



Sustainable removal of ammonia from anaerobic-lagoon swine waste effluents using an electrochemically-regenerated ion exchange process

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HIGHLIGHTS

- ▶ A new physico-chemical method for ammonia removal from swine wastes was tested.
- ▶ The method consists NH_4^+ ion exchange and electrochemical regeneration of the resin.
- ▶ Operation with swine wastes for prolonged time proved feasible and cost effective.
- ▶ Counter cations accumulation in recycled regenerant solution required short IX step.
- ▶ Overall treatment cost was \$3.057 per kg ammonia oxidized (OPEX amounting to 88.4%).

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ABSTRACT

A new process, based on ion-exchange and electrochemical regeneration, was tested for removing ammonia from effluents of swine-waste anaerobic lagoons. The process, consisting of a daily sequential operation of adsorption (180 min), chemical regeneration (125 min) and electrooxidation of ammonia in the regeneration solution (8 h, applied during low-cost electricity hours), was shown feasible for reducing the ammonia concentration in the wastewater from ~1000 to ~60 mg/L with a total cost estimated at ~\$3/kg N. The work focused on identifying the best operational conditions enabling continuous operation of the ion-exchange column and recycling of the regenerant solution without the need for replenishment of either. Chemical additions were restricted to in-line addition of NaOH to maintain constant pH during the electrolysis step and periodical addition of NaCl to compensate for Cl^- and Na^+ losses. It was found that removing NH_4^+ (by chabazite-zeolite) from swine wastewater characterized by $\text{NH}_4^+:\text{K}^+:\text{Ca}^{2+}:\text{Mg}^{2+}:\text{Na}^+$ ratio of 1:0.66:0.1:0.06:0.30 (g/g) could be carried out by the proposed treatment sequence at conditions of pseudo steady state, with an adsorption stage of 12.5 bed volumes and 14.5 min hydraulic retention time. Applying such conditions, the concentration of K^+ (the main competing cation) stabilized both in the regenerant solution and on the chabazite, enabling >90% NH_4^+ removal without need for replacing the regenerant solution. Electrooxidation efficiency constantly exceeded 90% due to the high Cl^- concentration (>17 g/L) maintained in the regeneration solution and because only a small mass of organic matter was transferred to the regenerant solution following the adsorption step.

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1. Introduction

The evolution of animal agriculture to meet the needs of a rapidly growing world population is evidenced by a consistent trend toward the replacement of small animal farms by large, industrial-scale animal feeding operations (AFOs), which maximize the number of livestock confined per unit of land area. Swine production is one of the biggest sources of meat in modern agriculture; in fact, pork is the most consumed meat in the world representing about 40% of the world's total meat consumption. In 2011, the

swine population in the European Union amounted to 148.6 million hogs [1]. Worldwide pork production was forecasted to amount to ~104 million metric tons in 2012, an increase of 2.7% from 2011 [2]. Swine wastes contain high concentrations of organic matter, nutrients (particularly N and P), pathogens, trace metals and salts. The effects of intense animal husbandry over relatively small areas have already been observed in many places. In Brittany (France), intensive pig-farming caused many surface and subsurface water resources to become contaminated by nitrate, with concentrations exceeding the European Community 50 mg/L drinking standard [3]. In Spain, the common practice of spreading swine wastes on agricultural soils in rural areas has impacted the quality of aquifers and surface waters to a degree that it jeopardizes the very existence of the industry. In Israel, more than 100,000 pigs

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are grown annually (in multiple farms of varying sizes) in a restricted area (near the town of Iblin, in northern Israel), producing $\sim 1000 \text{ m}^3/\text{d}$ of wastewater characterized by very high chemical oxygen demand (COD) and nutrient loads, equivalent to the loads produced by a medium-size city. The organic matter in the wastes, as well as the orthophosphate component, are reduced considerably (>60% and >90% removal, respectively; the P component presumably precipitates as hydroxyapatite) in anaerobic lagoons; however the ammonia component in the wastes is not treated, but rather discharged with the anaerobic lagoon effluents to a nearby wastewater treatment plant (the Haifa WWTP), where it contributes significantly to the ammonia load. Thus, an incentive (both economic and regulative) exists for developing a cost effective technology for reducing the ammonia concentration in the swine wastes before they arrive at the WWTP.

Current practices for removal of ammonia from swine wastes are predominantly based on biological means (nitrification–denitrification) either in (continuous) activated sludge configuration [4] or in sequencing batch reactor (SBR) mode (e.g. [5,6]). At present, most of the processes that are used for ammonia–nitrogen removal from wastewater are coupled with the removal of organic matter.

The most commonly-used technique for swine waste treatment to-date is anaerobic digestion, predominantly applied in anaerobic lagoons. Anaerobic treatment provides a convenient and simple method for stabilizing organic matter into less reactive compounds and biogas. Although efficient for COD removal (and methane production, in anaerobic digesters), anaerobic treatment does not provide a solution for ammonia removal. In fact, during lagoon and anaerobic digester treatment, the degradation of organic matter which contains nitrogen (both soluble and suspended) releases NH_3 to the water, thereby resulting in an increase in the dissolved ammonia concentration. Consequently, environmental regulations in most developed countries require additional treatment of the anaerobically treated wastes before they are discharged to water bodies, used for irrigation, or disposed to sewage systems.

