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(54) **Title:** METHODS AND SYSTEMS FOR THE ELECTROCATALYSIS OF MUNICIPAL SLUDGE AND BIOSOLIDS

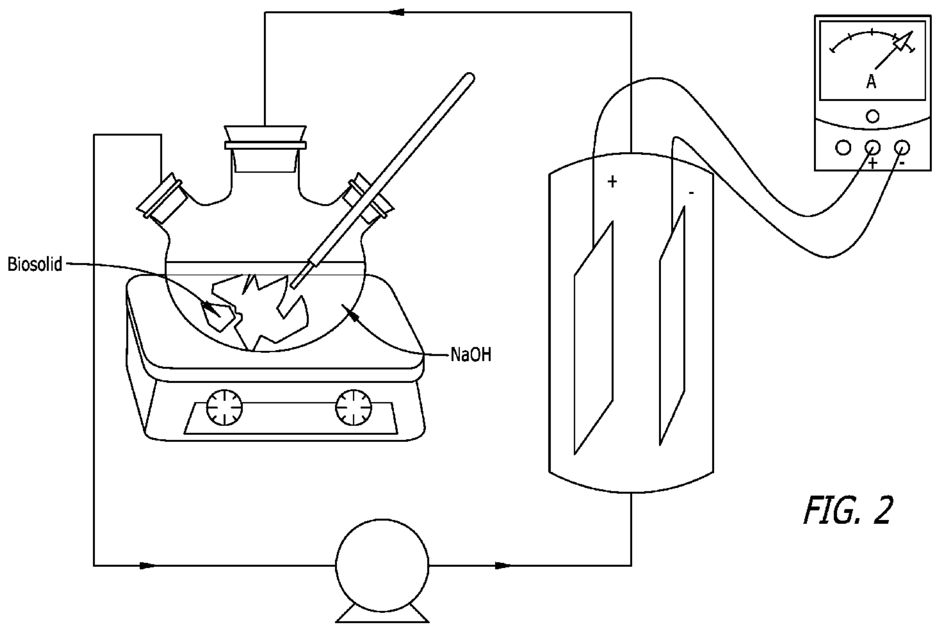

FIG. 2

(57) **Abstract:** Methods and systems for electrocatalysis of municipal sludge and biosolids. Such methods (and systems thereof) include selecting a sludge source; preparing a slurry, where the slurry comprises the sludge source and an electrolyte; adjusting a pH of the slurry, where the adjusting the pH of the slurry results in the slurry having an adjusted pH in a range between approximately (8) and (14); flowing the slurry through an electrochemical cell, where the electrochemical cell includes an anode, a cathode, and a catalyst; applying a potential between the anode and the cathode, where applying the potential includes oscillating a cell voltage between the anode and the cathode at an oscillation frequency; resultant to the applying the potential, breaking down carbon bonds in the slurry with nitrogen and phosphorus; releasing inorganic nitrogen and inorganic phosphorus; and obtaining an electrolyzed sludge, where the electrolyzed sludge includes an electrolyzed solid comprising nitrogen and phosphorus.

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PATENT COOPERATION TREATY

TITLE: METHODS AND SYSTEMS FOR THE ELECTROCATALYSIS OF MUNICIPAL SLUDGE AND BIOSOLIDS

INVENTOR: Gerardine G. Botte

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This application claims priority to U.S. Appl. Serial No. 63/506,601, filed June 7, 2023, entitled "Methods And Systems For The Electrocatalysis Of Municipal Sludge And Biosolids," which patent application is commonly owned by the owner of the present invention. This patent application is incorporated herein in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to an improved method and system for the electrolysis of biosolids, sludge, food waste, manure. In particular, the present disclosure relates to the electrocatalysis of sludge on transition metal based electrodes in order to produce synthetic nitrogen based fertilizer, phosphorus based fertilizer, and an electrolyzed solid organic fertilizer from waste activated sludge, manure from concentrated animal feeding operations, and food waste.

STATEMENT OF FEDERALLY FUNDED RESEARCH

[0003] The present invention was funded by the National Science Foundation Center for Advancing Sustainable and Distributed Fertilizer production, CASFER, NSF 20-553 Gen-4 Engineering Research Centers award # 2133576. The government has certain rights in the invention.

BACKGROUND

[0004] There is need to produce nitrogen based fertilizer and phosphorus based fertilizer from municipal sludge, sludge from concentrated animal feeding operations, food waste, and other like sources.

[0005] A tremendous amount of waste activated sludge ends up in landfilling even after a substantial retention time during anaerobic digestion. Waste activated sludge is the major byproduct of municipal wastewater treatment plants. Management and disposal of waste activated sludge create challenges for wastewater treatment plants such as high energy consumption and operational costs.

