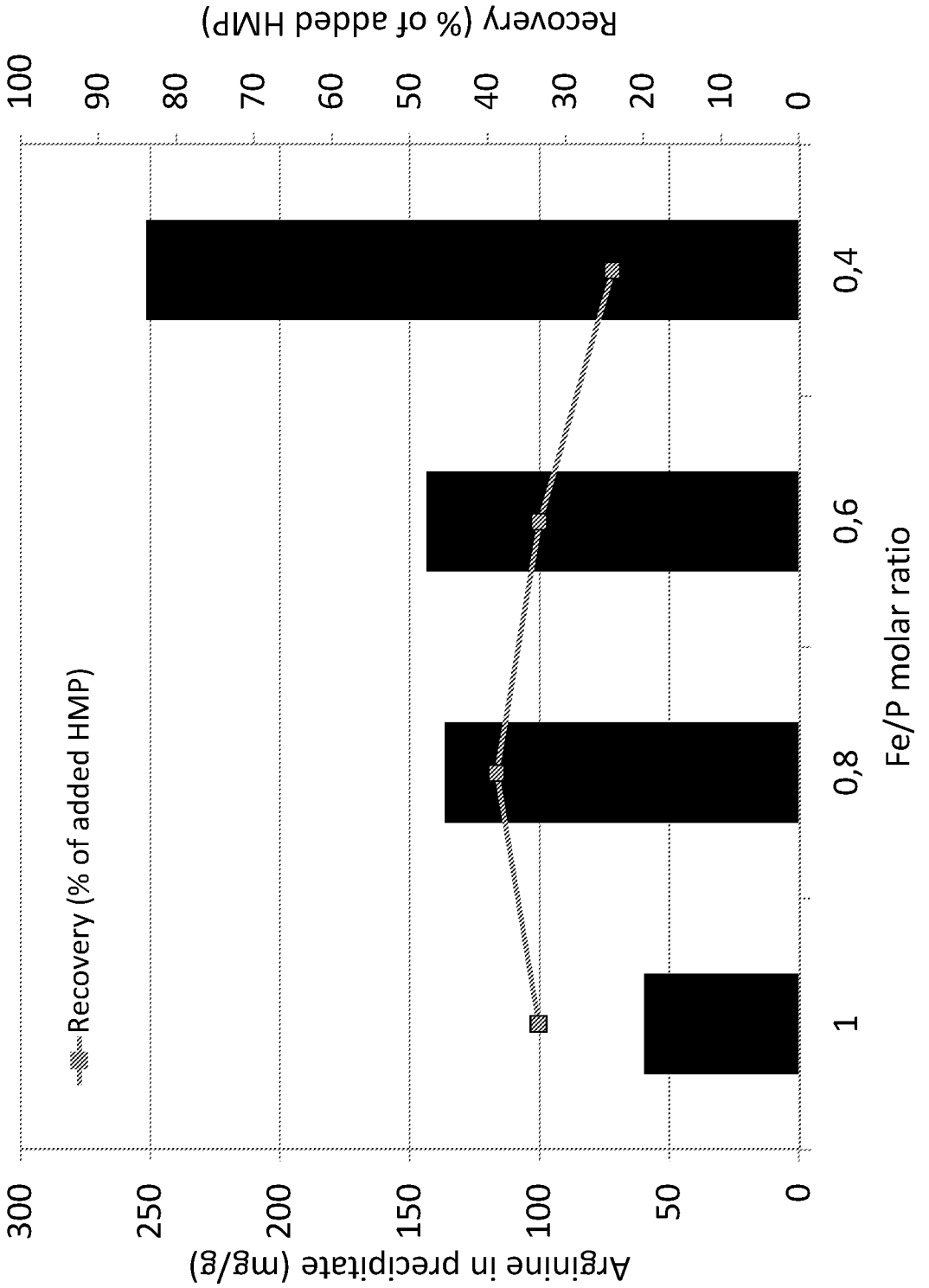

Arginine in precipitate (mg/g)
0
50
100
150
200
250
300
Recovery (% of added HMP)
0
10
20
30
40
50
60
70
80
90
100
Recovery (% of added HMP)
1
0,8
0,6
0,4
Fe/P molar ratio

Figure 4

Figure 5

Metal salt solution	Precipitation	Appearance of precipitate
$FeSO_4$	Yes	Green-grey (light to dark)
$FeCl_3$	Yes	Beige-white
$Al_2(SO_4)_3$	Yes	White
$Al_2(SO_4)_3$ + $FeSO_4$ (1:2)	Yes	Yellow-white
$MnSO_4$	Yes	White
$CaCl_2$	Yes	White
K_2SO_4	No	-

