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(71) **Applicant** *(for all designated States except US)*: **EKOBALANS FENIX AB** [SE/SE]; Forskningsbyn IDEON, S-223 70 Lund (SE).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **THELIN, Gunnar** [SE/SE]; Högseröd 134, S-240 33 Löberöd (SE).

(74) **Agent**: **AWAPATENT AB**; Box 5117, S-200 71 Malmö (SE).

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(54) **Title**: METHOD FOR THE PRODUCTION OF FERTILIZER PRODUCTS FROM RESIDUES

(57) **Abstract**: The present invention describes a process for the production of a fertilizer product from a residual product, said process comprising the steps of dewatering of the residual product and separation of the dry phase and the wet phase, collecting of the dry phase as a product no 1, precipitation of the wet phase to form at least phosphorous (P) in some solid form as a product no 2, stripping of the remaining wet phase to produce ammonia ((NH_3), (g)) which subsequently is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3 and agglomeration of at least one of the products no 2 and/or no 3 for the production of a fertilizer product.

METHOD FOR THE PRODUCTION OF FERTILIZER PRODUCTS FROM RESIDUES

Field of invention

The present invention relates to a process for the production of a fertilizer product from a residual product.

Technical Background

Different treatments of residual products, such as e.g. sludge or digestion residues, are known. It is e.g. known to dewater and separate a sludge and subsequently precipitate different substances for use as fertilizer additives. Different such processes have been disclosed. For e.g. in US4098006 there is disclosed a process for drying organic waste, such as sewage sludge, by contacting the organic waste with hot vapors. Partial dewatering of the organic waste is achieved by admixture with a recycled portion of dried solids followed by extrusion of the mixture. The resultant extrudate is then dried, and the unrecycled portion is extruded in a separate operation to form compacted granules said to have good flow characteristics and being suitable for application by commercial fertilizer spreaders. Moreover, in US5916448 there is described a method said to improve the dewatering and odor reduction characteristics of a liquid wastewater sludge, sediment, or soils to ultimately form a dewatered solid residual that includes nutrition enhancement of a resultant material that is suitable for distribution and marketing, and for incorporation in a fertilizer blend. The method includes the addition of selective acids, such as sulphuric acid, phosphoric acid or nitric acid, and bases, magnesium oxide, calcium oxide, potassium oxide, ammonia or calcium hydroxide, to the liquid sludge which forms insoluble precipitates, and enmeshes the solids in the sludge to form a granular product.

Although there exist several known processes today, none of these provide an optimal solution for producing fertilizer products from residual products. One aim of the present invention is to provide a process involving the optimal set of steps. Moreover, another purpose of the present invention is to provide improvements within different single steps of the process, such

as in relation to e.g. the first treatment of the residual product and also in relation to the end treatment when providing a fertilizer product.

Summary of invention

The first purpose above is achieved by a process for the production of a fertilizer product from a residual product, said process comprising the steps of:

- dewatering of the residual product and separation of the dry phase and the wet phase;
- collecting of the dry phase as a product no 1;
- precipitation of the wet phase to form at least phosphorous (P) in some solid form as a product no 2;
- stripping of the remaining wet phase to produce ammonia ((NH_3), (g)) which subsequently is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3;
- agglomeration of at least one of the products no 2 and/or no 3 for the production of a fertilizer product.

The residual product used for the present invention may e.g. be sludge (wastewater sludge), digestate(s), manure residues, such as liquid manure not being fermented, or the like.

The step of dewatering of the residual product and the separation of the dry phase and the wet phase is normally made simultaneously. Generally in this context, it is important to understand that different kind of process equipment types may be used to perform the process according to the present invention, such as continuous processing but also batch or semi-batch operations. Some steps are naturally performed batch-wise, however other steps may also be performed continuously.

