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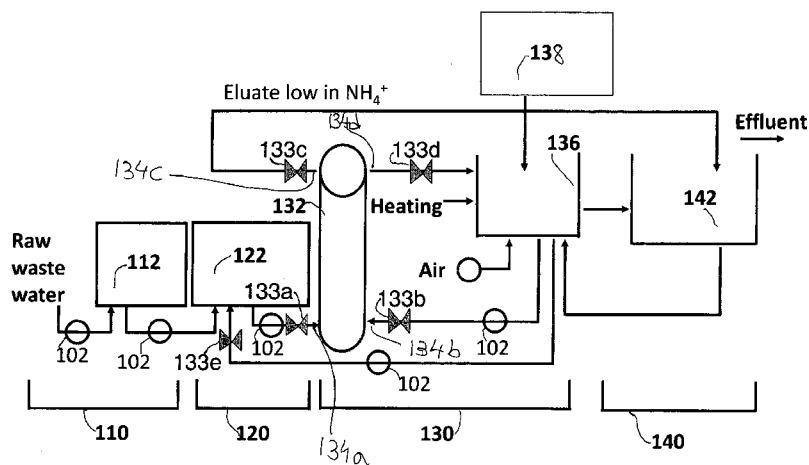


Figure 1

(57) Abstract: The present invention provides a new system for treatment of wastewater comprising organic materials, phosphate and ammonium. According to another aspect of the invention, a system for treatment of wastewater comprising organic materials, phosphate and ammonium is provided.

WASTE TREATMENT SYSTEM AND PROCESS

FIELD OF THE INVENTION

5 The present invention relates to treatment of wastewater containing high levels of organic material, ammonia and phosphate concentrations.

BACKGROUND

10 Animal manure is a worldwide environmental problem, which is constantly increasing due to increased meat demand. Swine production represents ~40% of the world's meat production. Its excrements contain high concentrations of organic matter, nutrients (particularly N and P), pathogens, trace metals and salts.

 Worldwide, anaerobic lagoons and land applications are currently the most
15 common wastewater partial treatment solutions. However, in recent years, due to increasingly stringent environmental legislation, mainly with regard to nitrogen species, further treatment of wastewater is required. A number of new treatment processes have been introduced, both at the field and at laboratory scale.

 Most of the new processes are aimed at obtaining a complete solution to
20 wastewater, which includes organic material and nutrients removal. In addition, current governmental endorsement and market demand for green energy solutions promote the use of anaerobic digesters for green energy production. In other cases a solid separation unit is employed to reduce the organic component in the wastes and then the wastewater is treated by anaerobic lagoons.

25 However, anaerobic digester effluents require further treatment with respect to ammonia and phosphate.

 Processes based on organic material reduction followed by nitrification-denitrification are known.

 In these processes an anaerobic digestion or solid separation first step is
30 typically followed by a second step of treatment of the effluent from the first step in a nitrification-denitrification unit. Such units are in operation, for example, in South Korea.

One such technology, the so-called Super Soil technology, is based on chemically enhanced solid separation followed by a nitrification/denitrification unit and a phosphorus removal unit (via calcium phosphate precipitation). This system is the only aqueous phase technology that had met the environmental performance standards set by the program: "Government-industry framework for developing alternatives to lagoon treatment and land application in North Carolina State".

The Super Soil method had to be combined with one of the four technologies found suitable by the same program for solid phase treatment: (A) High-temperature (thermophilic) anaerobic digester (ORBIT); (B) Centralized composting system (Super Soil Systems); (C) Gasification; (D) Fluidized bed combustion (BEST) (Williams, 2009).

Other treatment processes, which include recovery of both methane and nutrients, are known. Bonmati et al. (2003) presented a process composed of anaerobic digestion and water evaporation in order to obtain a solution for commercial use, which contained a high concentration of N, P and K. Preez et al. (2005) introduced the BIOREK process, which includes anaerobic digestion followed by ammonia stripping and recovery, to achieve an aqueous fertilizer for commercial use.

Ammonium may be nitrified to nitrite and nitrate by nitrifying bacteria, and in many wastewater treatment plants, nitrate is reduced by denitrifying bacteria into nitrogen gas. In some occasions, when the inherent organic matter present in the water is insufficient for full NO_3^- reduction, rather expensive organic compounds such as methanol, ethanol or acetate are added to the wastewater to provide an electron donor and carbon source for the denitrification bacteria.

Several approaches focusing on maximizing methane production from anaerobic digestion, combine advanced nitrogen transformation units for complete nitrogen removal. For example, Hwang et al. (2006) presented the ADEPT-SHARON-ANAMMOX concept, where ammonia is converted to nitrogen gas by Anammox bacteria. Karakashev et al. (2008) introduced the PIGMAN concept, in which the wastewater is first treated in an anaerobic digester, then in a separation unit (decanter centrifuge), followed by UASB (Upflow Anaerobic Sludge Blanket) post digestion, partial oxidation and nitrogen removal via anaerobic ammonia oxidation (the so called OLAND process). However, these processes require careful control since they are based on very sensitive slow growing bacteria and their economical and technological feasibility as well as sustainability have yet to be proven on full scale.

The common method for removal of ammonium and organic pollutants remains biological treatment, but ion exchange offers a number of advantages, including very short hydraulic retention times (in the order of minutes), very high reliability, the ability to handle shock loadings and the ability to operate under a wider range of temperatures. In addition, it has been shown that more often than not, the presence of organic compounds enhances the uptake of ammonium ions onto the ion exchangers (T.C. Jorgensen and L. R. Weatherley, Water Research 37 (2003), 1723-1728).

US4,098,690 to the University of Illinois Foundation and US4,370,234 to William P. Marsland describe the regeneration of ion exchange ammonium sorbents by nitrifying bacteria.

