

(43) International Publication Date
16 June 2016 (16.06.2016)(10) International Publication Number
WO 2016/090490 A1

(51) International Patent Classification:

C02F 11/06 (2006.01) *C02F 1/72* (2006.01)
B09B 3/00 (2006.01) *C02F 9/12* (2006.01)
C02F 1/30 (2006.01)

(74) Agents: **KONDOR, George F.** et al.; c/o OYEN WIGGS GREEN & MUTALA LLP, 480 - The Station, 601 West Cordova Street, Vancouver, British Columbia V5X 1Z8 (CA).

(21) International Application Number:

PCT/CA2015/051303

(22) International Filing Date:

10 December 2015 (10.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/089,965 10 December 2014 (10.12.2014) US

(71) Applicant: **THE UNIVERSITY OF BRITISH COLUMBIA** [CA/CA]; University-Industry Liaison Office, #103-6190 Agronomy Road, Vancouver, British Columbia V6T 1Z3 (CA).(72) Inventors: **LO, Kwang Victor**; 4694 Northview Court, Burnaby, British Columbia V5H 1E3 (CA). **LIAO, Ping Huang**; 5640 Camden Place, Richmond, British Columbia V7C 3Z7 (CA). **SRINIVASAN, Asha**; 271, East 60th Avenue, Vancouver, British Columbia V5X 1Z8 (CA).(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, 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, KN, KP, KR, 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).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

(54) Title: PROCESS AND SYSTEM FOR TREATING SLURRIES OF ORGANIC SOLIDS

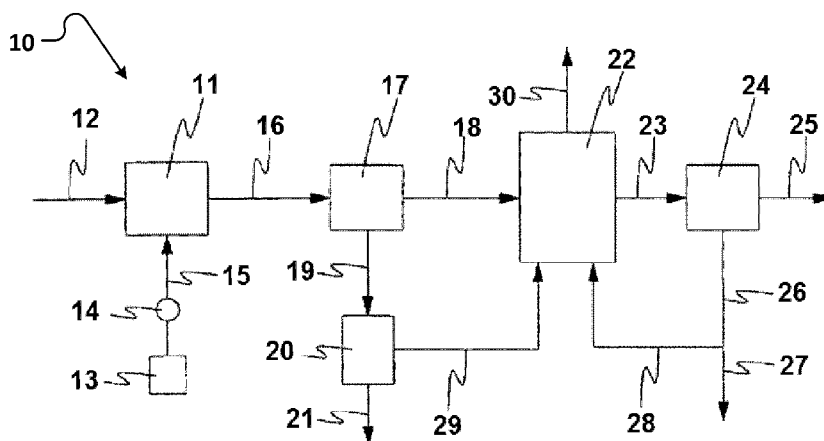


FIG. 1

(57) Abstract: Processes and systems for treating slurries of organic solids are disclosed. A slurry of organic solids is mixed with an oxidant, followed by exposure to radiofrequency radiation resulting in the heating of the mixture and enhanced hydrolysis of the organic solids. The AOP treated slurry can then be further treated in a variety of downstream processes, including solids separation, digestion, and fermentation. The supernatant portion of the AOP treated slurry can be a source from which to recover compounds such as nutrients (for example, nitrogen, phosphate, potassium, magnesium, calcium) or industrial organic compounds (such as acetic acid, propionic acid, butyric acid), or as a source of readily biodegradable organic compounds for supplementing a biological wastewater treatment process, digester, or fermenter.



WO 2016/090490 A1



Published:

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

PROCESS AND SYSTEM FOR TREATING SLURRIES OF ORGANIC SOLIDS

Technical Field

5 [0001] This application relates to the treatment of organic waste material, such as sludge resulting from sewage treatment facilities, animal manure, food processing waste, and/or industrial organic waste. In particular, this application relates to processes and systems for treating organic waste material using a combination of radiofrequency radiation and oxidants, such as hydrogen peroxide and/or ozone.

Background

10 [0002] The disposal of organic waste material such as sewage sludge, animal manure, food processing waste, industrial organic waste, and the like, presents environmental and public health concerns.

15 [0003] The production of large volumes of sludge as an end-product from wastewater treatment processes poses one of the biggest challenges to the wastewater treatment industry. The handling and disposal of sludge residuals has significant social, environmental, and economic implications. Treatment and disposal of sewage sludge from wastewater treatment plants can account for over half of the total cost of wastewater treatment plant construction and operation. Currently, residual sludge is commonly digested, incinerated, deposited in landfills, or used as fertilizer through agricultural land application of the residual biosolids.

20 [0004] In current wastewater treatment processes, toxic heavy metals become concentrated in the residual sludge. There may also be dangerous levels pathogenic organisms present in the residuals. For these reasons there are increasing concerns that land application of sludge residuals may be harmful to the environment and to public health. Under such social, environmental, and economic pressures, significant effort has been invested in developing new
25 methods of treating wastewater and wastewater sludges that result in smaller amounts of residual solids requiring disposal.

[0005] Anaerobic digestion is a very common solids reduction and stabilization technology, but is relatively inefficient due to the low biodegradability of the sludge. This poor biodegradability is particularly evident in the case of digesting secondary or waste activated sludge. The benefit of anaerobic digestion is that the methanogenesis stage of the process results in the production of methane (biogas) which can be used as an energy source. To improve the efficiency of the anaerobic digestion process, many techniques which enhance the biodegradability of these sludges have been developed in recent years.

[0006] The anaerobic degradation of particulate organics is considered to be a sequence of three steps: hydrolysis, acidogenesis, and methanogenesis. Among these, biological hydrolysis of the particulate organics has been considered to be the rate limiting step.

[0007] Many of the techniques recently developed to improve the biodegradability of sludges therefore focus on improving hydrolysis by other means. The processes most focused on are chemical oxidation disintegration by ozone, mechanical disintegration by various methods, and thermal or thermal/chemical disintegration. These techniques include those discussed in the following references:

- Ahn, K.-H., Park, K.Y., Maeng, S.K., Hwang, J.H., Lee, J.W., Song, K.G. and Choi, S. (2002). Ozonation of wastewater and ozonation for recycling. *Wat. Sci. Tech.*, 46(10), 71-77.
- Chiu, Y.C., Chang, C.N., Lim, J.G. and Huang, S.J. (1997). Alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion. *Wat. Sci. Tech.*, 36(11), 155-162.
- Hiraoka, M., Takeda, N., Sakai, S. and Yasuda, A. (1984). Highly efficient anaerobic digestion with thermal pre-treatment. *Wat. Sci. Tech.*, 17(4/5), 529-539.
- Kepp, U., Machenbach, I., Weisz, N. and Solheim, O.E. (2000). Enhanced stabilisation of sewage sludge through thermal hydrolysis - three years experience with full scale plant. *Wat. Sci. Tech.*, 42(9), 89-96.
- Recktenwald, M. and Karlsson, I. (2003). Recovery of wastewater sludge components by acid hydrolysis. Presented at IWA Specialised Conf. BIOSOLIDS 2003 Wastewater Sludge as a Resource, Trondheim, Norway, 23-25 June, 2003.

- Svanström, M., Modell, M. and Tester, J. (2004). Direct energy recovery from primary and secondary sludges by supercritical water oxidation. *Wat. Sci. Tech.*, 49(10), 201-208.
- Tiehm, A., Nickel, K., Zellhorn, M. and Neis, U. (2001). Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Research*, 35, 2003-2009.
- Weisz, N., Kepp, U., Norli, M., Panter, K. and Solheim, O.E. (2000). Sludge disintegration with thermal hydrolysis - cases from Norway, Denmark and United Kingdom. 1st IWA World Congress, Paris 3-7 July. Pre-prints Book 4, pp 288-295.
- Yasui, H. and Shibata, M. (1994). An innovative approach to reduce excess sludge production in the activated sludge process. *Wat. Sci. Tech.*, 30(9), 11-20.

[0008] Most of these prior processes operate either with large amount of chemical dosage or under high temperature and pressure conditions or both. Energy consumptions are typically large for many of these processes.

[0009] Various industries, such as the food processing, wood drying, and waste treatment industries, have applied dielectric heating techniques that use microwave (MW) radiation. MW radiation has been applied in sludge processing, medical waste treatment, contaminated soil remediation, wastewater cleanup, and degradation of organic compounds including pesticides and organic dyes. United States patent No. 8,444,861 describes the treatment of organic waste through a combination of microwave radiation and the use of oxidants such as hydrogen peroxide or ozone. For such processes, there are deficiencies in handling high volumes of organic waste material with high solids content in batch processes.

[0010] There remains a need for a cost-effective process to achieve solid waste disintegration, nutrient solubilisation, and pathogen destruction.

[0011] The foregoing examples of the related art and limitations related thereto are intended to be illustrative and not exclusive. Other limitations of the related art will become apparent to those of skill in the art upon a reading of the specification and a study of the drawings.

Summary

[0012] The following embodiments and aspects thereof are described and illustrated in conjunction with systems, tools and methods which are meant to be exemplary and illustrative, not limiting in scope. In various embodiments, one or more of the above-described problems
5 have been reduced or eliminated, while other embodiments are directed to other improvements.

[0013] The present invention has a number of aspects. One aspect of the present invention provide a method of treating a slurry of organic solids. The method includes admixing the slurry having a first suspended solids content with an oxidant to yield an admixed slurry and radiating the admixed slurry with radiofrequency radiation for a treatment period to yield a treated slurry
10 having a second suspended solids content less than the first suspended solids content.

[0014] In some embodiments, the oxidant includes one or more of hydrogen peroxide, ozone, and potassium persulfate.

[0015] In some embodiments, admixing the slurry with oxidant comprises introducing between about 0.03% and about 2.5% by volume (v/v) of hydrogen peroxide, preferably about 1% by
15 volume (v/v) of hydrogen peroxide.

[0016] In some embodiments, wherein admixing the slurry with the oxidant comprises introducing between about 0.025% and about 2.1% hydrogen peroxide per percent (%) total solids by weight, preferably about 0.8% hydrogen peroxide per percent (%) total solids by weight.

20 [0017] In some embodiments, the method further includes treating the slurry with ozone.

[0018] In some embodiments, treating the slurry with ozone comprises adding about 0.02 to about 0.1 g of ozone per gram total solids, preferably about 0.06 g of ozone per gram total solids.

[0019] In some embodiments, the method further includes increasing a treatment temperature of the admixed slurry during at least a portion of the treatment period to between about 60°C and
25 about 200°C, preferably about 60°C.

[0020] In some embodiments, increasing the treatment temperature includes heating the admixed slurry from a first temperature to a final temperature at a ramp rate of between about 3°C per minute to about 7°C per minute.

5 [0021] In some embodiments, increasing the treatment temperature includes radiating the admixed slurry with radiofrequency radiation.

[0022] In some embodiments, the treatment period is between about 5 minutes and about 60 minutes, preferably less than about 20 minutes.

[0023] In some embodiments, increasing the treatment temperature includes applying between about 1200 Watts and about 2500 Watts of radiofrequency power per litre of slurry.

10 [0024] In some embodiments, the method further includes acidifying the slurry. Acidifying the slurry may include adding one or more of a mineral acid and an organic acid, wherein the mineral acid may include one or more of sulphuric acid and hydrochloric acid and/or the organic acid may include oxalic acid. In some embodiments, the slurry is acidified to a pH of between about 2 to about 4, preferably about 4.

15 [0025] In some other embodiments, the pH of the slurry is maintained between about 6 to about 7.

[0026] In some embodiments, the method further includes maintaining the admixed slurry at a treatment pressure that is equal to or greater than atmospheric pressure during the treatment period.

20 [0027] In some embodiments, the second suspended solids content is at least 10% less than the first suspended solids content.

[0028] In some embodiments, the first suspended solids content is in the range of about 0.05% and about 30%, preferably about 0.1% to about 15%.

25 [0029] In some embodiments, the admixed slurry has a first soluble chemical oxygen demand and the treated slurry has a second soluble chemical oxygen demand in excess of the first soluble chemical oxygen demand, preferably by at least 30%.

[0030] In some embodiments, the treated slurry has a soluble chemical oxygen demand in excess of 30% of total chemical oxygen demand.

[0031] In some embodiments, the method further includes subjecting the treated slurry to a first downstream treatment process, wherein the first downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.

[0032] In some embodiments, the method further includes drawing off a supernatant portion from the treated slurry and recovering one or more of a dissolved mineral and dissolved organic compound from the supernatant portion. Recovering the dissolved mineral may include crystallizing the dissolved mineral. Recovering the dissolved organic compound may include one or more of solvent extraction, distillation, and direct use of the dissolved organic compound. Direct use of the dissolved organic compound may include using at least a portion of the supernatant portion as a source of readily biodegradable organic compounds to supplement a biological process, such as denitrification and/or enhanced biological phosphorus removal.

[0033] In some embodiments, the biodegradable organic compounds comprise volatile fatty acids.

[0034] In some embodiments, the dissolved mineral comprises phosphate.

[0035] In some embodiments, the dissolved mineral is recovered as struvite or a struvite analog.

[0036] In some embodiments, crystallizing the dissolved mineral includes adding ammonium or magnesium to the supernatant portion to create a supersaturation of the dissolved mineral.

[0037] In some embodiments, the method further includes subjecting a suspended solids-containing portion of the treated slurry remaining after drawing off the supernatant portion to a second downstream treatment process, wherein the second downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.

[0038] In some embodiments, the slurry comprises one or more of sewage sludge, solids separated manure, liquid fraction of separated manure, and unseparated manure.

[0039] In some embodiments, the treated slurry comprises about 60% of the organic solids present in the slurry in soluble form.

- 5 [0040] Another aspect of the present invention provides a system for treating a slurry of organic solids. The system includes an inlet for receiving the slurry, a reaction zone downstream from the inlet, one or more oxidant injection ports at or upstream from the reaction zone, a radiofrequency radiation source disposed to radiate the slurry in the reaction zone producing treated slurry, and an outlet for delivering the treated slurry downstream from the reaction zone.
- 10 The oxidant injection ports are connected to a supply of oxidant.

[0041] In some embodiments, the system further includes a separator connected to receive treated slurry from the outlet and separate the treated slurry into a supernatant portion and a suspended solids-containing portion.

- 15 [0042] In some embodiments, the system further includes a product recovery system connected to the separator for receiving the supernatant portion and crystallizing one or more of a dissolved mineral and dissolved organic compound. Crystallizing a dissolved mineral may include a means for adding soluble ammonium or magnesium to the supernatant portion.

- 20 [0043] In some embodiments, the system further includes a downstream treatment process, wherein the downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.

- 25 [0044] In addition to the exemplary aspects and embodiments described above, further aspects and embodiments will become apparent by reference to the drawings and by study of the following detailed descriptions.

Brief Description of Drawings

[0045] Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

5 [0046] Figure 1 is a schematic illustration of a system and process for treating a slurry of organic solids according to an example embodiment of the present invention.

[0047] Figure 2 is a schematic illustration of a system and process for treating a slurry of organic solids according to an example embodiment of the present invention, wherein an AOP reactor according to an example embodiment of the present invention is integrated into a pre-existing
10 wastewater treatment system.

[0048] Figure 3 is a graph showing a sample response surface profile of unseparated dairy manure for ortho-phosphate concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)).

[0049] Figure 4 is a graph showing a sample response surface profile of unseparated dairy
15 manure for SCOD concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)).

[0050] Figures 5A is a graph showing a particle size distribution profile of sewage sludge as a percentage of volume.

[0051] Figures 5B is a graph showing a particle size distribution profile of sewage sludge as a
20 percentage of volume.

[0052] Figures 5C is a graph showing a particle size distribution profile of sewage sludge as a percentage of volume.

[0053] Figure 6 is a graph showing dewaterability of sewage sludge as a function of capillary suction time.

25 [0054] Figure 7 is a graph showing sample settleability profiles of sewage sludge.

[0055] Figure 8 is a graph showing a sample response surface profile of separated dairy manure for ortho-phosphate concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)).

[0056] Figure 9 is a graph showing a sample response surface profile of separated dairy manure for SCOD concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)).

[0057] Figure 10A is a graph showing a sample response surface profile of separated dairy manure for ortho-phosphate concentration as a function of temperature (°C) and holding time (minutes).

[0058] Figure 10B is a graph showing a sample response surface profile of separated dairy manure for ortho-phosphate concentration as a function of temperature (°C) and hydrogen peroxide dose (% (v/v)).

[0059] Figure 10C is a graph showing a sample response surface profile of separated dairy manure for ortho-phosphate concentration as a function of holding time (minutes) and hydrogen peroxide dose (% (v/v)).

[0060] Figure 11A is a graph showing a sample response surface profile of separated dairy manure for SCOD concentration as a function of temperature (°C) and holding time (minutes).

[0061] Figure 11B is a graph showing a sample response surface profile of separated dairy manure for SCOD concentration as a function of temperature (°C) and hydrogen peroxide dose (% (v/v)).

[0062] Figure 11C is a graph showing a sample response surface profile of separated dairy manure for SCOD concentration as a function of holding time (minutes) and hydrogen peroxide dose (% (v/v)).

Description

[0063] Throughout the following description specific details are set forth in order to provide a more thorough understanding to persons skilled in the art. However, well known elements may not have been shown or described in detail to avoid unnecessarily obscuring the disclosure.

Accordingly, the description and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

[0064] Unless context dictates otherwise, the term “slurry of organic solids” (as used herein) means waste materials, such as sewage sludge, animal manure, food processing waste, industrial organic waste, and/or the like, suspended in a solvent, such as water. Unless context dictates otherwise, the term “supernatant” (as used herein) means the liquid wastewater solution separated from a slurry of organic solids, for example by means such as gravity sedimentation, floatation, filtration, centrifugation, and/or the like.

[0065] Unless context dictates otherwise, the term “advanced oxidation process” or “AOP” (as used herein) means a thermo-chemical process that employs oxidation to hydrolyze a slurry of organic solids.

[0066] Unless context dictates otherwise, the term “oxidant” (as used herein) means a chemical species that functions as an oxidizing agent. Unless context dictates otherwise, the term “oxidizing agent” (as used herein) means a chemical species that removes an electron from another chemical species and/or transfers electronegative atoms, such as oxygen, to the chemical species.

[0067] Unless context dictates otherwise, the term “upstream” (as used herein in relation to a system for treating a slurry of organic compounds and components thereof) means a position that is more near an inlet end of the system for treating a slurry of organic compounds relative to a position that is more near an outlet end. Unless context dictates otherwise, the term “downstream” (as used herein in relation to a system for treating a slurry of organic compounds and components thereof) means a position opposite to upstream, i.e. a position that is more near the outlet end of the system for treating a slurry of organic compounds relative to a position that is more near an inlet end.

[0068] Unless context dictates otherwise, the term “chemical oxygen demand” or “COD” means the amount of organic compounds in a solvent, such as water. COD is typically expressed in mg/L or g/L. Unless context dictates otherwise, the term “soluble chemical oxygen demand” or “soluble COD” or “SCOD” means the amount of soluble organic compounds in a solvent, such as water. SCOD is typically expressed as mg/L or g/L. Unless context dictates otherwise, the

term “total chemical oxygen demand” or “total COD” or “TCOD” means the total amount of organic compounds in a solvent, such as water. TCOD is typically expressed as mg/L or g/L.

[0069] Unless context dictates otherwise, the term “total Kjeldahl nitrogen” or “TKN” means the sum of organic nitrogen, ammonia (NH_3), and ammonium (NH_4^+) in the chemical analysis of

5 water and/or wastewater.

[0070] Unless context dictates otherwise, the term “about” (as used herein) means near the stated value (i.e. within $\pm 5\%$ of the stated value).

[0071] Hereinafter, preferred embodiments of the present invention are described with reference to the accompanying drawings. However, the present invention is not limited thereto.

10 [0072] Figure 1 is a schematic diagram of a system **10** according to one aspect of the present invention and a process for treating a slurry of organic solids using the system. System **10** includes an advanced oxidation process (AOP) reactor **11** arranged between a downstream treatment vessel **22** and slurry supply conduit **12**. An oxidant supply tank **13** is connected to AOP reactor **11** via an oxidant supply conduit **15**. Conduit **15** may be equipped with a pump **14**
15 for supplying oxidant to AOP reactor **11**.