Moreover, according to the present invention there may be a negative pressure applied from the dewatering to the stripping and subsequent reaction between ammonia ((NH_3), (g)) and an acid or a mixture of two or several acids and/or salt solutions. This implies that a negative pressure (underpressure) is applied from the dewatering step and forward to drive any produced gaseous (volatilized) ammonia towards and into the container

intended to collect this gas component, i.e. the container where ammonia is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3. Such ammonia may e.g. be produced in minor amounts already at the dewatering step or for instance in the precipitation.

As may be noted from above, the process according to the present invention comprises dewatering/separation, precipitation, ammonia generation, acid treatment and provision of end product, the latter being made by agglomeration, such as e.g. granulation, pelletization and compaction.

Detailed description

The present invention provides a method for treatment of residual products which focuses on optimization of total yield of nutrients and hence provides economic advantages in comparison to today known processes. In view of the purpose disclosed above and dependent on the residual product, it may be of interest to pretreat the influx before the dewatering and separation. Such known pretreatments today only have the purpose of providing a mixture which is easier to dewater. According to the present invention, however, the optional pretreatment is provided to optimize the total yield of nutrients as well as providing a mixture which is easy to dewater and separate. According to one specific embodiment of the present invention, the pretreatment is any one of flocculation, fiber addition, pH adjustment, addition of a divalent ion solution, magnetic field provision or a combination thereof.

Generally, flocculation is a process where colloids come out of suspension in the form of floc or flakes. In this case, flocculation is performed by adding a substance, e.g. a polymer, which improves the dewatering ability of the residual product by binding organic material into larger aggregates.

Added fiber improves the dewatering ability as suspended organic material (SOM) is bound to the added fibers. The fibers can act as “filter material” in the filtering process. When a sludge including fibers is filtered, fibers will be deposited on the filter and this will greatly enhance the specific surface area available for binding of SOM. This effect can also be used by first filtering a small amount of sludge with fiber added and then sludge without fiber. Alternatively, the sludge can be filtered through a fiber material.

Fiber addition may be a better alternative than polymer addition, since the intended types of fiber is much cheaper than polymers, and the added fiber can be used as energy in the dry phase. The risk of both flocculation and fiber addition is that too large nutrient fractions are allocated to the dry phase.

Increasing the pH value using e.g. sodium hydroxide before dewatering will lead to the release of positively charged nutrient ions into the wet phase and will decrease the need for pH increase later in the precipitation step. However, the dewatering ability will probably decrease, since the addition of monovalent cations will disperge the organic material. When negatively charged ends of the organic material are occupied by monovalent cations the different pieces of organic material will repel each other.

The addition of a divalent ion solution, e.g. calcium or magnesium hydroxide, will release positively charged nutrient ions and lower the need for pH increase later in the precipitation step, as in the above case. However, addition of divalent cations will not disperge the organic material, but instead bind it together. A divalent calcium ion can bind to two different pieces of organic material and thus probably improve the dewatering ability.

If a residual product is pumped through a container or a pipe where a strong magnetic field is applied across the container or pipe cell membranes will rupture and nutrients contained within cells will enter into the solution and increase the share of nutrients that end up in the wet phase after dewatering. This will probably reduce the dewatering ability of the residual product. Therefore, the technique will probably be used in combination with anyone of flocculation, fiber addition or addition of a divalent ion solution. UV-light or ultrasound are alternatives to a magnetic field, and also possible to use according to the present invention. Moreover, pretreatments such as treatment with ozone are also possible according to the present invention.

There are also other advantages with the process disclosed according to the present invention. One such is the removing of ecologically harmful substances in the process. Therefore, according to one specific embodiment of the present invention, the step of dewatering of the residual product and separation of the dry phase and the wet phase also involves removing of heavy metal compounds which are collected in the dry phase. Heavy metals

in the residual product are to a very high degree strongly bound to the organic material. Thus a dewatering step removing organic material from the solution will simultaneously remove the bulk of the heavy metals from the solution. This effect can be increased by the addition of substances with a high capacity of binding heavy metals.