The SBR technique, which is gaining momentum in the context of swine waste treatment, as manifested by the operation of a few full-scale plants [6,7], applies a sequence of fill and draw cycles. This technology allows the decrease of both organic matter and nitrogen concentrations (both ammonia through nitrification and nitrate through denitrification). Since biological denitrification requires the availability of readily degradable carbon, prior to anaerobic removal of COD from piggery effluent, a portion of the COD should be allocated to the denitrification step if successful denitrification without the use of costly external carbon sources is planned [8]. Lee et al. [9] used fermented wastes of a pig farm as a carbon source to reach enhanced nutrient removals by SBR. The reactor was fed with farm wastewater and was run through the following stages: 10 min anoxic feeding, 13 h oxic feeding, 7 h anoxic feeding, 3 h oxic feeding, 40 min sedimentation and 10 min withdrawal from the reactor. 90% nitrogen removal and 89% phosphorous removal were obtained using this method. Bernet et al. [10] suggested treating swine wastewater by a combined anaerobic–aerobic system. Using two laboratory-scale sequencing batch reactors, 85–91% TOC and 85–91% TKN removals were attained. Edger-ton [11] achieved 99% total ammonia nitrogen (TAN) and 79% COD removal in a pilot-scale SBR.

Best available techniques (BATs) for swine wastes treatment have been suggested in two places: In Cyprus, in locations where nutrients had to be removed from the wastes (but where odor was not a concern) the recommended treatment sequence consisted of solids separation followed by SBR aerobic treatment and storage or agricultural reuse of the solid waste [12]. The North Carolina State government–industry framework for developing alternatives to lagoon treatment and land application for swine

wastes tested five technologies that met, in their view, minimum environmental performance standards. Only the technology termed “Super soil”, which is based on polymer assisted liquid–solid separation followed by nitrification–denitrification units and a chemical phosphorus removal unit, met the technical performance criteria defined for the aqueous-phase treatment [13,14].

Despite being the first choice of most professionals, processes that rely on biological ammonia removal suffer from several drawbacks: Nitrifying autotrophic bacterial efficiency is highly dependent on temperature; bacterial communities in reactors that treat ammonia and organic matter simultaneously are subject to competition between heterotrophs and autotrophs, which under certain conditions may result in washout of the nitrifying population, resulting in process failure. Moreover, since in many cases the preferred method for organic matter removal is anaerobic digestion accompanied by CH_4 production, the need to leave sufficient labile organic matter for the denitrification step may become a liability. These shortcomings may be overcome by implementation of physico-chemical processes, which are advantageous due to their potential for stable operation, reduction of startup and recovery times after failure, and relative ease of control; these factors are essential for the operation of a treatment unit that is located in a hog-house, where professional intervention is limited.

With regard to physico-chemical swine treatment methods, attempts have been made to remove ammonia from swine wastes by electrochemical means, together with the oxidation of organic matter [15]. In another study NH_4^+ was reported to be removed from swine wastes by conventional ion exchange, using zeolite [16]. Such a process, however, cannot be economical because of the high costs associated with the chemical regeneration of the zeolite and the safe discharge of the produced brine. In the latter study, the authors reported that the presence of organic compounds in the wastes enhanced the uptake of the ammonium ion by the zeolite. This conclusion is in par with Lahav and Green [17], who showed that the capacity and kinetics of chabazite–zeolite for NH_4^+ adsorption was hardly changed by the growth of a bacterial biofilm on the surface of the ion exchanger exposed to domestic wastewater for prolonged periods of time.

Judging by the very small number of full-scale swine wastewater facilities operated to-date it appears that despite the intensive research focusing in the last two decades on swine manure treatment there is still a clear need for the development of economical, reliable and easy to operate treatment concepts. Moreover, considering that many farms already apply some sort of anaerobic treatment (either anaerobic lagoons or intensive anaerobic digestion) a particular focus should be put on nitrogen species removal from the wastes, which, to-date, constitutes the least effective element of most of the implemented treatment methods.

2. The proposed process and the practical challenges related to its operation

In order to overcome the drawbacks of the present biological processes for ammonia removal from swine wastewater, a new physico-chemical process, comprising ion exchange and electrochemical regeneration, was tested. This batch-mode process is described schematically in Fig. 1. The anaerobic lagoon swine effluent is first pumped through a chabazite–zeolite reactor for a predetermined number of bed volumes (simulating the volume of the swine wastewater generated daily). The effluents from the ion exchange (IX) reactor, now with low total ammonia nitrogen (TAN) concentration, are discharged to a nearby WWTP. Second, a highly concentrated NaCl solution (1 M) is passed through the zeolite column and the NH_4^+ is released into the regeneration solution, which, thereafter, is recirculated through an electrolyzer, which converts

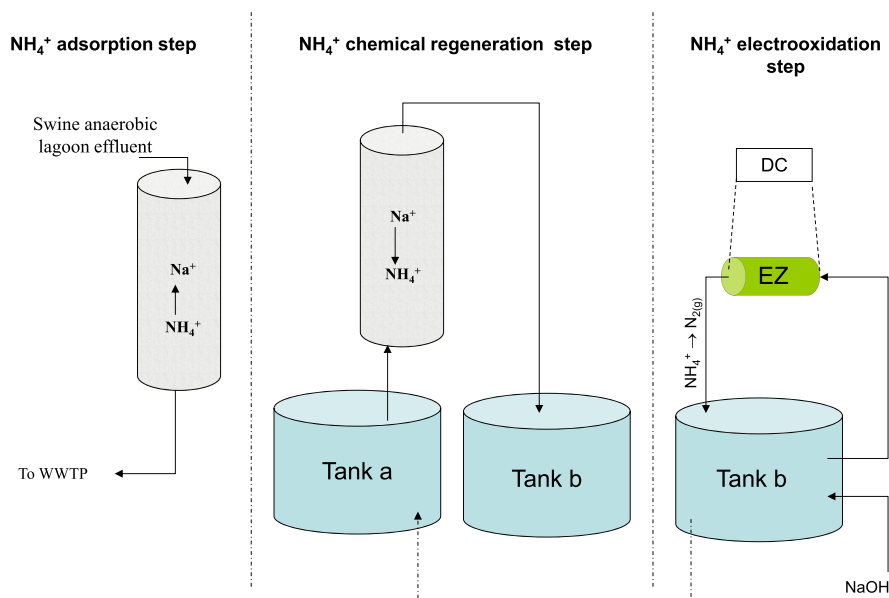
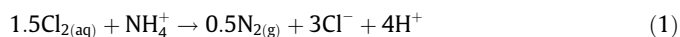


Fig. 1. Schematic of the three steps of the proposed process (reactions simplified).

all TAN into innocuous $N_{2(g)}$ via indirect oxidation of ammonia (i.e. through the generation of $Cl_{2(aq)}$ at the anode, which initiates a series of reactions resulting in ammonia oxidation to $N_{2(g)}$), as described in the following overall oxidation reaction (for elaboration see [18]).