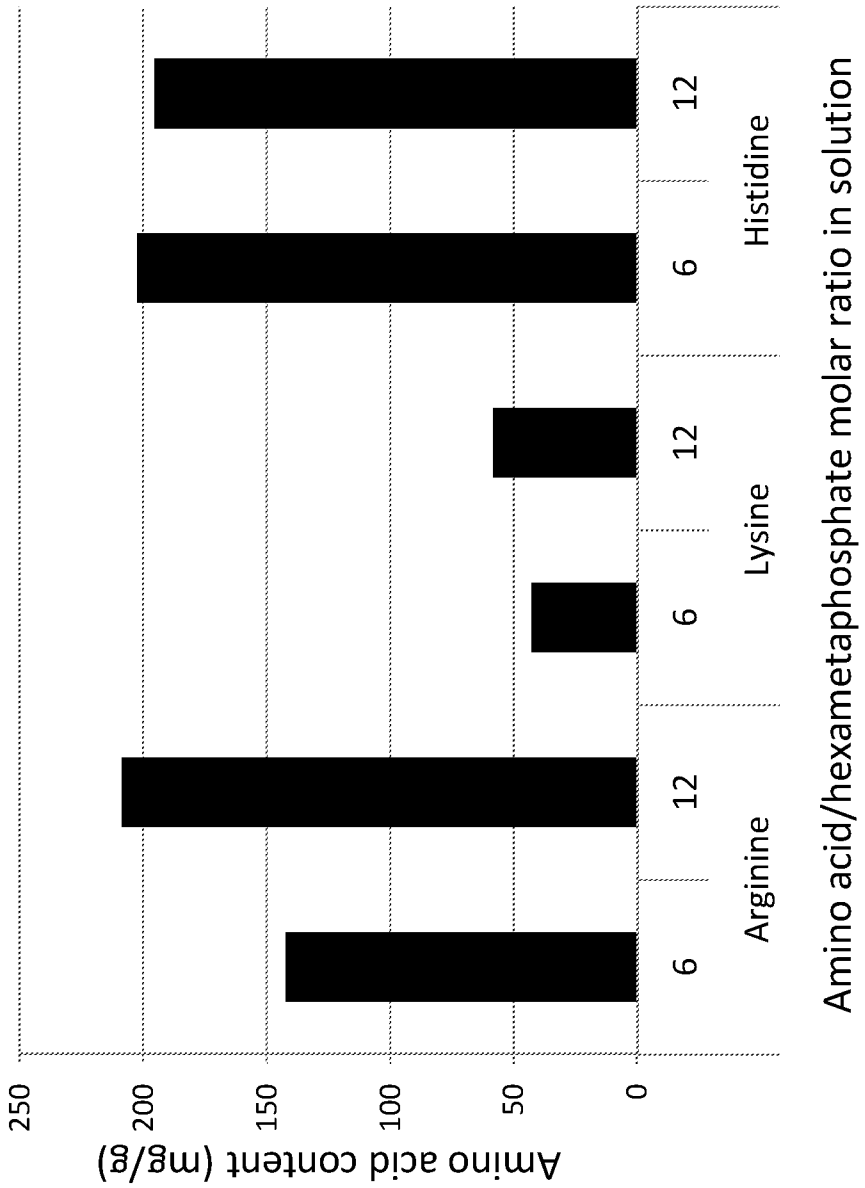

Amino acid content (mg/g)
250
200
150
100
50
0
Arginine
Lysine
Histidine
6
12
6
12
6
12
Amino acid/hexametaphosphate molar ratio in solution

Figure 6

Figure 7

Sample	Composition (in addition to HMP)	Amino acid/HMP ratio in solution	N/P ratio in solution	N/P ratio in precipitate
ref	$FeSO_4$	0	0	0.1
E2	arg + $FeSO_4$	3	2	0.5
E4	arg + $FeSO_4$	12	8	1
E4:2	arg + $FeCl_3$	12	8	2.4
A2	lys + $FeSO_4$	12	4	0.5
A3	his + $FeSO_4$	6	3	1
M3	arg + $MnSO_4$	6	4	0.8
M4	arg + $CaCl_2$	6	4	0.7
M6	arg + $Al_2(SO_4)_3$ + $FeSO_4$	6	4	0.4