As may be understood from above, the heavy metals follow the dry phase. However, the heavy metals shall eventually also be separated from the dry phase and be deposited. Such separation from the dry phase may be performed both before, such as by use of a substance with a high capacity of binding heavy metals as disclosed above, and also after the combustion of the dry phase. In the case of separation after the combustion of the dry phase (or product no 1), this may be performed either by first removal of phosphorous and other nutrients from the ash so that the heavy metals afterwards will be found in a residue, or by first removal of the heavy metals from the ash so that the nutrients will be found in a residue. Therefore, according to one specific embodiment of the process according to the present invention, the heavy metal compounds are separated either from the dry phase (product no 1) before combustion, or from the ash after combustion of the dry phase (product no 1).

Generally, in the context of the present invention it is important to realize that the dry phase may be seen as or called the organic phase. According to the process of the present invention, organic material is intended to be collected in the dry phase. Fact is that the maximum level of organic material in the wet phase is intended to be set at 5%. In other words, the separation of a dry and wet phase may also be seen as a separation of organic material so that the level of such organic material is depressed in the wet phase.

Besides the none-active process step of collecting of the dry phase, precipitation of the wet phase to form at least phosphorous (P) in some solid form is performed after the separation step. According to the present invention, different solid P forms are possible. Examples thereof are struvite (ammonium magnesium phosphate, formula $((NH_4)MgPO_4 \cdot 6H_2O)$), apatites, other calcium phosphates or combinations thereof. Apatite is a group of

phosphate minerals, usually referring to hydroxyapatite, fluorapatite, chlorapatite and bromapatite. The formulas of the admixtures of the four most common are written as $Ca_{10}(PO_4)_6(OH, F, Cl, Br)_2$. It is important to understand that many other solid forms are possible according to the present invention, such as e.g. calcium phosphate ($Ca_3(PO_4)_2$).

The precipitate, in this example struvite, may be produced by e.g. adding magnesium dichloride ($MgCl_2$) and sodium hydroxide (NaOH), either in one container e.g. simultaneously or in different containers sequentially. Either of them may be added first in the process. The precipitate may also be produced by increasing the pH value of the wet phase by stripping CO_2 (g) from the mixture. At pH value about 8-9, struvite begins to precipitate. After achieving a struvite solution, as particles and struvite from a magnesium chloride treatment container, as struvite solution from a sodium hydroxide treatment container, or in fact as both from a combined treatment container, this solution is fed to a filter, where the precipitate struvite is separated and thereafter obtained by dewatering. Filtration is one suitable technique for this step, however also other separation techniques are possible to use.

Irrespective of actual pretreatment and type of produced precipitation, it is according to present invention possible to precipitate at least 95% of the phosphorous in the wet phase.

It is important to understand that when describing precipitations, both crystalline and amorphous precipitations, as well as combinations thereof, are contemplated in relation to the present invention. One advantage of producing struvite is the fact that it crystallizes very clearly. Moreover, seed charging may be used during the precipitation to increase the efficiency of the process step. Furthermore, e.g. struvite may in fact be produced in minor amounts to function as a seed promoting the precipitation of other amorphous and/or crystalline precipitates. In other words, in this case struvite only functions as a precipitation promoter and is not intended as the main precipitation component to be produced.

As mentioned above, $MgCl_2$ and NaOH may be used as precipitation promoting substances for precipitation of P solids. Other known such substances are magnesium sulphate ($MgSO_4$), calcium chloride ($CaCl_2$),

calcium hydroxide ($Ca(OH)_2$), calcium sulphate (gypsum, $CaSO_4$* ½H_2O) and in fact also sea water or bittern, a residual product after the evaporation and crystallization of sodium chloride from brines and sea water. Bittern contains, in concentrated form, the calcium and magnesium chlorides and sulfates, bromides, iodides, and other chemicals originally present in the brine. These substances are known for usage in precipitation steps as according to above. However, the present invention also provides one new substance not known for such usage. Therefore, according to one specific embodiment of the present invention, green liquor sludge is used as the precipitation promoting substance. Green liquor sludge is a residual product from pulping processes and it contains inter alia metal salts, mainly sulphides including magnesium sulphide.