US 7,160,430 to Enpar Technologies Inc. describe a system in which ammonium may be taken out of a stream of wastewater by ion exchange, then flushed by a regenerant-water from the column, as the regenerant-water contains cations that replace the ammonium adsorbed on the column, cations such as sodium, potassium or calcium ions. An electrolysis step, which is carried out on the secondary-water, converts the flushed ammonium to nitrogen gas. However, US 7,160,430 does not describe a system or method to remove other wastewater components that should be removed, such as organic materials and phosphates.

There is a need for efficient systems and methods, with interconnected treatment units that allow share, use and/or reuse of materials at suitable levels and conditions for each unit, that allow effective removal of multiple components, such as organic materials, phosphates and ammonium from wastewater.

SUMMARY OF THE INVENTION

According to one aspect, a system for treatment of wastewater comprising organic materials, phosphate and ammonium is provided, the system comprising:

at least one anaerobic digester, each comprising a vessel, a wastewater inlet and a digester outlet fluidly connected thereto, the vessel comprising anaerobic digesters;

at least one struvite precipitation reactor, each comprising a vessel, a first and a second precipitation reactor inlet and a precipitation reactor outlet fluidly connected thereto, the first precipitation reactor inlet fluidly connectable to said digester outlet;

5 at least one ion exchange (IX) column, each comprising a column, a first and a second column valved inlet and a first and a second column valved outlet fluidly connected thereto, the column comprising resin having a high affinity to ammonium and a low affinity to magnesium ions, the first column inlet fluidly connectable to the precipitation reactor outlet;

10 an ion exchange column regenerator, comprising a vessel, a first regenerator inlet and a first regenerator outlet connected thereto, the vessel comprising a source of magnesium ions, wherein the first regenerator outlet is fluidly connectable to the second column inlet, and

15 at least one ammonium-nitrogen converter, each comprising means for conversion of ammonium into nitrogen gas ($N_2(g)$), at least one converter inlet and a first and a second converter outlet connected thereto, the first converter inlet fluidly connectable to the first column outlet and the first converter outlet fluidly connectable to the second precipitation reactor inlet,

20 the source of magnesium ions allowing magnesium ions in the regenerator to be fed to the IX column at a concentration allowing release of ammonium from the column when a level of ammonium in a wastewater eluate exceeds a first predetermined level, and precipitating the phosphates in wastewater fed from the digester to the struvite precipitation reactor together with ammonium in the wastewater.

According to another aspect, a system for treatment of wastewater comprising organic materials, phosphate and ammonium is provided, the system comprising:

25 at least one anaerobic digester, at least one struvite precipitation reactor fluidly connectable thereof, at least one ion exchange column fluidly connectable thereof, an ion exchange column regenerator, fluidly connectable thereof and an ammonium-nitrogen converter and a column regenerator comprising a source of magnesium ions, the converter and regenerator fluidly connectable thereof, the system configured to allow
30 anaerobic digestion of the wastewater in the digester, followed by precipitation of the phosphate out the wastewater in the struvite precipitation reactor, followed by adsorption of the ammonium in the wastewater on the IX column, followed by desorption

of the ammonium on the IX column, followed by conversion of the ammonium into nitrogen,

the source of magnesium ions allowing magnesium ions in the regenerator to be fed to the IX column at a concentration allowing release of ammonium from the IX column when a level of ammonium in a wastewater eluate exceeds a first predetermined level, and to precipitate the phosphates in wastewater fed from the digester to the reactor together with ammonium in the wastewater.

In some embodiments, the converter comprises: an aerated nitrification reactor and a denitrification reactor fluidly connectable thereto, and means for conversion of ammonium into nitrogen comprising: chemolithotrophic nitrifying bacteria in the aerated nitrification reactor, the chemolithotrophic nitrifying bacteria being capable of oxidizing ammonium to nitrate, and heterotrophic bacteria in the denitrification reactor, the heterotrophic bacteria being capable of converting nitrate to nitrogen gas;

wherein the nitrification reactor is fluidly connectable to the first column outlet; the ammonium released from the column is circutable between the column and the nitrification reactor, until a level of ammonium in a wastewater eluate drops below a second predetermined level;

wherein ammonia concentration in the nitrification reactor is controllable to allow for favorable conditions to the nitrifying bacteria; pH is settable in the nitrification reactor to prevent precipitation of magnesium hydroxide, and the system is configured to allow the amount of organic material remaining in the wastewater after the digester to fulfill an organic material/nitrate ratio needed for complete denitrification in the denitrification reactor.

In other embodiments, the converter comprises an electrochemical reactor, wherein ammonium is oxidizable to nitrogen gas.

Preferably, the embodiments further comprise at least one filter between the precipitation reactor and the columns, configured to remove suspended solids comprising struvite and solid organic matter from the wastewater before it is introduced into the IX column.

The systems may further comprise at least one ammonium-selective electrode, wherein the electrodes are positioned in at least one location selected from the group comprising: the first column outlet, the second column outlet, the first converter outlet and the second converter outlet.

5 The source of magnesium ions preferably comprises: magnesium oxide, magnesium hydroxide, magnesium chloride and mixtures thereof.

The vessel of the regenerator may further comprise a source of chloride, selected from one or more of the salts sodium chloride, potassium chloride and magnesium chloride.

10 The vessel of the regenerator preferably further comprises a composition capable of maintaining a constant pH through the addition of OH⁻ donating chemicals, the composition comprising: magnesium oxide, magnesium hydroxide, sodium hydroxide, potassium hydroxide and mixtures thereof.

15 The denitrification reactor may be fluidly connectable to the second column outlet, whereby eluates from the columns are conveyed directly to the denitrification reactor after a level of ammonium in a wastewater eluate drops below the second predetermined level, and until a level of ammonium in a wastewater eluate exceeds the first predetermined level.