[0006] Waste activated sludge contains organic material like lignocellulosic waste that could be converted to produce high value chemicals such as volatile fatty acids. Accordingly, the leftover activated sludge is an organic-rich material with the high potential to produce value-added chemicals such as short chain fatty acids.

[0007] Currently, municipal sludge disposal is expensive. For example, nearly sixty percent of the operational costs in a municipal wastewater treatment plant cost between $220 and $1,000 per ton of nitrogen, and over 1.4 million tons of nitrogen from sludge are disposed in land fields each year.

[0008] Typically, sludge cannot be used as a fertilizer due to the presence of micro-organisms and other organic contaminants that can be found in municipal sludge.

[0009] Sludge in concentrated animal feeding operations, such as lagoons, also contain nitrogen varying from 5 to 10% weight. Phosphorus is also present in these streams with most of the concentration in the solids.

[0010] Currently, concentrated animal feeding operations in the United States generate nitrogen waste equivalent to 16 to 22 million tons per year. The amount of nitrogen generated is greater than that needed per year for the annual domestic consumption of nitrogen based fertilizer.

[0011] Livestock facilities in the United States produce up to 20 times more manure than people, equivalent to 1.3 billion tons of waste. Nonetheless, there are no treatment plants for those livestock facilities. Therefore, manure management technologies are also of need for concentrated animal feeding operations, as most facilities are not located at points where manure can be applied to the field.

[0012] In addition, excessive direct application of untreated manure to the field creates environmental challenges, as nutrients overwhelm the absorptive capacity of the soil, and either run off or are leached into the groundwater.

[0013] Accordingly, there is a need for a production of synthetic like nitrogen based fertilizer and phosphorus based fertilizer from concentrated animal feeding operations that can lead to a holistic solution that addresses food production, environmental, economic, equity and health concerns.

[0014] It is therefore an objective of the present disclosure to determine the electrochemical conversion rate of municipal sludge to inorganic nitrogen and phosphorus on nickel-based electrodes and identify model compounds for sludge that can be implemented for electrocatalysts discovery in order to facilitate the production of synthetic nitrogen based fertilizer and phosphorus based fertilizer from waste activated sludge and concentrated animal feeding operations.

SUMMARY OF THE DISCLOSURE

[0015] The present disclosure is directed to an improved method and system for the electrolysis of biosolids, sludge, food waste, manure. In some embodiments, the method and system involve the electrocatalysis of sludge on transition based electrodes (such as for example, nickel (Ni), copper (Cu), iron (Fe), cobalt (Co), chromium (Cr), manganese (Mn), Scandium (Sc), etc.). From this, certain embodiments of the present disclosure involve the production of synthetic nitrogen based fertilizer and phosphorus based fertilizer from waste activated sludge and concentrated animal feeding operations.

[0016] In general, in one embodiment, the disclosure features a method for electrocatalysis of sludge. The method can include selecting a sludge source. The method also can include preparing a slurry. The slurry can include the sludge source and an electrolyte. The method also can include adjusting a pH of the slurry. The adjusting the pH of the slurry can result in the slurry having an adjusted pH in a range between approximately 8 and 14. The method also can include flowing the slurry through an electrochemical cell. The electrochemical cell can include an anode, a cathode, and a catalyst. The method also can include applying a potential between the anode and the cathode. Applying the potential can include oscillating a cell voltage between the anode and the cathode at an oscillation frequency. The method also can include, resultant to the applying the potential, breaking down carbon bonds in the slurry with nitrogen and phosphorus. The method also can include releasing inorganic nitrogen and inorganic phosphorus. The method also can include obtaining an electrolyzed sludge. The electrolyzed sludge can include an electrolyzed solid organic fertilizer comprising nitrogen and phosphorus. The method can also include the introduction of a separator or membrane between the two electrodes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Other advantages of the present disclosure will be apparent from the following detailed description of the disclosure in conjunction with embodiments as illustrated in the accompanying drawings, in which:

[0018] FIG. 1 depicts a process for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer with an organic fertilizer/carbon sink, in accordance with certain embodiments of the present disclosure.

[0019] FIG. 2 depicts a system for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer, in accordance with certain embodiments of the present disclosure.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0020] The present disclosure relates to an improved method and system for the electrolysis of biosolids, sludge, food waste, manure. In particular, the present disclosure relates to the electrocatalysis of sludge on transition based electrodes in order to produce synthetic nitrogen based fertilizer and phosphorus based fertilizer from waste activated sludge and concentrated animal feeding operations.

[0021] FIG. 1 depicts a process for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer with an organic fertilizer/carbon sink, in accordance with certain embodiments of the present disclosure. **FIG. 2** depicts a system for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer, in accordance with certain embodiments of the present disclosure.