There are other nutrients which may be recovered by the process according to the present invention. According to one specific embodiment of the present invention, also potassium (K) and/or nitrogen (N) in some solid form is precipitated in the step of precipitation of the wet phase. The amount of potassium in the residual product used varies a lot. The purpose of the invention, is of course to obtain as much potassium as possible from the start residual product. If potassium is present, it is present in the wet phase after separation according to the invention. According to the present invention it is possible to precipitate at least 50%, such as at least 70%, e.g. in the range of 70-95%, of the potassium present in the wet phase. Nitrogen may be produced in different solid forms. According to one specific embodiment of the present invention, nitrogen (N) is precipitated in some solid nitrate form.

As is mentioned above, according to the present process, ammonia production is involved. Such a production may comprise further processing of the wet phase before the actual stripping. According to one specific embodiment, the wet phase is further processed to an ammonium (NH_4^+) enriched solution which is subsequently stripped to produce ammonia ((NH_3), (g)) which then is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3. According to yet another specific embodiment, the wet phase is further processed to an ammonium (NH_4^+) enriched solution by contacting the

remaining wet phase with at least one ion exchanger. Such treatment may e.g. be performed in a zeolite container where also an eluent, such as sodium chloride (NaCl), is added. Zeolite functions as an ion exchanger, but it is important to understand that also other such exchangers may be used. After this step "clean" water solution, which may be recirculated back to the dewatering or in fact used as clean process water, and ammonium solution is produced. The ammonium solution is fed to a stripper, e.g. holding a pressure of 0.5-0.9 bar, where ammonia ((NH_3), (g)) and "clean" water solution is produced, the latter e.g. processed together with clean water solution from the ion exchange treatment. The ammonia is flowed into an acid tank so that remaining nitrogen (N) is produced in some solid form. Different acids may be used, such as e.g. sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3), the latter however not in clean form as ammonium nitrate (NH_4NO_3), which is explosive, of course is undesirable. Moreover, a mixture of two or several acids and/or salt solutions may also be used. For instance if sulphuric acid is used, ammonium sulphate ($(NH_4)_2SO_4$) is produced as the nitrogen solid form after the acid treatment. The nitrogen solid form is obtained after sedimentation. After this treatment, the present process achieves a level of at least 90% of the nitrogen (N) in the wet phase being collected in a solid form.

As mentioned above, the last step according to the present process is the agglomeration of at least one of the obtained solid products from the process for the production of a fertilizer product. Moreover, according to one specific embodiment of the present invention, substances from ash from combusted product no 1, i.e. obtained from the separation, or from other types of ash is admixed with at least one of the products no 2, i.e. obtained from the precipitation, and/or 3, i.e. from the acid treatment, for the production of a fertilizer product.

The agglomeration may according to the present invention be performed in different ways and by different means. According to one specific embodiment of the present invention, the agglomeration is performed by granulation, pelletization or compaction. Granulation may be preferred in

some applications according to the invention. Granulation may e.g. be performed by drum granulation or by means of a fluidized bed.

Furthermore, the agglomeration step may besides the actual mechanical treatment also involve other treatment, such as e.g. adding at least one agglomeration promoting substance. According to one specific embodiment of the present invention, the agglomeration is performed by granulation and the granulation involves adding a binder, said binder in this case being the agglomeration (granulation) promoting substance.

Generally, it is important to understand that different steps of the process according to the present invention may be performed in different plants, e.g. if this is efficient or necessary for a specific case or application.

