Electrochemical Oxidation for Denitrification of Ammonia: A Conceptual Approach for Remediation of Ammonia in Poultry Barns

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S *Supporting Information*

ABSTRACT: Ammonia in poultry barns produced by microbial action on the birds' excreta can be removed by scrubbing into aqueous solution at pH ~4. However, disposal of the resulting solution remains a problem. In this work, ammonia was oxidized electrochemically in the presence of unreactive electrolytes ($NaClO_4$, Na_2SO_4), but the conditions were not compatible with treatment inside or outside a poultry barn (high pH, closed electrochemical reactor, and high ammonia concentration). Efficient denitrification is possible without pH adjustment of the scrubbed solution when chloride ion is also present in the scrubbing solution. This reaction is based on electrochemical hypochlorination, which is similar to breakpoint chlorination for the chemical elimination of ammonia. This work confirms a recent mechanistic proposal that efficient denitrification at pH ~3 is the result of concomitant oxidation of water and acidification at the anode, but shows in addition that the mechanisms of both chemical and electrochemical hypochlorination are similar at acidic pH. These results allow us to propose that ammonia scrubbed into acidic brine can be oxidized to elemental nitrogen with high current efficiency without pH adjustment and without chemical additives, providing a "green" solution to the problem at hand.

KEYWORDS: *Ammonia oxidation, Graphite anode, Electrochemical hypochlorination, Scrubbers*
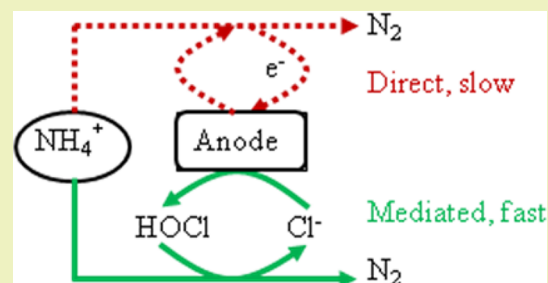
■ INTRODUCTION

Gas-phase ammonia is of concern in the context of poultry barns both because of toxicity toward the birds and to human workers[1−5] and because of fugitive emissions to the wider environment. In the first context, the industrial criterion (threshold limit value, TLV) is 25 ppmv (17 mg m^{-3}), time-weighted over an 8 h working day, with 35 ppmv as a 15 min short-term exposure limit.[6] Concentrations above the TLV represent a health hazard to both humans and poultry and impact negatively on the birds' productivity.[7−9] Ventilation and manure management practices (solid versus liquid systems and frequency of manure removal) have a profound influence on whether ambient ammonia concentrations exceed the TLV.[10] For the wider environment, the main issues are contributions to acidic precipitation after atmospheric oxidation[10−13] and toxicity toward aquatic life downstream of aqueous ammonia discharges.[14−18] In North America, the focus is principally on amelioration on high concentrations of ammonia in the barn in winter, when ventilation rates are low to conserve energy; in Europe, the main focus to date has been to avoid fugitive emissions to the outdoor environment.

A Spanish study of the production of ~19 000 broilers illustrates the magnitude of the ammonia problem. Ammonia emission rates were in the range 18−20 mg h^{-1} per bird for a total emission of 0.4 t ammonia per 48 day cycle, most of which was produced during the final 14 days.[19] Emissions from layer hens are of a similar order of magnitude.[20,21]

The most commonly used method to prevent fugitive emissions is scrubbing ammonia into dilute sulfuric acid solution at pH ~4 before the air is exhausted.[22−24] In this work we propose to treat the resulting aqueous solution of ammonium sulfate by electrochemical oxidation to elemental nitrogen (denitrification). Although the ultimate goal is the treatment of solutions in which ammonia is scrubbed from the air of poultry barns, this proof-of-concept study involved synthetic solutions of ammonia and no economic analysis was considered.

The course of electrochemical oxidation depends on the choice of anode. It may be initiated by direct transfer of one or more electrons from the substrate to the anode, or the substrate may be oxidized indirectly by intermediates formed by oxidation of water.[25−27] Ammonia can be oxidized to N_2 with excellent chemical and current efficiency at noble metal anodes, but several factors make the approach impractical for the proposed application. These include the high cost of noble metals, the need for highly alkaline pH to convert NH_4^+ into the more easily oxidized NH_3, and careful control of the anode potential to avoid overoxidation to nitrate. Much less is known about the direct oxidation of ammonia at other anodes.[28]

The electrochemical oxidation of ammonia can also be carried out indirectly in the presence of chloride ion, which is

oxidized at the anode to hypochlorite (HOCl or OCl$^-$, depending on the pH). Hypochlorite oxidizes ammonia to N_2, with reduction back to chloride ion; hence, the reaction is the electrochemical analogue of "breakpoint chlorination" of drinking water.[29−34]

In this work, we first attempted to determine whether direct oxidation could be practical, using a variety of anodes, including graphite. Graphite has been long and widely used as an anode in electrolyses,[35] although little work has been reported on the oxidation of ammonia at this anode.[36] We also studied graphite for the option of electrochemical hypochlorination of ammonia to nitrogen, because this is efficient at oxidizing chloride ion to hypochlorite.[37−39] An important consideration was whether the proposed process could be used directly on an acidic scrubbing solution, in order to avoid the cost of chemicals for changing the pH from acidic (scrubber) to alkaline (electrolyzer) and back.[40]

MATERIALS AND METHODS

Reagents. Ammonium perchlorate, sodium perchlorate, sodium citrate, and phenol were supplied by Sigma-Aldrich (Oakville, Canada). Sodium chloride, sodium hydroxide, sodium nitroprusside, sodium sulfite, and concentrated sulfuric acid were obtained from Fisher Scientific (Toronto, Canada). Bleach (sodium hypochlorite) was purchased from Loblaws (Toronto, Canada), and ethanol was made available from Commercial Alcohols Inc. (Brampton, Canada). All solutions were prepared using deionized water.