The overall electrochemical (predominant) ammonia removal reaction, including cathodic production of hydrogen gas, is described in by the following equation:



The idea of separation of NH_4^+ from concentrated waste solutions using ion exchange resins (particularly zeolites) and their subsequent regeneration via electrochemical means is not new. It was first suggested (in the general context of wastewaters, not specifically for swine wastes) in a patent by a Canadian company [19], mentioned in [20] in the context of ammonia removal from recirculating aquaculture systems and it also appears in a few papers represented by [21]. In the latter study, a synthetic $(NH_4)_2SO_4$ solution was pumped through a zeolite column which was thereafter regenerated by 1 g/L NaCl solution. Subsequently, the regeneration solution was recycled through an electrochemical cell and ammonia was oxidized directly to $N_{2(g)}$ according to Eq. (1). The authors repeated this cycle five times and reported no loss of ion exchange capacity and electrochemical efficiency. Li et al. [21] therefore concluded that the regeneration solution could be reused for many cycles without need for replenishment. However, in [21] the suggested process was neither tested in the presence of competing cations nor with actual wastewater. It is obvious, however, that the absorption of competing cations, present in the wastewater, on the zeolite during the adsorption step and their subsequent (partial) release into the regenerant solution in the chemical regeneration step, will inevitably lead to a decrease in ammonia removal efficiency during long-time operation. For example, if the first cycle is carried out with a zeolite occupied completely with Na^+ , in the next adsorption cycle some of the zeolite sites will be occupied by K^+ , Ca^{2+} and perhaps also Mg^{2+} , in addition to Na^+ . In the following cycles more and more sites will be occupied by cations with higher affinity toward the zeolite than that of Na^+ and NH_4^+ (such as Ca^{2+} and K^+ , when using chabazite-zeolite, as in the present

study) making the pseudo-equilibrium of NH_4^+ adsorption less favorable, thereby causing a deterioration in the NH_4^+ breakthrough curves. The extent of the deterioration is a function of the initial wastewater cation composition, the affinity sequence of the specific zeolite used towards the relevant cations and the number of bed volumes (BVs) of wastewater passed through the zeolite in the adsorption step. The latter operational parameter is of considerable importance since on the one hand when many BV can be treated in a single cycle, the volume of the resulting adsorption reactor becomes relatively small, and vice versa. On the other hand, passing a large volume of wastewater (i.e. more BV) through the zeolite column increases the rate at which competing cations adsorb onto the zeolite. This reduces the NH_4^+ removal efficiency and shortens the period of time between consecutive renewals of the zeolite column (either by chemical regeneration or by replacement of the IX material) and replacement of the regeneration solution.

Accordingly, the goal of the present study was to define the operational conditions that are both feasible from an engineering standpoint and cost effective, for the removal of ammonia from typical lagoon swine effluents, using the electro-regenerated IX method. Once appropriate operational conditions were defined, a secondary goal was to assess the operational (OPEX) and capital (CAPEX) costs associated with the process.

3. Materials and methods

3.1. Experimental system

A general depiction of the experimental system is shown in Fig. 2. During an adsorption stage, effluent taken from the outlet of a sequence of anaerobic lagoons treating actual swine wastewater (#1 in Fig. 1) was pumped (#2) through an ion exchange column (#3) containing 450 g of chabazite (Herschelik sodium chabazite, CABSORB-ZS500H, distributed by GSA Resources, AZ, US) with a nominal capacity of ~ 2.5 meq/g and an approximate affinity sequence (in parentheses: numerical affinity ratio in meq:meq) of $K^+(1) > Ca^{2+}(2.4) > NH_4^+(3.75) > Na^+(12.2) > Mg^{2+}(33.2)$ [22]. Following preliminary experiments (results not shown) the hydraulic retention time (HRT) was set at 14.5 min to allow for sufficient time for the high NH_4^+ concentration to be adsorbed

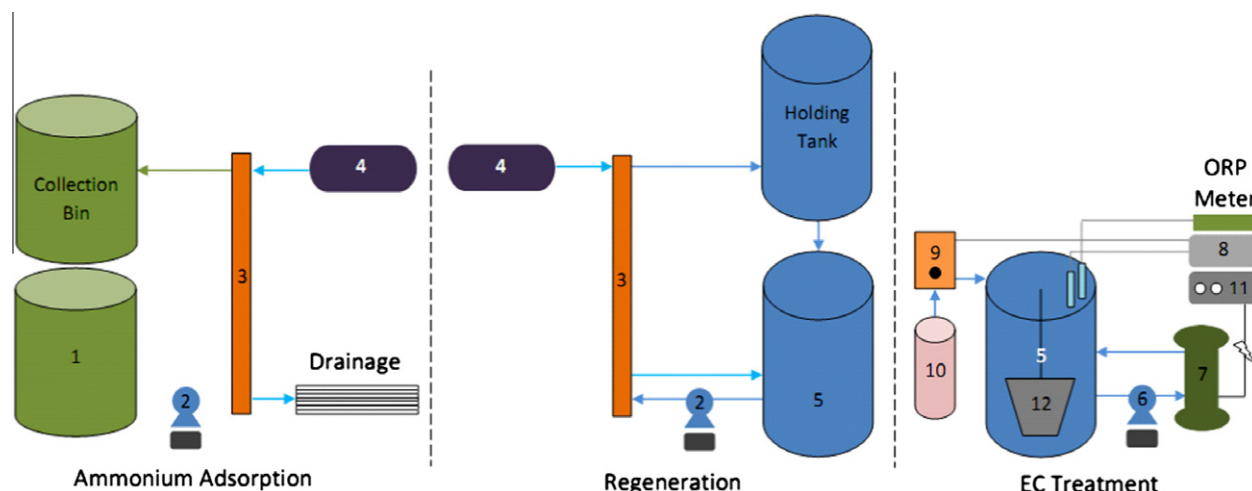


Fig. 2. Schematic of the experimental ammonium removal system tested. Labeled numbers correspond to the numbers referred to in the text.