[0073] In some embodiments, a solid-liquid separation tank **17** is arranged between AOP reactor **11** and downstream treatment vessel **22**. Solid-liquid separation tank **17** is connected to AOP reactor **11** via a conduit **16** and to downstream treatment vessel **22** via a conduit **18**. Solid-liquid separation tank **17** may be connected to a product recovery system **20** via a conduit **19** for
20 recovering nutrients, minerals, and/or organic compounds from the slurry of organic compounds treated by AOP reactor **11**. In such embodiments, product recovery system **20** may be connected to downstream treatment vessel **22** via a conduit **29** to feed a liquid fraction of the AOP treated slurry to downstream treatment vessel **22** following the recovery of nutrients, minerals, and/or organic compounds via a conduit **21**.

25 [0074] In some embodiments, downstream treatment vessel **22** is connected to a solid-liquid separation tank **24** via a conduit **23**. Conduits **25** and **26** are connected to solid-liquid separation tank **24** for removing liquid effluent and dewatered solids, respectively, from tank **24**. Conduit **26** may dispose of residual solids or return solids to downstream treatment vessel **22** for further

processing. Alternatively, conduit **26** may branch into two or more conduits. For example, a conduit **27** may be provided to dispose of residual solids and a conduit **28** may be provided to return solids to downstream treatment vessel **22** for further processing. Where downstream treatment vessel **22** comprises an anaerobic process, downstream treatment vessel **22** may include a vent **30** for venting biogas.

[0075] In operation, a slurry of organic solids is introduced into AOP reactor **11** via conduit **12**. An oxidant, such as hydrogen peroxide (H_2O_2) and/or ozone, is added to the slurry via conduit **15** at the inlet of AOP reactor **11** and the slurry is simultaneously exposed to RF radiation and oxidant inside AOP reactor **11**. Pump **14** works to supply the oxidant in solution from supply tank **13** to AOP reactor **11** via conduit **15**.

[0076] Thermo-chemical treatment of the slurry of organic solids using a combination of an oxidant, such as hydrogen peroxide, and RF radiation serves to solubilize organic solids, provides microbiocidal activity, breaks down organic molecules, and/or reduces the mass of residual organic matter within the slurry. For example, insoluble substances in the slurry, such as fibers and cell walls, may be converted to readily biodegradable, soluble chemical oxygen demand (COD). In some embodiments, the combination of hydrogen peroxide and RF radiation may serve to solubilize up to between about 60% and about 75% of the organic solids present in the slurry. The solubilized organic solids may be recovered or processed further. For example, the solubilized organic solids may enhance anaerobic digestion thereby shortening digestion times, increasing the yield of digested biogas, and/or reducing the amount of solid waste ultimately disposed of.

[0077] The solids content of the slurry of organic compounds effectively thermo-chemically treated within AOP reactor **11** may be between about 0.05% to about 30%. In some embodiments, the solids content of the slurry of organic compounds thermo-chemically treated within AOP reactor **11** may be between about 0.1% to about 15%. Below a solids content of about 0.05%, the energy and chemical requirements to thermo-chemically treat the slurry are likely to become uneconomical. Above a solids content of about 30%, the slurry becomes difficult to convey using conventional fluid pumping equipment and efficient mixing of the oxidant in the slurry becomes difficult due to the viscosity of the slurry.

[0078] Depending on the solids content of the slurry of organic compounds and/or the target treatment results, the amount of oxidant, the heating temperature inside AOP reactor **11**, and/or the period of RF radiation may be varied. For example, the slurry and oxidant mixture may be treated with RF radiation for 5 minutes while maintaining the temperature within AOP reactor **11** between about 60°C to about 200°C. At temperatures less than about 60°C, organic solids within the slurry are not efficiently solubilized. For a given amount of oxidant, increasing the temperature within AOP reactor **11** typically increases the solubilisation of organic solids within the slurry. However, applying temperatures greater than about 200°C and/or supplying excessive amounts of oxidant (for example, greater than 2.5% H₂O₂ by volume (v/v) and/or 2.1% H₂O₂ per percent of total solids (TS) by weight) are unnecessary and/or uneconomical.

[0079] Hydrogen peroxide is a powerful oxidant. Hydrogen peroxide may be converted into highly reactive hydroxyl radicals using RF radiation. Hydroxyl radicals possess a greater oxidation potential than unconverted hydrogen peroxide. The amount of hydrogen peroxide (H₂O₂) added to a slurry of organic solids to be thermo-chemically treated within AOP reactor **11** should be at least 0.03% (v/v) H₂O₂ and/or 0.025% H₂O₂ per percent of TS by weight) in the admixed slurry, or 0.3 g of H₂O₂ per litre of admixed slurry. Below this amount, the effects of thermal hydrolysis by RF radiation alone are not significantly enhanced.

[0080] RF radiation is used to increase the temperature of the admixed slurry to a desired temperature, and thereafter to maintain the temperature for a period of about 0 to about 60 minutes (i.e. RF radiation holding times of about 0 to about 60 minutes). Typically, solubilisation of the organic solids within the admixed slurry is achieved within a holding time of 60 minutes in a batch reactor. Exposure to RF radiation for longer periods of holding time may not improve the degree of solubilisation of the organic compounds. Certain types of slurries of organic compounds may however benefit from longer exposure to RF radiation. For example, slurries containing organic compounds that are more resistant to oxidation and thermal hydrolysis may require longer RF radiation exposure. In some embodiments, the temperature is maintained for a period of 20 minutes at a desired ramp rate of about 3°C/min to about 7°C/min.

[0081] In some embodiments, thermo-chemical treatment within AOP reactor **11** described elsewhere herein may be used to convert up to about 60% of the insoluble COD and phosphorus present in a slurry of organic compounds to soluble COD (SCOD) and ortho-phosphate,

respectively, to convert at least some of the total nitrogen present in the slurry to ammonia, to convert at least some of the insoluble nutrients present in the slurry to a soluble form, and/or to destroy up to about 80% of the volatile solids suspended in the slurry.

[0082] Many processes may be used to further process the AOP treated slurry. Since, as described elsewhere herein, a large fraction of the insoluble COD contained in the slurry has been converted to SCOD, the solid organics fraction of any remaining solids has been reduced. Further treatment of the remaining solids will therefore result in a relatively minor breakdown of any remaining organics. Thus, in some embodiments, it may be beneficial to separate the AOP treated slurry from any remaining solids via solid-liquid separation using known methods.

[0083] In some embodiments, the AOP treated slurry is fed to solid-liquid separation tank **17** via conduit **16** and separated into a solids fraction and a liquids fraction. The solids fraction may be fed to downstream treatment vessel **22** via conduit **18** for further processing. The liquids fraction (i.e. supernatant) may be rich in nutrients such as ortho-phosphate and ammonia and may be fed to product recovery system **20** via conduit **19** to recover the nutrients. Here, the nutrients may be crystallized and recovered from the supernatant via conduit **21**. For example, ortho-phosphate may be recovered as nutrient pellets of struvite, struvite analogs, or other phosphate-containing compounds. The resulting supernatant may be fed to downstream treatment vessel **22** via conduit **29**. The resulting supernatant may be rich in SCOD. In some other embodiments, the liquids fraction may contain volatile fatty acids, such as acetic, propionic, and butyric acids, that may be recovered through one or more of distillation, solvent extraction, and liquid/liquid separation processes.

[0084] In some other embodiments, the AOP treated slurry is fed directly to downstream treatment vessel **22** for further processing.

[0085] In some embodiments, downstream treatment vessel **22** may comprise an anaerobic digestion tank or a fermentation reactor. Biogas produced in anaerobic digestion may be recovered from vessel **22** via vent **30**. Acetate produced during fermentation may be used in industrial processing.

[0086] The digested/fermented slurry of organic solids within downstream treatment vessel **22** may be fed to solid-liquid separation tank **24** via conduit **23** and separated into a solids fraction

and a liquids fraction. The liquids fraction may be discharged from tank **24** via conduit **25** and may be further processed for use as land fertilizer. The solids fraction may be discharged from tank **24** as described elsewhere herein and may be further processed, taken to a solids storage facility, and/or used as fertilizer.

5 **[0087]** Persons skilled in the art will recognize that various upstream and/or downstream processes may be integrated with AOP reactor **11**. Figure 2 schematically illustrates an example embodiment in which AOP reactor **11** is integrated into a wastewater treatment system **40**.

10 **[0088]** System **10** offers a cost-effective means to treat a slurry of organic solids to recover energy and resources in the forms of, for example, soluble organic compounds, nutrient pellets, and/or digested biogas.

15 **[0089]** In some embodiments, pre-treatment of a slurry of organic compounds with ozone may improve solubilisation of the organic compounds during thermo-chemical treatment in AOP reactor **11**. In some other embodiments, the slurry of organic compounds may be first treated with ozone and/or hydrogen peroxide before it is exposed to RF radiation in AOP reactor **11**. In some embodiments, ozone is produced in situ using an ozone generator. In some embodiments, the slurry is ozonated at a flow rate of 1 L/min for 20 minutes before exposing the slurry to RF radiation in AOP reactor **11**. In some embodiments, about 0.02 g to about 0.1 g of ozone per gram of TS may be added. In some embodiments, about 0.06 g of ozone per gram of TS is added.

20 **[0090]** For the treatment of some slurries of organic compounds, such as dairy manure, acidification of the slurry to a pH of between about 2 to about 4 using a strong acid, such as sulphuric acid, may improve the solubilisation of organic compounds within the slurry through acid hydrolysis. Acidification may occur before or after thermo-chemical treatment within AOP reactor **11**.

25 **[0091]** For the treatment of some secondary sewage sludge slurries from an aerobic treatment stage, pH adjustment may be of some but minor benefit to solubilizing COD and reducing suspended solids levels via thermo-chemical treatment thereof. In such cases, a pH in the range of about 6 to about 7 may be desirable.

[0092] Persons skilled in the art will recognize that:

- downstream treatment vessel **22** may comprise one or more of an anaerobic digester, a fermenter, a fixed-film bioreactor, an upflow anaerobic sludge blanket reactor, a hybrid suspended/attached growth bioreactor, and other similar known treatment systems;
- 5 • product recovery system **20** may comprise one or more of solvent extraction, distillation, crystallization precipitation, ion exchange, and direct nutrient use;
- oxidants such as ozone and/or potassium persulfate may be used in place of or in addition to hydrogen peroxide to thermo-chemically treat a slurry of organic compounds according to the present invention;
- 10 • various upstream and/or downstream processes may be integrated with AOP reactor **11** depending on the outcome of needs assessment and the nature of the slurry being treated;
- AOP reactor **11** may be retrofit to existing systems for treating a slurry of organic compounds;
- AOP reactor **11** may comprise a batch process system or a continuous flow process
15 system. The batch process system may comprise a reactor in which a slurry of organic compounds is first introduced and mixed with an oxidant, such as hydrogen peroxide. Persons skilled in the art will recognize that the slurry and oxidant may be admixed before entering the reactor. The admixed slurry is then irradiated with RF radiation inside the reactor to obtain a desired temperature profile before it is discharged using a pump
20 and/or the pressure built-up within the reactor. The continuous flow system may comprise a mixing vessel in which a slurry of organic compounds and an oxidant are admixed and a flow-through vessel in which the admixture of slurry and oxidant are passed. The flow-through vessel is enclosed within a RF radiation chamber and the admixture is exposed to RF radiation to obtain a desired temperature profile as it passes
25 through the flow-through vessel. Untreated slurry is continuously pumped into the mixing vessel and then through the radiation chamber before it is discharged. The slurry treated by either system may be passed through a heat exchanger to preheat untreated slurry. The AOP treated slurry may be further processed downstream and/or subjected to recovery

processes. The slurry may be pretreated upstream before it is treated within the AOP reactor.

[0093] EXAMPLE 1

[0094] Dairy manure was obtained from the Dairy Education & Research Centre, University of British Columbia in Agassiz, British Columbia, Canada. In Part A, a set of ten experiments were performed to investigate the effects of various hydrogen peroxide concentrations and various RF radiation holding times on RF/H₂O₂-AOP with the objective of achieving solids and nutrient solubilisation from the manure. In part B, a set of 15 experiments were performed to investigate the effects of various RF radiation input power intensities, various hydrogen peroxide concentrations, and various RF radiation holding times on RF/H₂O₂-AOP with the objective of achieving solids and nutrient solubilisation from the manure.

[0095] The dairy manure of Part A samples 1.1-1.2 and 2.1-2.4 was comprised of the solid fraction obtained via solid-liquid separation of the manure. Each sample contained about 4% total solids (TS). The dairy manure of Part A samples 1.1 and 1.2 contained about 174 mg/L of total phosphorus (TP) and about 1635 mg/L of total Kjeldahl nitrogen (TKN). The dairy manure of Part A samples 2.1-2.4 contained about 142 mg/L of TP and about 1133 mg/L of TKN. The dairy manure of Part A samples 3.1-3.4 and Part B samples 1-15 comprised unseparated dairy manure containing about 8.1% and about 12.2% TS, respectively. The dairy manure of Part A samples 3.1-3.4 contained about 841 mg/L of TP and about 2877 mg/L of TKN. The dairy manure of the Part B samples contained about 800 mg/L to about 1148 mg/L of TP and about 3630 mg/L to about 4670 mg/L of TKN. The dairy manure samples were each acidified using sulphuric acid (certified ACS plus, Fischer Chemical) to pH 4.0.

[0096] In Part A, the experiments were carried out with RF radiation holding times of 20, 30, and 50 minutes and 0, 0.5, or 1% (v/v) H₂O₂ was added to the manure of each sample. In Part B, the experiments were carried out with RF radiation holding times of 20, 50, and 80 minutes and 0.5, 1, or 1.5% (v/v) H₂O₂ was added to the manure of each sample.

[0097] A RF unit (RF Specialists Ltd., Canada) with a maximum output of 6 kW was used in this study. The unit consisted of an aluminum box with a door at one side and an electrode suspended from polypropylene insulators inside the box. A transmission line connected a

generator output to the electrode. Commercially available microwave safe plastic containers with an aluminum plate moulded to each bottom surface were used as reaction vessels. The vessels were each covered with an aluminum lid. Temperature was measured using a Neoptix (trademark) fiber optic probe inserted into each vessel through a hold in the lid. The ramp time depended on the power intensity used for each sample, which was maintained at the desired level to maintain a uniform rate of heating up to the desired experimental temperature. The experiments in Part A were carried out at an RF radiation input power intensity of 50% (i.e. 2 kW/L). The experiments in Part B were carried out at RF radiation input power intensities of 50, 60, and 70% (i.e. 2 kW/L, 2.7 kW/L, and 3.3 kW/L, respectively). Experiments in both Parts A and B were carried out at a temperature of 90°C. TABLES 1 and 2 list the experimental design of the experiments in Parts A and B, respectively.

[0098] The soluble concentrations of nutrients (i.e. ortho-phosphate and ammonia), COD, and volatile fatty acids (VFA) of the Part A and B samples are listed in TABLES 1 and 2, respectively. Chemical analyses were carried out following the procedures outlined in American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 20th Edition, American Public Health Association, Washington, D.C., 1998 (APHA, 1998). Ortho-phosphate and soluble ammonia were determined using a flow injection system (Lachat Quik-Chem 8000 Automatic Ion Analyzer (trademark)). VFA was determined using a Hewlett Packard 6890 Series II (trademark) gas chromatograph equipped with a flame ionization detector (FID).

[0099] TABLE 1

Sample	Total solids content, %	RF holding time, min	H ₂ O ₂ dose, % (v/v)	Ortho-PO ₄ ³⁻ , mg/L	Ammonia, mg/L	Total COD (TCOD), g/L	SCOD, g/L	VFA, g/L
Raw	4.3±0.2	-	-	43±1	653±2	29.9±8.7	6.4±0.4	0.5±0.1
1.1	3.5±0.7	30	0	148±3	750±12	23.5±1.2	6.5±0.8	1.6±0.1
1.2	2.7±0.2	30	0.5	160±4	816±16	6.2±5.2	6.1±1.0	1.7±0.03
Raw	4.5±0.4	-	-	56±4	634±17	37.2±9.4	3.1±0.3	2.1±0.4
2.1	4.2±0.2	20	0.5	56±4	634±17	37.2±9.4	3.1±0.3	2.1±0.4
2.2	3.8±0.1	50	0.5	127±5	737±10	24.9±16.3	4.3±0.8	2.3±0.0
2.3	4.3±0.1	20	1	116±3	673±7	28.1±14.9	8.4±0.4	2.3±0.0
2.4	4.4±0.2	50	1	119±2	737±17	32.5±9.8	6.1±0.1	2.3±0.0

Sample	Total solids content, %	RF holding time, min	H ₂ O ₂ dose, % (v/v)	Ortho-PO ₄ ³⁻ , mg/L	Ammonia, mg/L	Total COD (TCOD), g/L	SCOD, g/L	VFA, g/L
Raw	9.9±0.1	-	-	281±34	1250±184	115.4±16.3	24.9±6.2	-
Acidified	10.7±0.1	-	-	360±27	1424±120	101.3±3.8	7.3±2.3	6.1±0.6
3.1	8.4±0.0	20	0.5	432±15	1627±58	82.4±0.6	30.7±8.1	6.9±0.3
3.2	8.1±0.2	50	0.5	508±8	1885±93	58.1±4.5	20.7±1.9	7.2±0.2
3.3	7.9±0.9	20	1	550±10	1900±33	56.2±8.1	22.9±1.1	7.1±0.1
3.4	-	50	1	430±18	1707±30	80.9±9.9	25.2±0.4	6.8±0.2

[0100] TABLE 2

Sample	Total solids content, %	Power intensity, %	RF holding time, min	H ₂ O ₂ dose, % (v/v)	Ortho-PO ₄ ³⁻ , mg/L	Ammonia, mg/L	Total COD (TCOD), g/L	SCOD, g/L	VFA, g/l
Raw	12.2	-	-	-	276	480	12	102	6.3
Acidified	12±0	-	-	-	756±127	588±48	9.4±1.3	104±3	5.7±0.4
1	12±0	60	20	0.5	638±129	519±102	16.9±2.5	116±3	4.9±1.5
2	12±0	50	50	0.5	788±20	653±13	22.0±1.1	104±7	6.0±0.1
3	12±1	60	80	0.5	698±31	576±28	19.5±1.6	113±4	5.2±0.1
4	12±0	70	50	0.5	577±44	594±56	23.2±2.1	110±10	5.8±0.4
5	11±0	60	50	1	589±48	619±38	25.3±2.4	114±6	5.9±0.2
6	11±0	50	80	1	732±24	699±14	24.2±0.7	112±5	6.1±0.2
7	12±1	70	20	1	777±33	672±26	24.7±1.8	93±25	5.8±0.1
8	12±1	60	50	1	689±70	721±73	28.0±1.8	117±3	6.2±0.2
9	12±0	70	80	1	631±57	644±31	26.1±2.2	112±7	6.0±0.1
10	12±0	50	20	1	761±31	667±34	23.8±1.0	102±16	5.7±0.2
11	12±0	60	50	1	649±60	651±59	26.2±1.2	113±1	6.0±0.1
12	11±0	60	80	1.5	573±28	646±37	26.2±1.6	102±11	6.1±0.2
13	12±1	70	50	1.5	712±57	692±37	28.7±1.7	119±3	6.0±0.2
14	11±0	50	50	1.5	542±48	590±47	24.7±2.3	117±7	5.5±0.4
15	12±1	60	20	1.5	713±21	625±21	24.4±0.3	101±15	5.5±0.1

[0101] TABLE 1 shows the concentration of soluble ortho-phosphate (ortho-PO₄³⁻) after

5 treatment at the three tested hydrogen peroxide concentrations (0, 0.5, and 1 % (v/v)) and the three RF holding times (20, 30, and 50 minutes). The results showed that RF/H₂O₂-AOP treatment increased ortho-phosphate concentrations. However, ortho-phosphate concentrations were lower for the samples with higher hydrogen peroxide concentration and longer RF holding

time. For example, an ortho-phosphate concentration increase of 41% was observed for sample 3.2 (RF heating for 50 minutes and hydrogen peroxide concentration of 0.5% (v/v) and 20% for sample 3.4 (RF heating for 50 minutes and hydrogen peroxide concentration of 1% (v/v)). An ortho-phosphate concentration increase of 53% was observed for sample 3.3 (RF heating for 20 minutes and hydrogen peroxide concentration of 1% (v/v)) and 20% for sample 3.1 (RF heating for 20 minutes and hydrogen peroxide concentration of 0.5% (v/v)).