Cyclic Voltammetry. Voltammetry was performed using a DY2113 potentiostat from Digi-Ivy Inc. (Austin, U.S.A.). A 0.5 mm diameter HB pencil lead from Pentel Ltd. (Tokyo, Japan) provided a working electrode (immersed area of 1.77 mm^2). Because of the change in voltammograms produced during multiple cycles of voltammetry due to modification of the electrode surface, a new microelectrode was used for each experiment. Platinum wire or a Ag/AgCl electrode were the reference electrodes used, and platinum foil (immersed surface area of 2 cm^2) was the counterelectrode. Both platinum electrodes were obtained from Sigma-Aldrich (Oakville, Canada); the Ag/AgCl electrode was obtained from Thermo Scientific (Beverly, U.S.A.). All experiments were conducted in a 50 mL glass beaker.

Batch-Cell Electrolysis. Open-cell electrolyses were performed in a 100 mL glass beaker containing 50 mL of solution to be electrolyzed. Two graphite rods 6.3 mm in diameter with a length of 150 mm (Alfa Aesar, Ward Hill, U.S.A.) were used as anode and cathode (immersed area 7.24 cm^2). The electrodes were fixed in the center of the beaker, with an interelectrode gap of 1.5 cm. A Princeton Applied Research model 363 Potentiostat Galvanostat was used as the power supply for the electrolyses, alongside an Agilent U1242A True RMS Multimeter to monitor the voltage between the electrodes. In experiments to compare anode materials, Ti/RuO$_2$ from ELTECH Systems Corporation (Painesville, U.S.A.) and boron-doped diamond on niobium mesh (Nb/BDD) from Condias (Itzehoe, Germany) were tested alongside a graphite rod cathode as previously described, also with an interelectrode distance of 1.5 cm. The Ti/RuO$_2$ and Nb/BDD had immersed surface areas of 5.25 cm^2.

Electrolyses performed in closed conditions were carried out using a 150 mL glass beaker with a tightly fitting lid. The lid had four separate ports, two of which allowed the graphite rod electrodes to be inserted into the cell. Plastic tubing ran from an argon gas tank from Linde Gas (Mississauga, Canada), through the third port, down into the bottom of the reactor, and the fourth port was connected to a T-joint that allowed samples to be collected using a syringe attached to tubing at the bottom of the cell, as well as providing an outlet flow of gas to a 50 mL acid trap (1 M H$_2$SO$_4$). Laboratory film was used to seal all the joints of the cell airtight.

'Electrolyses in both open and closed reactors were carried out amperostatically for 6 h with periodic sampling and mixing using a magnetic stir bar and a Fisher Scientific Thermix stirrer. Samples were

analyzed after diluting 0.5 mL of solution from the reactor with deionized water to 10 mL in a volumetric flask. The diluted samples were analyzed for total nitrogen, using a Shimadzu TOC-V$_{CPN}$, with the TOC + TN protocol, which monitors the luminescence of NO$_2$, following oxidation of the nitrogenous compounds. In some experiments the diluted sample was also analyzed for ammonia spectrophotometrically,[41] by treatment with phenol, sodium nitroprusside, and an alkaline citrate buffer with sodium hypochlorite to form indophenol blue. The absorbance of the resulting solution at 640 nm is proportional to the ammonia present; therefore, unknown samples taken from an electrolysis can be compared to a standard calibration curve and quantified with reasonable accuracy. A Pharmacia LKB-Novaspec II spectrophotometer was used to measure absorbance in this analysis.

Chemical Hypochlorination. Sodium hypochlorite was added to a 100 mL glass beaker containing 50 mL of varying concentrations of ammonia (most often 50 mM). The solution was stirred rapidly and sampled five minutes after addition of each aliquot of bleach. Analysis followed the same methodology used in the electrolysis experiments. The pH of the reaction was measured constantly using a Beckman Φ 340 pH/Temp meter, and the pH was adjusted using dropwise additions of 1 M H$_2$SO$_4$ and 1 M NaOH.