20 According to another aspect, treatment of wastewater comprising organic materials, phosphate and ammonium is provided, the treatment comprising:

anaerobically digesting organic material in the wastewater;

25 precipitating phosphate from the wastewater with ammonium and magnesium ions;

extracting ammonium from the wastewater by eluting the wastewater with at least one ion exchange column;

eluting ammonium from the column with eluent comprising magnesium ions, and

30 converting ammonium in an eluate from the column into nitrogen gas, wherein the magnesium ions in the eluent are at a concentration allowing elution of ammonium from the column when a level of ammonium in a

wastewater eluate exceeds a first predetermined level, and phosphates are precipitated with magnesium in an eluate from the column.

The conversion of ammonium in an eluate from the column into nitrogen gas may comprise: nitrifying the ammonium to nitrate in at least one
5 nitrification reactor with autotrophic bacteria, and denitrifying the nitrate to nitrogen in at least one denitrification reactor with heterotrophic bacteria, the treatment further comprising:

circulating eluate from eluting ammonium from the column
between the column and the nitrification reactor, until a level of
10 ammonium in a wastewater eluate drops below a second predetermined level;

aerating the eluate in the nitrification reactor;

controlling the ammonium concentration in the nitrification
reactor to allow for favorable conditions to the chemolithotrophic
15 nitrifying bacteria;

setting pH in the nitrification reactor to prevent precipitation therein,

conveying wastewater eluates from the columns directly to the
denitrification reactor after a level of ammonium in a wastewater eluate
20 drops below a second predetermined level, and until a level of ammonium in a wastewater eluate exceeds the first predetermined level, and

allowing a sufficient amount of organic material to remain in the
wastewater in the denitrification reactor to fulfill an organic
25 material/nitrate ratio needed for complete denitrification.

The treatment may further comprise minimizing the amount of organic material in the nitrification reactor to allow encouragement of the growth of the autotrophic bacteria over heterotrophic bacteria.

The circulation velocity is preferably adjusted, thereby preventing IX
30 column clogging by suspended solids emanating from the nitrification reactor, and maintaining a stable concentration of ammonium in the nitrification reactor sufficient to disallow toxic conditions to the autotrophic bacteria.

The treatment may further comprising at least one of: heating the eluate from eluting ammonium from the column, maintaining the pH of the nitrification unit at about 6 and the pH of the denitrification unit at about 6.

The treatment may further comprise maximizing CH₄ formation when anaerobically digesting organic material in the wastewater, by minimizing organic matter oxidation when converting ammonium in an eluate from the column into nitrogen gas.

The treatment may comprise further maximizing CH₄ formation, by electrolyzing the eluate together with chloride ions at about pH 4-5 to form nitrogen gas, the treatment excluding nitrification of ammonium to nitrate ions and denitrification of the nitrate ions, whereby further minimizing organic matter oxidation is performed.

Preferably, a source of the magnesium ions is reagents MgO or Mg(OH)₂, said reagents allowing;

- a) the eluting ammonium from the column with eluate without promoting subsequent precipitation of solids during the extracting ammonium from the wastewater and
- b) removing phosphorus from the anaerobic digester effluents by its precipitation as struvite in the struvite precipitation reactor.

BRIEF DESCRIPTION OF THE FIGURES

For a better understanding of the invention and to show how it may be carried into effect, reference will now be made, purely by way of example, to the accompanying drawings.

With specific reference now to the drawing in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of embodiments only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the

invention; the description taken with the drawing making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

In the accompanying drawings:

5 Fig. 1 is a schematic drawing describing a process and system aimed at removing organic, nitrogen and phosphorus species from swine manure, according to some embodiments, and

10 Fig. 2 is a schematic drawing of an electrochemical regeneration subsystem in a process according to some other embodiments.

DETAILED DESCRIPTION OF THE SELECTED EMBODIMENTS

Various embodiments of wastewater treatment are disclosed herein below.

15 For simplicity sake, the embodiments describe a process and system that were used to treat swine wastewater, which may be particularly suitable for the process due the high levels of organic material, phosphate and ammonium therein. The process and system may be used as is described, or with adjustments known to the skilled in the art, to treat other wastewater, such as various industrial wastes.

20 A treatment process and system 100, according to one aspect, is described merely for the sake of convenience as including four modules 110, 120, 130 and 140, as shown in Figure 1.

The first module 110 is the anaerobic digester 112, designed to decrease the swine waste organic material concentration and produce methane.

25 The second module 120 recovers struvite ($\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a solid that can be further used as a fertilizing product in agriculture, which decreases the phosphate and ammonium concentrations in the wastewater while concurrently preventing subsequent clogging of the ion exchange column 132 by Ca- and Mg-phosphate precipitants.

30 The third module 130 is composed of a cation ion exchange column(s) 132, used for removing ammonium ions from the wastewater, an ion exchange column regenerator 134, comprising a source of magnesium ions for an eluent capable of eluting ammonium ions adsorbed to the columns 132, and a batch nitrification reactor

136 for (biological) regeneration of the ion exchange resin (not shown) in the column 132.

The fourth module 140 comprises a denitrification reactor 142 for treating the nitrate-rich excess water volume (blow down) from the nitrification reactor 136, and optionally low ammonium-leveled effluents from the ion exchange columns 132, which also contain the organic matter required for the denitrification reaction.

The wastewater may be conveyed through inlets and outlets 134 in units in the system 100, with the help of pumps 102. For example, a solution containing magnesium ions may be conveyed by a pump 102 from nitrification reactor 136 through its outlet 133e and inlet 133f to struvite precipitation reactor 133e. Control over elution may be performed by control of valves 133a-d, at inlets 134a-b and outlets 134c-d.