[0102] Samples 2.1-2.4 also showed that more than 96% of TP present in these samples was released into solution and that 70% of TP was in the form of soluble ortho-phosphate.

[0103] RF treatment of acidified manure resulted in an increase in soluble ammonia and soluble TKN concentration by 14 to 33% and 27 to 47%, respectively, for all samples. The presence of a higher percentage of soluble TKN than soluble ammonia indicates that nitrogen compounds are solubilized but not converted to ammonia.

[0104] Concentrations of soluble volatile fatty acids (VFA) were observed to increase following RF/H₂O₂-AOP treatment for samples 1.1 and 1.2; however, soluble VFA concentrations did not significantly increase for samples 2.1-2.4 or 3.1-3.4. VFA are intermediate products of thermal and/or oxidation treatment. Two distinct processes are involved in thermal-oxidative treatment: the first process involves the breakdown of large particular organic matter into smaller and more soluble organic components (i.e. thermal decomposition) and the second process involves further oxidation or gasification of some of the resulting organic products (Shanableh et al., Treatment of Sewage Using Hydrothermal Oxidation Technology Application Challenge, 2000, Water Sci. Technol., vol. 41: 85-92).

[0105] Concentrations of SCOD varied among the samples in Part A. For example, the SCOD increased from 20 to 60% for samples 2.1-2.4; however, SCOD trends were not clearly defined in the case of samples 3.1-3.4. Samples 3.1-3.4 had a higher total solids (TS) content than samples 2.1-2.4 (i.e. about 10% compared to about 4%) and the dose of hydrogen peroxide used per gram TS may have been insufficient to solubilize COD.

[0106] In general, the results in TABLE 1 indicate that RF/H₂O₂-AOP treatment under acidic conditions is effective in treating separated solid dairy manure and raw (i.e. unseparated) dairy manure for nutrient release and solids disintegration.

[0107] Nutrient release

[0108] TABLE 2 shows the concentration of soluble ortho-phosphate (Ortho-PO_4^{3-}) after RF/ H_2O_2 -AOP treatment for the three tested hydrogen peroxide concentrations (0.5, 1, and 1.5 % (v/v)), the three RF holding times (20, 50, and 80 minutes), and the three input power intensities (50, 60, and 70%).

[0109] The results showed that ortho-phosphate concentrations were highest for sample 2 (RF heating for 50 minutes, hydrogen peroxide concentration of 0.5% (v/v), and input power intensity of 50%). The yield of ortho-phosphate following only RF was between 58 to 69% of TP while only 24% of TP for the untreated dairy manure.

[0110] The following proposed model is based on the regression coefficients for the concentration of ortho-phosphate remaining in RF/ H_2O_2 treated manure samples 1-15:

$$Y = 2993 - 65P + 3.4T - 785.6D + 0.4P^2 + 0.05T^2 - 115.4D^2 - 0.1PT + 19.1PD - 3.3TD \quad [1]$$

where Y is ortho-phosphate concentration (mg/L), P is input power (%), T is holding time (minutes), and D is H_2O_2 dose (% (v/v)). A correlation coefficient (R^2) of 0.92 was obtained.

Concentrations of ortho-phosphate predicted using equation [1] correlate with the experimentally determined concentrations for samples 1-15.

[0111] According to equation [1], increasing hydrogen peroxide dose decreases the release of ortho-phosphate. Also, increasing the input power intensity decreases ortho-phosphate concentration. Holding time has little effect on ortho-phosphate release. The magnitude of the effect of hydrogen peroxide dose on ortho-phosphate concentration was observed to be greater than the magnitude of the effect of input power intensity.

[0112] A sample response surface profile for ortho-phosphate concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)) is shown in Figure 3. This profile shows that ortho-phosphate concentration was optimized when input power intensity was 64.3%, RF holding time was 65 minutes, and hydrogen peroxide does was 1% (v/v).

[0113] Solids disintegration

[0114] Solids disintegration is represented in terms of SCOD concentration and VFA present in the treated sample. SCOD concentration levels represent the solubilisation of total organic substances in a slurry of organic compounds. VFA are intermediate products in RF/H₂O₂-AOP treatment.

[0115] The TABLE 2 results show that SCOD concentration increased by increasing holding time; however, the SCOD concentration decreased slightly at 80 minutes. Input power intensity was observed to have a negative effect on SCOD concentrations.

[0116] The TABLE 2 results also show that the concentration of ammonia is increased by increasing the dose of hydrogen peroxide but is decreased by increasing input power intensity. . Ammonia is a constituent of struvite, a known potent fertilizer.

[0117] The following proposed model is based on the regression coefficients for the concentration of SCOD in RF/H₂O₂ treated manure samples 1-15:

$$Y = 27969 - 756.5P + 252.5T + 17051.5D + 5.6P^2 - 2.5T^2 - 9636.5D^2 + 0.8PT + 141.6PD - 14.3TD \quad [2]$$

where Y is SCOD concentration (mg/L), P is input power (%), T is holding time (min.), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.92 was obtained. Concentrations of SCOD predicted using equation [2] correlate with the experimentally determined concentrations for samples 1-15.

[0118] A sample response surface profile for SCOD concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)) is shown in Figure 4. It is clear from Figure 4 that high SCOD concentrations were obtained using higher hydrogen peroxide concentrations. The profile also demonstrates that SCOD concentration was optimized when input power intensity was 48.4%, RF holding time was 53 minutes, and hydrogen peroxide dose was 1.2% (v/v).

[0119] The TABLE 2 results show that RF/H₂O₂-AOP treatment yielded digestible compounds, such as VFA. For example, at an input power intensity of 50%, RF holding time of 50 minutes,

and hydrogen peroxide dose of 1.5% (v/v), a VFA concentration of 6.49 g/L was observed. In general, higher VFA concentrations were obtained where hydrogen peroxide dose was higher and input power intensity was lower.

[0120] Hydrogen peroxide dose, reaction time, and power intensity all contributed to nutrient release and COD solubilisation. The effects of each parameter on the soluble materials studied varied. For example, an increase in hydrogen peroxide dose decreased ortho-phosphate release but improved COD solubilisation. Input power intensity negatively affected both ortho-phosphate release and COD concentration, indicating that as input power increased, these soluble materials decreased. The effect of holding time was not as significant as the other two parameters.

[0121] Comparison of RF and MW Processes

[0122] TABLE 3 lists the soluble concentrations of ortho-phosphate and COD after RF/H₂O₂-AOP and MW/H₂O₂-AOP treatment. Dairy manure samples were each acidified using sulphuric acid (certified ACS plus, Fischer Chemical) to pH 4.0. Chemical analyses were carried out following the procedures outlined in APHA, 1998 and using the equipment described elsewhere herein.

[0123] TABLE 3

H ₂ O ₂ dose, % (v/v)	Temp., °C	RF holding time, min	Total solids content, %	Initial ortho- PO ₄ ³⁻ as TP, %	Final ortho- PO ₄ ³⁻ as TP, %	Initial SCOD as total COD (TCOD), %	Final SCOD as total COD (TCOD), %
1 ^e	70	10	0.5	7.7	17.9	1.5	2.2
5 ^e	70	10	1.6	33.3	108.7	17.1	8.9
5 ^f	80	7.5	5.1	20.5	46.8		N/A
8.5	80	7.5	4.3	17.5	35.4		
7	80	10	4.7	19.0	45.6		
1 ^d	120	10	0.5	14.4	22.8	1.2	2.1
3 ^d	120	10	1.6	10.4	88.5	7.1	9.9
6	120	10	3.4	37.5	162.5	8.6	17.7
1.5 ^g	60	10	1.5	10.0	71		N/A
1.5 ^g	90	10	1.5	10.0	72		
1.5	120	10	1.5	10.0	85		

H ₂ O ₂ dose, % (v/v)	Temp., °C	RF holding time, min	Total solids content, %	Initial ortho- PO ₄ ³⁻ as TP, %	Final ortho- PO ₄ ³⁻ as TP, %	Initial SCOD as total COD (TCOD), %	Final SCOD as total COD (TCOD), %
1.5	170	10	1.5	10.0	85		
3 ^h	120	30	6.6	8.4	38.8		N/A
3 ^h	120	30	6.6	8.4	22.8	5.0	9.57 ^b
0.5, 1, 1.5	90	20, 50, 80 ^d	12.2	24.0	50.5 – 90	11.3	14.6 – 26.5

^a Solid dairy manure obtained via solid-liquid separation was used; ^b This dairy manure sample was acidified using hydrochloric acid; ^c Unseparated dairy manure was used; ^d Refers to holding time only (i.e. ramp time is not included); ^e Kenge, et al., 2009, Treating solid dairy manure using microwave-enhanced advanced oxidation process, J. Environ. Sci. Health Part B, vol. 44: 606-612; ^f Kenge, A., 2008, Enhancing nutrient solubilisation from organic waste using microwave technology, MASc thesis, University of British Columbia, Vancouver, Canada; ^g Pan, et al., 2006, Microwave pretreatment for enhancement of phosphorus release from dairy manure, J. Environ. Sci. Health Part B, vol. 41(4): 451-458; ^h Jin, et al., 2009, Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment, Water Res., vol. 43(14): 3493-3502.

[0124] TABLE 3 shows that the results of RF/H₂O₂-AOP treatment are comparable to those of MW/H₂O₂-AOP treatment at similar operating temperatures despite the manure sample treated using RF/H₂O₂-AOP having a higher total solids content (i.e. 12.2% compared to ≤ 6.6%). While RF radiation processes required longer heating times than the MW radiation processes, less energy was required by the RF radiation processes. For example, the energy required by the RF/H₂O₂-AOP systems was in the range of about 289 to about 314 kJ/L. In contrast, the energy required by the MW/H₂O₂-AOP systems was in the range of 200 to 577 kJ/L. Energy estimation was based on the method used by Danesh, P., et al., 2008, Phosphorus and heavy metal extraction from wastewater treatment plant sludges using microwaves for generation of exceptional quality biosolids, Water Environ, Federation, 80(9), 784-795.

[0125] In batch processes, the RF radiation processes were also capable of handling higher volumes of manure and slurries having a higher total solids content than the MW radiation processes.

[0126] Temperature was one of the most significant factors affecting treatment efficiency of MW/H₂O₂-AOP. Treatment efficiency was observed to be greatest when MW/H₂O₂-AOP

temperature was 120°C. For example, increasing temperature increased SCOD concentration. RF/H₂O₂-AOP was studied at only 90°C and so no temperature trends were observable.

[0127] H₂O₂ dose was one of the most significant factors affecting treatment efficiency (i.e. nutrient release and solids disintegration) of both MW/H₂O₂-AOP and RF/H₂O₂-AOP. For RF/H₂O₂-AOP, the effect of H₂O₂ dose on treatment efficiency was greater than the effect of either heating time or input power intensity. By increasing the hydrogen peroxide dose, SCOD, ammonia, and VFA release were improved. However, hydrogen peroxide dose had a negative effect on ortho-phosphate release, as discussed elsewhere herein, suggesting that high concentrations of hydrogen peroxide are not required to solubilize phosphate at the treatment temperature employed during RF/H₂O₂-AOP treatment. For MW/H₂O₂-AOP, increasing the hydrogen peroxide dose increased ortho-phosphate release; however, this is not necessarily required since most ortho-phosphate is solubilized upon acid addition (Lo, et al., 2010, The effects of irradiation intensity on the microwave-enhanced advanced oxidation process, J. Environ. Sci. Health Part A, vol. 45: 257-262). Initial ortho-phosphate concentrations in untreated manure were observed to vary, which may be due to the age of the manure experimented on. The greater the age of the manure the higher the ortho-phosphate content. Increasing the H₂O₂ dose also increased the SCOD/total COD (TCOD) ratio at 120°C.

[0128] Input power intensity was observed to affect the extent of nutrient release and solids disintegration of dairy manure for MW/H₂O₂-AOP treated samples. For example, the highest concentration of ortho-phosphate was observed when the MW radiation power level was 1000W and the ramp rate was 20°C/minute. SCOD concentration was greatest when the ramp rate was 30°C/minute. In contrast, RF/H₂O₂-AOP input power intensity was observed to have a negative effect on treatment efficiency. This may be attributed to the variable ramp times associated with the studied input power intensities. For example, the average ramp times associated with 50, 60, and 70% power input intensities were about 10, 8, and 6.5 minutes (i.e. about 7, 9, and 11°C/minute), respectively. Therefore, a process that operates at a lower input power intensity operates for a longer period of time and may release higher concentrations of nutrients. Also, the total reaction time, which includes ramp time required to reach a desired temperature and heating time, was longer for RF/H₂O₂-AOP than MW/H₂O₂-AOP.

[0129] Heating time and ramp rates significantly affected treatment efficiency of both MW/H₂O₂-AOP and RF/H₂O₂-AOP. Improved solubility of ortho-phosphate and COD is observed with longer heating times. Heating time was observed to have a positive coefficient in the regression equations [1] and [2] for RF/H₂O₂-AOP, indicating that solubilisation is increased with longer heating times. However, for RF/H₂O₂-AOP, the effect of heating time on treatment efficiency was less pronounced than the effects of hydrogen peroxide dose and input power intensity. This may be due to the longer heating times used to study RF/H₂O₂-AOP compared to those used to study MW/H₂O₂-AOP (i.e. 20, 50, and 80 minutes for RF/H₂O₂-AOP and 7.5, 10, and 30 minutes for MW/H₂O₂-AOP).

[0130] The TABLE 3 results show that the fraction of ortho-phosphate present as a function of total phosphorus increased after both MW/H₂O₂-AOP and RF/H₂O₂-AOP. For MW/H₂O₂-AOP, the fraction of ortho-phosphate increased from 20.5% to 46.8% for a manure sample containing 5.1% TS and treated at 80°C, while it increased from 24% to as high as 69.8% for a manure sample containing 12.2% TS and treated at 90°C by RF/H₂O₂-AOP.

[0131] In summary, RF/H₂O₂-AOP treatment was at least as effective as MW/H₂O₂-AOP treatment in releasing nutrients and disintegrating solids from dairy manure. In spite of the longer heating times used during RF/H₂O₂-AOP treatment, the capacity of this system to efficiently treat higher volumes of manure with higher solids contents makes RF/H₂O₂-AOP batch processing favourable in some instances over MW/H₂O₂-AOP.

[0132] EXAMPLE 2

[0133] Aerobic sludge was obtained from the pilot-plant wastewater treatment facilities located at the University of British Columbia (UBC) campus. The facilities use membrane-enhanced biological phosphorus removal consisting of three stages (anaerobic, anoxic, and aerobic) to remove carbonaceous materials, nitrogenous compounds, and phosphorus from wastewater. The sludge retention time (SRT) was maintained at approximately 25 days and processes were operated with a hydraulic retention time (HRT) of 10 hours.

[0134] Unless context dictates otherwise, the term “SRT” (as used herein) means the average time the activated sludge solids are in the system and is typically expressed in days. Unless

context dictates otherwise, the term “HRT” (as used herein) means the average residence time of wastewater in an aeration tank.

[0135] In Part A, a set of four experiments was performed and in part B a set of five experiments was performed to investigate the effects of radiofrequency heating, ozone, and/or various hydrogen peroxide concentrations on solids and nutrient solubilisation from the sludge.

[0136] The RF unit (RF Specialists Ltd., Canada) described in Example 1 was used in both parts of this study. Each experiment in Parts A and B was carried out at an RF temperature of 95°C and an RF radiation input power level of 20% (i.e. 800 Watt/L). Where required, ozone was produced in situ using an ozone generator (VMUS-4 AZCO Ind., Canada) and the sludge was ozonated at a flow rate of 1 L/min for 20 minutes. The experimental conditions used in Parts A and B are presented in TABLES 4 and 5, respectively.

[0137] TABLE 4

Sample	Description	Oxygen rate, L/min	Ozone duration, min	H ₂ O ₂ dose, % (v/v)	RF temperature, °C	RF ramp time, min	RF holding time, min
	Raw	0	0	0			
	Ozone	1	20	0			
1.1	Ozone + RF	1	20	0	95	9.3	20
1.2	Ozone/RF + H ₂ O ₂	1	20	0.1	95	6.5	20
1.3	H ₂ O ₂ + RF	0	0	0.2	95	7.9	20
1.4	H ₂ O ₂ + RF	0	0	0.1	95	6.5	20

[0138] TABLE 5

Sample	Description	Oxygen rate, L/min	Ozone duration, min	H ₂ O ₂ dose, % (v/v)	RF temperature, °C	RF ramp time, min	RF holding time, min
	Raw						
2.1	RF	0	0	0	95	9.6	20
	Ozone	1	20	0			
2.2	Ozone + RF	1	20	0	95	13	20
2.3	Ozone/RF + H ₂ O ₂	1	20	0.2	95	9	20

Sample	Description	Oxygen rate, L/min	Ozone duration, min	H ₂ O ₂ dose, % (v/v)	RF temperature, °C	RF ramp time, min	RF holding time, min
2.4	H ₂ O ₂ + RF	0	0	0.2	95	6.9	20
	H ₂ O ₂ + Ozone	1	20	0.2			
2.5	H ₂ O ₂ + ozone/RF	1	20	0.2	95	8.1	20

[0139] TABLES 6 and 7 list the total solids content, volatile solids (VS) content, the total concentration of COD, and the soluble concentrations of COD and VFA after treatment for the experiments in Part A and B, respectively. Chemical analyses were carried out following the procedures outlined in APHA, 1998 and using the equipment described elsewhere herein.

5 [0140] TABLE 6

Sample	Description	pH	Total solids content, %	VS, %	SCOD, mg/L	TCOD, mg/L	VFA, mg/L
	Raw	6.5	0.49	0.38	0	5008±278	8.7±4.3
	Ozone	5.9	0.5	0.35	626±87	3216±174	23.1±0.8
1.1	Ozone + RF	5.1	0.38	0.35	1088±79	3134±492	33.3±1.8
1.2	Ozone/RF + H ₂ O ₂	3.9	0.45	0.32	1784±102	2561±209	64.4±1.4
1.3	H ₂ O ₂ + RF	5.8	0.49	0.37	982±25	3879±128	35.2±2.5
1.4	H ₂ O ₂ + RF	6.3	0.53	0.38	319±69	3658±35	27.4±3.4

[0141] TABLE 7

Sample	Description	pH	Total solids content, %	VS, %	SCOD, mg/L	TCOD, mg/L	VFA, mg/L
	Raw	6.3	0.41	0.32	0	4536±16	1.2±0.1
2.1	RF	6.1	0.38	0.29	1353±80	3956±129	13.1±1.9
	Ozone	5.7	0.39	0.31	705±39	4002±496	24.8±1.2
2.2	Ozone + RF	5.4	0.39	0.3	1698±107	3570±256	36.3±3.9
2.3	Ozone/RF + H ₂ O ₂	3.2	0.38	0.28	2304±125	3024±182	91.6±3.6
2.4	H ₂ O ₂ + RF	5.7	0.43	0.33	1046±0	3945±48	39.0±5.8
	H ₂ O ₂ + Ozone	5.9	0.39	0.3	1243±189	4017±443	27.5±0.8
2.5	H ₂ O ₂ + ozone/RF	5.5	0.41	0.31	1486±35	3934±79	40.7±6.4

[0142] TABLES 8 and 9 list the soluble concentrations of nutrients and metals after treatment. Chemical analyses were carried out following the procedures outlined in APHA, 1998 and using the equipment described elsewhere herein. TP and TKN were determined using a flow injection system (Lachat Quik-Chem 8000 Automatic Ion Analyzer (trademark)). Calcium (Ca),
5 magnesium (Mg), and potassium (K) were determined using a Varian Spectra 220 Fast Sequential Atomic Absorption Spectrometer (trademark).