RESULTS

Voltammetry. No oxidation current was observed at a graphite anode in the absence of ammonia at <0.7 V vs Pt (+1.4 V vs SHE) in a supporting electrolyte of 0.1 M NaOH, and the oxidation of the anode surface began at less positive potentials than the oxidation of water (Supporting Information, Figure 1). Figure 1 shows cycle 5 abstracted from Supporting Information,
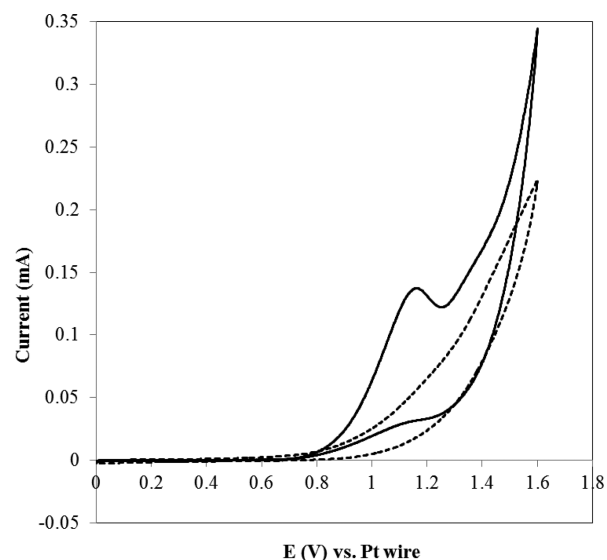

Figure 1. Cyclic voltammograms of multiple cycles experiments (only cycle 5 presented); pencil lead working electrode, platinum wire reference electrode, and platinum foil counter electrode; — 0.1 M NaOH; — — — 0.1 M NaOH + 0.1 M NH$_4$ClO$_4$.

Figure 1, as well as cycle 5 when ammonia was also present. No voltammetric current separate from the oxidation of water could be seen even with concentrated (d = 0.88 g cm^{-3}) ammonia (Supporting Information, Figure 2), but the presence of ammonia appeared to suppress the oxidation of the graphite surface. Analogously, Ji et al.[42] saw a well-defined peak for the oxidation of ammonia at boron doped diamond (BDD) but not at various samples of graphite.

Electrolyses in the Absence of Chloride. In a preliminary study in an open, undivided cell, the oxidation of

ammonia at graphite, Ti/RuO$_2$, or Nb/BDD anodes was negligibly slow at pH 3 (Figure 2). In alkaline solution there
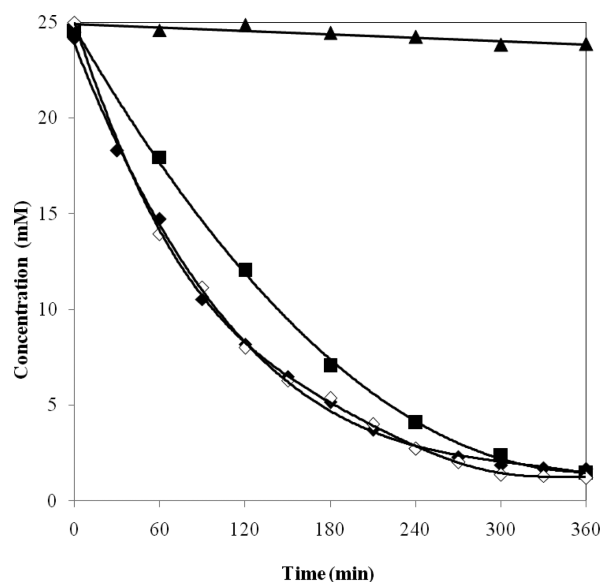

Figure 2. Electrolysis of 50 mL of 25 mM NH$_4$ClO$_4$ at 100 mA. Graphite rods were used as both the anode and cathode. An identical solution had argon gas bubbled through it slowly over the same amount of time; ▲ electrolysis at pH 3; ♦/◊ electrolysis at pH 14; ■ argon stripping at pH 14; filled symbols, analysis by TN; open symbols, indophenol method.

appeared to be rapid loss of ammonia, but this was an artifact; almost all the loss of ammonia was due to gas stripping. All further experiments in alkaline solution were therefore carried out in closed cells, one of whose ports was connected to a trap containing dilute sulphuric acid. The loss of ammonia from the electrolyzate was corrected for the amount of ammonia in the trap.

In a series of experiments in alkaline solution at different starting concentrations of ammonia, the rate of loss of ammonia increased with the initial concentration, indicating a mass transport controlled reaction (Figure 3). Care was taken to distinguish electrochemical oxidation from gas stripping, whose rate also increases with concentration. In Figure 3 the point at time zero was omitted from the regression because we consistently found a faster loss of ammonia prior to the first sampling time, suggesting that the unused graphite surface is initially more active than one in continued use. Throughout the electrolyses, all the total nitrogen was in the form of ammonia (there was no overoxidation to nitrate). The current efficiency increased with the initial ammonia concentration, consistent with competitive oxidation of water. The reaction rate was directly proportional to the current below 50 mA but tended toward a constant value at higher currents (Supporting Information, Figure 3). This suggests mixed kinetics: current control at low current (k_{obs} independent of [NH$_3$]), tending toward mass transport control (k_{obs} independent of current) as the current increased.