Fig. 8

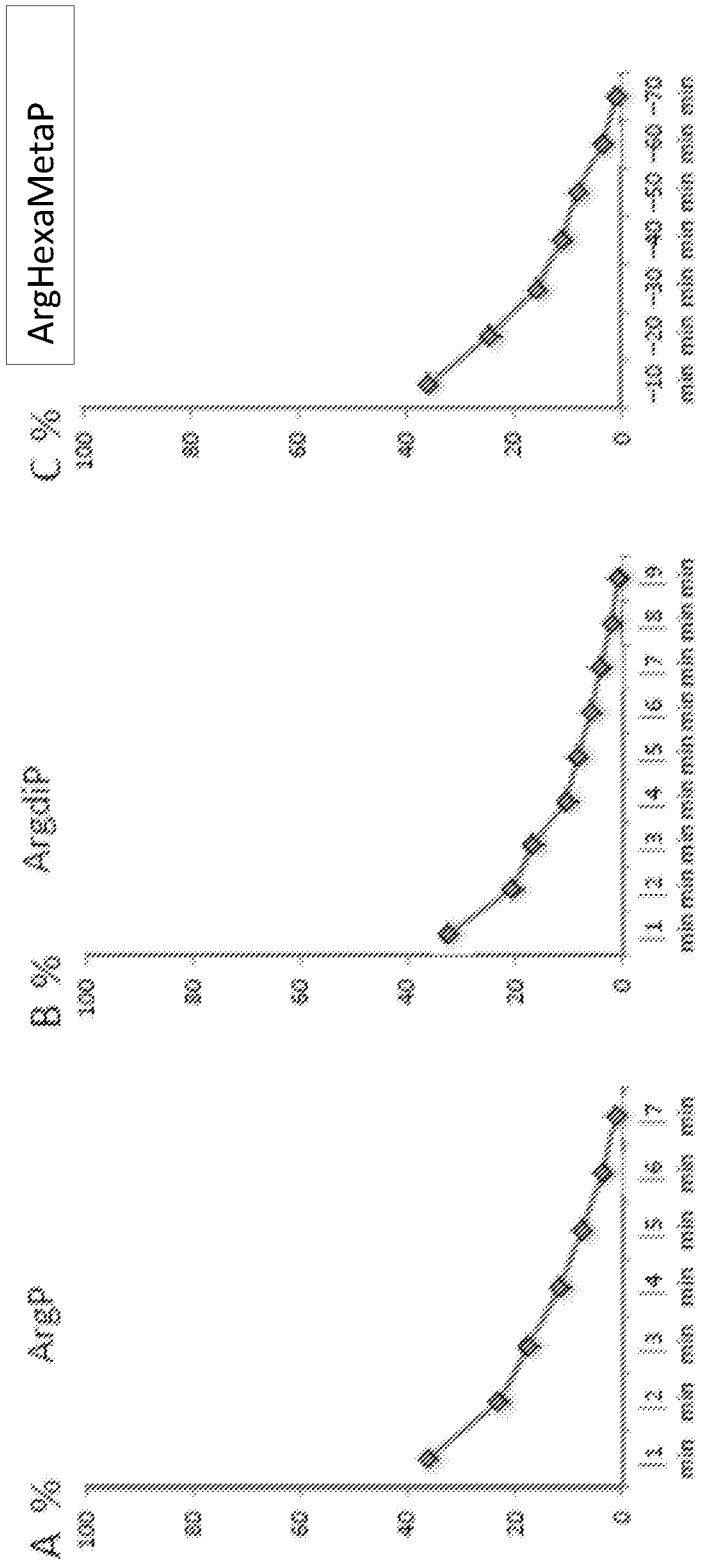

A %
ArgP
B %
ArgdiP
C %
ArgHexaMetaP
100
80
60
40
20
0
1 min
2 min
3 min
4 min
5 min
6 min
7 min
8 min
9 min
10 min
20 min
30 min
40 min
50 min
60 min
70 min

Fig. 9

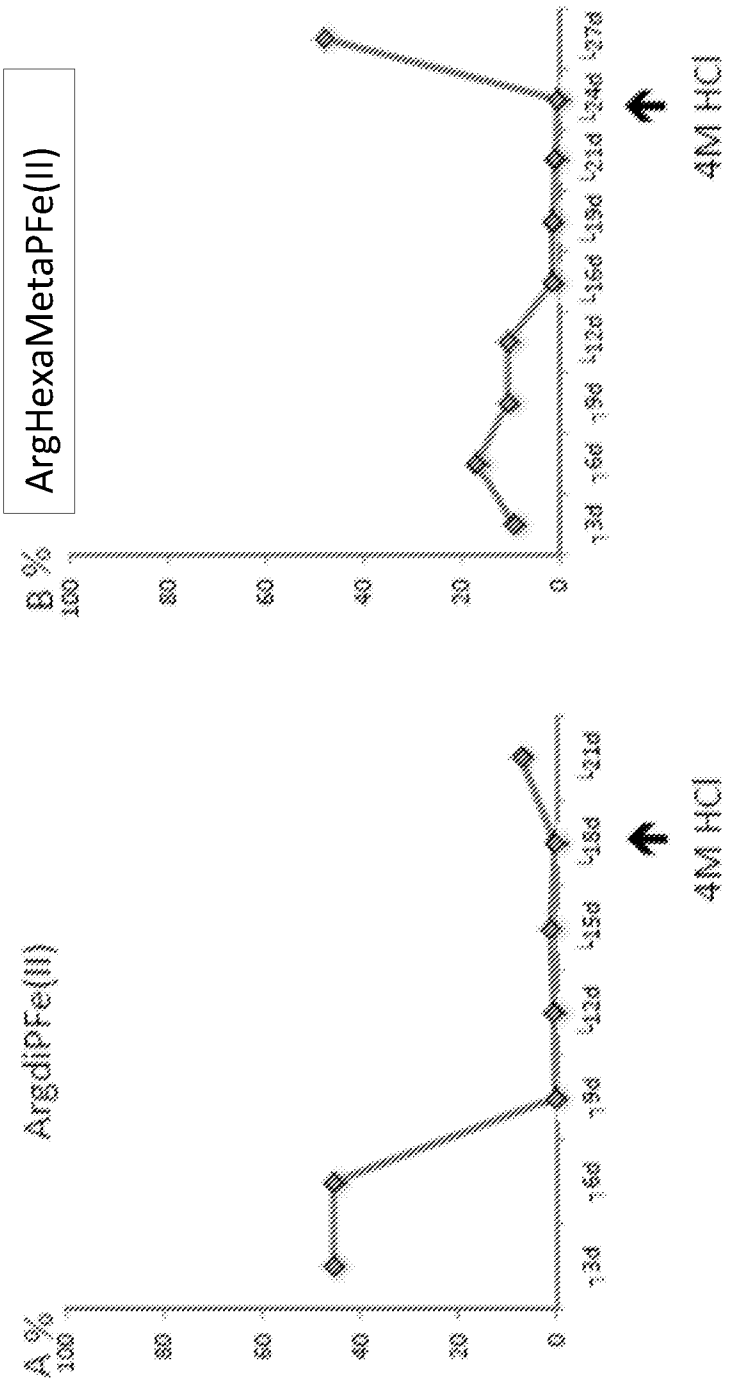

ArgdiPFe(III)
A %
100
80
60
40
20
0
1:24
1:48
1:96
1:120
1:168
1:192
1:216
4M HCl
ArgHexaMetaPFe(II)
B %
100
80
60
40
20
0
1:24
1:48
1:96
1:120
1:168
1:192
1:216
1:240
1:272
4M HCl