[0022] As shown in FIG. 1, the present disclosure relates to a method and system for the electrolysis of biosolids, sludge, food waste, manure. The process, as shown in FIG. 1, the process may transform municipal sludge, manure, concentrated animal feeding operations sludge, and food waste into nitrogen based fertilizer, phosphorus based fertilizer, ammonia, slow-release organic fertilizer, and carbon sink char. The process of FIG. 1 provides the conversion and valorization of municipal and concentrated animal feeding operations sludge into value products such as ammonia, low-release organic fertilizer, phosphorus, and soil enhancement nutrient with the ability to serve as a carbon sink.

[0023] The process may result in the products of inorganic nitrogen-based fertilizer, inorganic phosphorus based fertilizer, fatty acids, hydrogen, and organic N-P fertilizer. For example, in some embodiments, the inorganic nitrogen-based fertilizer may be ammonia, ammonium salts, calcium nitrate, or combinations thereof. For example, in some embodiments, the inorganic phosphorus-based fertilizer may be one or more calcium phosphates.

[0024] In some embodiments, for example, the slow-release organic fertilizer may be or include electrolyzed biosolids. In such an embodiment, the fertilizer may contain consistent nitrogen and phosphorus content and a microstructure to enhance plant growth due to slow release of nitrogen increasing nutrient use efficiency. In some embodiments, the method and system for the electrolysis can include carbon sink material, since electrolyzed biosolids, such as those in a slow-release organic fertilizer, have the property to absorb carbon dioxide.

[0025] As shown in FIG. 1, the process may begin with the introduction of sludge. In some embodiments, the sludge may be sewage. In other embodiments, the sludge may be manure. In certain embodiments, the sludge may be a combination of one or more of municipal sludge, manure, concentrated animal feeding operations sludge, and food waste.

[0026] The process may continue with the preparation of a slurry. In such an embodiment, the slurry can include the sludge and an electrolyte. The sludge may include between approximately 0.5 percent and 40 percent solids as a mass percentage of solute in the solution.

[0027] The process may involve, in certain embodiments, the adjustment of the pH of the slurry. In some embodiments, the pH of the slurry may be adjusted between 8 and 14 using potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium oxide (CaO), or other equivalent salt. These salts can also serve as electrolyte in the slurry. Operating the process at higher pH values is feasible but the range provided presents an economic advantage.

[0028] As shown in FIG. 1, the process can include flowing the slurry through an electrochemical cell containing two electrodes, an anode and cathode. In some embodiments, the electrochemical cell can also include a membrane or separator. In such an embodiment, the addition of separator allows the separation of hydrogen gas that can evolve under certain applied voltages. In certain embodiments, the electrochemical cell can contain an anode, a cathode, a membrane or separator for collecting hydrogen, an electrolyte, and a reference electrode.

[0029] In some embodiments, the anode may include a conductive material, support, such as for example but not limited to, (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof. In some embodiments, the anode may include any conductive material that is resistant to corrosion based on the electrolyte, cell voltage and temperature of the system. In some embodiments, the supports can include carbon, carbon fibers, graphene. In some embodiments, the anode may include a catalyst that includes metals such as nickel (Ni), iron (Fe), cobalt (Co), chromium (Cr), copper (Cu), zinc (Zn), ruthenium (Ru), rhodium (Rh), vanadium (V), manganese (Mn), titanium (Ti), Scandium (Sc) and combinations thereof. In some embodiments, the catalyst may include composites of graphene metal combinations. The catalyst may have loadings 0.1 mg/cm^2 to 2 mg/cm^2. The catalysts can also be used as a direct metal or support in certain embodiments.

[0030] In some embodiments, the cathode may include a conductive material, support, such as for example but not limited to, nickel (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof. In some embodiments, the anode may include any conductive material that is resistant to corrosion based on the electrolyte, cell voltage and temperature of the system. In some embodiments, the supports can include carbon, carbon fibers, graphene. In some embodiments, the anode may include a catalyst that includes metals such as nickel (Ni), iron (Fe), cobalt (Co), chromium (Cr), copper (Cu), zinc (Zn), ruthenium (Ru), rhodium (Rh), vanadium (V), manganese (Mn), titanium (Ti), Scandium (Sc) and combinations thereof. In some embodiments, the catalyst may include composites of graphene metal combinations. The catalyst may have loadings 0.1 mg/cm^2 to 2 mg/cm^2. The catalysts can also be used as a direct metal or support in certain embodiments.

[0031] In some embodiments, a membrane and/or a separator may be included in the electrochemical cell. Specifically, in some embodiments, the electrochemical cell may contain a membrane such as for example but not limited to nafion, fritted glass, and/or separators, such as for example but not limited to polyethylene.