We showed previously[35] that the functionalization of the graphite surface leads to mineralization and disintegration at the graphite surface. When the same anode was used three times for electrolysis of ammonia in 0.1 M NaOH at 100 mA, the average loss of ammonia and the cell voltage were constant (19% over 5 h and 3.7 V, respectively), but by the third use, the
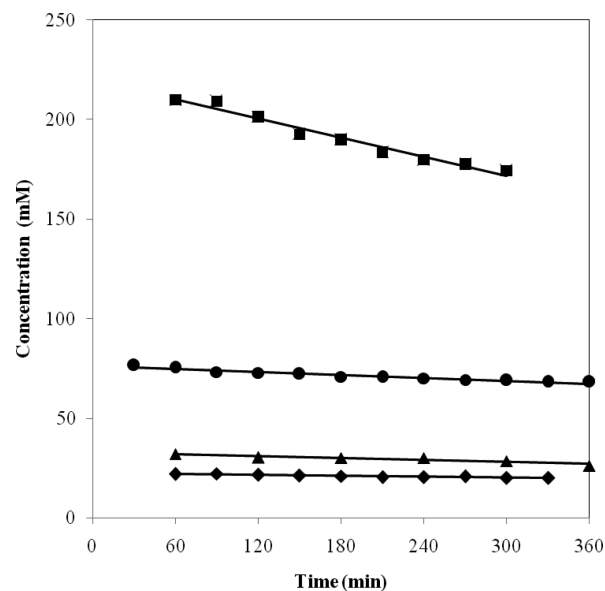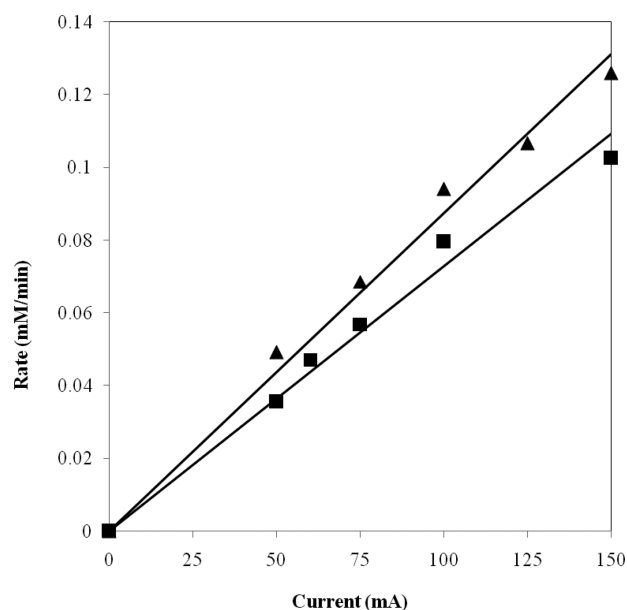

Figure 3. Electrolysis of NH$_4$ClO$_4$ at different initial concentrations in 1 M NaOH at 100 mA using a closed-cell reactor with Ar gas bubbling; the moles of NH$_3$ from H$_2$SO$_4$ trap were included in the calculation of the NH$_3$ concentration at the time of sampling; ♦ 25 mM (current efficiency of 3.6%); ▲ 40 mM (current efficiency of 6.3%); ● 90 mM NH$_4$ClO$_4$ (current efficiency of 12.6%); ■ 250 mM (current efficiency of 53%).

anode became pitted and black particles were found in the solution.

Electrolytic and Chemical Hypochlorination. Preliminary experiments showed that the electro-oxidation of ammonia was much faster in the presence of chloride ion under various conditions: alkaline solution with acid trap; neutral NaCl solution; divided or undivided cell. Complete denitrification was achieved upon electrolysis of 25 mM NH$_4$ClO$_4$ and 0.5 M NaCl at 100 mA. At all times the TN was equal to c(NH$_3$), again showing that ammonia had been oxidized to N$_2$ rather than to nitrate (Supporting Information, Figure 4). The loss of ammonia increased almost proportionately with the current, but the slope of the line k_{obs} versus current was slightly larger when a new graphite anode was used for each electrolysis than when the same anode was used throughout (Figure 4), indicating gradual degradation of anode performance. At constant ionic strength, constant current, and constant initial concentration of NH$_4$ClO$_4$ (25 mM), the rate of denitrification increased (but more than proportionately) with c(NaCl) (Figure 5).

There has recently been debate about mechanistic differences between chemical and electrochemical hypochlorination in the presence of ammonia. When the chemical process is carried out near neutral pH, the TN of the solution does not decrease significantly until the ratio [added hypochlorite]/[initial ammonia] > 1, because the first aliquots of hypochlorite convert NH$_3$ to NH$_2$Cl, which does not remove TN from solution. Further hypochlorite converts NH$_2$Cl to NHCl$_2$; these react together to eliminate TN as N$_2$. In contrast, the electrochemical process has been observed to show a linear decrease of TN from the very beginning of electrolysis.[43−45]

In electrolyses carried out with a Ti/PtO$_x$−IrO$_2$ anode at pH ∼6 (at which HOCl is the main "positive chlorine" species), Kapalka et al.[44] proposed that the electrochemical process generates high local concentrations of NH$_2$Cl and NHCl$_2$,