[0143] TABLE 8

Sample	Description	Total Kjeldahl nitrogen (TKN), mg/L	Soluble total Kjeldahl nitrogen, TKN, mg/L	Ammonia, mg/L	Total phosphorus (TP), mg/L	Ortho-PO ₄ ³⁻ , mg/L	Ca	Mg	K
	Raw	323±9.2	5±2.3	0.6±0.1	178±7.8	5.0±2.7	2.8±0.1	0	12.3±1.6
	Ozone	270±7.8	84±5.7	2.6±0.1	148±2.8	35.6±12.0	6.5±2.4	5.1±1.5	48.9±6.6
1.1	Ozone + RF	270±1.5	122±20	4.6±0.3	151±4.5	119.2±3.9	21.9±1.8	24.4±0.9	64.7±2.3
1.2	Ozone/RF + H ₂ O ₂	255±22	184±6.5	12±0.7	140±4.0	103.7±19.5	26.5±0.4	25.9±1.3	64.8±4.6
1.3	H ₂ O ₂ + RF	287±8.1	119±3.4	9.1±0.6	153±5.9	89.6±3.1	13.3±1.5	17.4±0.6	68.8±6.8
1.4	H ₂ O ₂ + RF	300±0.7	87±8.2	6.1±0	159±2.1	103.1±1.0	11.7±0.7	18.0±1.7	60.5±0.5

[0144] TABLE 9

Sample	Description	Total Kjeldahl nitrogen (TKN), mg/L	Soluble total Kjeldahl nitrogen, TKN, mg/L	Ammonia, mg/L	Total phosphorus (TP), mg/L	Ortho-PO ₄ ³⁻ , mg/L	Ca	Mg	K
	Raw	356±58	25±4.0	0.8±0	127±4.2	5±1.8	1.2±0.6	0	6.6±0.8
2.1	RF	285±50	80±7.1	3.4±0	109±9.1	15.0±4.3	3.4±2.4	5.7±2.0	39.6±2.9
	Ozone	313±37	99±1.9	2.0±0.7	121±11	30.0±9.0	2.8±0.7	1.5±0.4	30.9±1.0
2.2	Ozone + RF	283±41	133±5.5	5.4±0.2	99±5.9	60.8±8.1	14.2±1.6	11.7±1.2	43.1±7.2
2.3	Ozone/RF + H ₂ O ₂	285±45	197±6.8	18±1.0	93±8.5	70.0±10.1	25.7±3.1	16.5±2.1	44.7±2.0
2.4	H ₂ O ₂ + RF	312±54	120±7.8	4.7±0	106±3.6	76.1±10.5	8.9±3.5	7.8±2.8	38.4±9.2
	H ₂ O ₂ + Ozone	313±36	83±7.5	10±1.6	106±7.1	62.6±14.1	3.1±0.4	1.7±1.0	31.9±3.3
2.5	H ₂ O ₂ + ozone/RF	299±45	123±3.5	5.9±0.1	108±1.5	54.1±1.9	9.9±0.5	8.8±1.1	40.3±1.4

[0145] Settleability was determined by first mixing the sludge with a glass rod and then settling the sludge in a 100 mL graduated cylinder over 60 minutes. The sludge level was recorded every 5 minutes. Dewaterability was determined in terms of capillary suction time (CST) using a Komline-Sanderson (trademark) capillary suction timer. Particle size measurements were conducted using a Malvern Instrument Mastersizer 2000 (trademark) with a Hydro S (trademark) automated sample dispenser unit. Particle size distribution is shown in TABLES 10 and 11, where $d(0.1)$, $d(0.5)$, and $d(0.9)$ represent 10%, 50%, and 90% volume distributed in the range from 0 μm to 0.1 μm , 0 μm to 0.5 μm , and 0 μm to 0.9 μm , respectively.

[0146] In general, larger flocs are more easily dewatered than smaller flocs and the presence of smaller flocs tend to reduce dewaterability. A particle size distribution profile may indicate the positive or negative effects on dewaterability (Neyens, et al., A Review of Thermal Sludge Pre-Treatment Process to Improve Dewaterability, 2003, J. Haz. Mat. B, vol. 98(1-3): 51-67).

[0147] Organics Solubility

[0148] During oxidation and/or thermal treatment, the cell wall of a microorganism is destroyed and cytoplasm is dissolved into sludge water. Water insoluble substances with high molecular weight are split into smaller, water soluble and biodegradable fragments.

[0149] SCOD concentration was observed to increase for each experiment in Parts A and B. Samples having a higher H_2O_2 dose had a higher SCOD concentration (see samples 1.3 and 1.4). Samples treated with ozone alone had SCOD concentrations of 626 mg/L and 705 mg/L. When these samples were subjected to RF heating, the SCOD concentrations increased to 1088 mg/L (sample 1.1) and 1698 mg/L (sample 2.2), respectively (see TABLES 6 and 7). When the ozonated samples were subjected to a combination of RF heating and hydrogen peroxide, the SCOD concentrations increased to 1784 mg/L (sample 1.2: 0.1% (v/v) H_2O_2) and 2304 mg/L (sample 2.3: 0.2% (v/v) H_2O_2). When the ozonated sample was subjected to hydrogen peroxide (i.e. H_2O_2 + ozone), the SCOD concentration was 1243 mg/L. Thus, a higher SCOD concentration was obtained for the sample treated with ozone and hydrogen peroxide than the sample treated with ozone alone. Without being limited to any theory, this may be attributable to a higher SCOD concentration being obtainable using a greater amount of oxidant and/or the

combination of hydrogen peroxide and ozone generating a greater amount of hydroxyl radicals resulting in a more reactive treatment than either oxidant used alone.

[0150] Samples 2.3 and 2.5 were treated with the same amount of oxidant; however, sample 2.3 was first ozonated and then treated with hydrogen peroxide and RF heating and sample 2.5 was ozonated with hydrogen peroxide treatment followed by RF heating. A higher SCOD concentration was obtained for sample 2.3 than for sample 2.5 (2304 mg/L compared to 1486 mg/L). Without being limited to any theory, it is possible that a synergistic effect is achieved between RF heating and hydrogen peroxide for sample 2.3. Persons skilled in the art will understand that hydrogen peroxide may be added to a slurry of organic solids before ozonation; however, it is thought that disintegration is enhanced by first ozonating a slurry of organic solids followed by hydrogen peroxide treatment (Duguet, et al., Improvement in the Effectiveness of Ozonation of Drinking Water through the use of Hydrogen Peroxide, 1985, J. International Ozone Association, vol. 7(3): 241-258). A one-factor analysis of variance (ANOVA) was conducted to determine the effect of ozone and hydrogen peroxide dose on SCOD release. The effect of each oxidant individually was significant ($p < 0.05$); however, a two-way ANOVA involving both oxidant doses was not significant.

[0151] SCOD results were comparable to previous microwave studies (Yin, et al., An Ozone/Hydrogen Peroxide/Microwave-Enhanced Advanced Oxidation Process for Sewage Sludge Treatment, 2007, J. Environ. Sci. Health Part A 42, 1177-1181).

[0152] TABLES 6 and 7 show the concentrations of VFA after treatment. RF heating alone (sample 2.1) yielded the lowest concentration of VFA (13.1 mg/L). Ozone and ozone/hydrogen peroxide treatments yielded VFA concentrations of 24 mg/L and 27.5 mg/L, respectively. A higher VFA concentration was obtained by thermal-oxidation treatment. The $O_3/RF + H_2O_2$ treated sludge (sample 2.3) had the highest concentration of VFA (91.6 mg/L) and the lowest pH (3.2). The reduced pH is attributable to the production of VFA in the treated sample (i.e. the higher the concentrations of VFA, the lower the pH).

[0153] VFA results were comparable to previous microwave studies (Liao, et al., Sludge Reduction and Volatile Fatty Acid Recovery Using Microwave Advanced Oxidation Process, 2007, J. Environ. Sci. Health A, vol. 42: 633-639).

[0154] Physical Properties

[0155] TABLES 10 and 11 show that the size of the majority of particles of sludge used in this study were in the range of 14 to 105 μm . This is smaller than the typical bacterial cell flocs found in activated sewage sludge where most of the particles are between 5 and 300 μm (Jorand, et al., Chemical and Structural (2D) Linkage Between Bacteria within Activated Sludge Flocs, 1995, Water Res., vol. 29: 1639-1647).

[0156] TABLE 10

Sample	Description	d(0.1) μm	d(0.6) μm	d(0.9) μm
	Raw	14.74	37.30	85.47
	Ozone	11.99	38.28	109.41
1.1	Ozone + RF	11.14	37.74	111.59
1.2	Ozone/RF + H_2O_2	8.31	33.33	130.16
1.3	H_2O_2 + RF	10.29	30.95	81.13
1.4	H_2O_2 + RF	11.55	32.81	82.47

[0157] TABLE 11

Sample	Description	d(0.1) μm	d(0.6) μm	d(0.9) μm
	Raw	17.02	41.41	104.62
2.1	RF	13.95	36.74	94.47
	Ozone	9.89	34.72	109.75
2.2	Ozone + RF	7.68	27.69	84.36
2.3	Ozone/RF + H_2O_2	11.62	32.15	82.73
2.4	H_2O_2 + RF	12.21	37.06	118.31
	H_2O_2 + Ozone	13.72	37.25	97.57
2.5	H_2O_2 + Ozone/RF	11.74	35.09	99.97

[0158] The presence of a large number of smaller flocs reduces the effluent quality and dewatering properties of the sludge. As seen in Figure 5A, with RF heating alone (sample 2.1), the size distribution profile shifted towards smaller particles sizes (i.e. an increase in percent volume was seen for a smaller particle range). This indicates that thermal treatment achieved particle breakdown. With RF heating and hydrogen peroxide treatment (sample 2.4), the distribution profile shifted towards even smaller particle sizes than with RF heating alone; however, percent volume increased slightly for the larger particle sizes. Without being limited to any theory, it is thought that the larger particle sizes were formed due to either chemical

reactions with the hydrogen peroxide or a coagulation of smaller particles on detachment of extracellular polymeric substances (EPS) from the sludge. A detachment of EPS from sludge was found to enhance coagulation (Neyens, et al., 2003, A review of thermal sludge pre-treatment process to improve dewaterability, J. Haz. Mat. B, vol. 93(1-3): 51-67)

[0159] Figure 5B shows the particle size distribution of raw sludge, ozone treated sludge, and ozonated sludge treated further with RF heating. With ozone treatment, percent volume increased in the higher and lower particle size ranges. Compared to the ozone treated sludge, RF heating shifted the distribution profile of the ozonated sludge towards smaller particle sizes.

[0160] Figure 5C shows the particle size distribution of raw sludge, sludge treated with ozone and hydrogen peroxide, ozonated sludge further treated with hydrogen peroxide and RF heating (sample 2.3), and sludge oxidized with ozone and hydrogen peroxide and further treated with RF heating (sample 2.5). Similar amounts of oxidants were used where required. The particle size distribution was observed to be smallest for sample 2.3, followed by sample 2.5, and then the sludge oxidated with ozone and hydrogen peroxide. These results mirror the observed SCOD concentration trends (i.e. SCOD concentration was highest for the ozonated sludge further treated with hydrogen peroxide and RF heating).

[0161] Figure 6 shows the dewaterability results. CST was observed to increase for all samples, except the ozonated sludge further treated with hydrogen peroxide and RF heating (sample 2.3). CST was greatest for the sample treated with RF heating alone (sample 2.1). A very high standard deviation of CST was observed for sample 2.1. This may be attributed to a duplicate sample deviating from the others. Without being limited to any theory, it is assumed that the release of EPS from the sludge increased CST indicating deteriorated dewaterability in the treated sludge. With RF heating, the amount of attached EPS was reduced thereby increasing CST.

[0162] Sludge dewaterability is thought to be relative to the amount of EPS attached to the cells present in the sludge. CST decreases with an increase in EPS to a point, beyond this point, a further increase in EPS deteriorates CST (Houghton, et al., 2001, Municipal wastewater sludge dewaterability and the presence of microbial extracellular polymer, Water Science Technol., vol. 44(2-3): 373-379). The microorganisms embedded in a matrix of EPS are thought to be mainly

responsible for the structural and functional integrity of the aggregates (Flemming, et al., 2001, Relevance of microbial extracellular polymeric substances (EPSs), Part 1, Structure and ecological aspects, *Water Sci. Technol.*, vol. 43(6): 1-8; Neyens et al., 2003, A review of thermal sludge pre-treatment process to improve dewaterability, *J. Haz. Mat. B*, vol. 98(1-3): 51-67). Thermal, chemical, and thermal-chemical treatment causes EPS to detach from a cell surface. The detached EPS may be further broken down into simpler forms, resulting in high concentrations of detached EPS and small particles in the sludge. The detached EPS and residual solids may block the pores of the filter paper used when measuring CST thereby preventing water from escaping the treated solution (Chen, et al., 2001, Effect of acid and surfactant treatment on activated sludge dewatering and settling, *Water Res.*, vol. 35(11): 2615-2620).

[0163] CST was observed to increase for samples treated with ozone and with hydrogen peroxide and ozone; a higher CST was observed for the ozonated sample than the sample treated with ozone and hydrogen peroxide. The reaction mechanism of ozone and hydrogen peroxide treatment differs from that of ozone treatment alone. It is thought that the reaction for the ozone and hydrogen peroxide reaction occurs within a biofilm, and only degrades extracellular material matrix and not microorganisms (Christensen, et al., 1996, Degradation of double-stranded xanthan by hydrogen peroxide in the presence of ferrous ions: comparison to acid hydrolysis, *Carbohydrate Res.*, vol. 280: 85-99). Thus, smaller particles are produced with hydrogen peroxide and ozone treatment over ozone treatment alone. Unlike ozone and hydrogen peroxide treatment, ozonation alone destroys the cell walls of microorganisms thereby dissolving cell cytoplasm in the sludge. This results in more small particles in solution (Figure 5b and TABLES 10 and 11). An increase in the electrostatic repulsion between small particles causes deterioration of dewatering properties (Christensen, et al., 1990, Biofilm removal by low concentration of hydrogen peroxide, *Biofouling*, vol. 2: 165-175; Neyens, et al., 2003, A review of thermal sludge pre-treatment process to improve dewaterability, *J. Haz. Mat. B*, vol. 98(1-3): 51-67). Thus, ozone treatment had a negative effect on sludge dewaterability (Liu, et al., 2001, Extracellular polymers of ozonized waste activated sludge, *Water Sci. Technol.*, vol. 44(10): 137-142; Weemaes, et al., 2000, Anaerobic digestion of ozonized biosolids, *Water Res.*, vol. 34(8): 2330-2336).

[0164] The CST value observed for sample 2.3 was similar to that observed for untreated sludge. The pH observed for this sample (i.e. pH of 3.2) was near the isoelectric point of sewage sludge. It has been observed that a minimum dissociation constant occurs in the pH range of 2.6 to 3.6 (Liao, et al., 2002, Inter-particle interactions affecting the stability of sludge flow, *J. Colloid Interf. Sci.*, vol. 249: 372-380). The repulsive electrostatic interactions are minimized near the isoelectric point such that fine flocs can approach each other more closely. As a result, the sludge was more stable. The dewaterability of sludge has been shown to improve as pH decreases by Neyens, et al., 2003, A review of thermal sludge pre-treatment process to improve dewaterability, *J. Haz. Mat. B*, vol. 98(1-3): 51-67. Sample 2.3 had the highest SCOD and VFA concentrations in addition to the smallest particle sizes and fastest settling rates.

[0165] Figure 7 shows the sludge settleability profiles of the TABLES 4 and 5 samples. The profiles are categorized into four distinct groups: (i) very poor settling (raw sludge, RF, and $\text{H}_2\text{O}_2 + \text{O}_3$); (ii) moderate settling (ozone treatment alone); (iii) good settling ($0.2\% \text{ RF} + \text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2 + \text{O}_3/\text{RF}$, $0.1\% \text{ RF} + \text{H}_2\text{O}_2$, and O_3/RF), and (iv) excellent settling ($\text{O}_3/\text{RF} + \text{H}_2\text{O}_2$). The sludge used in Parts A and B of this study was observed to have very poor settling properties. This may be due to poor floc microstructure, resulting in the compact core of sludge flocs being too small (between about 20 to about 80 μm). Settleability was improved on addition of an oxidant, either ozone or hydrogen peroxide. It has been suggested that cations, specifically bivalent cations aid flocculation thereby improving settling (Tezuka, Y., 1969, Cation-dependent flocculation in a *Floavobacterium* species predominant in activated sludge, *Applied Microbiol.*, vol. 17: 222-226). Cations released into solution following treatment are listed in TABLES 8 and 9. The best settling was observed for the $\text{O}_3/\text{RF} + \text{H}_2\text{O}_2$ sample. This may be attributed to high oxidation and cell disintegration. As discussed elsewhere herein, EPS removed from the cell surface of sludge is beneficial for agglomerating the sludge, thereby improving settleability. Another possible reason is that a large amount of bivalent cations were present in the sample. For raw sludge and the sample treated with ozone and hydrogen peroxide, the sludge settled to the bottom and 10-15 mL of sludge flocs were suspended in a top layer. The clarified liquid of the samples treated with hydrogen peroxide had a lighter colour, depending on the hydrogen peroxide dose. The $\text{O}_3/\text{RF} + \text{H}_2\text{O}_2$ sample had excellent settling properties (i.e. rapid sludge settling) and the clarified liquid was very light in colour. The sludge settled to the bottom and appeared as a powder-like suspension, unlike what was observed for the other samples.

[0166] A two-way ANOVA was performed on samples 2.3 and 2.5 to determine the effects of hydrogen peroxide before and after ozonation on settling and the CST of treated sludge. The difference in settling and CST was statistically significant for both samples at 99% confidence interval (i.e. settling and CST values were different between the two samples). However, a similar two-way ANOVA performed on samples 2.3 and 2.5 conducted on SCOD concentration was not statistically significant. Nonetheless, sample 2.3 resulted in faster settling than sample 2.5. Lower CST and higher SCOD concentration was observed for sample 2.5 over sample 2.3. Thus, overall, sample 2.3 performed better than sample 2.5.

[0167] Nutrient and Metal Release

[0168] TABLES 8 and 9 list the soluble concentrations of nutrients and metals after treatment. Soluble phosphorus was observed to increase with RF heating (sample 2.1). Phosphorus was also released into solution upon all oxidation treatments. For Parts A and B, ortho-phosphate concentration for samples treated with RF heating and oxidation was in the narrow range of 89 to 119 mg/L and 60 to 74 mg/L, respectively. In previous studies, oxidants have not been observed to play a significant role in phosphorus release (Wong et al., 2007, Factors affecting nutrient solubilisation from sewage sludge in microwave advanced oxidation process, J. Environ. Science Health Part A, vol. 42(6): 825-829. These results are consistent with previous microwave studies (Yin et al., 2007, An ozone/hydrogen peroxide/microwave-enhanced advanced oxidation process for sewage sludge treatment, J. Environ. Sci. Health Part A, vol. 42: 117-1181).

[0169] Oxidant dose was observed to play a significant role in the release of ammonia into solution. A higher oxidant concentration yielded higher soluble TKN and ammonia concentrations. High soluble TKN concentrations were observed for all samples; however, low ammonia concentrations were observed. It is speculated that most of the soluble TKN was in the form of protein, amino acid, and other nitrogen containing species, but not ammonia. Oxidant dose was observed to influence soluble TKN concentration (see sample 1.3 vs. sample 1.4 and sample 1.2 vs. sample 2.3). The treatment sequence also affected soluble TKN concentrations (see sample 2.3 vs. sample 2.5). The O₃/RF + H₂O₂ sample (sample 2.3) was observed to have the highest soluble TKN concentration. A paired t-test was applied to test the difference in the concentration of ammonia and soluble TKN for all samples. The difference was found to be statistically similar ($p < 0.05$) for each sample in Parts A and B at 95% confidence interval. The

trend observed for ammonia concentration was the same as that for soluble TKN concentration. Yi et al., 2014, Effects of microwave, ultrasonic and enzymatic treatment on chemical and physical properties of waste activated sludge, J. Environ. Sci. Health Part A, vol. 49(2): 203-209 reported that most protein and amino acids are liberated from particulate into soluble form in microwave-oxidation treatment; however, they are not converted into ammonia. The results of this study are consistent with previous microwave studies (Wong, et al., 2007, Factors affecting nutrient solubilisation from sewage sludge using microwave-enhanced advanced oxidation process, J. Environ. Sci. Health Part A, vol. 42: 825-829; Yin et al., 2007, An ozone/hydrogen peroxide/microwave-enhanced advanced oxidation process for sewage sludge treatment, J. Environ. Sci. Health Part A, vol. 42: 117-1181; Yi et al., 2014, Effects of microwave, ultrasonic and enzymatic treatment on chemical and physical properties of waste activated sludge, J. Environ. Sci. Health Part A, vol. 49(2): 203-209).