[0032] In some embodiments, the electrolyte may have a strong and weak basis. For example, the electrolyte may include potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium oxide (CaO), or combinations thereof. The electrolyte may be present at concentrations such that pH is maintained between approximately 8 and 14.

[0033] The process also can include applying an oscillation of potential between the two electrodes. For example, the cell voltage can be applied between the anode and the cathode of the cell. In some embodiments, a current is applied instead of a voltage. In some embodiments, the voltage can be oscillated with a frequency of 1, 10, 30, 60 seconds and 15, 30 minutes. In some embodiments, the effective cell voltage may be up to 2.0V (discounted by the ohmic resistance, counters, wires, etc.), depending on the type of electrolyte used and the temperature. The cell voltage for the electrochemical cell may vary from 0.8V to 2.0V excluding the ohmic resistance. The cell voltage applied can prevent water oxidation at the anode of the cell, and the oxidation potential is a function of the electrolyte and temperature used.

[0034] During the oscillation, in some embodiments, the temperature is controlled. For example, the temperature may be controlled between approximately 20 °C to 80 °C.

[0035] By doing so, in some embodiments, the applied potential breaks down carbon bonds with nitrogen and phosphorus. As a result, in such an embodiment, the process can include releasing the nitrogen and phosphorus as inorganic phosphorus and nitrogen. For example, inorganic phosphorus may include phosphates. For example, inorganic nitrogen may be ammonia, nitrates, or combinations thereof.

[0036] The product of the process may include an electrolyzed solid containing a fraction of nitrogen and phosphorus in organic form which can be applied as an organic fertilizer. The microstructure of the electrolyzed sludge may, in some embodiments, serve as a sink for the absorption of carbon dioxide (CO_2) from the atmosphere.

[0037] Accordingly, in some embodiments, the process of FIG. 1 may reduce the time for producing organic fertilizer. In some embodiments, the fertilizer may include carbon, nitrogen, and phosphorus. For example, biological process takes 30 to 45 days to digest organic waste into fertilizer. Whereas, in the process of FIG. 1, sludge electrolysis reduces the digestion time to less than six hours. Residence time for conversion for the process of FIG. 1 may be two hours. This residence time for conversion in the process of FIG. 1 is significantly lower than processes using anaerobic digestors, which typically take approximately 10 to 20 days.

[0038] The process of FIG. 1 can result in a reduction of 24.85 percent in total solids and 46.42 percent in volatile solids, which represents approximately a 25 percent reduction in sludge disposal cost when compared to conventional treatment methods.

[0039] In some embodiments, the process can result in the conversion of 68% of the organic nitrogen into inorganic nitrogen.

[0040] **<u>Working Example 1</u>**

[0041] A slow-release fertilizer (electrolyzed sludge) was produced using the process for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer with an organic fertilizer/carbon sink. In the working example, the electrolyzed sludge (solids after electrolysis) decreased the carbon content by 20-40%, while pathogens have been destroyed. In addition, the microstructure of the material changed, creating surfaces with micro and nanoparticles. This material contained nitrogen and phosphorus in concentrations like compost. The microstructure change enabled a slow release of the fertilizer, creating an advantage in the soil. The change in the micro-structure can minimize the release of inorganic fertilizer when mixed in the soil with synthetic inorganic fertilizer.

[0042] **<u>Working Example 2</u>**

[0043] A carbon sink material, electrolyzed sludge was produced using the process for the electrolysis of sludge for the production of nitrogen based fertilizer and phosphorus based fertilizer with an organic fertilizer/carbon sink. The electrolyzed sludge released the volatile carbon. Because of the change in the microstructure, the product behaves similar to an activated carbon, enabling the absorption of carbon dioxide (CO_2) and other contaminants. The other contaminants may include methane, benzene, toluene, or combinations thereof.

[0044] Consistent with the above disclosure, the examples of systems and methods enumerated in the following clauses are specifically contemplated and are intended as a non-limiting set of examples.

[0045] Clause 1. A method for electrocatalysis of sludge including selecting a sludge source; preparing a slurry, where the slurry includes the sludge source and an electrolyte; adjusting a pH of the slurry, where the adjusting the pH of the slurry results in the slurry having an adjusted pH in a range between approximately 8 and 14; flowing the slurry through an electrochemical cell, where the electrochemical cell includes an anode, a cathode, and a catalyst; applying a potential between the anode and the cathode, where applying the potential includes oscillating a cell voltage between the anode and the cathode at an oscillation frequency; resultant to the applying the potential, breaking down carbon bonds in the slurry with nitrogen and phosphorus; releasing inorganic nitrogen and inorganic phosphorus; and obtaining an electrolyzed sludge, where the electrolyzed sludge includes an electrolyzed solid comprising nitrogen and phosphorus.