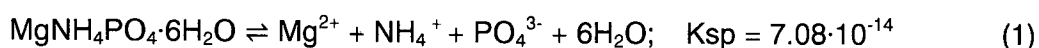
Module 1. Anaerobic digestion

The anaerobic digester is used to sharply decrease organic material concentrations and pathogens and produce methane as a green energy source. While efficient anaerobic digestion greatly reduces organic material in swine wastewater, anaerobic digester effluent still requires significant treatment, namely the removal of N and P species such as ammonium and phosphate, before it can be released to the environment. The effluent composition of the anaerobic digester is imperative for efficient operation of the process. Optimal effluent organic material/N ratio for complete denitrification is achieved by controlling the anaerobic process (hydraulic retention time [HRT], and solids residence time [SRT]) to on the one hand allow for sufficient degradable organic matter in the effluent for use in the denitrification process, while on the other hand maximizing the methane production of the anaerobic reactor.

Since high ammonia concentrations are well known to severely inhibit methanogenic activity (Hansen et al., 1998), the option of placing another IX reactor before the anaerobic treatment may have significant advantages (this will be decided specifically based on the conditions at a given site).

Module 2. Phosphorus removal and recovery

Struvite is formed according to Equation (1).



In order to reduce phosphate concentration by struvite precipitation, the initial struvite precipitation potential (PP) has to be set according to the desired residual phosphate concentration. Struvite PP, is mainly a function of the pH value, and the total ammonium, phosphate and magnesium ion concentrations.

- 5 In some embodiments, a blow-down volume from the nitrification reactor (rich in Mg^{2+}) is used to increase the struvite PP (see outlet 133e to inlet 133f). The ratio of the solution volume from the nitrification reactor 136 to the wastewater volume from the anaerobic digester depends on the actual Mg^{2+} concentration in the nitrification reactor 136 and the phosphorus, ammonium and Mg^{2+} concentrations in the digester effluent.
- 10 In some cases when the pH of the wastewater is low, aeration may be applied to increase the PP via controlled $CO_{2(g)}$ stripping.

Module 3. Ion exchange and ammonia oxidation

- Soluble ammonium ions may be removed from swine wastewater by absorbing
- 15 them onto a natural ion exchange (IX) material (for example natural or synthetic zeolites such as chabazite or clinoptilolite, which have a high affinity towards NH_4^+ and a lower affinity towards Mg^{2+} ions, or any other IX resin with similar properties – such as Dowex G-26, manufactured by DOW) that is subsequently regenerated. The process of ammonia removal and IX regeneration is operated as a SBR (sequencing batch reactor)
- 20 with two main operating steps:

- (1) a column packed with zeolite (or other specific resin) is used for ammonium removal from the effluent of anaerobic swine waste treatment.
- When NH_4^+ breakthrough occurs or the level of ammonium exceeds a first predetermined level, or after a predetermined volume of wastes has been pumped
- 25 through the bed, the system switches to the bio-regeneration mode. (2) During the bio-regeneration phase, a regenerating solution containing a sufficiently high concentration of counter cations (namely Mg^{2+} but possibly also Na^+ , K^+ , etc.) is circulated between the ion exchange column and the nitrification reactor. As a result, NH_4^+ is released from the resin and oxidized by common aerobic nitrifying
- 30 bacteria to NO_2^- , and subsequently to NO_3^- (final product). This operation is continued until the IX material is practically empty of NH_4^+ ions and ready for a new adsorption cycle.

Practical operation: a column packed with zeolites (resin) is used for ammonium ions removal from the effluent of anaerobic swine waste treatment (following P and NH_4^+ removal by struvite precipitation). The wastewater is pumped through the ion exchange bed. The breakthrough point has to be planned in advance to meet local environmental requirements with respect to allowed average effluent NH_4^+ concentration (typically 25 to 50 mg/l as N, which is the concentration range which is allowed to be introduced to municipal wastewater treatment plants). Based on the desired breakthrough concentration, the number of BV until breakthrough (typically 7 to 10 BV) and the hydraulic retention time (typically 15 to 20 min) in the bed (i.e. fluid velocity) are determined.

During the regeneration phase the velocity of the circulated water from the nitrification reactor is designed to expand the IX zeolites in a manner that will prevent it from clogging by suspended solids (mainly bacteria flocs). To do this the water is pumped at a vertical velocity typically higher than 25 m/h to provide a significant expansion of the resin particles (typically >25% expansion). The required vertical velocity may change according to the suspension characteristics of the particular IX resin used.

The ammonium concentration in the nitrification reactor is controlled to allow for favorable conditions to the nitrifying bacteria (i.e. ammonium concentration in the range 5 to 15 mg/l as N). Ammonia control may be performed by controlling the flow rate through the IX resin based on inline NH_4^+ measurement.

pH is set so that no solids precipitation will occur (the main concern is $\text{Mg}(\text{OH})_2$ precipitation, due to the typically high Mg^{2+} concentration maintained in the nitrification reactor emanating from the use of $\text{Mg}(\text{OH})_2$ or MgO as the buffer source). A suitable pH is 6. At such pH, both $\text{Mg}(\text{OH})_2$ and $\text{Mg}_3(\text{PO}_4)_2$ are not expected to precipitate.

Note that a phosphate containing chemical (e.g. Na_3PO_4) may be added in the nitrification reactor at low concentrations (typically 0.5 mgP/l), as soluble phosphate is required for the nitrification reaction to proceed.

Although the nitrifying bacteria may optimally grow and nitrify at different pH levels, they can readily be acclimated to adequately function at ~pH6.

Preferably, constant circulation is not applied, to prevent the development of excessively high ammonia concentrations and decreased oxidation rate. Rather, the circulation rate is adjusted, for example intervals of circulation are followed by time periods with no circulations to maintain relatively stable ammonia concentration in the nitrification reactor.

Aeration and/or heating control in the nitrification reactor 136 may help encourage growth and thriving of the nitrifying bacteria.

Moreover, an ammonia selective electrode may be used to control the process.

To meet the alkalinity requirements in the nitrification reaction two or more alkalinity agents/sources may be dosed, such as NaOH or KOH and MgO and/or $\text{Mg}(\text{OH})_2$. Another option is to recycle a fraction of the effluents of the denitrification reactor (water high in alkalinity and low in nitrate and NH_4^+) to the nitrification reactor.