[0170] In Part A, total metal concentrations of the raw sludge were 48 ± 4.9 , 49.2 ± 3.2 , and 67.7 ± 8.1 mg/L for Ca, Mg, and K, respectively. In Part B, total metal concentrations of the raw sludge were 40.3 ± 1 , 42.1 ± 1.9 , and 52.5 ± 11.8 mg/L for Ca, Mg, and K, respectively. The trend of metal release was similar to that of solids disintegration and nutrient release upon treatment. For sludge treated with RF heating (sample 2.1), Ca and Mg concentrations increased slightly, while most K was released into solution. The metal concentrations of the sludge treated with ozone were similar to those observed for sample 2.1. Thermal-oxidation treatment increased all metal concentrations. Ca, Mg, and K release was highest for the $O_3/RF + H_2O_2$ sample: about 65% of total Ca, about 70% of total Mg, and most of the total K.

[0171] RF heating and/or oxidation treatment damages microbial cell structure releasing nutrients into solution. The effectiveness of the tested treatment processes was in the following order, from most to least effective: RF heating-oxidation, oxidation, and RF heating. RF heating-oxidation treatment increased cell disintegration and nutrient release, improved settleability and dewaterability, and decreased particle sizes. The $O_3/RF + H_2O_2$ treated sample had the highest SCOD, VFA, ammonia, and metal ion concentrations, as well as the smallest CST and excellent settling properties.

[0172] EXAMPLE 3

[0173] Dairy manure was obtained from the Dairy Education & Research Centre, University of British Columbia in Agassiz, British Columbia, Canada. The manure was separated by adding water to and decanting water from the manure to remove sand. The separated manure containing 4.4% TS was acidified using sulphuric acid (certified ACS plus, Fischer Chemical) to pH 4.0.

[0174] Dairy manure contains fats, proteins, lignin, carbohydrates, and inorganic residue. It is rich in a variety of nutrients including nitrogen, phosphorus, and minerals. The solids fraction of dairy manure following liquid-solids separation results in a manure with a higher lignocellulosic and phosphorus content than unseparated manure. Separated solids dairy manure is considered to be a better substrate for nutrient and energy recovery than unseparated manure (Barnett, G.M., 1994, Phosphorus forms in animal manure, *BioRes. Technol.*, vol. 49: 139-147; Rico, et al., 2007, Characterisation of solid and liquid fractions of dairy manure with regard to their component distribution and methane production, *Bioresource Technol.*, vol. 98: 971-979; Hjorth, et al., 2010, Solid-liquid separation of animal slurry in theory and practice: A review, *Agron. Sustain. Dev.*, vol. 30: 153-180). Lignocellulosic components can be converted into fermentable saccharides, which can be further converted into ethanol and other useful organic products (Cantrell, et al., 2008, Livestock waste-to-bioenergy generation opportunities, *Bioresource Technol.*, vol. 99(17): 7941-7953; Sun, et al., 2002, Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technol.*, vol. 83: 1-11). Nutrients and metals can be recovered via crystallization processes to yield struvite (magnesium ammonium phosphates), K-struvite (magnesium potassium phosphates), calcium phosphate, and other phosphate compounds (Zhang, H., 2013, Pilot scale application of microwave technology for dairy manure treatment and nutrient recovery through struvite crystallization, MSc. Thesis, University of British Columbia, Canada).

[0175] The RF unit (RF Specialists Ltd., Canada) used in EXAMPLE 1 was also used in this study. A set of fifteen experiments were performed to optimize RF/H₂O₂ methods for treating the solids portion of separated dairy manure. Using a statistical program (MINITAB (trademark), version 16.0), the experimental design of the fifteen samples listed in TABLE 12 was selected (Minitab, 2007, Meet Minitab 15 for Windows, Minitab Inc., USA). The Box-Benken design for response surface plots was selected for the experiments. TABLE 12 lists the experimental design

of those fifteen experiments. The experiments were carried out with RF radiation input power levels of 50, 60, and 70%, RF radiation holding times of 20, 50, and 80 minutes, and hydrogen peroxide doses of 0.5, 1.0, and 1.5% (v/v). Heating ramp rates were controlled based on input power as discussed elsewhere herein. The experiments were carried out a temperature of 90°C. Initially, the power control was set to a desired setting level until the sample reached 90°C, after which they were held at that temperature for the desired holding time.

[0176] TABLE 12

Sample	Input power intensity, %	RF holding time, min.	H ₂ O ₂ dose, % (v/v)
1	60	20	0.5
2	50	50	0.5
3	60	80	0.5
4	70	50	0.5
5	60	50	1
6	50	80	1
7	70	20	1
8	60	50	1
9	70	80	1
10	50	20	1
11	60	50	1
12	60	80	1.5
13	70	50	1.5
14	50	50	1.5
15	60	20	1.5

[0177] TABLE 13 lists the TCOD and the soluble concentrations of nutrients, COD, and VFA after treatment. Chemical analyses were carried out following the procedures outlined in APHA, 1998 and using the equipment described elsewhere herein. For ortho-phosphate analysis, dairy manure samples were determined at 0.5% TS to ensure correct measurement (Wolf, et al., 2005, Development of a water-extractable phosphorus test for manure: An interlaboratory study, Soil Sci. Soc. Am., vol. 69: 695-700).

[0178] TABLE 13

Sample	Total solids (TS), %	Ortho- PO ₄ ³⁻ , mg/L	Ammonia, mg/L	SCOD, g/L	TCOD, g/L	VFA, g/L
Raw	4.1 – 4.4	42 - 76	348 – 613	2.3 – 6.5	30 - 41	0.7 - 3
Acidified	4.2 – 5.0	52 - 155	412 - 731	1.7 – 8.4	28 - 40	1.1 - 3
1	5.4±1.6	134±11	673±31	6.6±0.7	28±2.2	2.8±0.1
2	5.4±1.6	128±5.6	689±47	6.8±0.2	31±0	2.9±0.1
3	4.7±1.4	101±6.9	631±11	6.6±0.5	36±14	2.8±0.1
4	5.9±3.3	142±21	706±116	7.4±0.3	38±0.9	2.8±0.1
5	4.2±0.1	160±3.9	756±17	4.0±0.2	44±22	2.1±0.1
6	4.8±3.4	122±13	680±47	9.6±0.2	35±10	2.8±0.1
7	4.2±0	62±4.4	613±11	2.6±0.2	47±6.9	1.8±0.1
8	4.2±0.2	74±6.3	610±27	3.5±0.1	59±11	1.9±0
9	5.9±3.3	140±25	769±118	11±1.0	38±2.5	2.9±0.1
10	4.4±0.2	147±17	781±76	4.7±0	48±12	2±0.2
11	4.2±0.2	77±1.9	622±40	3.7±0.1	57±6.6	1.8±0.1
12	5.4±1.5	139±13	687±36	11±0.9	36±5.5	2.7±0
13	3.7±0.2	103±2.4	452±7.5	2.4±0.3	49±15	1.4±0.1
14	3.7±0.1	92±3.5	459±7.8	2.0±0.1	57±7.5	1.4±0
15	3.9±0.1	86±13	655±14	3.5±0.6	54±8.5	1.9±0.1

[0179] Nutrient Release

[0180] TABLE 13 shows that ortho-phosphate concentrations for the raw manure sample varied from 42 to 76 mg/L. This can be attributed to anaerobic decomposition during manure storage. The longer the manure is allowed to age, the higher the concentration of ortho-phosphate. Ortho-phosphate concentrations also varied after acidification with sulphuric acid from 52 to 155 mg/L.

[0181] After RF/H₂O₂-AOP treatment, ortho-phosphate concentration ranged from 62 to 160 mg/L and the yield of ortho-phosphate was between 39 to 75% of TP. In a study using unseparated manure, the yield of ortho-phosphate was between 58 to 91% of TP (Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of dairy manure, J. Environ. Chem. Eng., vol. 3(3): 2155-2160). Thus, the ratio of ortho-phosphate/TP was higher for unseparated dairy manure than for separated manure. For both types of manure, the ratio of ortho-phosphate/TP was highest for sample 13 (70% input power intensity, 50 minutes RF

holding time, and 1.5% (v/v) H₂O₂): 91% for the unseparated dairy manure and 75% for the separated dairy manure.

[0182] Despite different substrates and environmental conditions, the results of this study were comparable to the results elsewhere reported for microwave enhanced advanced oxidation processes. For example, for MW/H₂O₂-AOP, the percent TP released as ortho-phosphate has been observed to increase from 21 to 47% at 80°C (Kenge, et al., 2009, Treating solid dairy manure using microwave-advanced oxidation process, J. Environ. Sci. Health Part B, vol. 44: 606-612).

[0183] The percent TP released as ortho-phosphate from dairy manure following RF/H₂O₂-AOP treatment was lower than that released from sewage post-treatment. This may be attributed to dairy manure containing many forms of phosphate, including inorganic, acid soluble organic phosphate, lipid phosphate, and nucleic phosphate, which are difficult to solubilize. Sewage sludge, in contrast, is essentially microbial cells which are relatively easy to release phosphorus from when disrupted (Barnett, G.M., 1994, Phosphorus forms in animal manure, BioRes. Technol., vol. 49: 139-147; Liao, et al., 2005, Advanced oxidation process using hydrogen peroxide/microwave system for solubilisation of phosphate, J. Environ. Sci. Health Part A, vol. 40(9): 1753-1761; Jin, et al., 2009, Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment, Water Res., vol. 43(14): 3493-3502).

[0184] The following proposed model is based on the regression coefficients for the concentration of ortho-phosphate remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 781 - 6.95T - 116D - 14.3P + 0.01T^2 + 17.9D^2 + 0.08P^2 + 1.40DT + 0.09PT - 0.18PD \quad [3]$$

where Y is ortho-phosphate concentration (mg/L), P is input power (%), T is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.52 was obtained. The low R^2 value may be attributed to each raw sample having variable ortho-phosphate content.

[0185] According to equation [3], an increase in hydrogen peroxide dose decreases the release of ortho-phosphate. Input power intensity and holding time were observed to have a negative effect on ortho-phosphate concentration (i.e. as these parameters increase, ortho-phosphate

concentration decreases). The interaction between hydrogen peroxide dose and input power and the interaction between holding time and input power were found to be significant factors in ortho-phosphate release. The magnitude of the factor affecting ortho-phosphate concentration in solution was observed as follows: H₂O₂ dose > second order interaction effect of H₂O₂ dose > input power intensity > holding time.

[0186] A sample response surface profile for ortho-phosphate concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)) is shown in Figure 8. This profile shows that ortho-phosphate concentration was optimized when input power intensity was 62.9%, RF holding time was 55.9 minutes, and hydrogen peroxide dose was 1.1% (v/v). These results are similar to those observed for the untreated manure (Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of dairy manure, J. Environ. Chem. Eng., vol. 3(3): 2155-2160).

[0187] For untreated separated manure, the ammonia/TKN ratio was between 0.26 and 0.51, compared to a ratio of 0.11 for untreated unseparated manure. Following RF/H₂O₂-AOP treatment, ammonia concentration ranged from 452 ± 7.5 mg/L to 781 ± 76 mg/L and the percent TKN released as ammonia ranged from 35% to 57%. For both separated and unseparated manure, sample 13 resulted in the highest ammonia/TKN ratio and sample 1 resulted in the lowest ratio. A similar trend was observed for ortho-phosphate/TP.

[0188] The following proposed model is based on the regression coefficients for the concentration of ammonia remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 775 - 20.2T + 510D + 6.88P + 0.07T^2 - 287D^2 - 0.14P^2 + 0.69DT + 0.21PT - 1.24 DP \quad [4]$$

where Y is ammonia concentration (mg/L), P is input power (%), T is holding time (minutes), and D is H₂O₂ dose (% (v/v)). Equation [4] indicates that a high degree of nitrogen solubilisation may be achieved using higher hydrogen peroxide doses, shorter holding times, and higher input power intensities. The magnitude of the factor affecting ammonia concentration in solution was observed as follows: H₂O₂ dose > second order interaction effect of H₂O₂ dose > holding time > input power intensity. Holding time was observed to have a negative effect on ammonia concentration. This was also observed in previous studies on RF and MW treatment of dairy manure. Hydrogen peroxide dose was a significant factor affecting ammonia solubilisation

(Yawson, et al., 2011, Two-stage dilute acid hydrolysis of dairy manure for nutrient release, solids reduction and reducing sugar production, *Natural Resources*, vol. 2: 224-233; Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of dairy manure, *J. Environ. Chem. Eng.*, vol. 3(3): 2155-2160). Ammonia concentration was optimized when input power intensity was 59.2%, RF holding time was 51.5 minutes, and hydrogen peroxide dose was 0.8% (v/v).

[0189] Solids Disintegration

[0190] The following proposed model is based on the regression coefficients for the concentration of ammonia remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 49124 - 513T - 12588D - 942P + 3.2T^2 + 2715D^2 + 6.9P^2 + 118TD + 2.9PT - 14.3PD \quad [5]$$

where Y is SCOD concentration (mg/L), P is input power (%), T is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.84 was obtained.

[0191] A sample response surface profile for SCOD concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)) is shown in Figure 9. Hydrogen peroxide dose, holding time, and input power intensity all had a negative statistical coefficient; however, the statistical coefficient for the interaction effects was all positive with the exception of the interaction of input power and hydrogen peroxide dose. A low input power requires a longer reaction time to reach the desired temperature. However, holding time was observed to have a negative effect on SCOD concentration.

[0192] The interaction effect of holding time and hydrogen peroxide dose was found to be statistically significant ($p < 0.05$). The magnitude of the statistical coefficients of hydrogen peroxide and its interaction with itself was higher than all of the rest suggesting that hydrogen peroxide dose was a significant factor in COD solubilisation. Previous studies on MW/H₂O₂-AOP disclosed in Wong, et al., 2007, Factors affecting nutrient solubilisation from sewage sludge using microwave-enhanced advanced oxidation process, *J. Environ. Sci. Health Part A*, vol. 42: 825-829 showed that the significant factors affecting SCOD concentration, from most to least, were: microwave heating temperature, hydrogen peroxide dose, and heating time. However, the statistical coefficient for H₂O₂ dose was negative in this study. This may be

attributed to insufficient amounts of hydrogen peroxide used in this study to react with the manure particles. Figure 9 shows that ortho-phosphate concentration was optimized when input power intensity was 70.6%, RF holding time was 4.5 minutes, and hydrogen peroxide dose was 2.4% (v/v). This hydrogen peroxide dose value was outside of the doses studied, therefore, the effect of H₂O₂ dose on varying levels of solids disintegration for RF heating-oxidation processes was investigated in EXAMPLE 4.

[0193] TABLE 14 lists the SCOD/TCOD ratio for separate solids manure (SS) and unseparated whole manure (WM) for samples 1-15.

[0194] TABLE 14

Sample	Ortho-PO ₄ ³⁻ /TP		SCOD/TCOD		Ammonia/TKN	
	SS	WM	SS	WM	SS	WM
Raw	0.32-0.37	0.24	0.05-0.21	0.11	0.26-0.51	0.11
Acidified	0.34-0.62	0.73-0.75	0.04-0.21	0.08-0.1	0.29-0.41	0.12-0.14
1	0.29	0.58	0.23	0.15	0.25	0.12
2	0.60	0.72	0.21	0.21	0.57	0.15
3	0.32	0.63	0.18	0.17	0.35	0.13
4	0.43	0.60	0.20	0.21	0.39	0.13
5	0.72	0.67	0.09	0.22	0.44	0.15
6	0.39	0.66	0.27	0.22	0.43	0.15
7	0.32	0.68	0.05	0.26	0.37	0.14
8	0.36	0.75	0.06	0.24	0.38	0.15
9	0.51	0.75	0.30	0.23	0.52	0.14
10	0.59	0.75	0.1	0.23	0.46	0.14
11	0.38	0.76	0.07	0.23	0.40	0.16
12	0.38	0.69	0.30	0.26	0.35	0.15
13	0.75	0.91	0.05	0.24	0.54	0.18
14	0.56	0.68	0.04	0.21	0.39	0.16
15	0.42	0.70	0.06	0.24	0.42	0.14

[0195] The SCOD/TCOD ratio indicates the process efficiency of solubilisation. For the separated solids manure, the highest SCOD/TCOD ratio was observed for samples 9 and 12, while samples 7 and 12 showed the highest ratio for the unseparated whole manure. This indicates that the interaction effect of holding time and hydrogen peroxide dose results in higher SCOD release. This effect was found to be statistically significant ($p < 0.05$) for both manure types (Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of

dairy manure, J. Environ. Chem. Eng., vol. 3(3): 2155-2160). The highest SCOD/TCOD ratio observed for separated manure was 30%, while it was only 26% for unseparated whole manure. It should be noted that ramp times and rates for the two studies varied as the two manure types had different composition and, therefore, the dielectric properties of the two manure types may have been different from one another. RF heating of separated manure had a ramp rate of about 2.7, 4, and 5.8°C/min for input power levels of 50, 60, and 70%, respectively. For unseparated whole manure, ramp rates of 7, 9, and 11°C/min for the same respective power levels were used. Further, the TS of the unseparated whole manure was 12.2%. Thus, the hydrogen peroxide dose added per gram of TS may have been insufficient to break down the solids present. The lowest SCOD/TCOD ratio for the unseparated whole manure was observed for samples 1 and 3. As discussed elsewhere herein, the 0.5% (v/v) H₂O₂ used may not have been sufficient to break down the solids present. However, for separated manure, samples 1-4 had comparatively higher SCOD/TCOD ratios despite low hydrogen peroxide doses. This may be attributed to a fresh sample of separated solids being used. In the other samples, this was not the case. Poor SCOD/TCOD ratios were observed for samples 7, 8, 13, 14, and 15. The manure used in these samples was stored for a longer period of time than the other samples and therefore the effect of aging would be more pronounced.

[0196] RF/H₂O₂-AOP treatment yielded high VFA concentrations (TABLE 13). VFA concentration ranged from 1389 ± 33 mg/L to 2941 ± 82 mg/L. The highest VFA concentration was observed for sample 9, which showed a 92% increase over the initial VFA concentration. For samples 13 and 14, no increase in VFA concentration was observed. The concentrations of SCOD, ammonia, and ortho-phosphate were also observed to be low for these samples indicating that the age of the manure tested is important.

[0197] The following proposed model is based on the regression coefficients for the concentration of VFA remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 5814 - 62.8T - 3167D - 18.8P + 0.48T^2 + 764D^2 + 0.02P^2 + 10.5TD + 0.27PT + 3.09PD \quad [6]$$

where Y is VFA concentration (mg/L), P is input power (%), T is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R²) of 0.84 was obtained. The statistical coefficients of each factor were negative, meaning that as they increase VFA production

decreases. Hydrogen peroxide dose had a higher influence on VFA concentration than the other factors. A similar trend was observed for COD solubilisation. The interaction effects were all positive with the interaction effect between hydrogen peroxide dose and holding time having the greatest influence on VFA concentration. Lo, et al., 2012, Microwave enhanced advanced oxidation process for treating dairy manure at low pH, J. Environ. Sci. Health Part B, vol. 47: 362-367 reported temperature and hydrogen peroxide dose having the greatest influence on VFA concentration for MW/H₂O₂-AOP treated samples. This disparity in results may be attributed to the lower hydrogen peroxide doses (0.5-1.5% (v/v)) used in this study compared to past MW/H₂O₂-AOP studies (1-8.5% (v/v)). Equation [6] supports that VFA concentration was optimized when input power intensity was 43.8%, RF holding time was 33.9 minutes, and hydrogen peroxide dose was 1.8% (v/v).

[0198] Energy Estimation

[0199] The energy required by RF/H₂O₂-AOP was estimated using the method of Danesh, et al., 2008, Phosphorus and heavy metal extraction from wastewater treatment plant sludges using microwaves for generation of exceptional quality biosolids, Water Environ. Federation, vol. 80(9): 784-795. The energy required by the RF/H₂O₂-AOP batch system for the separated manure used in this study was between about 71 to 85 kJ/g TS. For unseparated whole manure, it was between 25.6 to 28.5 kJ/g TS. The lower energy required by the unseparated whole manure may be attributed to the higher TS content (12.2%) of the unseparated manure compared to the TS content (4.4%) of the separated manure. The energy required for RF heating separated manure was comparable to that required by MW/H₂O₂-AOP batch systems (i.e. 76 to 128 kJ/g TS (Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of dairy manure, J. Environ. Chem. Eng., vol. 3(3): 2155-2160)).

