

A PHOSPHATE-BASED PRODUCT RECOVERY METHOD

Technical Field

The present invention relates to a method of recovering a phosphate-based product.

5 Background

Phosphorus is a non-renewable resource which is usually expensive to recover from waste. For example, phosphorus is found in sewage sludge in large amounts. The phosphorus is sometimes recovered but, in many instances, the sewage sludge is disposed in landfills. Current methods for recovering the phosphorus involve high cost in
10 view of high temperature conditions or energy intensive conditions required for the recovery or the use of many process steps in recovering the phosphorus.

Thus, there is a need for an improved process for recovering phosphates.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved
15 method for recovering phosphates.

According to a first aspect, the present invention provides a method of recovering a phosphate-based product, the method comprising:

- mixing a phosphate-containing material with an ammonium-based solution, wherein the mixing is at a temperature of 15-95°C to form a slurry;
- 20 - filtering the slurry to separate solids from a filtrate; and
- adjusting the pH of the filtrate to precipitate the phosphate-based product from the filtrate.

The phosphate-based product recovered may comprise ≥ 35 wt % phosphates based on
25 the total weight of the phosphate-based product.

The ammonium-based solution may be any suitable ammonium-based solution. For example, the ammonium-based solution may comprise a mineral acid.

The mixing may be under suitable conditions. According to a particular aspect, the mixing may be carried out at a low pressure. For example, the pressure may be 1-2 bars.

The mixing may comprise mixing a suitable amount of the phosphate-containing material with a suitable amount of the ammonium-based solution. According to a particular aspect, the mixing may comprise mixing the phosphate-containing material with the ammonium-based solution in a solid:liquid ratio of 1:3-1:8.

- 5 The solids separated from the filtering may comprise calcium-based product. The calcium-based product may be any suitable calcium-based product. For example, the calcium-based product may be for use in sequestering carbon dioxide.

The adjusting the pH may comprise adjusting the pH to a suitable pH. For example, the pH may be in the range of 5-12. The pH may be adjusted using any suitable solvent. For
10 example, the adjusting may comprise adding an ammonium-containing fluid. The ammonium-containing fluid may be an ammonium-containing gas, an ammonium-containing solution, or a mixture thereof.

The method may further comprise recycling liquid effluent collected following the adjusting pH of the filtrate, wherein the liquid effluent comprises the ammonium-based
15 solution.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary
20 embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of the method according to one embodiment; and

Figure 2 shows the weight percentage of products recovered by the method according to one embodiment.

25 Detailed Description

As explained above, there is a need for an improved method of recovering phosphates.

In general terms, the present invention provides an improved phosphate-based product recovery which is green and efficient and which results in less waste being generated from the method. In particular, some of the end product of the method may be reused in
30 the method, thereby leading to reduced cost of the overall method. The method avoids

utilisation of strong acids and high temperatures, making the method more economical and greener particularly at a larger scale.

According to a first aspect, there is provided a method of recovering a phosphate-based product, the method comprising:

- 5 - mixing a phosphate-containing material with an ammonium-based solution, wherein the mixing is at a temperature of 15-95°C to form a slurry;
- filtering the slurry to separate solids from a filtrate; and
- adjusting the pH of the filtrate to precipitate the phosphate-based product from the filtrate.

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The method enables the recovery of a phosphate-based product comprising ≥ 35 wt % phosphates based on the total weight of the phosphate-based product. In particular, the phosphate-based product may comprise 35-55 wt %, 40-50 wt %, 42-48 wt %, 43-45 wt % phosphates based on the total weight of the phosphate-based product.

- 15 The phosphate-containing material may be any suitable phosphate-containing material such as, but not limited to, sewage sludge ash, incineration ash, low grade phosphate ore, food waste residues, or a mixture thereof. For example, the food waste residues may comprise suitable phosphate-containing material such as, but not limited to, bones.

- 20 The ammonium-based solution may be any suitable ammonium-based solution. For example, the ammonium-based solution may comprise a mineral acid. In particular, the ammonium-based solution may comprise an acidic ammonium salt of a mineral acid in an aqueous solution. The mineral acid may be any suitable mineral acid, such as but not limited to, sulphuric acid, hydrochloric acid, nitric acid, or a mixture thereof. Even more in particular, the ammonium-based solution may comprise ammonium bisulphate
- 25 solution, ammonium chloride, ammonium nitrate, or a mixture thereof.

The mixing may be under suitable conditions, such as temperature and pressure. According to a particular aspect, the mixing may be at a temperature of 15-95°C. For example, the mixing may be at a temperature of 20-90°C, 25-85°C, 30-80°C, 35-75°C, 40-70°C, 45-65°C, 50-60°C. In particular, the temperature may be 25-35°C.

According to a particular aspect, the mixing may be carried out at a low pressure. For example, the pressure may be 1-2 bars. In particular, the mixing may be carried out at atmospheric pressure.