The Mg^{2+} cation provided with the alkalinity agent is also used for struvite precipitation (and thus further ammonia and phosphate removal). If the concentration of Mg^{2+} that develops in the nitrification reactor is insufficient to extract the NH_4^+ ions from the zeolites (resin) column such that the level of ammonium eluted drops below a second predetermined level, such as to properly maintain the NH_4^+ concentration in the nitrification reactor, preferably in the range of 5 to 15 mg/l, until almost the end of the regeneration step, other chemicals (e.g. NaCl) may be dosed with the buffer during the regeneration period, or independently.

Module 4. Denitrification

In the process scheme in Figure 1, a biological denitrification reactor is used to treat the effluent of the ion exchange (containing organic material not degraded in the anaerobic digester) mixed with the blow down (high in nitrate concentration) from the nitrification reactor. In the denitrification reactor reduction of organic material occurs along with the conversion of nitrate to N_2 gas by heterotrophic bacteria. As noted before, the amount of biodegradable organic material remaining in the effluent after anaerobic digestion is designed to fulfill the organic material/ NO_3^- ratio needed for complete denitrification.

The nitrification is a batch operation that may last for around 20 hours. At the end of the nitrification the reactor is allowed to settle, and a part of the supernatant (typically between 5% and 15%) is pumped to the denitrification reactor. Another

volume is pumped to the struvite precipitation reactor. The denitrification reactor receives the electron donor from the raw sewage that passes the IX reactor in the adsorption step (which typically lasts 3 h). At the end of the denitrification step water with low NO_3^- and high alkalinity may be returned to the nitrification reactor to
5 compensate for the water lost to the denitrification reactor and the struvite reactor.

The IX – chemical regeneration followed by biological nitrification process may be used for treating swine wastewater. However, its application is not limited to the agricultural market. In general the process may be applied for two wastewater treatment scenarios (1) any wastewater that requires combined removal of high levels
10 of organic material, phosphate and ammonia (2) if the IX system is placed at the inlet to the digester with the aim of reducing ammonium concentrations before the wastewater is introduced to the anaerobic digester, it may help preventing ammonia inhibition within the anaerobic reactor itself.

The configuration combines a bio-regenerated ion exchange unit for treating
15 ammonia. Since the bio-regeneration relies on a biological nitrification step which is acidic (2 moles of protons are released for each mole of ammonia oxidized to nitrate) it requires the addition of an alkalinity source. MgO and $\text{Mg}(\text{OH})_2$ were identified as alkalinity sources that can be further used in the treatment process for P removal, thus allowing for the combined operation of the different units in a highly effective manner,
20 which not only maximizes the performance of each unit but also minimizes potential clogging of the IX reactor during the adsorption step. Moreover, the ion exchange unit not only separates the ammonia but also allows for higher methane formation in the anaerobic unit (see further explanation below). The IX unit is only cost-effective when combined with MgO and $\text{Mg}(\text{OH})_2$ as both magnesium and alkalinity sources, and
25 further use of the Mg^{+2} cations for struvite precipitation and for preventing the clogging of the ion exchange reactor by Ca- and Mg-phosphate precipitants.

The system 100 has several advantages over conventional systems and methods for treating wastewater such as swine manure wastewater:

1. Maximization of organic material oxidation to CO_2 which is proportional to the

30 CO_2 mass that is reduced to form methane (CH_4) in the anaerobic digester.

In some conventional nitrification-denitrification processes wastewater is continuously circulated between nitrification and denitrification reactors. This results in COD (Chemical Oxygen Demand, a quantitative measure of the

electron donating capacity of a solution, which is often used to characterize the energy derived from organic materials in a solution) being aerobically oxidized in the nitrification reactor leading to a high overall COD/NH₄⁺ ratio required at the influent of the nitrification-denitrification unit to achieve complete denitrification.

Decreasing the ratio would allow to oxidize more organic material in the anaerobic digester and thus produce more CH₄. Since in the provided process COD is not introduced to the nitrification reactor, and is not circulated between the nitrification and denitrification reactors, no COD is aerobically oxidized in the nitrification reactor, i.e. a relative low COD/NO₃⁻ ratio is required for complete denitrification, thereby increasing the organic material portion that can be oxidized in the anaerobic digester.

2. Decrease in operational costs.

Oxygen supplementation constitutes a major component in the cost of traditional nitrification-denitrification systems. Oxygen is required for ammonia and COD oxidation in the nitrification reactor. In the provided process, since COD is not introduced to the nitrification reactor, less oxygen is required in the nitrification reactor, i.e. operational costs are reduced.

3. Maximizing phosphate recovery without increasing operational costs. Normally a high struvite PP is achieved by increasing pH through aeration and addition of external Mg²⁺ (common Mg²⁺ sources are MgO, Mg(OH)₂ and MgCl₂). In the provided process since MgO and/or Mg(OH)₂ is used as at least a part of the buffering agent, the Mg⁺² ions are supplied as blow-down from the nitrification reactor and no further chemical dosing is required.

4. Providing favorable conditions for the nitrifying bacteria.

Nitrifying bacteria, being autotrophic, are slow-growing relative to heterotrophic bacteria. Minimization of organic matter presence in the nitrification reactor encourages the growth of ammonium oxidizing bacteria over heterotrophic bacteria.

Furthermore, since the volume of water in the nitrification reactor is relatively low (and nitrifying bacteria concentration is high), the water can be

heated in winter to allow for optimal conditions for nitrification (Temp > 20 °C).

5 Maintaining high ammonia concentrations and/or rapid changes in ammonia concentrations in the nitrification reactor may result in a decrease in the nitrification rate. In the presented process tight control is maintained over the ammonia concentrations in the nitrification tank, providing yet again favorable conditions for the nitrifying bacteria.