[0200] In summary, the RF/H₂O₂-AOP system was capable of handling dairy manure with various solids content and manure that was either liquid-solids separated or unseparated. The system proved effective for nutrient release and solids disintegration from separated solids fraction of dairy manure. The system released up to 72% of TP from separated dairy manure as ortho-phosphate and had a SCOD/TCOD ratio of 30%. The energy required by the RF/H₂O₂ batch process on separated solids was higher than that for unseparated whole manure.

[0201] EXAMPLE 4

[0202] In this study a set of fifteen experiments were performed to investigate the effects of higher hydrogen peroxide doses and shorter holdings times on solids disintegration and nutrient solubilisation from separated dairy manure. The manure was obtained from the Dairy Education & Research Centre, University of British Columbia in Agassiz, British Columbia, Canada as prepared as described above in EXAMPLE 3. The separated manure contained 5.5% TS. TABLE 15 lists the experimental design of the fifteen experiments selected as described in EXAMPLE 3. The experiments were carried out with RF radiation holding times of 20, 40, and 60 minutes and hydrogen peroxide doses of 1.5, 2.0, and 2.5% (v/v), which are equivalent to 0.1, 0.3, and 0.5% H₂O₂ per % TS. The experiments were carried out a temperature of up to 95°C. Initially the input power intensity was set at 35% (1167 Watt/L) until the manure samples reached the desired temperature, after which temperature was held constant for the desired holding time.

[0203] TABLE 15

Sample	Temperature, °C	Holding time, min.	H ₂ O ₂ dose, % (v/v)
1	95	40	2.5
2	85	20	1.5
3	95	60	2
4	85	20	2.5
5	85	60	2.5
6	85	60	1.5
7	85	40	2
8	75	40	1.5
9	75	40	2.5
10	85	40	2
11	85	40	2
12	75	60	2
13	75	20	2
14	95	40	1.5
15	95	20	2

[0204] Nutrient Release

[0205] TABLE 16 lists the TCOD and the soluble concentrations of nutrients, COD, and VFA after treatment. Chemical analyses were carried out following the procedures outlined in APHA, 1998 and using the equipment described elsewhere herein.

[0206] TABLE 16

Sample	Total solids (TS), %	Ortho- PO_4^{3-} , mg/L	Ammonia, mg/L	SCOD, g/L	TCOD, g/L	VFA, g/L
Raw	5.5±0.3	14±6.6	626±30	7.1±0.7	50±11	0.9±0
Acidified	5.4±0.3	135±8.1	885±15	8.5±0.4	54±3.7	0.6±0
1	5.3±0.4	93±7.7	778±12	9.4±0.4	52±5.7	5.5±0.1
2	5.3±0.2	117±13	790±26	8.8±0.3	55±0.4	5.3±0.5
3	5.1±0.0	94±2.9	832±25	8.8±0.5	54±4.9	5.1±0.3
4	5.1±0.3	109±5.9	800±18	8.9±0.5	47±15	5.1±0.2
5	5.5±0.0	105±46	835±33	8.3±0.2	49±16	5.1±0
6	5.8±0.1	100±5.7	840±22	8.1±0.3	53±24	4.9±0.1
7	5.5±0.0	100±3.5	803±25	8.4±0.4	50±10	5.1±0.2
8	5.3±0.1	99±1.9	838±33	8.8±0.1	47±0.7	5.0±0.2
9	4.7±0.1	111±4.2	815±30	8.4±0.3	49±5.8	4.9±0
10	5.6±0.2	105±4.2	798±34	8.4±0.7	55±3.3	4.6±0.3
11	5.7±0.0	89±5.8	807±60	8.1±0.7	53±1.3	4.4±0.1
12	5.6±0.0	95±2.9	803±41	8.7±0.7	54±2.4	4.3±0.1
13	5.6±0.3	104±5.9	760±31	10±0.3	52±17	4.3±0.1
14	6.1±0.1	90±11	830±13	8.8±1.1	50±0.1	4.4±0.1
15	5.1±0.2	91±2.9	815±18	8.3±0.3	49±1.1	4.9±0.2

[0207] The raw sample of manure had 5.5% TS, an ortho-phosphate concentration of 14 mg/L, and TP of about 240 mg/L. At pH 4, the ortho-phosphate concentration increased to 135 mg/L, which represents about 60% of TP. This is an increase of almost nine-fold that of the raw sample. Acid was added to release phosphorus from solid dairy manure (Kenge, A., 2008, Enhancing nutrient solubilisation from organic waste using microwave technology, MASc Thesis, University of British Columbia, Vancouver, Canada). Ortho-phosphate concentration did not further increase with RF/H₂O₂-AOP treatment.

[0208] The following proposed model is based on the regression coefficients for the concentration of ortho-phosphate remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 98 - 5.2T - 3.5t + 1.6D + 2.9Tt - 2.1TD + 3.4tD - 5.8T^2 + 3.6t^2 + 6.1D^2 \quad [7]$$

where Y is ortho-phosphate concentration (mg/L), T is temperature (°C), t is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.78 was obtained.

[0209] Sample response surface profiles for ortho-phosphate concentration as a function of holding time (min.), temperature (°C), and hydrogen peroxide dose (% (v/v)) are shown in Figures 10A-10C. Statistical analysis of the results showed that temperature was the most important factor affecting ortho-phosphate concentration. The effect of each factor on ortho-phosphate release was observed to be: temperature > holding time > H₂O₂ dose.

[0210] Similar studies on MW/H₂O₂-AOP treatment of dairy manure have shown a strong relationship between heating temperature and soluble phosphorus release; an increase of soluble phosphate in solution was observed as microwave temperature increased from 60°C to 90°C (Pan, et al., 2006, Microwave pretreatment for enhancement of phosphorus release from dairy manure, J. Environ. Sci. Health Part B, vol. 41(4): 451-458). However, in RF/H₂O₂-AOP treatment, within the studied range (i.e. 75°C to 95°C), temperature had a negative effect on ortho-phosphate release. This indicates that higher ortho-phosphate concentrations may be achieved using lower RF temperatures. A maximum ortho-phosphate concentration of 117 mg/L was observed for sample 2 (temperature of 85°C, holding time of 20 minutes, hydrogen peroxide dose of 1.5% (v/v)). The samples treated at 95°C resulted in low ortho-phosphate release. Without being bound to any theory, one possible explanation for the low release is that more polyphosphates are released than ortho-phosphates at temperatures near 90°C. An ortho-phosphate to soluble TP ratio as low as 78% were observed for samples treated at 95°C. TABLE 16 shows that among the three holding times tested (20, 40, and 60 minutes), 20 minutes was sufficient to release most of soluble TP as ortho-phosphate.

[0211] It can be seen from Figures 10A-10C that ortho-phosphate concentration was optimized when temperature was 83°C, RF holding time was 55 minutes, and hydrogen peroxide dose was 1.8% (v/v). Hydrogen peroxide had a positive effect on ortho-phosphate release; however, its effect was lesser compared with RF temperature and reaction time. RF/H₂O₂-AOP and MW/H₂O₂-AOP studies on dairy manure have indicated that a high H₂O₂ dose may not be required to solubilize phosphate in lower temperature regions (Chan, et al., 2010, Effects of

irradiation intensity and pH on nutrients release and solids destruction of waste activated sludge using the microwave enhanced advanced oxidation process, *Water Environ. Res.*, vol. 82(11): 2229-2238; Srinivasan, et al., September 2015, Optimization of radiofrequency-oxidation treatment of dairy manure, *J. Environ. Chem. Eng.*, vol. 3(3): 2155-2160). In the present study, higher doses of hydrogen peroxide (1.5, 2.0 and 2.5% (v/v)) were used compared to those used in EXAMPLE 3. An increased dose of hydrogen peroxide permits RF/H₂O₂-AOP to be operated at lower RF temperatures and/or for shorter RF holding times while achieving comparable TP to ortho-phosphate conversion results.

[0212] TABLE 16 lists the soluble ammonia concentrations observed for each of the 15 samples. Raw dairy manure had an initial soluble ammonia concentration of 626 mg/L and a TKN value of 1588 mg/L. Samples RF treated with 1.5% (v/v) hydrogen peroxide achieved some of the highest ammonia concentrations (see samples 6, 8, and 14). The lowest ammonia concentration was observed at a temperature of 75°C, RF holding time of 20 minutes, and hydrogen peroxide dose of 2% (v/v) (sample 13). Overall, ammonia concentration did not increase by a significant amount following RF/H₂O₂-AOP treatment. Without being bound by any theory, a possible reason is that the majority of nitrogen present was degraded into intermediate products, such as amino acids or peptides, and only a small amount of ammonia was formed in the process. A similar trend was observed following MW/H₂O₂-AOP treatment (Lo, et al., 2011, Microwave enhanced advanced oxidation process application to treatment of dairy manure, *Microwave Heating*, ed. Dr. Usha Chandra, InTech, available online: <http://www.intechopen.com/books/microwave-heating/microwave-enhanced-advanced-oxidation-processapplication-to-treatment-of-dairy-manure>). No significant release of ortho-phosphate was observed over the temperature range of 60 to 80°C regardless of operating conditions (Chan, et al., 2010, Effects of irradiation intensity and pH on nutrients release and solids destruction of waste activated sludge using the microwave enhanced advanced oxidation process, *Water Environ. Res.*, vol. 82(11): 2229-2238). Acid addition helps solubilize ammonia (Wong, et al., 2007, Factors affecting nutrient solubilisation from sewage sludge using microwave-enhanced advanced oxidation process, *J. Environ. Sci. Health Part A*, vol. 42: 825-829). The TABLE 16 results support the use of acid as a catalyst for the treatment of dairy manure.

[0213] The following proposed model is based on the regression coefficients for the concentration of ammonia remaining in RF/H₂O₂-AOP treated manure samples 1-15:

$$Y = 803 + 54.8T + 18t - 8.8D - 6.7Tt - 7.1TD - 3.8tD - 0.6T^2 + 0.3t^2 + 13D^2 \quad [8]$$

where Y is ammonia concentration (mg/L), T is temperature (°C), t is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.60 was obtained.

[0214] Temperature was observed to be the most significant factor affecting ammonia release. The combined effects of temperature and holding time, as well as the second order interaction effect of H₂O₂ dose resulted in increased release of ammonia. The ammonia yielded in this study was comparable to that amount reported in MW/H₂O₂-AOP treatment of dairy manure (Pan et al., 2006, Microwave pretreatment for enhancement of phosphorus release from dairy manure, J. Environ. Sci. Health Part B, vol. 41(4): 451-458; Jin et al., 2009, Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment, Water Res., vol. 43(14): 3493-3502). From equation [8], ammonia concentration was optimized when temperature was 107°C, RF holding time was 29 minutes, and hydrogen peroxide dose was 2.4% (v/v). A temperature of 107°C is outside of the temperature range studied implying that more ammonia may be produced by increasing the temperature near 107°C.

[0215] Solids Disintegration

[0216] TABLE 16 lists the SCOD concentrations of the studied samples. The raw sample had an initial SCOD and TCOD of 7.1 g/L and 50 g/L, respectively. The SCOD concentration increased to as high as 10 g/L after RF/H₂O₂-AOP treatment. This represents an increase of about 41%. Hydrogen peroxide dose had a positive effect on SCOD release. For example, high SCOD concentrations were observed for samples 1 and 4, where 2.5% (v/v) hydrogen peroxide dose was used. The TCOD of RF/H₂O₂ dairy manure samples treated with 2.5% (v/v) hydrogen peroxide (i.e. samples 1, 4, 5, and 9) was found to decrease. A similar decreasing trend in TS was also observed for these samples. The highest SCOD concentration was observed for sample 13 (a temperature of 75°C, RF holding time of 20 minutes, and hydrogen peroxide dose of 2% (v/v)). For exclusively sample 13, the manure was acidified to 3.5. The settling properties of sample 13 were observed to be better than the other RF/H₂O₂ treated sets.

[0217] The following proposed model is based on the regression coefficients for the concentration of SCOD remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 8281 - 130T - 293t + 78D + 547Tt + 260TD + 19tD + 529T^2 + 223t^2 + 29D^2 \quad [9]$$

where Y is SCOD concentration (mg/L), T is temperature (°C), t is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.75 was obtained. From equation [9], SCOD concentration was optimized when temperature was 83°C, RF holding time was 60 minutes, and hydrogen peroxide dose was 1.7% (v/v).

[0218] Sample response surface profiles for ortho-phosphate concentration as a function of input power intensity (%) and hydrogen peroxide dose (% (v/v)) are shown in Figures 11A-11C. RF temperature and holding time were observed to have a negative effect on SCOD release. Without being bound to any theory, this could be attributed to SCOD being oxidized and/or decomposed into CO₂ at higher temperatures and/or longer reaction times. Therefore, SCOD concentration would decrease, as shown in samples 4 and 8. The combined effect of temperature and holding time and temperature and hydrogen peroxide dose were also observed to be important factors in SCOD release.

[0219] VFA concentration of the raw manure was 0.9 g/L and increased to 5.5 g/L after RF/H₂O₂-AOP treatment. VFA was mainly present in the form of acetic acid; however, other VFA such as propionic, butyric, and valeric acids were also present following RF treatment.

[0220] The following proposed model is based on the regression coefficients for the concentration of VFA remaining in RF/H₂O₂ treated manure samples 1-15:

$$Y = 4.7 + 0.18T - 0.025t + 0.125D + 0.05Tt + 0.3TD + 0.1tD + 0.1T^2 + 0.05t^2 + 0.35D^2 \quad [10]$$

where Y is VFA concentration (mg/L), T is temperature (°C), t is holding time (minutes), and D is H₂O₂ dose (% (v/v)). A correlation coefficient (R^2) of 0.66 was obtained. From equation [10], VFA concentration was optimized when temperature was 89°C, RF holding time was 49 minutes, and hydrogen peroxide dose was 1.8% (v/v). VFA concentrations were observed to increase with increasing temperature and hydrogen peroxide dose. The lowest VFA concentrations were observed at a temperature of 75°C (samples 9, 12, and 13). In RF/H₂O₂-AOP treatment, organic matter present in the dairy manure will be transformed to VFA at high

temperatures via thermal decomposition and oxidation processes facilitated by hydrogen peroxide. Higher hydrogen peroxide doses therefore typically favour higher VFA production. However, an increase in holding time was found to result in lower VFA concentrations. The decrease in VFA concentration with longer RF holding times may be attributed to vaporization of VFA and/or oxidation of the VFA to CO₂ as described elsewhere herein.

[0221] In summary, the SCOD/TCOD ratio of the RF/H₂O₂ treated samples of this study was in the range of 15-19% regardless of operating conditions. Phosphorus release was mainly dictated by solution pH. Nonetheless, almost a nine-fold increase in ortho-phosphate release was achieved. A remarkable increase in VFA concentration was observed following RF/H₂O₂ treatment. SCOD and ortho-phosphate concentrations were optimized when the temperature was about 83°C, the RF holding time was about 55 to about 60 minutes, and the hydrogen peroxide dose was about 1.7 to about 1.8% (v/v).

[0222] While a number of exemplary aspects and embodiments have been discussed above, those of skill in the art will recognize certain modifications, permutations, additions and sub-combinations thereof. It is therefore intended that the following appended claims and claims hereafter introduced are interpreted to include all such modifications, permutations, additions and sub-combinations as are within their true spirit and scope.

WHAT IS CLAIMED IS:

1. A method of treating a slurry of organic solids, the method comprising:
admixing the slurry having a first suspended solids content with an oxidant to yield an admixed slurry; and
radiating the admixed slurry with radiofrequency radiation for a treatment period to yield a treated slurry having a second suspended solids content less than the first suspended solids content.
2. A method according to claim 1, wherein the oxidant comprises one or more of hydrogen peroxide, ozone, and potassium persulfate.
3. A method according to claim 2, wherein admixing the slurry with the oxidant comprises introducing between about 0.03% and about 2.5% by volume (v/v) of hydrogen peroxide.
4. A method according to claim 3, wherein admixing the slurry with the oxidant comprises introducing about 1% by volume (v/v) of hydrogen peroxide.
5. A method according to claim 2, wherein admixing the slurry with the oxidant comprises introducing between about 0.025% and about 2.1% hydrogen peroxide per percent (%) total solids by weight.
6. A method according to claim 5, wherein admixing the slurry with the oxidant comprises introducing about 0.8% hydrogen peroxide per percent (%) total solids by weight.
7. A method according to any one of claims 1 to 6, further comprising treating the slurry with ozone.
8. A method according to claim 7, wherein treating the slurry with ozone comprises adding about 0.02 to about 0.1 g of ozone per gram total solids.

9. A method according to claim 8, wherein treating the slurry with ozone comprises adding about 0.06 g of ozone per gram total solids.
10. A method according to any one of claims 1 to 9, further comprising increasing a treatment temperature of the admixed slurry during at least a portion of the treatment period to between about 60°C and about 200°C.
11. A method according to claim 10, wherein the treatment temperature is about 60°C.
12. A method according to either one of claims 10 and 11, wherein increasing the treatment temperature comprises heating the admixed slurry from a first temperature to a final temperature at a ramp rate of between about 3°C per minute to about 7°C per minute.
13. A method according to any one of claims 10 to 12, wherein increasing the treatment temperature comprises radiating the admixed slurry with radiofrequency radiation.
14. A method according to any one of claims 1 to 13, wherein the treatment period is between about 5 minutes and about 60 minutes.
15. A method according to claim 14, wherein the treatment period is less than about 20 minutes.
16. A method according to any one of claims 10 to 15, wherein increasing the treatment temperature comprises applying between about 1200 Watts and about 2500 Watts of radiofrequency power per litre of slurry.
17. A method according to any one of claims 1 to 16, further comprising acidifying the slurry.
18. A method according to claim 17, wherein acidifying the slurry comprises adding one or more of a mineral acid and an organic acid.

19. A method according to claim 18, wherein the mineral acid comprises one or more of sulphuric acid and hydrochloric acid.
20. A method according to either one of claims 18 and 19, wherein the organic acid comprises oxalic acid.
21. A method according to any one of claims 17 to 20, wherein the slurry is acidified to a pH of between about 2 to about 4.
22. A method according to claim 21, wherein the slurry is acidified to a pH of about 4.
23. A method according to any one of claims 1 to 16, wherein a pH of the slurry is maintained between about 6 to about 7.
24. A method according to any one of claims 1 to 23, further comprising maintaining the admixed slurry at a treatment pressure that is equal to or greater than atmospheric pressure during the treatment period.
25. A method according to any one of claims 1 to 24, wherein the second suspended solids content is at least 10% less than the first suspended solids content.
26. A method according to any one of claims 1 to 25, wherein the first suspended solids content is in the range of about 0.05% and about 30%.
27. A method according to any one of claims 1 to 26, wherein the first suspended solids content is in the range of about 0.1% to about 15%.
28. A method according to any one of claims 1 to 27, wherein the admixed slurry has a first soluble chemical oxygen demand and the treated slurry has a second soluble chemical oxygen demand in excess of the first soluble chemical oxygen demand.

29. A method according to claim 28, wherein the second soluble chemical oxygen demand exceeds the first soluble chemical oxygen demand by at least 30%.
30. A method according to any one of claims 1 to 29, wherein the treated slurry has a soluble chemical oxygen demand in excess of 30% of total chemical oxygen demand.
31. A method according to any one of claims 1 to 30, further comprising subjecting the treated slurry to a first downstream treatment process.
32. A method according to claim 31, wherein the first downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.
33. A method according to any one of claims 1 to 32, further comprising drawing off a supernatant portion from the treated slurry and recovering one or more of a dissolved mineral and dissolved organic compound from the supernatant portion.
34. A method according to claim 33, wherein recovering the dissolved mineral comprises crystallizing the dissolved mineral.
35. A method according to either one of claims 33 and 34, wherein recovering the dissolved organic compound comprises one or more of solvent extraction, distillation, and direct use of the dissolved organic compound.
36. A method according to claim 35, wherein direct use of the dissolved organic compound comprises using at least a portion of the supernatant portion as a source of readily biodegradable organic compounds to supplement a biological process.