[0046] Clause 2. The method of any foregoing clause, where the sludge source includes one or more of municipal sludge, manure, concentrated animal feeding operations sludge, and food waste.

[0047] Clause 3. The method of any foregoing clause, where the sludge source includes a solid in a mass percent in a range between approximate 0.5 and 40 percent.

[0048] Clause 4. The method of any foregoing clause, where adjusting the pH of the slurry further includes adding a salt to the slurry.

[0049] Clause 5. The method of any foregoing clause, where the salt includes using potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium oxide (CaO), or combinations thereof.

[0050] Clause 6. The method of any foregoing clause, where the electrochemical cell further includes a membrane.

[0051] Clause 7. The method of any foregoing clause, where the membrane includes nafion, fritted glass, or combinations thereof.

[0052] Clause 8. The method of any foregoing clause, where the electrochemical cell further includes a separator, where the separator separates hydrogen gas.

[0053] Clause 9. The method of any foregoing clause, where the separator is polyethylene.

[0054] Clause 10. The method of any foregoing clause, where the electrochemical cell further includes a reference electrode.

[0055] Clause 11. The method of any foregoing clause, where the anode includes (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof.

[0056] Clause 12. The method of any foregoing clause, where the cathode includes nickel (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof.

[0057] Clause 13. The method of any foregoing clause, where the catalyst includes composites of graphene metal combinations.

[0058] Clause 14. The method of any foregoing clause, where the oscillation frequency of 1, 10, 30, 60 seconds and 15, 30 minutes is applied.

[0059] Clause 15. The method of any foregoing clause, where the applying an oscillating cell voltage between the anode and the cathode further includes maintaining a controlled temperature, where the controlled temperature is in a range of approximately 20 °C and 80 °C.

[0060] Clause 16. The method of any foregoing clause, where the inorganic nitrogen includes ammonia, nitrates, or combinations thereof.

[0061] Clause 17. The method of any foregoing clause, where the inorganic phosphorus includes phosphates.

[0062] Clause 18. The method of any foregoing clause, where the electrolyzed sludge includes an organic fertilizer.

[0063] Clause 19. The method of any foregoing clause, where the electrolyzed sludge comprises a microstructure, where the microstructure of the electrolyzed sludge serves as a sink for the absorption of carbon dioxide (CO_2).

[0064] Clause 20. The method of any foregoing clause, where the cell voltage varies from approximately 0.8V to approximately 2.0V excluding ohmic losses.

[0065] Clause 21. The method of any foregoing clause, where the applying the potential between the anode and the cathode further includes preventing water oxidation at the anode.

[0066] Clause 22. The method of any foregoing clause, where the organic fertilizer comprises carbon, nitrogen, and phosphorus.

[0067] Clause 23. A electrolyzed solid organic fertilizer including nitrogen, carbon, and phosphorus.

[0068] Clause 24. The electrolyzed solid organic fertilizer of any foregoing clause, where the electrolyzed solid organic fertilizer promotes a nitrogen circular economy.

[0069] Clause 25. The electrolyzed solid organic fertilizer of any foregoing clause, where the electrolyzed solid organic fertilizer facilitates reduced runoff.

[0070] The foregoing description, for purposes of explanation, used specific nomenclature to provide a thorough understanding of the described embodiments. However, it should be apparent to one skilled in the art that the specific details are not required in order to practice the described embodiments. Thus, the foregoing descriptions of specific embodiments are presented for purposes of illustration and description. They are not intended to be exhaustive or to limit the described embodiments to the precise forms disclosed. It should be apparent to one of ordinary skill in the art that many modifications and variations are possible in view of the above teachings.

[0071] While embodiments of the disclosure have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the disclosure. The embodiments described and the examples provided herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the disclosure disclosed herein are possible and are within the scope of the disclosure. The scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[0072] Amounts and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a numerical range of approximately 1 to approximately 4.5 should be interpreted to include not only the explicitly recited limits of 1 to approximately 4.5, but also to include individual numerals such as

2, 3, 4, and sub-ranges such as 1 to 3, 2 to 4, etc. The same principle applies to ranges reciting only one numerical value, such as "less than approximately 4.5," which should be interpreted to include all of the above-recited values and ranges. Further, such an interpretation should apply regardless of the breadth of the range or the characteristic being described. The symbol "~" is the same as "approximately".

[0073] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which the presently disclosed subject matter belongs. Although any methods, devices, and materials similar or equivalent to those described herein can be used in the practice or testing of the presently disclosed subject matter, representative methods, devices, and materials are now described.

[0074] Following long-standing patent law convention, the terms "a" and "an" mean "one or more" when used in this application, including the claims.