Fig. 10

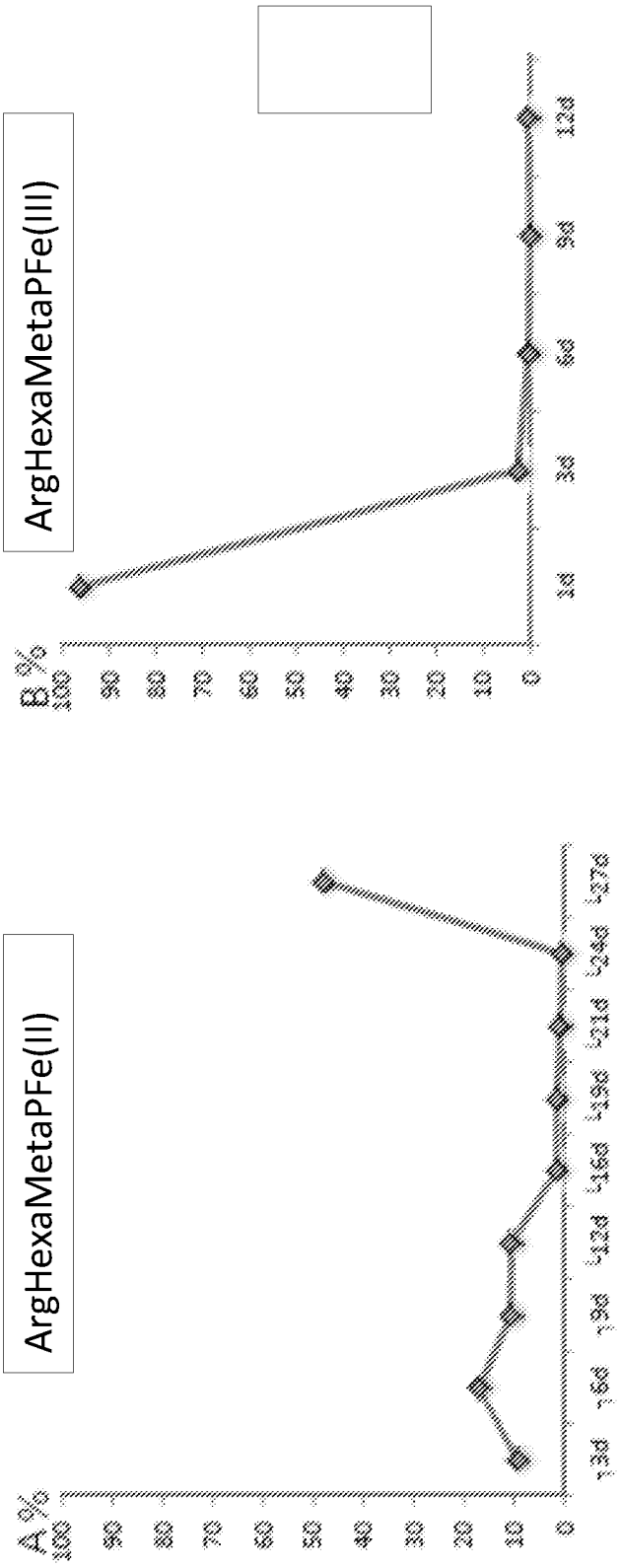

ArgHexaMetaPFe(III)
B %
100
90
80
70
60
50
40
30
20
10
0
1d
3d
6d
9d
12d
ArgHexaMetaPFe(II)
A %
100
90
80
70
60
50
40
30
20
10
0
13d
16d
19d
123d
156d
219d
244d
273d