According to another aspect, in system 200 the nitrification and denitrification modules are replaced with another module 250, including an electrochemical reactor 252, as shown in Figure 2.

Detailed description of the electrochemical ammonia oxidation step

The system 200 has three operational modules. Module 210 (anaerobic digestion) and Module 220 (phosphorous removal and recovery) are essentially identical to the system 100, while the biological units, modules 130 and 140) in system 100 are replaced by an electrochemical reactor 252 used to convert ammonium to $N_{2(g)}$. Ammonium electro-oxidation may theoretically be carried out directly by oxidation of the ammonium, or indirectly by "active chlorine" species formed at the anode. The adsorption-oxidation process comprises three steps: (1) adsorption of NH_4^+ on the ion exchange resin; (2) chemical regeneration of the resin using a regeneration solution from container 254 (ion exchange regenerator) comprised of a high cation concentration (1-2 M) and a correspondingly high Cl^- concentration; (3) electrochemical oxidation of ammonium in the regeneration solution (Container 252) which is characterized by high Cl^- (1-2 M) and NH_4^+ concentrations (several hundred mgN/l), at a working voltage of about 2 to 4 volts. Typically the anode in this application is made of titanium covered by a thin layer of RuO_2 and the cathode of titanium. During indirect ammonia oxidation, chloride ions compete with ammonium and OH^- at the anode, Eq. (2):



Simultaneously, Cl_2 (or $HOCl$ from reaction of the chlorine with water) reacts with NH_4^+ close to the anode to form $N_{2(g)}$ and Cl^- (Eq. (3)). At the cathode H^+ is reduced to $H_{2(g)}$ (Eq. (4)).



Combining Eqs. (2), (3) and (4), the overall (main) electrolytic cell reaction is:



- 5 As shown in Eq. (5), the overall proton balance of the electrolytic cell is acidic, i.e. protons are released to the solution at a molar ratio of 1 to 1 with the ammonia oxidized. Thus, an alkalinity containing agent has to be added to maintain constant pH, which is preferably in the range of pH4-pH5.

10 As in the biological mode, $\text{Mg}(\text{OH})_2$ and/or MgO are preferably used for neutralization of the hydronium ions. Once the electrolysis step comes to completion, the redox potential of the solution increases steeply from ~500 mV to 800 mV and pH goes up, both parameters serve as an indication that the ammonium concentration has dropped to nil and the process can be stopped.

15 The electro-oxidized solution, which is now devoid of NH_4^+ , can now be used for the next chemical regeneration cycle. A small portion of this solution is pumped to the struvite precipitation reactor for P removal and reuse, as described regarding the embodiments comprising biological treatment.

Therefore, in the electrooxidation IX regeneration mode the regeneration solution will be rich in Mg^{2+} (due to the alkalinity source) and Cl^- concentrations (typically higher
20 than 50 g Cl^-/L).

This recycled regeneration solution will also contain certain concentrations of Na^+ , Ca^{2+} and K^+ , since these cations are present in swine wastes, but at a relatively low concentration.

25 Further addition of NaCl during the chemical regeneration step may be carried out if transpires that faster NH_4^+ desorption kinetics is required.

The regeneration solution will be used intermittently as the chemical regeneration solution (using its high Mg^{2+} and possibly Na^+ concentrations) and as an efficient ammonia indirect electrooxidation solution (using its high Cl^- concentration).

The Mg^{2+} ions lost to the swine wastes in the adsorption step will be compensated by the addition of $\text{Mg}(\text{OH})_2$ and/or MgO in the electrooxidation step.

The cations (namely Mg^{2+}) and Cl^- ions pumped to the struvite reactor will be compensated by equal addition of NaCl .

5 As in the biological regeneration alternative, blow down from the regenerant solution (rich in Mg^{2+}) will be used to precipitate struvite from the effluent of the anaerobic digester, prior to introducing the water to the IX adsorption step.

At the end of the NH_4^+ electrooxidation step the regeneration solution is pumped back to Container 254 for use in the next chemical regeneration step, and so forth.

10 The system 200 may be used in many wastewater schemes in batch processing, whereby the wastewater is eluted through ion exchange columns, the elution of the wastewater is stopped when the ammonium level eluting from the column exceeds a first predetermined level, and then the column is flushed with a regenerating solution comprising (mainly) magnesium and sodium ions. Preferably, the process is designed in
15 size, capacity, velocity etc. to allow the electrolysis to occur in off-peak times when electricity costs are minimal.

In large systems that have to treat large volumes of wastewater with high levels of ammonium, a number of units such as columns 232 may be used, so that during regeneration of a column 232 the wastewater may be eluted through another column
20 232. Typically, the size of the reactors is fit to the ammonium mass that is absorbed in the IX step.

The scope of the present invention is defined by the appended claims and includes both combinations and sub combinations of the various features described hereinabove as well as variations and modifications thereof, which would occur to
25 persons skilled in the art upon reading the foregoing description.

In the claims, the word comprise, and variations thereof such as comprises, comprising and the like indicate that the components listed are included, but not generally to the exclusion of other components.