Table 1

Characterization of swine effluent collected from the Iblin swine treatment plant (before and after TAN normalization) for the two experimental sets ($n > 8$). The significant difference in TAN and K^+ concentrations between the seasons stems from the fact that during the summer the pigs are cooled by water sprinklers, making the wastewater more dilute. "Normalized composition" represents the actual wastewater quality used in the experiments. pH values in the collected swine effluents were closely scattered around pH 8.45.

| Solution composition | TAN (mg N/L) | K^+ (mg/L) | Ca^{2+} (mg/L) | Mg^{2+} (mg/L) | Na^+ (mg/L) | P_T (mgP/L) | COD (mg/L) | TSS (mg/L) |
|---|-------------------|-------------------|------------------|------------------|------------------|-----------------|----------------|----------------|
| Raw lagoon effluent (exp. set #1, winter) | 1371.7 ± 76.9 | 949.8 ± 52.7 | 92.7 ± 44.6 | 22.9 ± 7.3 | 350.9 ± 12.9 | 15.4 ± 12.0 | 5824 ± 989 | 1034 ± 192 |
| Normalized composition | 979.4 ± 88.8 | 681.8 ± 74.5 | 67.7 ± 32.8 | 15.5 ± 5.0 | 251.4 ± 28.4 | 11.0 ± 8.6 | 4403 ± 847 | 739 ± 137 |
| Raw lagoon effluent (exp. set #2, summer) | 801.4 ± 134.2 | 672.2 ± 127.4 | 97.1 ± 42.6 | 58.2 ± 7.2 | 312.7 ± 69.0 | – | – | – |
| Normalized composition | 1005.2 ± 12.1 | 660.5 ± 101.8 | 96.4 ± 43.5 | 57.6 ± 8.5 | 307.0 ± 57.9 | 7.0 ± 4.1 | 2413 ± 190 | 289 ± 148 |

efficiently. Following the adsorption stage the column was drained with the assistance of 50 psi compressed air (#4) to minimize organic matter transfer into the regenerant solution.

The regeneration stage started by passing the regenerant (initial NaCl concentration: 1 mol/L) through the column at an HRT of 3.6 min, with the aim of releasing all the NH_4^+ adsorbed in the adsorption step. Not all of the regeneration solution (total volume 55 L) was passed through the ion exchanger in this stage. Only a portion of the volume was passed through the IX, pumped to the holding tank and then returned to the original regeneration solution tank (#5). At the end of this stage the column was again drained with 50 psi of air pressure from a compressor (#4), with the drained volume flowing back to the regeneration solution (to minimize loss of the highly concentrated regenerant solution). This stage lasted 125 min (~ 35 BV).

The second regeneration stage consisted of electro-oxidation of the ammonia solution. The regenerant solution was recirculated (#6) at a rate of 3.0 L/min through a commercial electrolyzer (#7) (Titanium Tantalum Products Ltd., Chennai, model Klorogen M40; capacity 40 g Cl_2 /h; both anode and cathode defined as titanium gr.2 with precious metal oxide coating – presumably RuO_2) with an applied current density of 35.7 mA/cm². Ammonia electro-oxidation led to a drop in pH (#8) in the regenerant solution according to Eq. (2). pH was maintained constant (at pH 7.0 ± 0.05) by a dosing pump (#9) which continuously added a strong base (#10) [$NaOH$] = 1 mol/L. DC power (#11) was supplied to the electrolyzer at a constant current of 25 A with consequent cell potential ranging between 2.5 and 3.0 V. The solution was mechanically stirred (#12) during the electrolysis step.

3.2. Analyses

Total ammonia nitrogen concentration (TAN) was measured according to the colorimetric procedure described in [23] using a

Thermo Electron Co., model Genesys 10 UV spectrophotometer. All samples were tested against their absorption prior to reagent addition. Turbid samples were filtered with a 0.45 μm syringe filter. COD, TSS and chloride ion concentrations were determined via the closed reflux-titrimetric, argentometric and sampling drying at 103–105 °C methods, respectively [24]. The concentrations of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , total P and total S were measured by ICP (1CAP6300 Duo, Thermo Scientific). Nitrate was determined by the cadmium reduction method [24].

3.3. Characterization of the swine wastes used in the study

The swine wastewater used in the study was obtained from a pig farm located in Iblin, Israel, where pigs are raised in a far-row-to-finish operation. The treatment of the wastewater in Iblin up to the point of collection is as follows: pig excrement from below slotted floors is collected by flushing with water (in the summer the pigs are cooled with water sprinklers, making the wastewater more diluted). The wastewater, collected in one location from many farms, undergoes coarse filtration and then flows to an anaerobic lagoon with an HRT of approximately 14 d. Next, the wastewater enters a sedimentation tank followed by two smaller oxidation ponds with an HRT of approximately 3 d, from which the effluent flows to the Haifa WWTP. Approximately 100 L of wastewater were obtained once a week from the effluent of the latter ponds and stored at 7 °C until usage in the present work.