Fig. 11

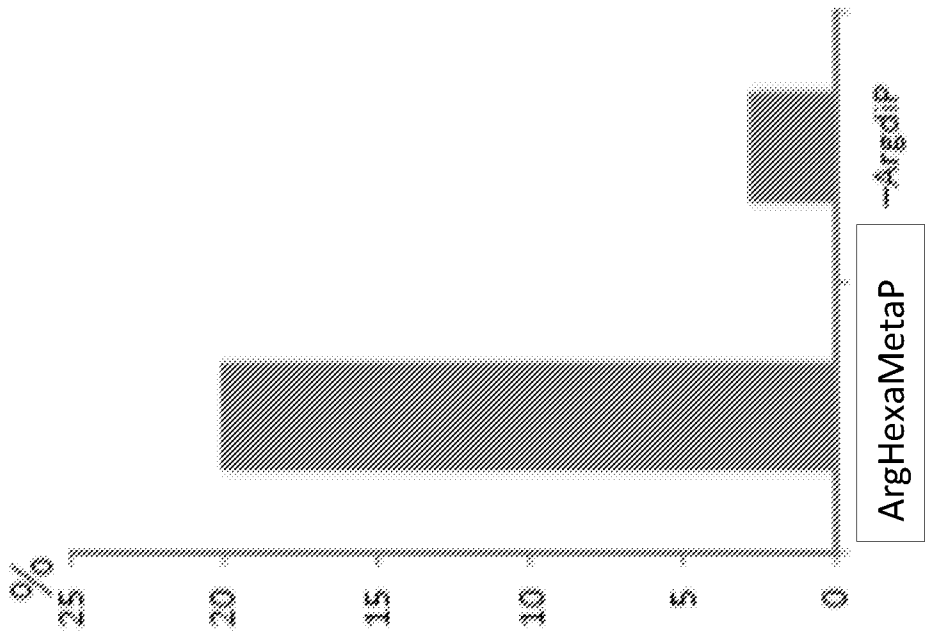


Fig. 12 A



Fig. 12 B

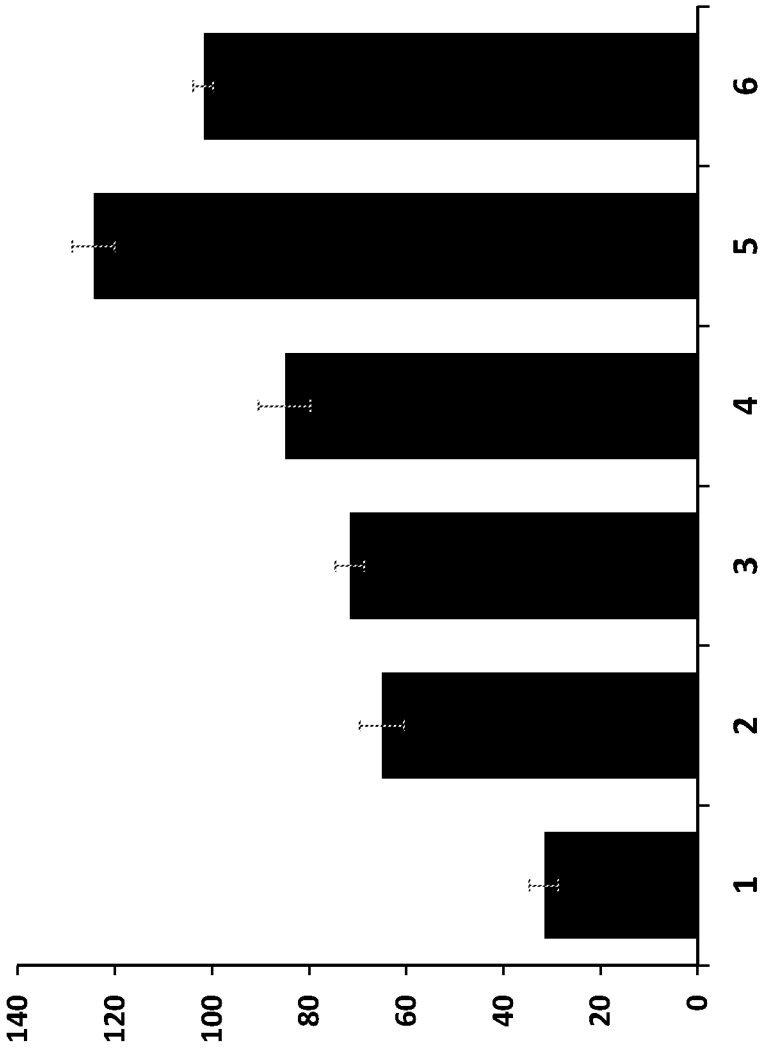


Fig. 12 C

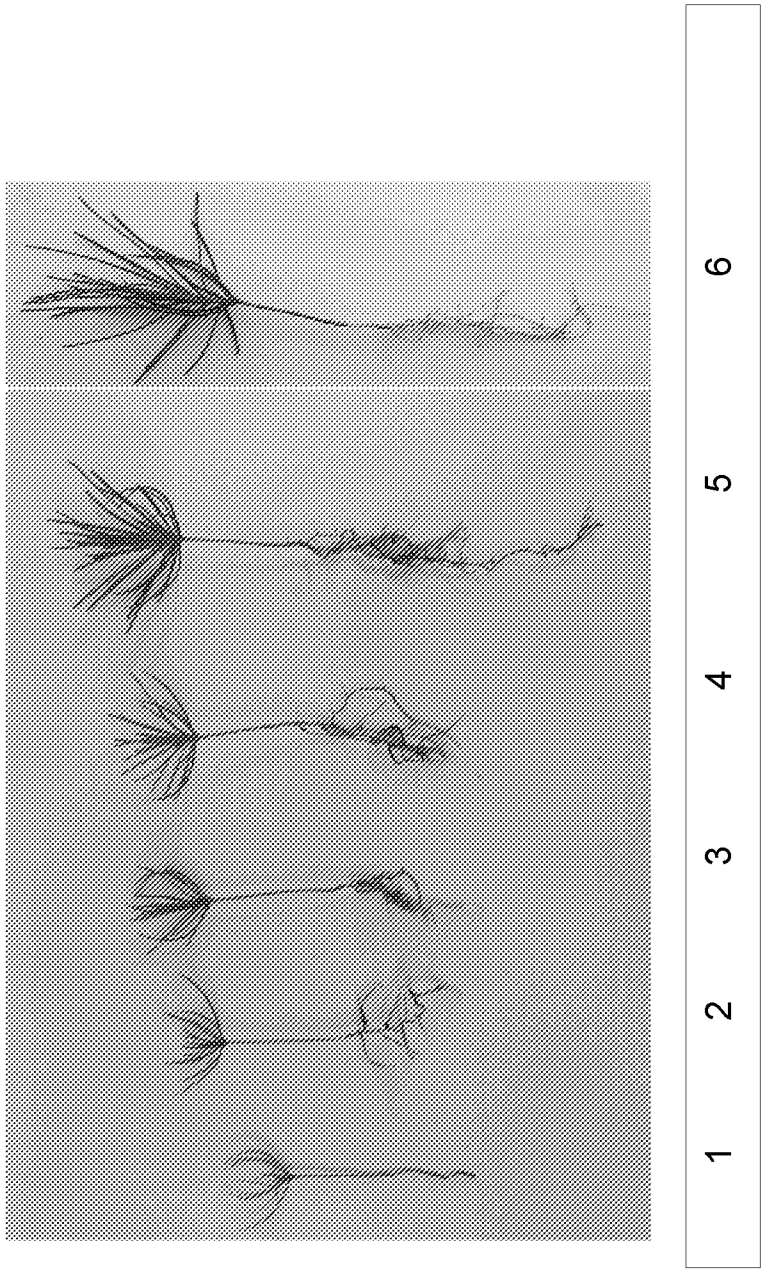


Fig. 13