Figure 4. Electrolysis of 25 mM NH$_4$ClO$_4$ in 0.5 M NaCl at different currents and graphite electrodes; ▲ new graphite anode for each experiment; ■ the same graphite anode used in all experiments.
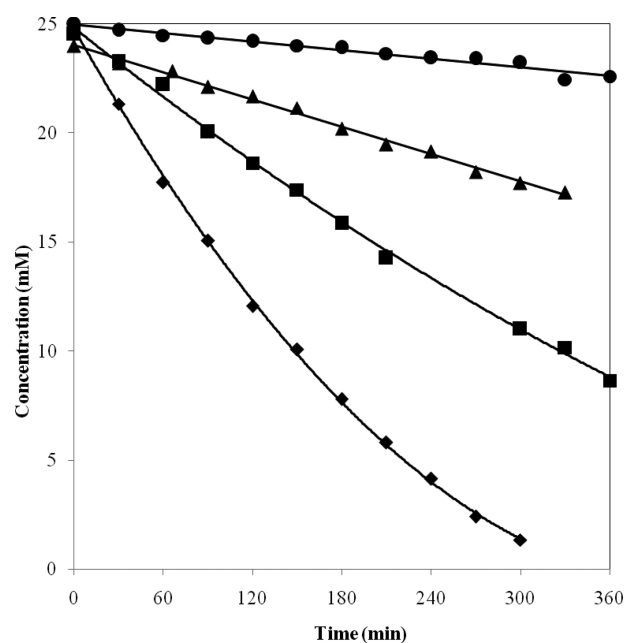
Figure 5. Electrolyses in a batch cell reactor of 25 mM NH$_4$ClO$_4$ at 100 mA with varying concentrations of NaCl but constant ionic strength using NaClO$_4$; ♦ 500 mM NaCl (initial rate 0.078 mM/min ± 0.0041, current efficiency 19%); ■ 375 mM NaCl (0.044 mM/min ± 0.0012, 11%); ▲ 250 mM NaCl (0.021 mM/min ± 0.00047, 5%); ● 100 mM NaCl (0.0064 mM/min ± 0.00044, 2%).

which react with each other close to the anode before diffusing into the bulk. This makes the concentrations of nitrogen species in the bulk solution irrelevant to the progress of the reaction. Gendel and Lahav[43] suggested instead that because water and Cl$^-$ are oxidized simultaneously, the solution near a Ti/RuO$_2$−TiO$_2$ anode becomes so acidic that the main active chlorine species is Cl$_2$ rather than HOCl. The essence of their proposal is that the oxidation of ammonia and chloramines is significantly faster with Cl$_2$ than with HOCl.

Our own work indicates two experimental complexities. First, there is an analytical discrepancy according to whether ammonia is analyzed as TN or spectrophotometrically. In a conventional (nonelectrochemical) hypochlorination experiment carried out at pH 7, the indophenol method showed the "classical" behavior, with a lag before the concentration of dissolved N fell significantly, but TN analysis indicated loss of TN from the earliest addition of hypochlorite (Figure 6). This
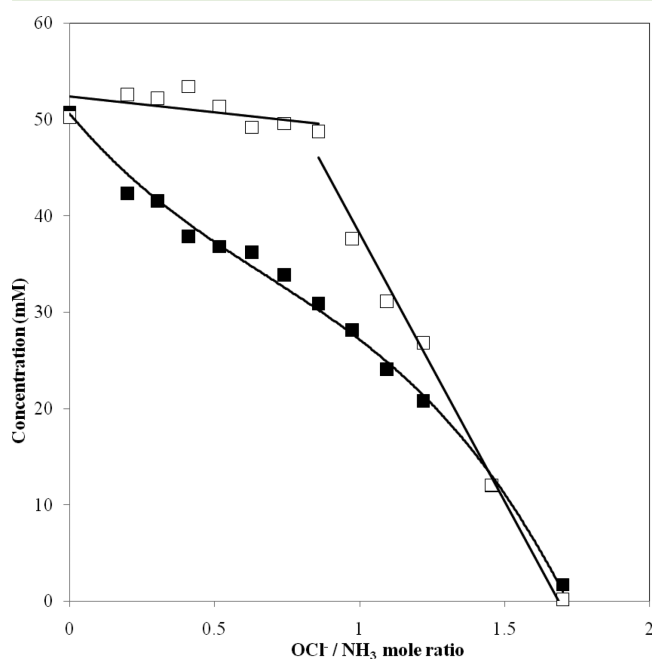
Figure 6. Sodium hypochlorite (0.39 M) was added periodically to 50 mL of 50 mM NH$_4$ClO$_4$ with the pH maintained at ∼7 by dropwise addition of 1 M H$_2$SO$_4$ and 1 M NaOH; ■ analysis by TN; □ analysis by indophenol method.

result was an artifact due to the different calibration sensitivities of ammonia and chloramines in the total nitrogen analyzer.[46] The evidence was that the "lost" TN was recovered when a partly hypochlorinated solution of ammonia was treated with sodium sulfite to reduce the chloramines back to ammonia (Table 1). No "loss" of ammonia was observed by the

Table 1. Oxidation of 25 mL of 50 mM NH$_4$ClO$_4$ Using 2 mL of 0.39 M Sodium Hypochlorite, Analyzed Using Both TN and the Standard Indophenol Method (Two Trials), Then Reacted with 1 mL of 1 M Sodium Sulfite, And Reanalyzed; Duplicate Experiments

| conditions	ammonia concentration (mM)	
	TN method	indophenol method
initial ammonia concentration	47.7; 47.4	47.7; 48.0
after adding 2.0 mL of 0.39 M NaOCl	40.5; 40.6	47.0; 47.4
after adding 1.0 mL of 1 M Na$_2$SO$_3$	46.3; 47.2	47.3; 49.3

indophenol method, because the chloramines equilibrate back to ammonia during the analytical procedure. The reaction between hypochlorite and ammonia was very rapid, with identical analyses at 1, 5, and 10 min after the addition of hypochlorite (Table 2). As before, the analyses by TN and the indophenol method were not in agreement.