The mixing may comprise mixing a suitable amount of the phosphate-containing material with a suitable amount of the ammonium-based solution. According to a particular aspect, the mixing may comprise mixing the phosphate-containing material with the ammonium-based solution in a solid:liquid ratio of 1:1-1:10. For example, the ratio may be 1:3-1:8, 1:3.5-1:7.5, 1:4-1:7, 1:4.5-1:6.5, 1:5-1:6. Even more in particular, the ratio may be 1:3-1:4.

The solids separated from the filtering may comprise calcium-based product. The calcium-based product may be any suitable calcium-based product. For example, the calcium-based product may be for use in sequestering carbon dioxide. The sequestering carbon dioxide may be by any suitable method. For example, the sequestering may be by the method as described in WO 2018/182506 A1.

The adjusting may comprise adjusting the pH to a suitable pH. For example, the pH may be in the range of 3-12. In particular, the range may be 5-12, 6-11, 7-10, 8-9. In particular, the pH may be adjusted to a pH of 5-7. The method utilises mild pH conditions, thereby avoiding the need for acid-resistant equipment and handling procedures. In addition, the milder pH conditions utilised by the method improves the leaching selectivity of phosphorus, with minimal quantities of heavy metals being co-extracted from the phosphate-containing material.

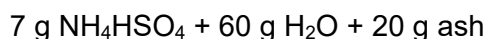
The pH may be adjusted using any suitable solvent. For example, the adjusting may comprise adding an ammonium-containing fluid. The ammonium-containing fluid may be an ammonium-containing gas, an ammonium-containing solution, or a mixture thereof. In particular, the ammonium-containing fluid may comprise, but is not limited to, ammonia gas, aqueous ammonia, or a mixture thereof.

The method may further comprise recycling liquid effluent collected following the adjusting pH of the filtrate, wherein the liquid effluent comprises the ammonium-based solution. In this way, the method is a green and efficient method since it would reduce the amount of solvents required for the method. Also, the amount of waste generated from the method is also reduced, thereby leading to reduced cost.

Having now generally described the invention, the same will be more readily understood through reference to the following example which is provided by way of illustration, and is not intended to be limiting.

5 **Example**

Ammonium bisulfate solution was mixed with sewage sludge ash in stoichiometric amounts as follows:



10 The mixture was agitated at room temperature for an hour, and then filtered to separate the solids from the liquid product.

Aqueous ammonia of 1M concentration was added to the liquid product to adjust the pH of the solution until off-white solids were precipitated at around neutral pH values (5 – 7). A schematic representation of the process is as shown in Figure 1.

15 The precipitated solids were filtered off and dried, and found to contain up to 50 wt % phosphates (measured as P_2O_5 using x-ray fluorescence (XRF)) as shown in Figure 2. Figure 2 shows the comparison of recovery of phosphate-based product when using sodium bisulphate vs ammonium bisulphate. The filtrate consisting of ammonium sulfate was then heated or adjusted with sulfuric acid to regenerate the solution for further use.

20 The solids from the first leaching step may be used for mineral carbonation to sequester CO_2 . When subjected to carbonation process according to the method disclosed in WO 2018/182506 (i.e. carbonation with 10% $(\text{NH}_4)_2\text{CO}_3$ at room temperature and pressure), the solids achieved a carbonation capacity of between 3 – 5%. This contrasts with a nil value previously for the sewage sludge when reacted as-is, without the treatment as described above.

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Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A method of recovering a phosphate-based product, the method comprising:
 - mixing a phosphate-containing material with an ammonium-based solution, wherein the mixing is at a temperature of 15-95°C to form a slurry;
 - filtering the slurry to separate solids from a filtrate; and
 - adjusting the pH of the filtrate to precipitate the phosphate-based product from the filtrate.
2. The method according to claim 1, further comprising recycling liquid effluent collected following the adjusting the pH, wherein the liquid effluent comprises the ammonium-based solution.
3. The method according to claim 1 or 2, wherein the ammonium-based solution comprises a mineral acid.
4. The method according to any preceding claim, wherein the mixing comprises mixing the phosphate-containing material and the ammonium-based solution in a solid:liquid ratio of 1:1-1:10.
5. The method according to claim 4, wherein the mixing comprises mixing the phosphate-containing material and the ammonium-based solution in a solid:liquid ratio of 1:3-1:8.
6. The method according to any preceding claim, wherein the mixing is carried out at a pressure of 1-2 bars.
7. The method according to any preceding claim, wherein the solids separated from the filtering comprise calcium-based product.
8. The method according to claim 7, wherein the calcium-based product is for use in sequestering carbon dioxide.

9. The method according to any preceding claim, wherein the adjusting the pH comprises adjusting the pH to a range of 3-12.

10. The method according to claim 9, wherein the adjusting the pH comprises
5 adjusting the pH to a range of 5-12.

11. The method according to any preceding claim, wherein the adjusting the pH is by adding an ammonium-containing fluid.

10 12. The method according to claim 11, wherein the ammonium-containing fluid comprises: ammonium-containing gas, ammonium-containing solution or a mixture thereof.

13. The method according to any preceding claim, wherein the phosphate-based
15 product comprises ≥ 35 wt % phosphates based on the total weight of the phosphate-based product.