[0075] Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification are approximations that can vary depending upon the desired properties sought to be obtained by the presently disclosed subject matter.

[0076] As used herein, the term "and/or" when used in the context of a listing of entities, refers to the entities being present singly or in combination. Thus, for example, the phrase "A, B, C, and/or D" includes A, B, C, and D individually, but also includes any and all combinations and subcombinations of A, B, C, and D.

[0077] The above discussion is meant to be illustrative of the principles and various embodiments of the present disclosure. Numerous variations and modifications will become apparent to those skilled in the art once the above disclosure is fully appreciated. It is intended that the following claims be interpreted to embrace all such variations and modifications.

REFERENCES

[0078] Environmental Protection Agency. Detecting and mitigating the environmental impact of fecal pathogens originating from confined animal feeding operations: Review (2005). (retrieved from http://www.farmweb.org/Articles/Detecting%20and%20Mitigating%20the%20 Environmental%20Impact%20of%20Fecal%20Pathogens%20Originating%20from%20Confined %20Animal%20Feeding%20Operations.pdf).

[0079] Jafari, M., Botte G.G. Electrochemical valorization of waste activated sludge for short-chain fatty acids production. Frontiers in Chemistry 10:974223 (2022).

[0080] Jafari, M., Botte, G.G. Electrochemical treatment of sewage sludge and pathogen inactivation. J Appl Electrochem **51**, 119–130 (2021).

[0081] Liu, H. et al. Phosphorus recovery from municipal sludge-derived ash and hydrochar through wet-chemical technology: A review towards sustainable waste management, Chemical Engineering Journal 417, 129300 (2021).

[0082] Lu, F., Botte G. G. Understanding the electrochemically induces conversion of urea to ammonia using nickel-based catalysts, Electrochimica Acta, 246, 564-571 (2017).

[0083] Schmalzried, H.D. & Fallon, L.F., Jr. Large-scale dairy operations: Assessing concerns of neighbors about quality-of-life issues. J. of Dairy Science, *90*(4), 2047-2051 (2007) (retrieved from http://jds.fass.org/cgi/reprint/90/4/2047?maxtoshow=&hits=10&RESULTFOR MAT=&fulltext=large-scale&searchid=1&FIRSTINDEX=0&volume=90&issue=4&resource type=HWC).

[0084] Zhuang, X. et al. The transformation pathways of nitrogen in sewage sludge during hydrothermal treatment, Bioresource Technology 245, 463-470 (2017)..

CLAIMS

WHAT IS CLAIMED IS:

1. A method for electrocatalysis of sludge comprising:

   (a) selecting a sludge source;

   (b) preparing a slurry, wherein the slurry comprises the sludge source and an electrolyte;

   (c) adjusting a pH of the slurry, wherein the adjusting the pH of the slurry results in the slurry having an adjusted pH in a range between approximately 8 and 14;

   (d) flowing the slurry through an electrochemical cell, wherein the electrochemical cell comprises:

      (i) an anode,

      (ii) a cathode, and

      (iii) a catalyst;

   (e) applying a potential between the anode and the cathode, wherein applying the potential comprises oscillating a cell voltage between the anode and the cathode at an oscillation frequency;

   (f) resultant to the applying the potential, breaking down carbon bonds in the slurry with nitrogen and phosphorus;

   (g) releasing inorganic nitrogen and inorganic phosphorus; and

   (h) obtaining an electrolyzed sludge, wherein the electrolyzed sludge comprises an electrolyzed solid comprising nitrogen and phosphorus.

2. The method of Claim 1, wherein the sludge source comprises one or more of municipal sludge, manure, concentrated animal feeding operations sludge, and food waste.

3. The method of Claim 1, wherein the sludge source comprises a solid in a mass percent in a range between approximately 0.5 and 40 percent.

4. The method of Claim 1, wherein adjusting the pH of the slurry further comprises adding a salt to the slurry.

5. The method of Claim 4, wherein the salt comprises using potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium oxide (CaO), or combinations thereof.

6. The method of Claim 1, wherein the electrochemical cell further comprises a membrane.

7. The method of Claim 6, wherein the membrane comprises nafion, fritted glass, or combinations thereof.

8. The method of Claim 1, wherein the electrochemical cell further comprises a separator, wherein the separator separates hydrogen gas.

9. The method of Claim 1, wherein the separator is polyethylene.

10. The method of Claim 1, wherein the electrochemical cell further comprises a reference electrode.

11. The method of Claim 1, wherein the anode comprises nickel (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof.

12. The method of Claim 1, wherein the cathode comprises nickel (Ni) gauze/mesh, stainless steel, Hastelloy, graphite, nickel (Ni), nickel (Ni) foam, copper (Cu), cobalt (Co), chromium (Cr), zinc (Zn), titanium (Ti), titanium (Ti) foam, aluminum (Al), aluminum (Al) foam, vanadium (V), manganese (Mn), Scandium (Sc), Ruthenium (Ru), Rhodium (Rh), Iron (Fe), Silver (Ag), Gold (Au), or combinations thereof.