Claims

1. Process for the production of a fertilizer product from a residual product, said process comprising the steps of:
- dewatering of the residual product and separation of the dry phase and the wet phase;
- collecting of the dry phase as a product no 1;
- precipitation of the wet phase to form at least phosphorous (P) in some solid form as a product no 2;
- stripping of the remaining wet phase to produce ammonia ((NH_3), (g)) which subsequently is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3;
- agglomeration of at least one of the products no 2 and/or no 3 for the production of a fertilizer product.

2. Process according to claim 1, wherein the wet phase is further processed before the stripping.

3. Process according to claim 2, wherein the wet phase is further processed to an ammonium (NH_4^+) enriched solution which is subsequently stripped to produce ammonia ((NH_3), (g)) which then is reacted with an acid or a mixture of two or several acids and/or salt solutions to produce nitrogen (N) in some solid form as a product no 3.

4. Process according to claim 3, wherein the wet phase is further processed to an ammonium (NH_4^+) enriched solution by contacting the remaining wet phase with at least one ion exchanger.

5. Process according to any of claims 1-4, wherein there is a negative pressure applied from the dewatering to the stripping and subsequent

reaction between ammonia ((NH_3), (g)) and an acid or a mixture of two or several acids and/or salt solutions.

6. Process according to any of claims 1-5, wherein pretreatment of the residual product is performed before the dewatering and which pretreatment is any one of flocculation, fiber addition, pH adjustment or addition of a divalent ion solution, magnetic field provision or a combination thereof.

7. Process according to any of claims 1-6, wherein the step of dewatering of the residual product and separation of the dry phase and the wet phase also involves removing of heavy metal compounds which are collected in the dry phase.

8. Process according to claim 7, wherein the heavy metal compounds are separated either from the dry phase (product no 1) before combustion, or from the ash after combustion of the dry phase (product no 1).

9. Process according to any of claims 1-8, wherein green liquor sludge is used as a precipitation promoting substance.

10. Process according to any of claims 1-9, wherein also potassium (K) and/or nitrogen (N) in some solid form is precipitated in the step of precipitation of the wet phase.

11. Process according to claim 10, wherein also nitrogen (N) in some solid nitrate form is precipitated in the step of precipitation of the wet phase.

12. Process according to any of the preceding claims, wherein substances from ash from combusted product no 1 or from other types of ash is admixed with at least one of the products no 2 and/or 3 for the production of a fertilizer product.

13. Process according to any of the preceding claims, wherein the agglomeration is performed by granulation, pelletization or compaction.

14. Process according to claim 13, wherein the agglomeration is performed by granulation.

15. Process according to claim 14, wherein the granulation is performed by drum granulation or by means of a fluidized bed.

16. Process according to any of the preceding claims, wherein the agglomeration involves adding at least one agglomeration promoting substance.

17. Process according to claim 14 or 15, wherein the agglomeration is performed by granulation and the granulation involves adding a binder.

INTERNATIONAL SEARCH REPORT

International application No.
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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: C02F, C05F

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20090206028 A1 (JIANG ANPING ET AL), 20 August 2009 (2009-08-20); paragraphs [0003], [0014], [0025], [0026], [0027]; figure 1 --	1-3, 5-17
X	US 6464875 B1 (WOODRUFF STEVEN R), 15 October 2002 (2002-10-15); column 2, line 55 - line 62; column 5, line 56 - line 59; column 6, line 2 - line 5; column 6, line 22 - line 26; column 7, line 19 - line 22; column 8, line 40 - line 45; figure 1 --	1-3, 5-17
A	WO 2006005733 A1 (HANS HUBER AG MASCH & ANLAGENB ET AL), 19 January 2006 (2006-01-19); page 10, line 28 - line 32; page 12, line 26 - line 28; page 13, line 15 - line 20; figure 1 -- --------	1-17

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

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Cited literature, if any, will be enclosed in paper form.

US	20090206028	A1	20/08/2009	US	7909995	B2	22/03/2011
US	6464875	B1	15/10/2002	NONE			
WO	2006005733	A1	19/01/2006	DE	102004033310	A1	26/01/2006
				EP	1768933	A1	04/04/2007