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CLAIMS

1. A system for treatment of wastewater comprising organic materials, phosphate and ammonium, the system comprising:

at least one anaerobic digester, each comprising a vessel, a wastewater inlet and a digester outlet fluidly connected thereto, the vessel comprising anaerobic digesters;

at least one struvite precipitation reactor, each comprising a vessel, a first and a second precipitation reactor inlet and a precipitation reactor outlet fluidly connected thereto, the first precipitation reactor inlet fluidly connectable to said digester outlet;

at least one ion exchange (IX) column, each comprising a column, a first and a second column valved inlet and a first and a second column valved outlet fluidly connected thereto, the column comprising resin having a high affinity to ammonium and a low affinity to magnesium ions, the first column inlet fluidly connectable to the precipitation reactor outlet;

an ion exchange column regenerator, comprising a vessel, a first regenerator inlet and a first regenerator outlet connected thereto, the vessel comprising a source of magnesium ions, wherein the first regenerator outlet is fluidly connectable to the second column inlet, and

at least one ammonium-nitrogen converter, each comprising means for conversion of ammonium into nitrogen gas ($N_{2(g)}$), at least one converter inlet and a first and a second converter outlet connected thereto, the first converter inlet fluidly connectable to the first column outlet and the first converter outlet fluidly connectable to the second precipitation reactor inlet,

the source of magnesium ions allowing magnesium ions in the regenerator to be fed to the IX column at a concentration allowing release of ammonium from the column when a level of ammonium in a wastewater eluate exceeds a first predetermined level, and precipitating the phosphates in wastewater fed from the digester to the struvite precipitation reactor together with ammonium in the wastewater.

2. A system for treatment of wastewater comprising organic materials, phosphate and ammonium, the system comprising:

at least one anaerobic digester, at least one struvite precipitation reactor fluidly connectable thereof, at least one ion exchange column fluidly connectable thereof, an ion exchange column regenerator, fluidly connectable thereof and an ammonium-nitrogen converter and a column regenerator comprising a source of magnesium ions, the converter and regenerator fluidly connectable thereof,

the system configured to allow anaerobic digestion of the wastewater in the digester, followed by precipitation of the phosphate out the wastewater in the struvite precipitation reactor, followed by adsorption of the ammonium in the wastewater on the IX column, followed by desorption of the ammonium on the IX column, followed by conversion of the ammonium into nitrogen,

the source of magnesium ions allowing magnesium ions in the regenerator to be fed to the IX column at a concentration allowing release of ammonium from the IX column when a level of ammonium in a wastewater eluate exceeds a first predetermined level, and to precipitate the phosphates in wastewater fed from the digester to the reactor together with ammonium in the wastewater.

3. The system of claim 1, wherein the converter comprises: an aerated nitrification reactor and a denitrification reactor fluidly connectable thereto, and means for conversion of ammonium into nitrogen comprising: chemolithotrophic nitrifying bacteria in the aerated nitrification reactor, the chemolithotrophic nitrifying bacteria being capable of oxidizing ammonium to nitrate, and heterotrophic bacteria in the denitrification reactor, the heterotrophic bacteria being capable of converting nitrate to nitrogen gas;

wherein the nitrification reactor is fluidly connectable to the first column outlet;

the ammonium released from the column is circutable between the column and the nitrification reactor, until a level of ammonium in a wastewater eluate drops below a second predetermined level;

wherein ammonia concentration in the nitrification reactor is
5 controllable to allow for favorable conditions to the nitrifying bacteria;

pH is settable in the nitrification reactor to prevent precipitation of magnesium hydroxide, and the system is configured to allow the amount of organic material remaining in the wastewater after the digester to fulfill an organic material/nitrate ratio needed for complete denitrification in the
10 denitrification reactor.

4. The system of claim 1, wherein the converter comprises an electrochemical reactor, wherein ammonium is oxidizable to nitrogen gas.

15 5. The system of any one of claims 1 to 4, further comprising a filter between the precipitation reactor and the columns, configured to remove suspended solids comprising struvite and solid organic matter from the wastewater before it is introduced into the IX column.

20 6. The system of any one of claims 1 to 4, further comprising at least one ammonium-selective electrode, wherein the electrodes are positioned in at least one location selected from the group comprising: the first column outlet, the second column outlet, the first converter outlet and the second converter outlet.

25 7. The system of any one of claims 1 to 4, wherein the source of magnesium ions comprises: magnesium oxide, magnesium hydroxide, magnesium chloride and mixtures thereof.

30 8. The system of claim 7, wherein the vessel of the regenerator further comprises a source of chloride, selected from one or more of the salts sodium chloride, potassium chloride and magnesium chloride.

9. The system of claim 8, wherein the vessel of the regenerator further comprises a composition capable of maintaining a constant pH through the addition of OH⁻ donating chemicals, the composition comprising: magnesium oxide, magnesium hydroxide, sodium hydroxide, potassium hydroxide and mixtures thereof.

10. The system of claim 3, wherein the denitrification reactor is fluidly connectable to the second column outlet, whereby eluates from the columns are conveyed directly to the denitrification reactor after a level of ammonium in a wastewater eluate drops below the second predetermined level, and until a level of ammonium in a wastewater eluate exceeds the first predetermined level.

11. Treatment of wastewater comprising organic materials, phosphate and ammonium, the treatment comprising:

anaerobically digesting organic material in the wastewater;
precipitating phosphate from the wastewater with ammonium and magnesium ions;

extracting ammonium from the wastewater by eluting the wastewater with at least one ion exchange column;

eluting ammonium from the column with eluent comprising magnesium ions, and

converting ammonium in an eluate from the column into nitrogen gas,

wherein the magnesium ions in the eluent are at a concentration allowing elution of ammonium from the column when a level of ammonium in a wastewater eluate exceeds a first predetermined level, and phosphates are precipitated with magnesium in an eluate from the column.

12. The treatment of claim 11, wherein the conversion of ammonium in an eluate from the column into nitrogen gas comprises: nitrifying the ammonium to nitrate in at least one nitrification reactor with autotrophic bacteria, and denitrifying the nitrate to nitrogen in at least one denitrification reactor with heterotrophic bacteria, the treatment further comprising:

circulating eluate from eluting ammonium from the column between the column and the nitrification reactor, until a level of ammonium in a wastewater eluate drops below a second predetermined level;

5 aerating the eluate in the nitrification reactor;

controlling the ammonium concentration in the nitrification reactor to allow for favorable conditions to the chemolithotrophic nitrifying bacteria;

10 setting pH in the nitrification reactor to prevent precipitation therein,

conveying wastewater eluates from the columns directly to the denitrification reactor after a level of ammonium in a wastewater eluate drops below a second predetermined level, and until a level of ammonium in a wastewater eluate exceeds the first predetermined level, and

15 allowing a sufficient amount of organic material to remain in the wastewater in the denitrification reactor to fulfill an organic material/nitrate ratio needed for complete denitrification.