Prior to entering the IX step, the pond's effluent was passed through a sand gravity filter (particle diameter in effective layer 1.5–2.5 mm) to prevent reactor clogging. However, the TSS value of the wastewater hardly changed in this step (on average TSS dropped by ~ 100 mg/L, i.e. $\sim 10\%$). Due to variations in wastewater composition with time and in order to operate the reactor with almost constant influent composition, the wastewater was either diluted with distilled water or dosed with NH_4Cl in order to maintain

a constant ammonium concentration of ~ 1000 mg N/L at the inlet of the IX step. Characterization of the measured swine lagoon effluents, before and after normalization is provided in Table 1.

The results derived from operating the tested treatment sequence were divided in this study into two experimental sets, the first conducted during the winter and the second during the summer. The wastewater collected in the summer period was much more diluted due to the action of cooling the pigs with water during the hot season. The phosphate concentration in the wastewater was very low throughout the study, presumably due to precipitation of hydroxyapatite in the anaerobic ponds.

4. Results and discussion

Comparing the values measured in the lagoon effluents collected in this study (Table 1) with average values obtained in a comprehensive study published by Barker and Overcash [25], who characterized raw swine wastes from many hog farms, several observations are noteworthy. The mass ratio among the cations NH_4^+ : K^+ : Ca^{2+} : Mg^{2+} : Na^+ in Barker and Overcash's study was 1:0.63:0.60:0.14:0.14 while the average ratio among the cations in the effluents used in this study (2nd experimental set) was: 1:0.66:0.1:0.06:0.30. The fact that the ratio K^+ to NH_4^+ was close to the one reported in [24] is significant because these two ions are the most influential with respect to the proposed method, and the similarity in the ratios makes the results more general. The differences in the magnesium and sodium ion concentrations were not predicted to have an effect on the system studied in this work (due to their low affinity to the chabazite). The lower Ca^{2+} : NH_4^+ ratio, relative to Barker and Overcash's [25] study, emanates, in all probability, from the precipitation of hydroxyapatite in the anaerobic lagoons sequence, as explained before ([25] characterized raw swine wastewater, i.e. prior to any treatment).

4.1. Results obtained from operating the suggested treatment sequence

Two main sets of experiments were conducted. In the first, the system was operated with an adsorption step of 18 BV. The reason for this particular length stemmed from the results of the first breakthrough curve, which was conducted with chabazite occupied entirely with Na^+ ions. The second set was conducted with 12.5 BV, based on the conclusions drawn from the 1st set. Since the more cost effective results were obtained from the operation of the 2nd experiment set, these are shown in more detail, however the main results from the first run are also shown, to elucidate the reasons that led to the choice of the (eventually recommended) process' operational conditions. In both experiments the goal was to reduce the average TAN concentration in the effluents of the IX step to below 70 mg N/L, a typical concentration in municipal wastewaters in Israel, that does not result in TAN overload when released to a nearby WWTP.

4.1.1. First experimental set

Fig. 3 shows selected breakthrough curves recorded in the 1st experimental set (adsorption of 18 BV) and Fig. 4 shows the change in the regenerant solution composition throughout the 30 cycle duration. From Fig. 3 it is clear that operating the adsorption step for more than 13 BV resulted in rapid deterioration of the breakthrough curves (operating at between 14 and 18 BV resulted in fact in very early NH_4^+ breakthroughs, i.e. $\text{TAN} > 70$ mg/L). Observing the results obtained after 13 BVs, it can be seen that at the 30th cycle, the TAN concentration arrived approximately at the desired threshold TAN concentration (70 mg N/L). The reason for the relatively rapid deterioration in the breakthrough curves of this experimental set is evidenced in Fig. 4: the K^+ concentration in

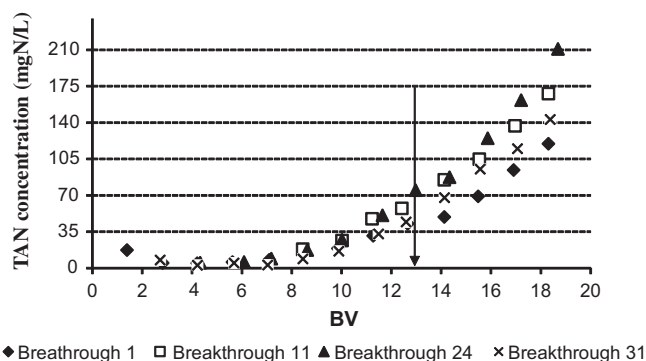


Fig. 3. Selected breakthrough curves in experiment set #1 (adsorption of 18 BV). The arrow indicates the number of bed volumes at which the defined threshold (70 mg N/L) was attained.

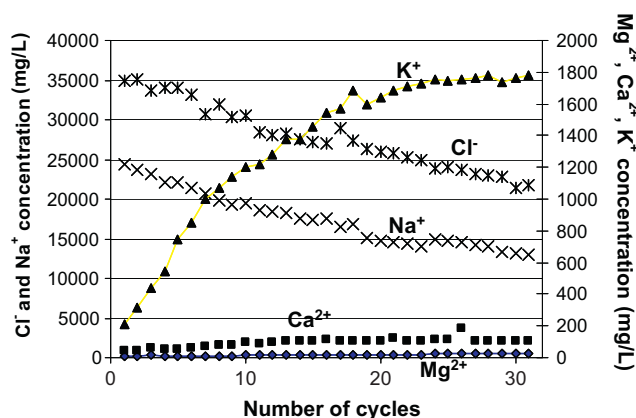


Fig. 4. Concentrations of ions in the regenerant solution as a function of the cycles applied (1st experimental set).