Table 2. Effect of Bleach Contact Time on the Ammonia Concentration: 4 mL of 0.39 M Bleach Was Added To 50 mL of 50 mM NH$_4$ClO$_4$ (OCl/NH$_3$ Mole Ratio of 0.63), and the Reaction Was Sampled at Different Times

|	ammonia concentration (mM)	
contact time	TN method	indophenol method
0	46	53
1	37	45
5	36	43
10	36	43

The second issue was that chemical hypochlorination gave different results at pH 3 compared with pH 7. At pH 3 there was a near-linear decrease in the analytical observable, by both the TN and indophenol methods, with little difference between them (Figure 7).
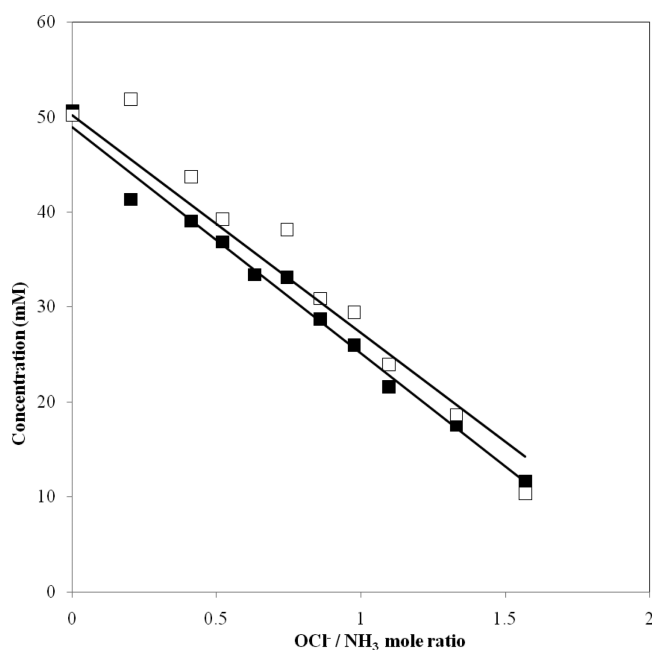
Figure 7. Sodium hypochlorite (0.39 M) was added periodically to 50 mL of 50 mM NH$_4$ClO$_4$; the pH was maintained at ~3 by dropwise addition of 1 M H$_2$SO$_4$ and 1 M NaOH; ■ analysis by TN; □ analysis by indophenol method.

The "conventional wisdom" about the mechanism of breakpoint chlorination is that the reaction is fastest near pH 8.5 when NH$_3$ reacts with HOCl.[30,33,34] However, the concentration of free NH$_3$ is negligible at pH 3, which is six pH units away from the pK_a of NH$_4^+$. We excluded the possibility of a photochemically induced radical reaction at pH 3 (involving either Cl$_2$ or HOCl), by showing that the rate of denitrification under ordinary laboratory illumination was the same as that of a parallel reaction that was carefully protected from the light (Supporting Information, Figure 5).

Electrochemical hypochlorinations were compared at the anodes Ti/RuO$_2$, Nb/BDD, and graphite, using 25 mM ammonium perchlorate in the presence of 0.5 M sodium chloride at 100 mA (Figure 8). The order of reactivity was Ti/RuO$_2$ > Nb/BDD > graphite. The high reactivity of Ti/RuO$_2$ is compatible with its use as the commonest dimensionally stabilized anode (DSA) used in the chlor-alkali process.
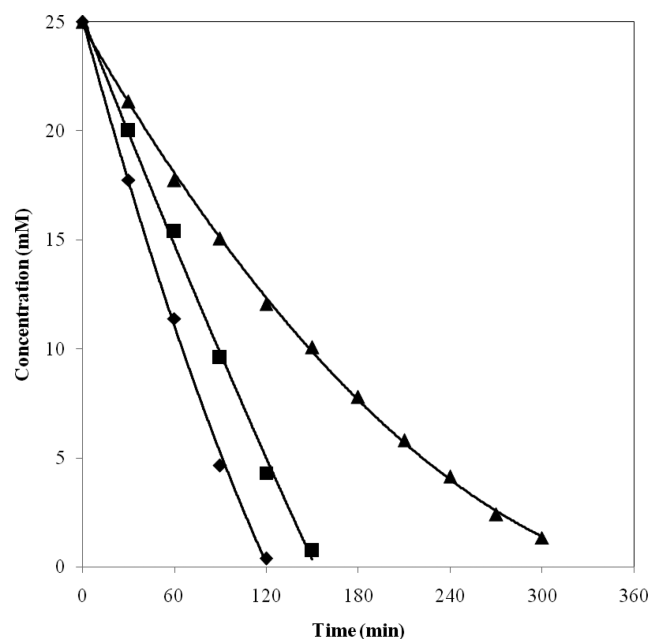
Figure 8. Electrolysis of 50 mL of 25 mM NH$_4$ClO$_4$ + 0.5 M NaCl at 100 mA, using a graphite rod cathode and different anode materials: ▲ graphite; ■ BDD; ♦ Ti/RuO$_2$.