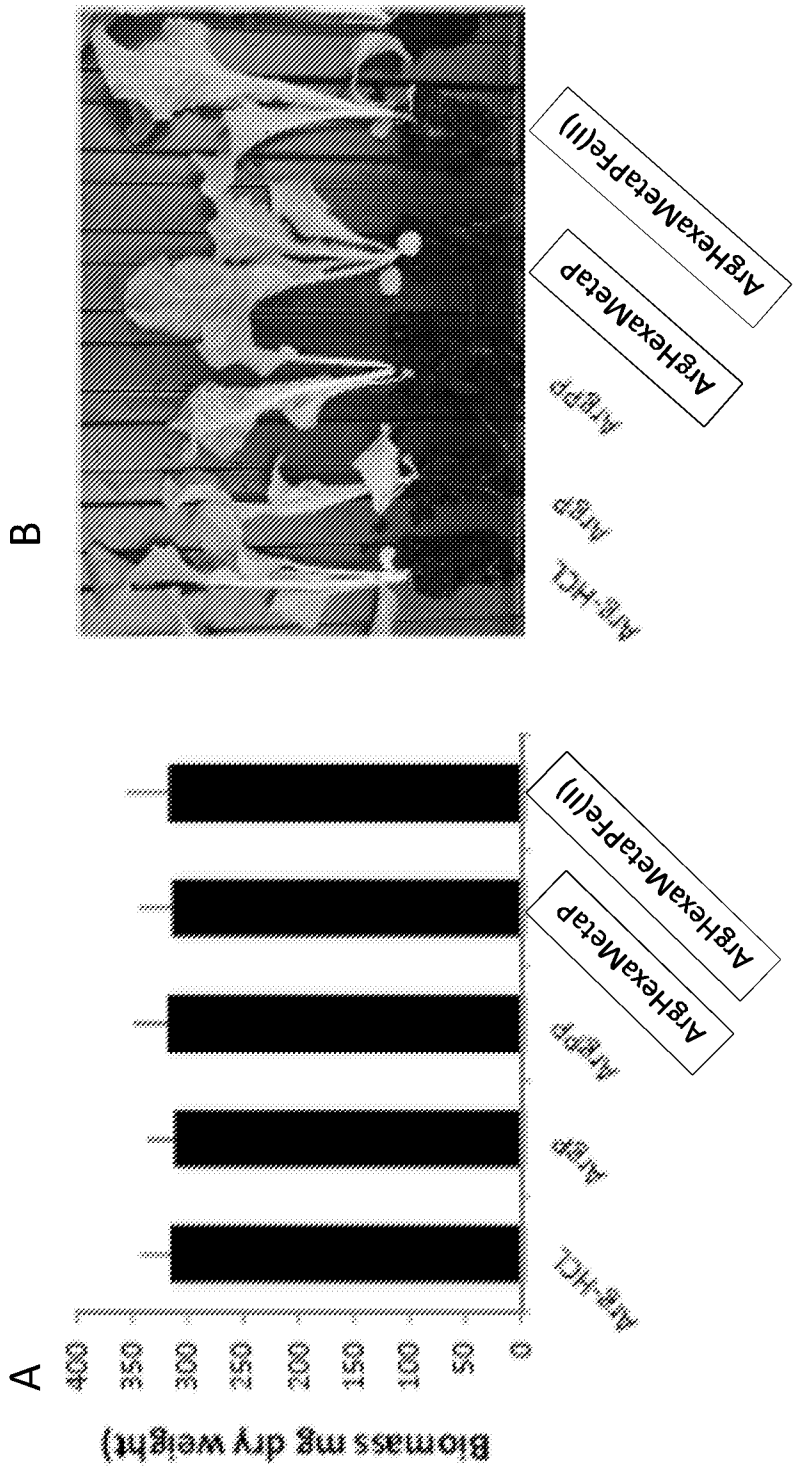

B
ArgHexaMetaPFe(II)
ArgHexaMetap
Argpp
Argp
Arg-HCl
A
Biomass mg dry weight)
400
350
300
250
200
150
100
50
0
ArgHexaMetaPFe(II)
ArgHexaMetap
Argpp
Argp
Arg-HCl