13. The method of Claim 1, where the catalyst comprises composites of graphene metal combinations.

14. The method of Claim 1, wherein the applying an oscillating cell voltage between the anode and the cathode further comprises maintaining a controlled temperature, wherein the controlled temperature is in a range of approximately 20 °C and 80 °C.

15. The method of Claim 1, wherein the inorganic nitrogen comprises ammonia, nitrates, or combinations thereof.

16. The method of Claim 1, wherein the inorganic phosphorus comprises phosphates.

17. The method of Claim 1, wherein the electrolyzed sludge comprises an organic fertilizer.

18. The method of Claim 1, wherein the electrolyzed sludge comprises a microstructure, wherein the microstructure of the electrolyzed sludge serves as a sink for the absorption of carbon dioxide (CO_2).

19. The method of Claim 1, wherein the cell voltage varies from approximately 0.8V to approximately 2.0V excluding ohmic losses.

20. The method of Claim 1, wherein the applying the potential between the anode and the cathode further comprises preventing water oxidation at the anode.

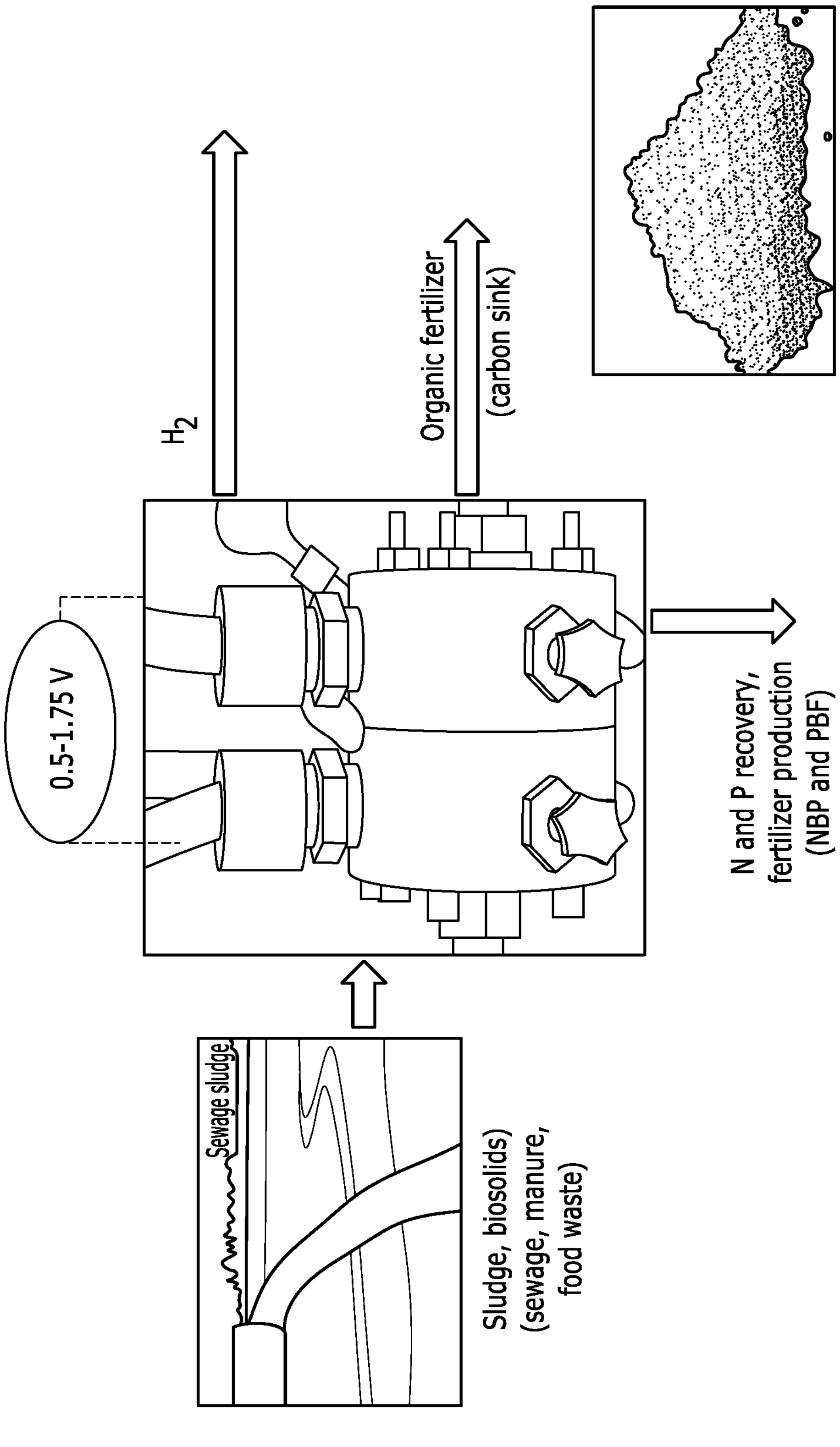
Sewage sludge
Sludge, biosolids)
(sewage, manure,
food waste)
0.5-1.75 V
H_2
Organic fertilizer
(carbon sink)
N and P recovery,
fertilizer production
(NBP and PBF)