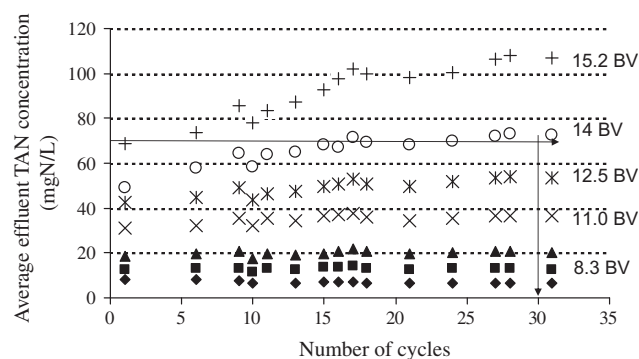


Fig. 5. Cumulative TAN concentrations in the effluent of adsorption step of experiment set #1, as a function of the cycle number. Marked is the 30th cycle at which the threshold TAN concentration (70 mg N/L) was exceeded at 14 BV operation.

the regenerant solution rose constantly, indicating that as the cycles progressed, the chabazite (which was in pseudo equilibrium with the regenerant solution) had become more and more occupied by K^+ , the cation with the highest affinity for the resin. A rough calculation showed that by the 30th cycle, K^+ occupied a significant percentage ($>50\%$) of the chabazite sites. Fig. 5 shows an analysis of the cumulative TAN concentration obtained from the IX column effluents collected in all the cycles, as a function of the cycle, separated into results recorded in each BV passing the

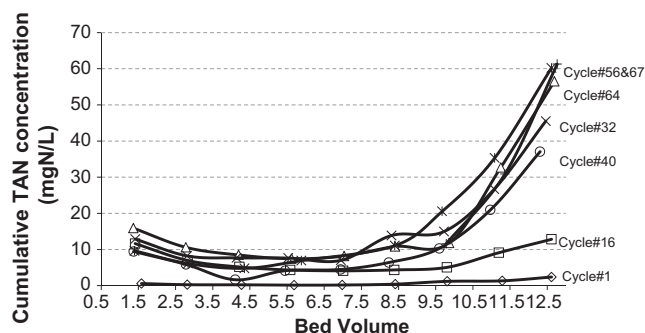


Fig. 6. Cumulative TAN breakthrough curves as a function of BV as obtained in the various cycles during the 2nd experimental set.

chabazite bed. It can be seen that at roughly 14 BV the system could be run for 30 cycles until the cumulative TAN concentration in the effluents equaled 70 mg N/L; that is, operating under such conditions the system (regenerant solution and resin) should be renewed every 30 cycles. Such operation would have resulted in excessive operational costs (not shown), mainly associated with the NaCl mass required for regenerating the chabazite and renewing the regenerant solution. However, observing that the TAN cumulative concentrations recorded at 12.5 BV and below were lower than the threshold, a hypothesis was raised that if the system applied a shorter adsorption step (i.e. less BV), the system could be operated with a much longer gap between renewals. Accordingly, the second set of experiments was designed with an adsorption step of 12.5 BV.

4.1.2. Second experimental set

The results of this experiment, which was operated for a much longer period of time (68 cycles, representing 68 consecutive days of operation) are summarized in Figs. 6–8. Due to gradual loss of regenerant solution due to the cyclic adsorption/regeneration sequence, 1257 g of NaCl was added to the regeneration solution at the end of Cycle #34 to raise the Cl^- concentration to its initial value (1 mol/L). Fig. 6 shows selected breakthrough curves recorded throughout the operation period. It can be clearly seen that the breakthrough curve stabilized at operation with 12.5 BV without exceeding the defined TAN threshold. More specifically, no significant changes were observed in the breakthrough curves starting roughly from Cycle #40 until the end of the experiment (Cycle #68). It is interesting to note the relatively high TAN concentrations recorded at the beginning (two first BVs) of the adsorption curves – this known phenomenon stemmed from the fact that the chemical regeneration was done in the same direction as the

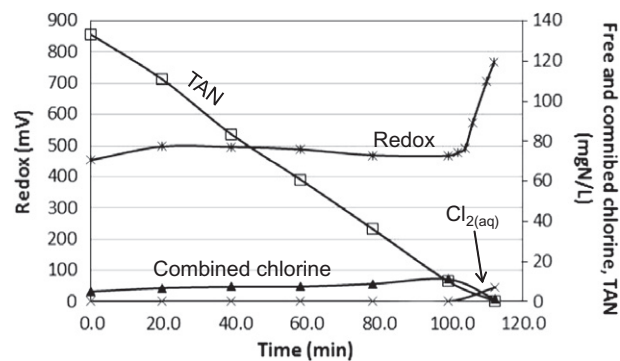


Fig. 8. Results from a typical electrolysis run (Cycle #56) showing an almost linear drop in TAN concentration (zero order kinetics) and the rise in chlorine and redox concurrent with TAN and chloramines concentration tending towards zero.

adsorption (upflow, in both cases). As corroboration for the fact that the breakthrough curves in this experiment had reached pseudo steady state, Fig. 7 shows the change in the concentrations of the main ions in the regenerant solution, as measured right after the end of the electrolysis step in each of the cycles. Fig. 7 shows that the concentration of the main competing cation (K^+) along with the concentrations of Ca^{2+} and Mg^{2+} had stabilized in the regenerant solution roughly after 40 cycles. The K^+ concentration, being the cation with the highest affinity for the chabazite and due to its relative high concentration in the swine wastes, stabilized (with fluctuations ascribed to variations in the cation concentrations in the swine wastes) at the highest concentration range (2000–2400 mg/L). The stabilization of the cations in the regeneration solution indicated that the percentage of the chabazite sites occupied by K^+ and Ca^{2+} had stabilized as well, leading to a roughly constant resin cation composition at the start of the adsorption steps, which resulted in stabilization of the adsorption step breakthrough curves (Fig. 6). Concurrently, the Cl^- and Na^+ concentrations dropped steadily until Cycle #34 (and thereafter again, until Cycle #68), after which NaCl was added to compensate for the loss. While the mass balance for Cl^- was rather simple: chloride ions were lost in the exchange between adsorption and regeneration steps, the mass balance for Na^+ was more complex: Na^+ ions were lost both because of regenerant solution losses but also due to ion exchange for mainly NH_4^+ , K^+ , Ca^{2+} , during the adsorption step. The loss of Na^+ ions to the wastewater is a drawback of the presented process, because (for example) in Israel the effluents from the WWTP are reused for agricultural irrigation, in which Na^+ is unwelcome due to its contribution in increasing the Sodium