Fig. 14A

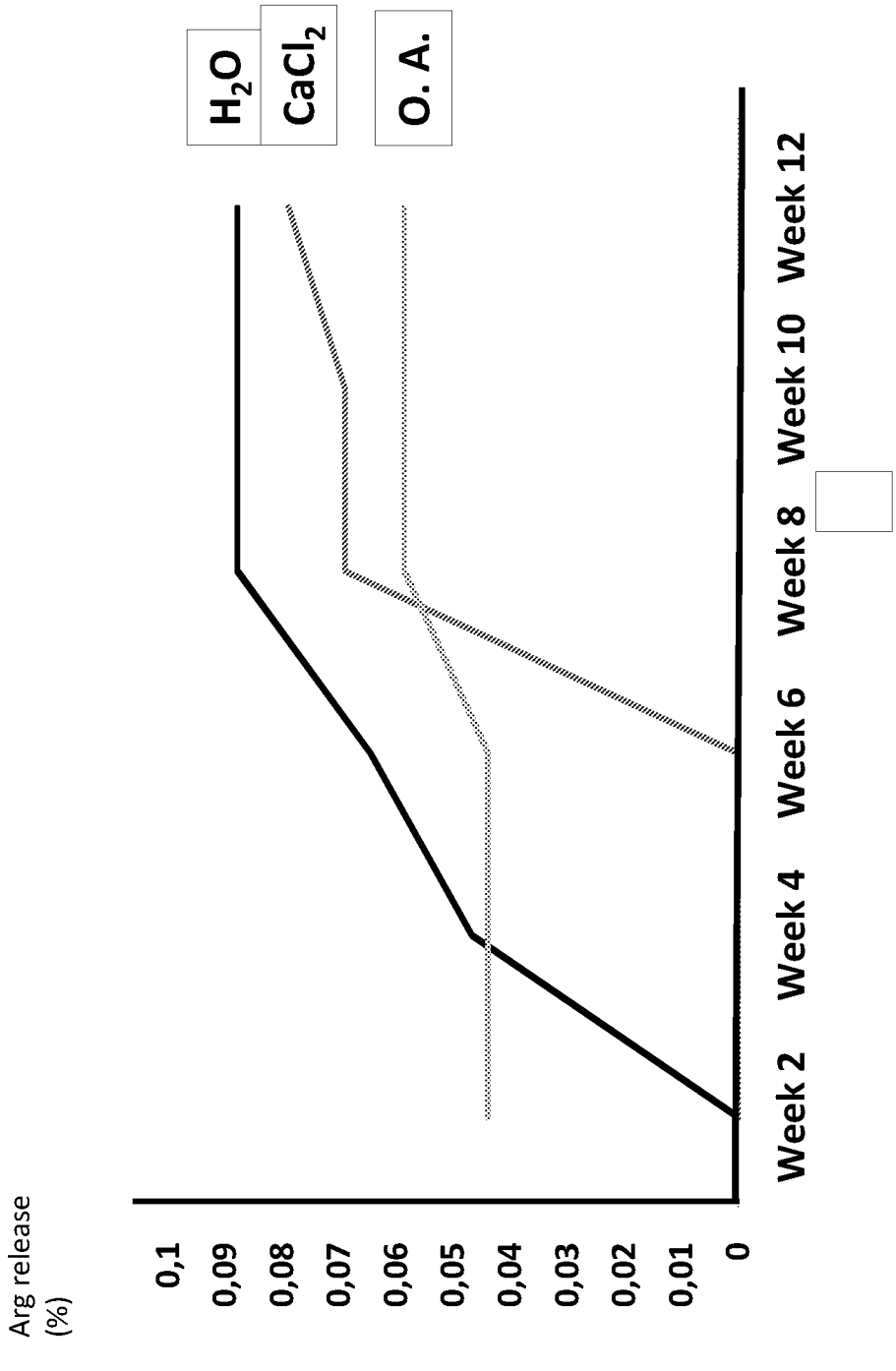
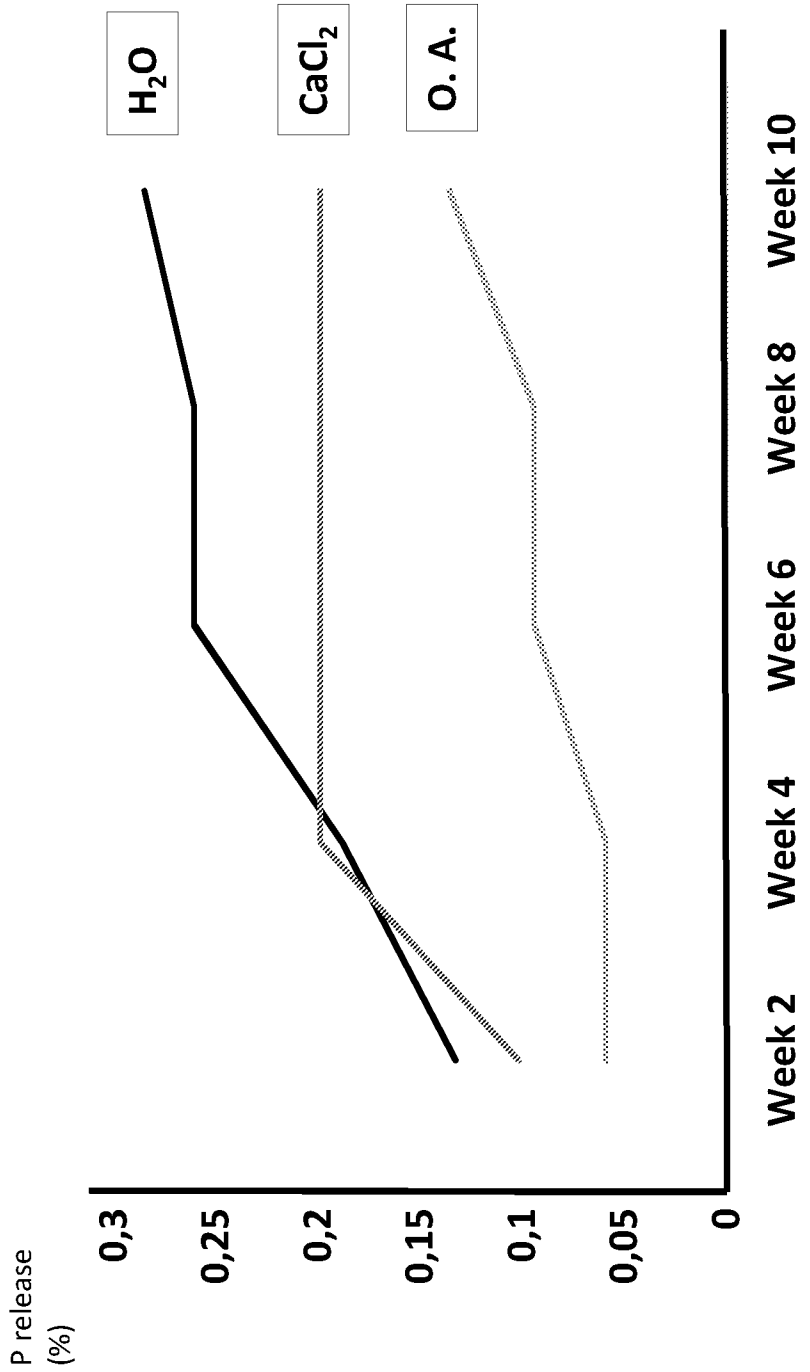