■ DISCUSSION

Mechanical pencil "leads", which are inexpensive and disposable, provide a convenient method of carrying out voltammetry at graphite,[47−51] as they have similar voltammetric behavior to the massive graphite anodes used in bulk electrolyses.[35,49] Repeated cycling of a graphite microelectrode into the potential range of oxygen evolution functionalizes the surface of the anode, as shown by changes to the appearance of the voltammogram.[35] Concerning the work by Ji et al.,[42] who saw an oxidation peak for ammonia at BDD but not at graphite, BDD has a much wider useful anodic potential range than graphite. This is because the sp^3 carbons on its surface are more resistant to oxidation than the sp^2 carbons of graphite. At graphite, the oxidation current for ammonia is obscured by the oxidation of water in the same potential range.

Although conditions were found under which ammonia was oxidized with high current efficiency at graphite in the absence of chloride, it would be difficult to make this approach practical in the context of ammonia scrubbed from poultry barns. First, significant adjustment is needed to change the pH of the scrubbing solution to that needed for electrolysis. This makes recycling of the solution impractical due to the build-up of salts in the solution when the pH is changed back and forth; this requirement for added chemicals also negates the "green" advantage of using electrolytic rather than chemical oxidation.[40] Second, high current efficiency was achieved only at very high ammonia concentrations. Although no oxidation current was observed at a graphite microelectrode under conditions of voltammetry, the rate of electrochemical oxidation in the absence of chloride was concentration-dependent, increasing with the concentration of ammonia in solution. Mechanistic possibilities include either that ammonia is oxidized competitively with water or (as we proposed previously for acetaminophen[35]) that oxidation of ammonia involves oxygen transfer to ammonia from an oxidized graphite surface, following oxidation of water. Third, alkaline conditions necessitated a closed electrolytic cell to avoid loss of ammonia

to the atmosphere due to gas stripping by the O_2 and H_2 byproducts of electrolysis. This would be technologically impossible for a recirculating system. Previously, little success was achieved in an attempt to oxidize ammonia at pH 5.5 using a boron-doped diamond anode (BDD),[45] even though Ji et al.[42] had observed voltammetric oxidation currents proportional to $c(NH_3)$ at BDD. Although BDD promotes efficient oxidation of many substrates by the hydroxyl radical mechanism, the low reactivity of NH_3 and NH_4^+ is probably due to their slow rate constants for reaction with the hydroxyl radical.[52,53]

The electrolysis of ammonia in the presence of chloride ion is generally considered to be similar, but not identical, to the nonelectrochemical process known as breakpoint chlorination, which is used to remove ammonia from wastewater[34,54−57] or drinking water sources concurrently with disinfection.[29−34] In breakpoint chlorination the fastest reaction involves the interaction between neutral ammonia (NH_3) and hypochlorous acid (HOCl), and the optimum pH range for the reaction of ∼8.5 lies between the pK_a values of HOCl and NH_4^+. The stoichiometric reaction is given by eq 1, although the mechanism of denitrification involves chloramine species as intermediates.

$$3HOCl + 2NH_3 \rightarrow N_2 + 3Cl^- + 3H_2O \qquad (1)$$

The electrochemical oxidation of ammonia was much more efficient in the presence of chloride ion (current efficiencies up to 19% depending on the concentration of NaCl). The low cost of electricity compared with chemical oxidants makes this current yield acceptably efficient. Independent of apparent differences in mechanism between conventional chemical and electrochemical hypochlorination in neutral solution resulting from analytical artifacts, there is an inherent difference between pH 7 and pH 3 in the progress of the elimination of nitrogen from solution under chemical conditions. Rapid denitrification occurs at pH 3 at low ratios of $[HOCl]/[NH_3]$. This is compatible with the explanation of Gendel and Lahav[43] that the acidic pH generated at the anode is responsible. However, rapid denitrification at pH 3 remains unexpected because in this pH range ammonia is almost entirely in the non-nucleophilic form of NH_4^+, which has no obvious mode of reactivity with an electrophilic species such as Cl_2 or HOCl. Our tentative suggestion, which requires mechanistic follow-up, is that water promotes this reaction by acting as a general base catalyst.