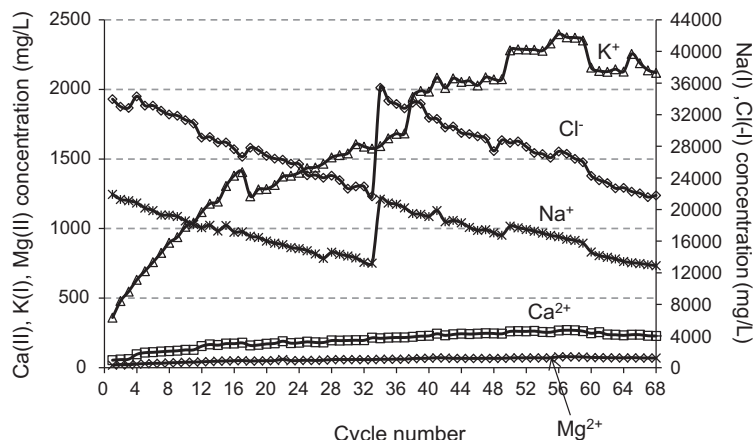


Fig. 7. Concentrations of ions in the regenerant solution as a function of the cycles applied (2nd experimental set).

Table 2Summary of operating expenses of the TAN removal method suggested in this work for swine lagoon effluents, normalized per 1 kg of ammonia oxidized to $N_{2(g)}$.

| Element | NaCl compensation | Electricity consumed in electrolysis step | Alkalinity compensation (NaOH) | Chabazite annual renewal (10%) | Labor | Total |
|-------------------------|-------------------|---|--------------------------------|--------------------------------|-------|-------|
| Cost (\$/kg N oxidized) | 0.24 | 0.996 | 1.43 | 0.016 | 0.025 | 2.707 |

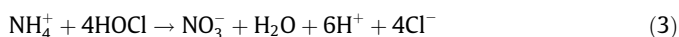
Adsorption Ratio (SAR) value. To overcome this problem and also reduce the costs associated with the buffering agent used in the study (NaOH), the process can be probably operated with either $Ca(OH)_2$ or $Mg(OH)_2$ (or a combination thereof) as the alkalinity agent and $CaCl_2/MgCl_2$ as the main salt. Such operation, which naturally results in a different steady state working point, is not reported in this paper.

The conclusion from the second experimental set was that an adsorption step of 12.5 BV (strictly speaking, with the cation composition tested in this study, whose cation ratios were shown earlier to be rather general) allows operating the treatment system sequence without the need to replace or chemically regenerate the ion exchange material, or to replace the regenerant solution, apart from addition of NaCl every 34 days. This is an important result, because it leads to a significantly reduced operational process cost, since the cost of replacing the regeneration solution is substantial.

Fig. 8 shows results from a typical electrooxidation run (Cycle #56 in experimental set #2). A typical ammonia removal current efficiency of 91.6% was recorded in this run. Current efficiencies were calculated in this study by comparing the actual ammonia removal rate with the rate obtained from the theoretical Faraday's law, which was calculated under the assumption that ammonia oxidation is the only oxidation reaction occurring on the anode. Current efficiency of 91.6% means that 91.6% of the electrons supplied to the solution through the external current were utilized for conversion of TAN to $N_{2(g)}$. The high current efficiencies imply that unwanted side reactions such as organic matter oxidation, ammonia oxidation to nitrate (and its possible reduction of nitrate back to ammonia on the cathode) and chlorate formation, were minimal. With respect to organic matter: a small concentration of organic matter (TOC = 5–10 mg/L per cycle) entered the regeneration solution in the course of switching from the adsorption to the regeneration steps. However, the current demand of this organic component was very limited, as manifested by the high observed current efficiencies (moreover, the current efficiencies observed when the system was operated with simulative wastewater and real wastewater were practically similar). With respect to the TAN oxidation reactions: a zero order TAN oxidation rate was recorded in all the runs, down to almost negligible TAN concentrations. TAN electrooxidation was accompanied by the formation of low total chloramines concentration, which developed during the run and dropped steeply (down to almost nil) once the TAN concentration dropped to below 1 mg/L and concurrently the free chlorine concentration rose to 7.6 mg Cl_2/L . The redox potential pattern is also noteworthy; particularly the steep rise at the end of the experiment signaled the drop of the TAN concentration to nil and, in practical terms, the end of the electrooxidation step. Thus, redox potential can be used efficiently within the process to control the time required for the electrooxidation step (important mainly when the NH_4^+ mass adsorbed in each cycle is not constant due to fluctuations in the quality of the swine wastewater). In addition to $N_{2(g)}$, another possible product of ammonia electrooxidation is nitrate, as shown in Eq. (3). Production of nitrate is unwanted because it reduces the current efficiency for ammonia removal. In the current study the nitrate concentration that developed in the regenerant solution after 68 runs was ~ 112 mg N/L, representing an average (net) growth of 1.64 mg/L per cycle, which

is approximately 1% of the ammonia absorbed in each cycle. In par with the slow nitrate accumulation rate, the very high ammonia current efficiencies recorded throughout the study indicated that loss of efficiency associated with nitrate production was insignificant.

For elaboration on the mechanism of indirect ammonia electro-oxidation, which includes detailed description of the reactions taking place and mechanistic explanation related to the low chloramines concentration observed in the runs (relative to classical breakthrough chlorination), the reader is referred to [18].