Arg release (%)
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
Week 2
Week 4
Week 6
Week 8
Week 10
Week 12
H2O
CaCl2
O. A.
A

Fig. 14B


P release (%)
0,3
0,25
0,2
0,15
0,1
0,05
0
Week 2
Week 4
Week 6
Week 8
Week 10
H_2O
$CaCl_2$
O. A.
B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2017/050504

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: C05B, C05G

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

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, BIOSIS, CHEM ABS Data, COMPENDEX, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016035090 A1 (CHAUDHRY SUUNIL SUDHAKAR), 10 March 2016 (2016-03-10); page 11, paragraph [0004]; page 13, paragraph [0002] --	1-27
A	US 20100035308 A1 (SUMMER PAUL ET AL), 11 February 2010 (2010-02-11); abstract; claim 1 --	1-27
A	CN 103772069 B (SHANDONG SIWEI TECHNOLOGY CO LTD), 7 May 2014 (2014-05-07); abstract; claim 1 --	1-27
A	WO 2015066691 A1 (UNIV FLORIDA), 7 May 2015 (2015-05-07); claims 1-3 --	1-27

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04-07-2017	04-07-2017

Name and mailing address of the ISA/SE	Authorized officer
Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Moa Emling Telephone No. + 46 8 782 28 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2017/050504

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20040035162 A1 (WILLIAMS RICHARD HENRY ET AL), 26 February 2004 (2004-02-26); abstract; claims 21-22	1-27
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A	CN 104355841 A (HEFEI BULAOCHUANQI HEALTH CARE TECHNOLOGY CO LTD), 18 February 2015 (2015-02-18); abstract; claim 1	1-27
	--	
A	CN 105439739 A (GUIZHOU RES INST OF CHEMICAL IND), 30 March 2016 (2016-03-30); abstract; claim 1	1-27
	--	

International application No.
PCT/SE2017/050504

Continuation of: second sheet

International Patent Classification (IPC)

C05G 1/00 (2006.01)
C05B 15/00 (2006.01)

WO	2016035090	A1	10/03/2016	AU	2014101391	A4	15/01/2015
				CA	2953914	A1	10/03/2016
				US	20170166488	A1	15/06/2017
US	20100035308	A1	11/02/2010	US	8262765	B2	11/09/2012
CN	103772069	B	07/05/2014	NONE			
WO	2015066691	A1	07/05/2015	NONE			
US	20040035162	A1	26/02/2004	NONE			
CN	104355841	A	18/02/2015	NONE			
CN	105439739	A	30/03/2016	NONE			