FIG. 1

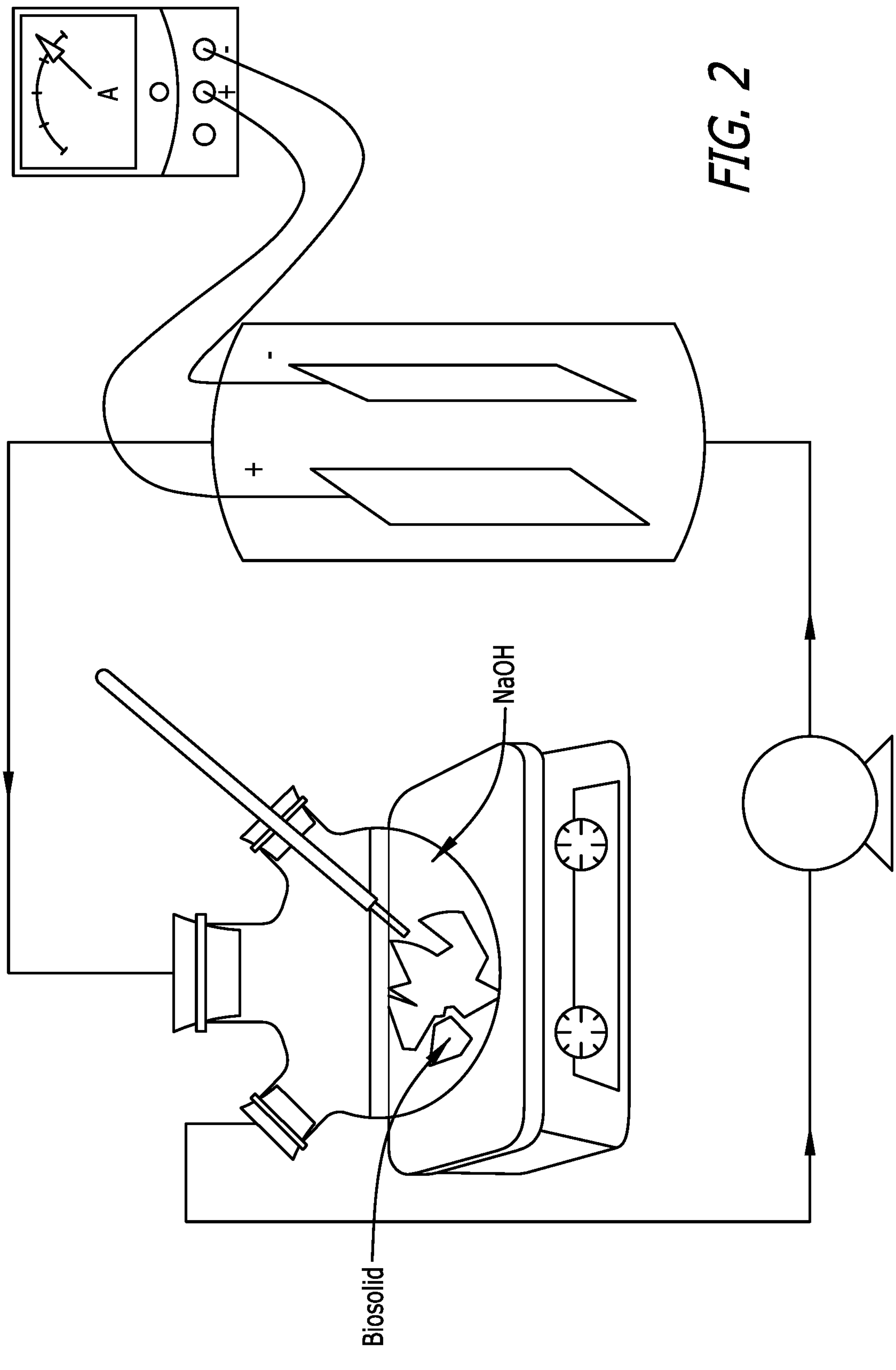

FIG. 2