4.2. Estimation of the operational and capital costs associated with the proposed treatment approach

4.2.1. Assessment of operating expenses (OPEX)

For estimating the operational expenses the following cost list was assumed, based on published information: NaCl: \$52 per ton; Price of tap water: \$0.50 per m^3 ; Discounted "time of use" (TOU) electricity price: \$0.06/kW h, NaOH: \$500 per ton; Chabazite: \$500 per ton. From the operational standpoint the following parameters were assumed, based on the experimental system data: Working voltage: 2.6 V; assumed current efficiency: 90%. A summary of the operating expenses of the system is presented in Table 2, based on the results of the 2nd experimental set. All calculations were performed based on an average of 8.076 g TAN removed from the wastewater in a single cycle. Calculation of the NaCl compensation mass was performed based on a 34 cycle run between NaCl dosages. Note that the rate of chloride loss throughout the experiments was mostly dependent on losses incurred as a result of remnant regenerant volume left over in the IX bed and therefore operating conditions (i.e. compressor pressure) employed in the experiments in this work. It is likely that a commercial system will employ a more thorough drainage of the reactor and therefore more cycles (i.e. more ammonium will be treated) prior to NaCl dosage, leading to a cheaper cost for the NaCl compensation component. NaOH consumption and electricity demand, as practiced in this work, are based on stoichiometric relationships. To reduce costs, alkalinity compensation could be perhaps attempted with the much cheaper $Ca(OH)_2$ chemical, however, in such case the most dominant competing cation would be Ca^{2+} and a new set of experiments would have to be conducted to determine whether the system would stabilize with an acceptable breakthrough curve and the new length of the operation cycle under such conditions.

The electricity demand in the electrolysis stage was calculated based on discounted "time of use" (TOU) electricity price of \$0.06/kW h, working voltage of 2.6 V and electrolysis efficiency of 90%, yielding required energy of 16.6 kW h and cost of \$0.996 per kg of oxidized ammonia (as N). Additional electricity costs (e.g. for pumping, etc.) are negligible relative to the electrolysis demand due to the low daily volumes and pumping pressures. The cost of the alkalinity agent addition, calculated with \$500/ton of NaOH and 1:1 M ratio of NaOH added per removed NH_4^+ (Eq. (2)), was determined at \$1.43 per kg of ammonia (as N) oxidized. Labor costs: the system was designed to work automatically, with

minimal manual intervention. As such, 25% occupation of an unskilled worker would probably be sufficient, amounting to \$0.025/kg N removed.

4.2.2. Assessment of capital expenses (CAPEX)

The capital expenses comprise the electrolyzing equipment (electrolyzing unit + DC converter) and the chabazite reactors. Assuming a 1000 m³/d wastewater flow rate and 12.5 BV adsorption step, the required chabazite volume would be 1000/12.5 = 80 m³. At an assumed cost of \$500/ton chabazite (1 ton ~ 1.72 m³ of chabazite) the cost of the zeolite material is ~\$23,500. Assuming two 50 m³ packed bed reactors, at \$80,000 per reactor (including control and paraphernalia), the IX component costs are estimated at \$183,500. Electrolyzer costs were estimated at \$1,100,000 based on a web publication of a commercial entity [26] reduced by 50%, and assuming 8 h of operation per day (low electricity hours), i.e. oxidation of ~1000*0.93/8 = 116 kg N per h, necessitating electrolyzers capable of producing 883 kg Cl₂ per h (7.6 kg Cl₂ per kg TAN). The overall CAPEX amounts to ~\$1,300,000. Assuming \$1,500,000 as the capital cost figure (15% unforeseen costs), 5% interest and a 20 year average equipment serviceable lifespan, the estimated normalized capital cost is \$0.35 per kg NH₄-N, i.e. about 13% of the OPEX. Therefore, even under the assumption that the capital costs are 50% higher than the estimation in this section, since the effect of the CAPEX on the overall cost is relatively low, such an error would not change the cost picture significantly.

In summary, the overall cost (OPEX and CAPEX) calculated for the suggested process was estimated at \$3.057/kg N, which, to the best of the writers knowledge, is competitive, as compared with the typically-applied biological alternatives (i.e. nitrification–denitrification).

5. Summary and conclusions

A new treatment concept, comprising IX and electrochemical regeneration, was tested under realistic operational conditions for the removal of ammonia from effluents of swine wastewater anaerobic treatment processes. The method was applied for a prolonged period of time with actual swine effluents and found feasible from both process (robust reduction of TAN concentration from 1000 to ~60 mg N/L) and cost effectiveness standpoints. For the particular composition of wastewater tested in the study, the following operational conditions enabled operating the treatment sequence at pseudo steady state: an IX adsorption step of 12.5 BV at an HRT of 14.5 min, a chemical regeneration step lasting 35 BV (HRT = 3.6 min) using a regenerant solution of ~1 mol/L (see Fig. 7 for detailed ionic composition) and an electrooxidation step of two hours ($I = 25$ A, cell potential = 2.7–2.8 V), operated at current efficiencies above 90%. The operational costs, normalized per 1 kg N, amounted to \$2.707, of which the dominant costs were the electricity requirement for the electrooxidation step and the base dosed to the electrolyte for maintaining constant pH during the electrolysis step. The overall cost of the process was estimated at \$3.057/kg N removed, out of which the capital cost, comprising mainly electrolysis system-related costs, amounted to 11.4%. The system tested in this study assumed a constant TAN concentration of 1000 mg N/L and a specific (rather typical) ratio between cations. Under conditions of a different TAN concentration or a different ratio between cations, the steady state point is expected to be different (a higher or lower adsorption step length, corresponding to a lower or higher zeolite reactor volume), however, unless the conditions are significantly different, the concept is expected to remain valid. From an environmental standpoint the system can be improved by replacing the main cation in the regenerant solution from Na⁺ to Ca²⁺/Mg²⁺ by applying Ca(OH)₂/Mg(OH)₂ as the pH

control agent and CaCl₂/MgCl₂ as the main salt(s). Work is underway to determine the steady state working point under such conditions and associated costs. The proposed system can help reducing the large-scale adverse environmental effects stemming from the release of ammonia-rich swine effluents to soils and water bodies in many parts of the world.

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