20 13. The treatment of claim 12, further comprising minimizing the amount of organic material in the nitrification reactor to allow encouragement of the growth of the autotrophic bacteria over heterotrophic bacteria.

25 14. The treatment of claim 12, wherein the circulation velocity is adjusted, thereby preventing IX column clogging by suspended solids emanating from the nitrification reactor, and maintaining a stable concentration of ammonium in the nitrification reactor sufficient to disallow toxic conditions to the autotrophic bacteria.

30 15. The treatment of claim 11 or 12, further comprising at least one of: heating the eluate from eluting ammonium from the column, maintaining the pH of the nitrification unit at about 6 and the pH of the denitrification unit at about 6.

16. The treatment of claim 11, further comprising maximizing CH_4 formation when anaerobically digesting organic material in the wastewater, by minimizing organic matter oxidation when converting ammonium in an eluate from the column into nitrogen gas.

5

17. The treatment of claim 16, comprising further maximizing CH_4 formation, by electrolyzing the eluate together with chloride ions at about pH 4-5 to form nitrogen gas, the treatment excluding nitrification of ammonium to nitrate ions and denitrification of the nitrate ions, whereby further minimizing organic matter oxidation is performed.

10

18. The treatment of claim 15 or 17, wherein a source of the magnesium ions is reagents MgO or $\text{Mg}(\text{OH})_2$, said reagents allowing;

- a) the eluting ammonium from the column with eluate without promoting subsequent precipitation of solids during the extracting ammonium from the wastewater and
- b) removing phosphorus from the anaerobic digester effluents by its precipitation as struvite in the struvite precipitation reactor.

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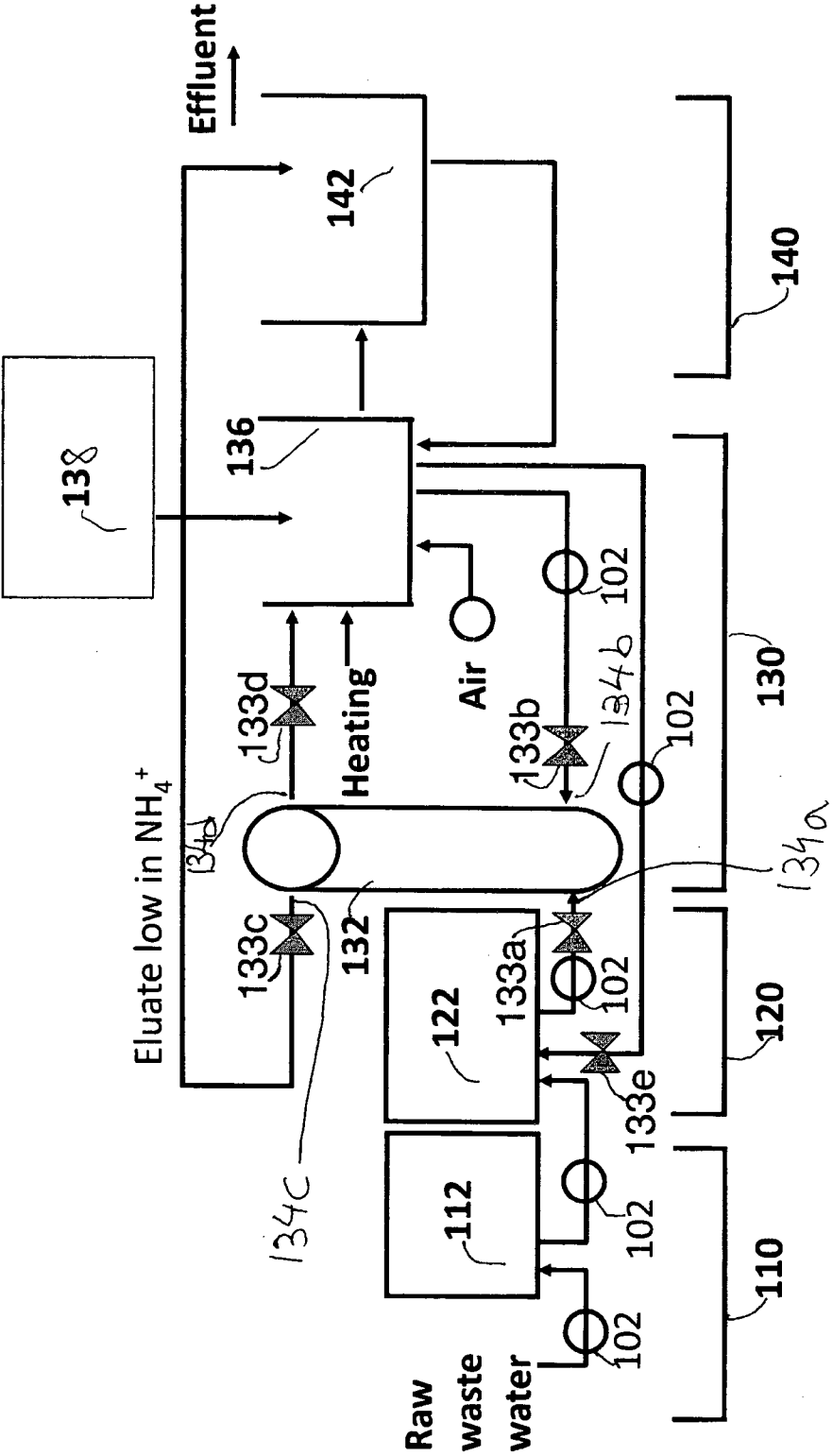


Figure 1