37. A method according to claim 36, wherein the biodegradable organic compounds comprise volatile fatty acids.
38. A method according to either one of claims 36 and 37, wherein the biological process is denitrification or enhanced biological phosphorus removal.
39. A method according to either one of claims 33 and 34, wherein the dissolved mineral comprises phosphate.
40. A method according to either one of claims 33 and 34, wherein the dissolved mineral is recovered as struvite or a struvite analog.
41. A method according to claim 34, wherein crystallizing the dissolved mineral comprises adding ammonium or magnesium to the supernatant portion to create a supersaturation of the dissolved mineral.
42. A method according to any one of claims 33 to 41, further comprising subjecting a suspended solids-containing portion of the treated slurry remaining after drawing off the supernatant portion to a second downstream treatment process.
43. A method according to claim 42, wherein the second downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.
44. A method according to any one of claims 1 to 43, wherein the slurry comprises one or more of sewage sludge, solids separated manure, liquid fraction of separated manure, and unseparated manure.

45. A method according to any one of claims 1 to 44, wherein the treated slurry comprises about 60% of the organic solids present in the slurry in soluble form.
46. A system for treating a slurry of organic solids, the system comprising:
an inlet for receiving the slurry;
a reaction zone downstream from the inlet;
one or more oxidant injection ports at or upstream from the reaction zone, the oxidant injection ports connected to a supply of oxidant;
a radiofrequency radiation source disposed to radiate the slurry in the reaction zone, producing treated slurry; and
an outlet for delivering the treated slurry downstream from the reaction zone.
47. A system according to claim 46, further comprising a separator connected to receive treated slurry from the outlet and separate the treated slurry into a supernatant portion and a suspended solids-containing portion.
48. A system according to claim 47, further comprising a product recovery system connected to the separator for receiving the supernatant portion and crystallizing one or more of a dissolved mineral and dissolved organic compound.
49. A system according to claim 48, wherein crystallizing a dissolved mineral comprises a means for adding soluble ammonium or magnesium to the supernatant portion.
50. A system according to any one of claims 46 to 49, further comprising a downstream treatment process.
51. A system according to claim 50, wherein the downstream treatment process is selected from the group consisting of one or more of: anaerobic digestion, fermentation, treatment in a fixed film bioreactor, treatment in an upflow anaerobic sludge blanket reactor, treatment in a hybrid suspended/attached growth bioreactor, and treatment in an acid hydrolysis reactor.

52. Methods having any new and inventive steps, acts, combination of steps and/or acts, or sub-combinations of steps and/or acts as described herein.
53. Apparatus having any new and inventive feature, combination of features, or sub-combination of features as described here.

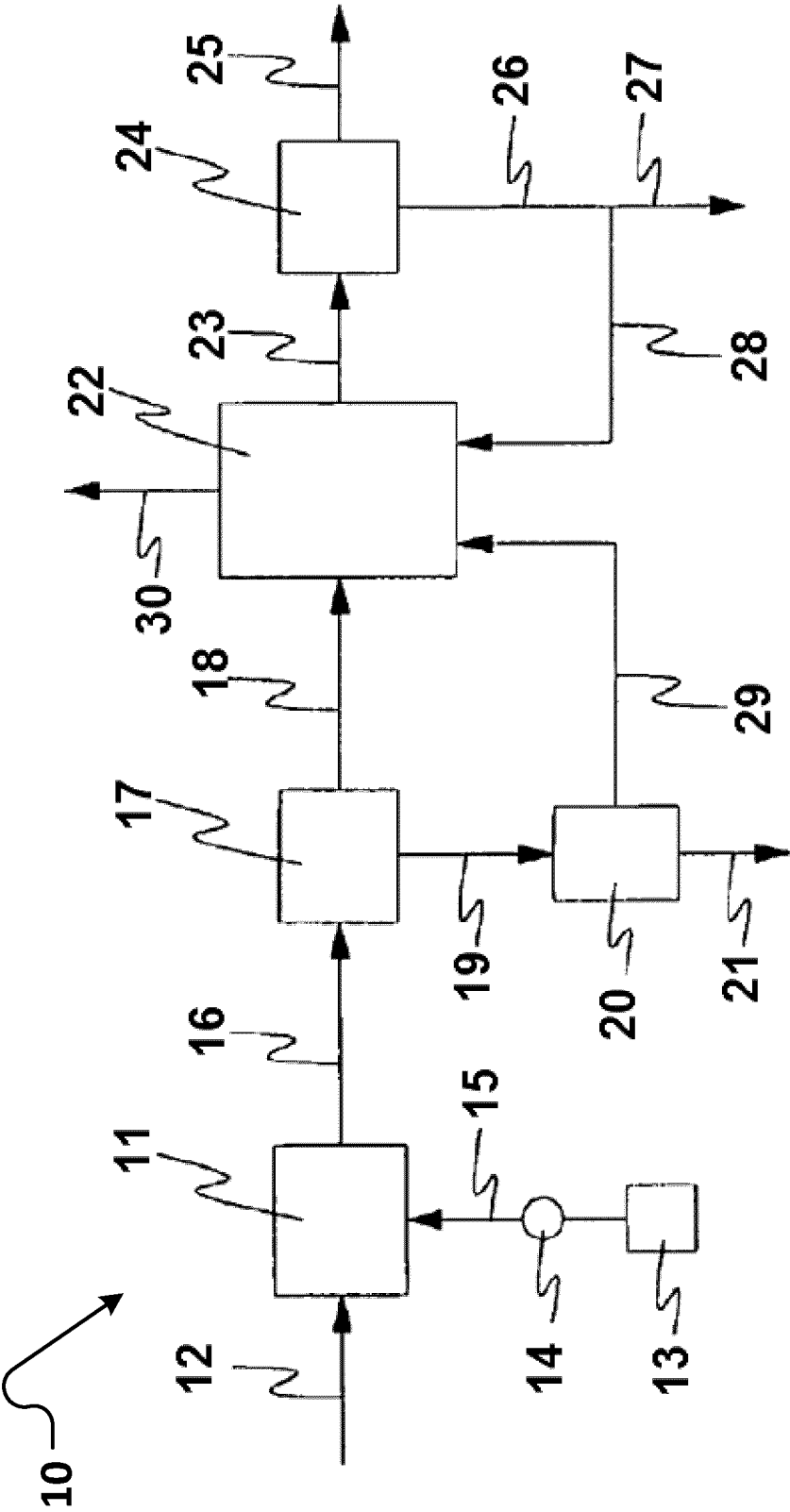


FIG. 1

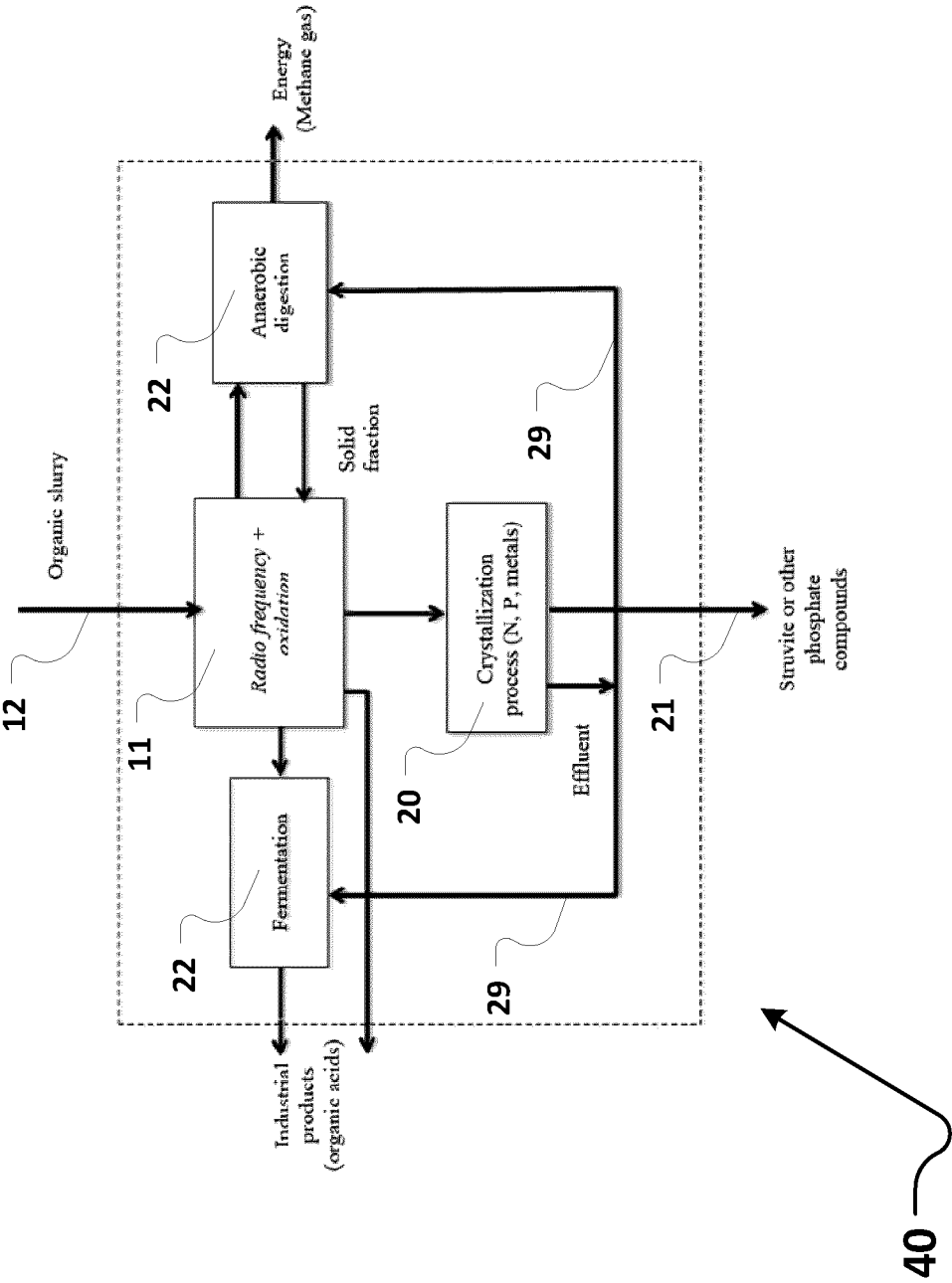


FIG. 2

3/9

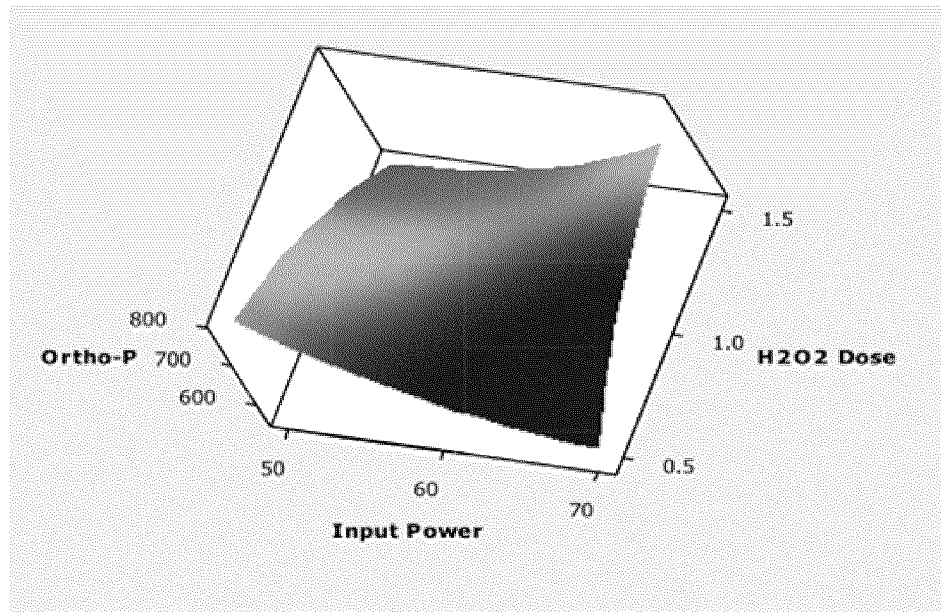


FIG. 3

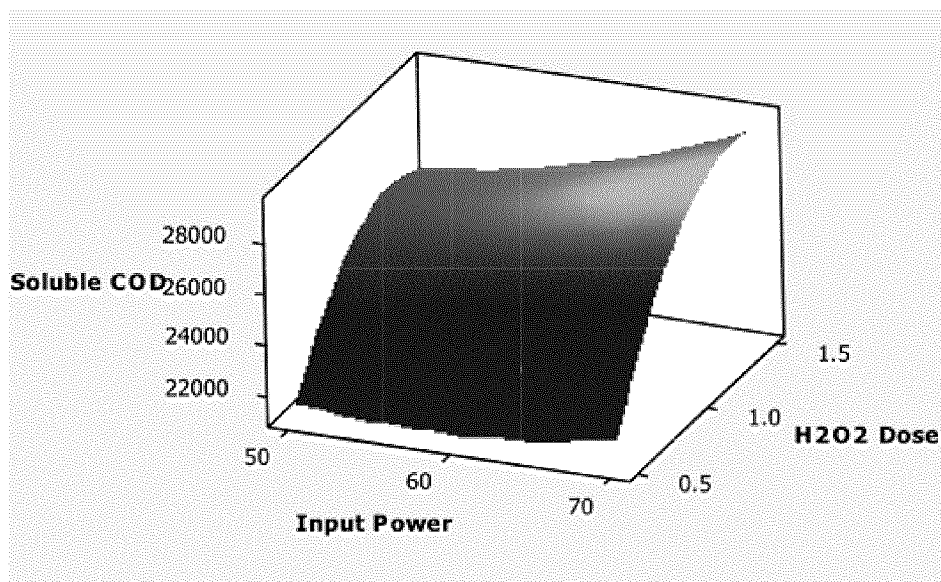


FIG. 4

4/9

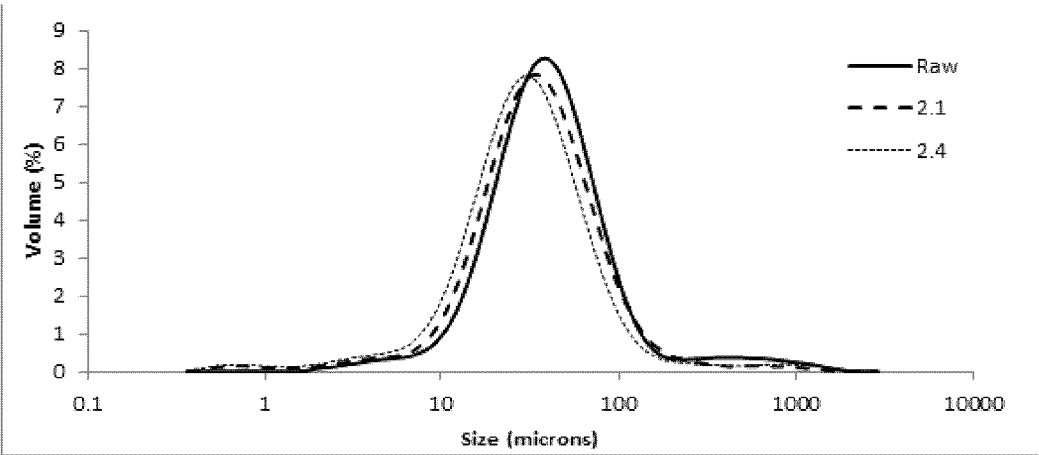


FIG. 5A

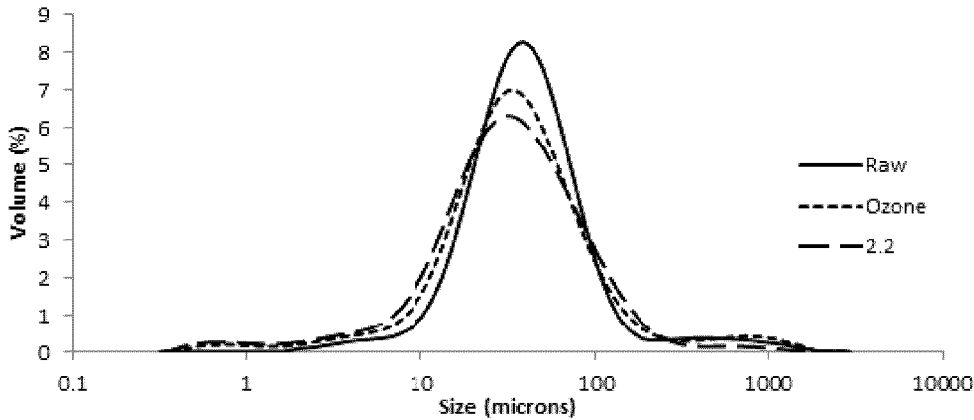


FIG. 5B

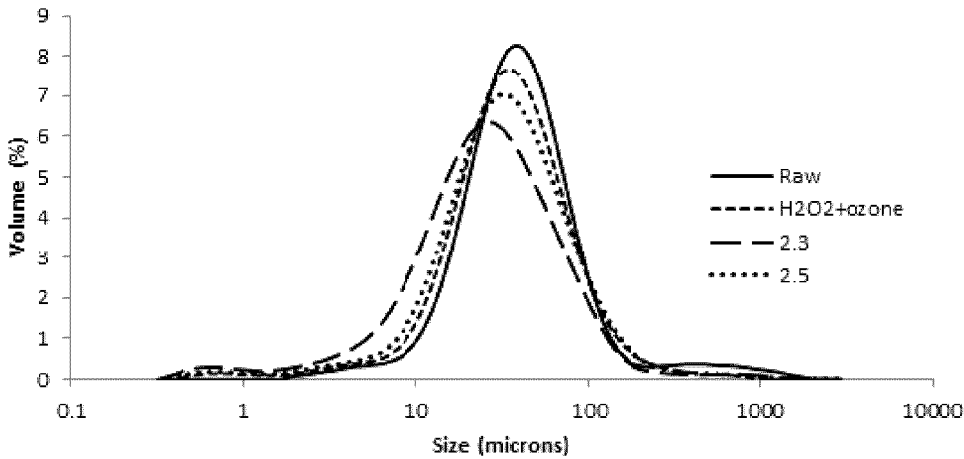


FIG. 5C

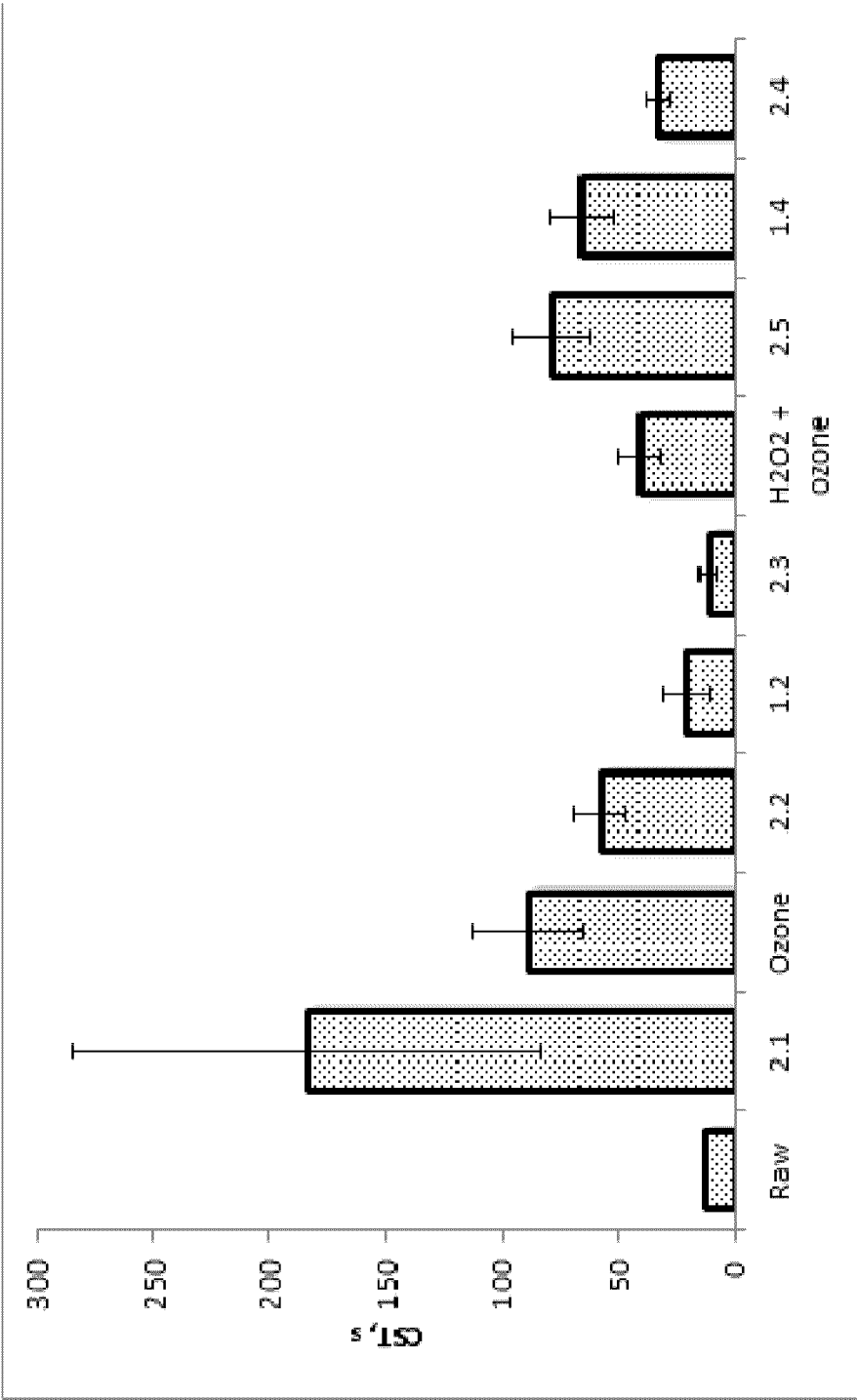


FIG. 6

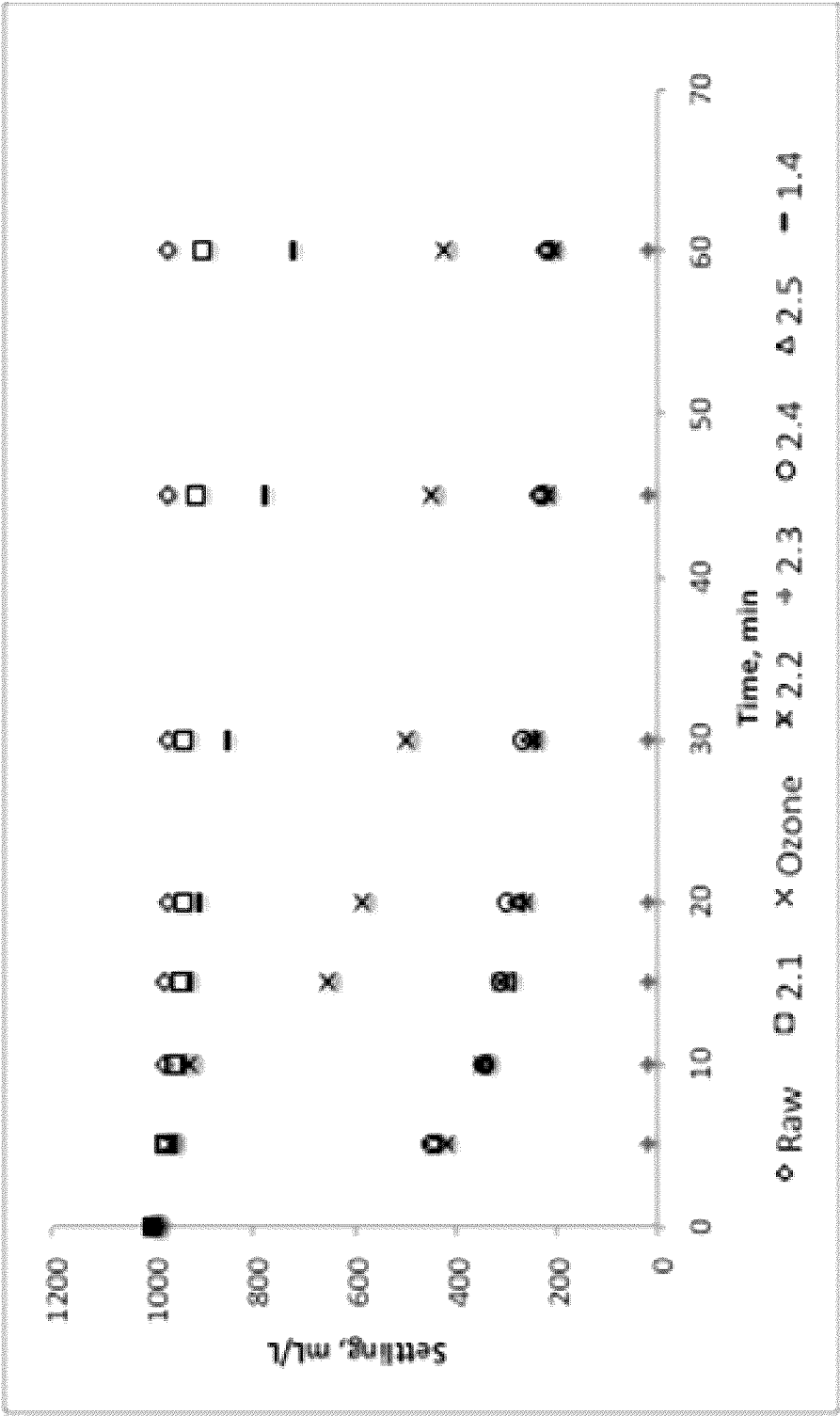


FIG. 7

7/9

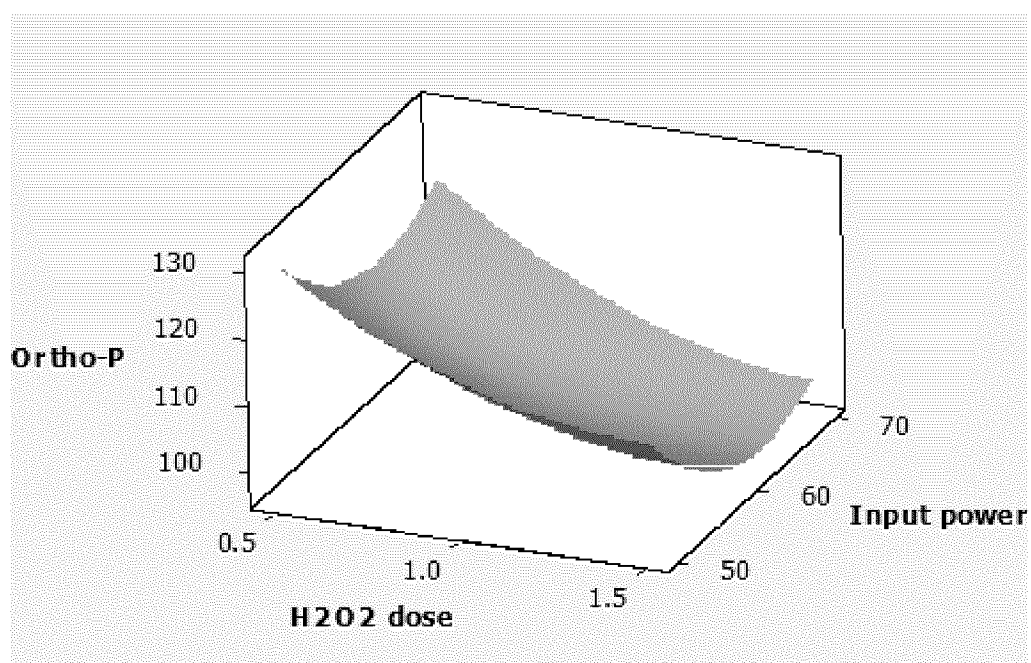


FIG. 8

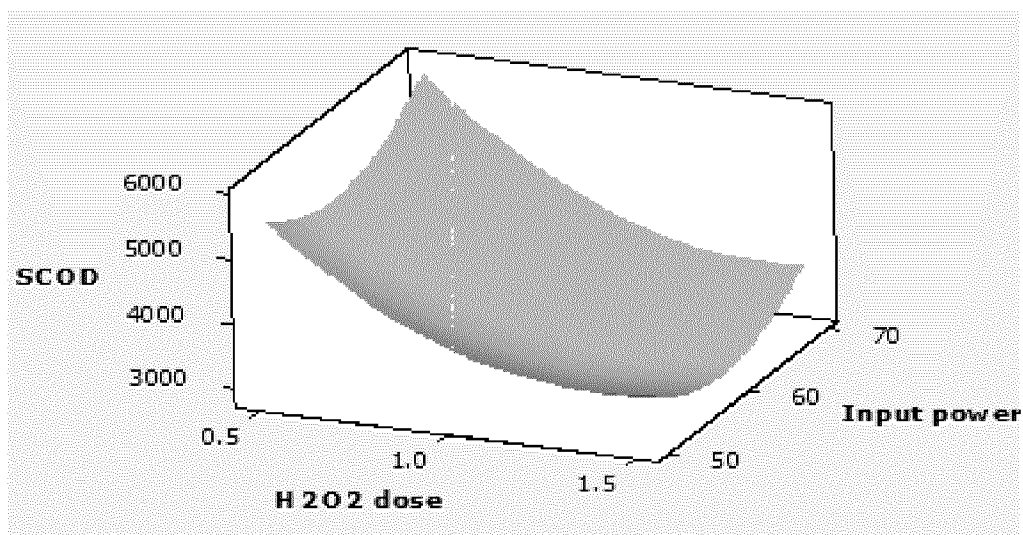


FIG. 9

8/9

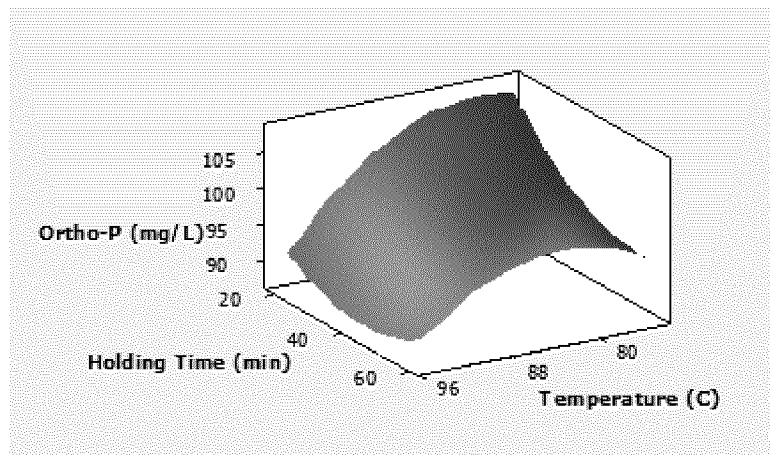


FIG. 10A

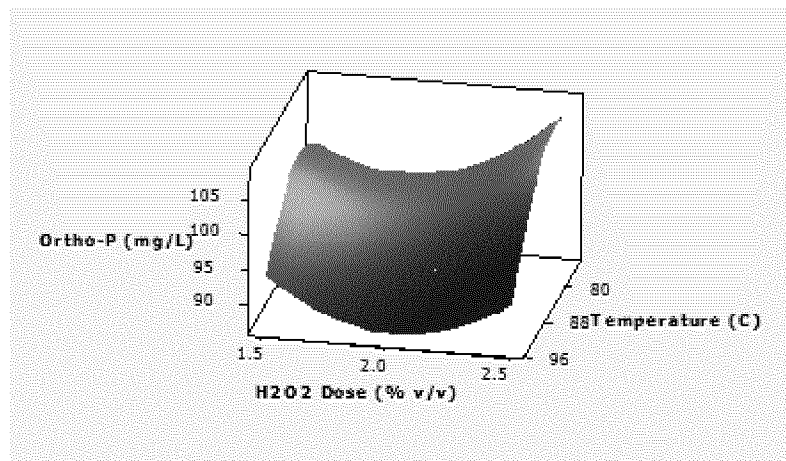


FIG. 10B

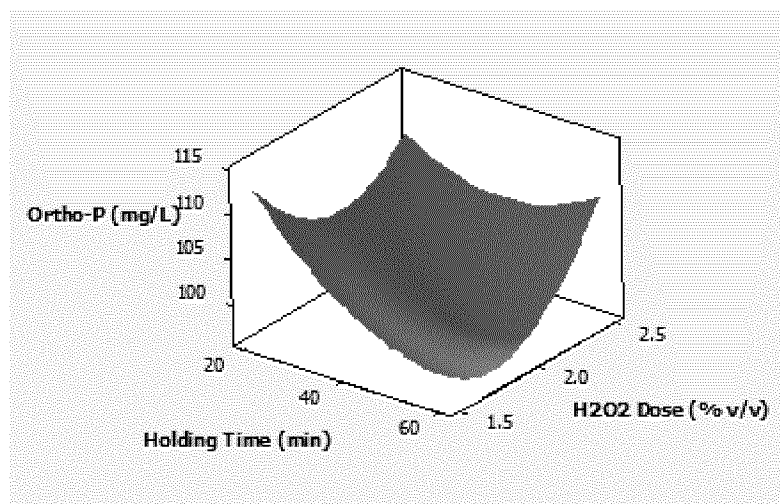


FIG. 10C

9/9

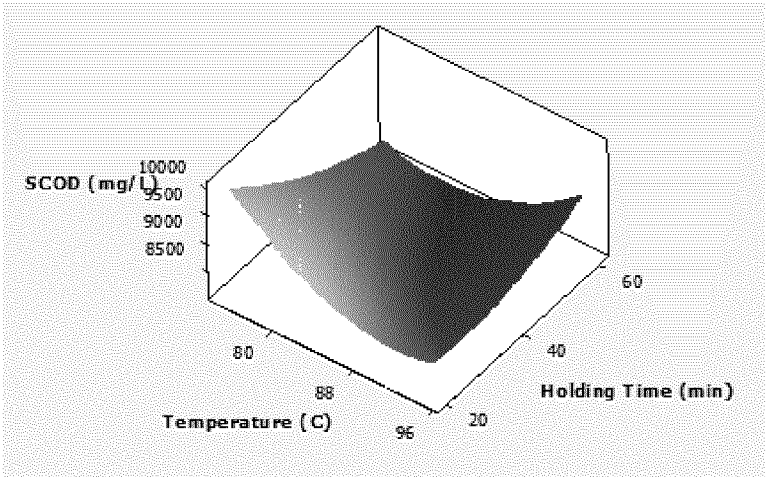


FIG. 11A

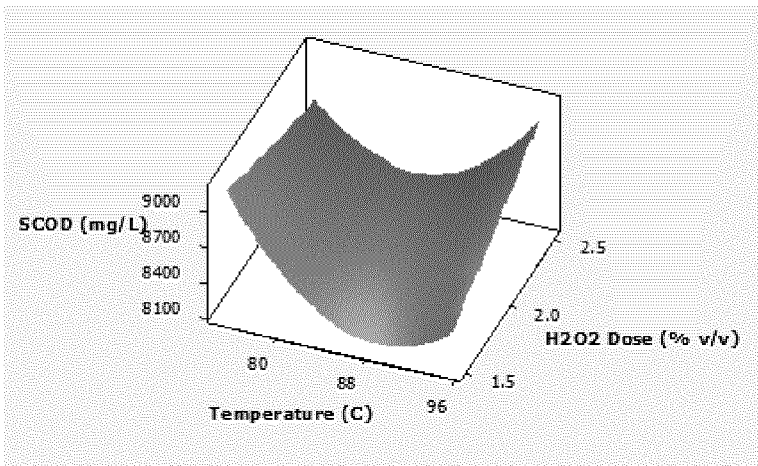


FIG. 11B

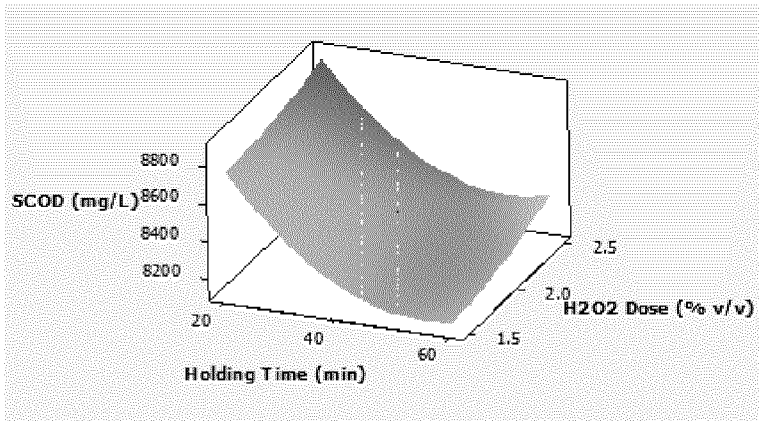


FIG. 11C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/051303

A. CLASSIFICATION OF SUBJECT MATTER IPC: <i>C02F 11/06</i> (2006.01), <i>B09B 3/00</i> (2006.01), <i>C02F 1/30</i> (2006.01), <i>C02F 1/72</i> (2006.01), <i>C02F 9/12</i> (2006.01) 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) <i>C02F 11/06</i> (2006.01), <i>B09B 3/00</i> (2006.01), <i>C02F 1/30</i> (2006.01), <i>C02F 1/72</i> (2006.01), <i>C02F 9/12</i> (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Questel Orbit, CIPO Library Discovery tool, see Examiner's Notes.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 894 248 B1 (CUENIN et al.) 15 February 2008 (15-02-2008) *whole document*	1, 10, 11, 13, 25, 28, 31, 32, 44, 46, 50, and 51
Y	(with LO et al.)	1-51
Y	WO 2008/017137 (LO et al.) 14 February 2008 (14-02-2008) *whole document*	1-51
☒ 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	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 13 February 2016 (13-02-2016)		Date of mailing of the international search report 01 March 2016 (01-03-2016)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476		Authorized officer Michelle Barriault (819) 639-8422

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2015/051303**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim Nos.: 52 and 53
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
These are omnibus claims.

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

- Remark on Protest**
- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2015/051303

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	LAGUNAS-SOLAR et al., "Disinfection of dairy and animal farm wastewater with radiofrequency power". J. Dairy Sci., 2005, Vol. 88(11), pp. 4120-4131. *pages 4126 and 4127 in particular* (with LO et al.)	1-51
Y	SRINIVASAN et al., "Briefing: A continuous-flow 915-MHz microwave treatment of dairy manure". Journal of Environmental Engineering and Science, 1 May 2014 (01-05-2014), Vol. 9(3), pp. 155-157. *abstract and Conclusions* (with LO et al.)	1-51
P, X	SRINIVASAN et al., "Optimization of radiofrequency-oxidation treatment of dairy manure". Journal of Environmental Chemical Engineering, 30 July 2015 (30-7-2015), Vol 3, pp. 2155-2160.	1-51
P, X	SRINIVASAN et al., "Effect on hydrogen peroxide on radiofrequency-oxidation of dairy manure". Journal of Environmental Engineering and Science, Vol. 10(2), 40-45.	1-51
A	GUIQING et al., "An ozone/hydrogen peroxide/microwave-enhanced advanced oxidation process for sewage sludge treatment" Journal of Environmental Science and Health Part A (2007). Vol 42, 1177-1181.	
A	SRINIVASAN et al., "Effects of acidifying reagents on microwave treatment of dairy manure". Journal of Environmental Science and Health, Part B (2014), Vol. 49, pp. 532-539.	
A	PING et al., "Advance oxidation process using hydrogen peroxide/microwave system for solubilisation of phosphate". Journal of Environmental Science and Health (2005), Vol. 40, pp. 1753-1761.	
A	ASIF et al., "Microwave treatment and struvite recovery potential of dairy manure" Journal of Environmental Science and Health Part B (2008), Vol.43, pp.350-357.	
A	LO et al., "Briefing: H2O2 dosing strategy on microwave treatment of sewage sludge" Journal of Environmental Engineering and Science, Vol. 9(3), pp. 158-161.	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2015/051303

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
FR2894248A1	08 June 2007 (08-06-2007)	FR2894248A1 FR2894248B1	08 June 2007 (08-06-2007) 15 February 2008 (15-02-2008)
WO2008017137A1	14 February 2008 (14-02-2008)	WO2008017137A1 CA2660181A1 CA2660181C US2010044306A1 US8444861B2 US2012067796A1	14 February 2008 (14-02-2008) 14 February 2008 (14-02-2008) 21 January 2014 (21-01-2014) 25 February 2010 (25-02-2010) 21 May 2013 (21-05-2013) 22 March 2012 (22-03-2012)