Our results suggest possible technical conditions for applying electrochemical oxidation to the aqueous phase obtained by scrubbing ammonia into mildly acidic solution. Chloride ion must be present in the scrubbing solution at moderate (e.g., 0.5 M/30 g L^{-1}) concentrations to promote the mediated oxidation in which chloride ion is oxidized electrochemically to a positive chlorine compound (principally HOCl in the pH range of the scrubbed solution) and reduced back to chloride ion during the denitrification step. This combines the pre-existing scrubbing technology for ammonia, only using acidified brine as the scrubbing solution, with recirculation between the scrubbing and electrolysis compartments. Critically, neither pH adjustment nor chemical additives are required.[40] Issues not yet addressed are possible interference to the hypochlorination method by other contaminants in the scrubbed solution, and an evaluation of capital and operating costs of the system. The proposed technology differs from the approach in which ammonia is scrubbed continuously into the acid solution over a protracted period to build up a high concentration of ammonium sulfate that can be used then as fertilizer. In temperate regions there are limited seasons when the solution can be spread. In the present proposal, ammonia is denitrified as it is scrubbed and never builds up to high concentrations; the electrolyzer unit can be incorporated into existing technology between the scrubbing unit and the recirculatory pump. The ability to recirculate avoids the disposal cost of the discharge water, which can be a significant operational cost of an acid scrubber.[58] An additional advantage of a hypochlorite-based technology is that it inherently incorporates disinfection of recirculating water of acid scrubbers due to aerial emissions from the birds.[59] Although the same overall chemistry could be achieved by simply adding elemental chlorine or sodium hypochlorite to the scrubbed solution, this would not be a "green" answer to the problem. More NaOCl would need to be added at each cycle in recirculation mode. Eventually, this would build up the NaCl byproduct to very high concentrations. The same problem would arise if the hypochlorite were generated electrochemically in a separate process (on-site generation) and bled into a recirculatory system.

Several purely chemical reagents for the oxidation of ammonia are in principle competing technologies for the present proposal, but all of these require stoichiometric amounts of the oxidant and can never be "green". Ozone, either alone or in combination with hydrogen peroxide (the peroxone system),[60−62] and potassium ferrate[63] oxidize ammonia to nitrate ion, leaving the same problem as with ammonia itself—a need for further treatment of the dilute solution to a useful product or denitrification. Ozone plus bromide ion achieves oxidation of ammonia to N_2 via hypobromination,[64−66] but this is merely a more complicated and more costly analogue of chemical hypochlorination.

Unlike chemical processes, electrochemical hypochlorination uses electrical charge rather than chemical oxidants and is inherently "green" provided that the solution contains sufficient electrolyte. In the present instance, inexpensive NaCl functions as both electrolyte and electroactive species. Regarding the choice of anode material, dimensionally stable anodes such as Ti/RuO_2 are known for their longevity in oxidizing chloride ion. However, graphite might also be considered on the grounds of low cost, its ability to be formed into a diversity of shapes, and the possibility of reverse polarity to avoid cathode fouling if hard water sources are used.

This proposal is completely compatible with the present technology in which ammonia is scrubbed into dilute sulfuric acid, producing a solution of ammonium sulfate that must either be treated further or stored for use as nitrogenous fertilizer in the growing season. By adding a chloride salt (NaCl) to the scrubbing solution, with an electrolyzer unit in the recycle loop, ammonia (NH_4^+) can be continuously oxidized to N_2 without addition of further chemicals for either oxidation or pH adjustment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This consists of five additional figures (voltammograms and results of electrolyses), as cited in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) http://www.omafra.gov.on.ca/english/livestock/swine/facts/93-001.htm, accessed August 2012

(2) Senthilselvan, A.; Beach, J.; Feddes, J.; Cherry, N.; Wenger, I. A prospective evaluation of air quality and workers' health in broiler and layer operations. *Occup. Environ. Med.* **2011**, *68*, 102.

(3) Létourneau, V.; Nehmé, B.; Mériaux, A.; Massé, D.; Duchaine, C. Impact of production systems on swine confinement buildings bioaerosols. *J. Occup. Environ. Hyg.* **2010**, *7*, 94.

(4) Von Essen, S.; Moore, G.; Gibbs, S.; Larson, K. L. Respiratory issues in beef and pork production: Recommendation from an expert panel. *J. Agromed.* **2010**, *15*, 216.

(5) Willson, P. J.; Khozani Talaei, T.; Juurlink, B. H. J.; Senthilselvan, A.; Rennie, D. C.; Gerdts, V.; Gawaziuk, J.; Schneberger, D.; Burch, L. H.; Dosman, J. A. In vitro production of tumor necrosis factor-alpha by human monocytes stimulated with lipopolysaccharide is positively correlated with increased blood monocytes after exposure to a swine barn. *J. Toxicol. Environ. Health, A* **2008**, *71*, 1401.

(6) http://www.osha.gov/dts/chemicalsampling/data/CH_218300.html, accessed August 2012

(7) Green, A. R.; Wesley, I.; Trampel, D. W.; Xin, H. Air quality and bird health status in three types of commercial egg layer houses. *J. Appl. Poult. Res.* **2009**, *18*, 605.

(8) Drake, K. A.; Donnelly, C. A.; Dawkins, M. S. Influence of rearing and lay risk factors on propensity for feather damage in laying hens. *Brit. Poultry Sci.* **2010**, *51*, 725.

(9) Dawkins, M. S.; Donnelly, C. A.; Jones, T. A. Chicken welfare is influenced more by housing conditions than by stocking density. *Nature* **2004**, *427*, 342.

(10) Tuomisto, H. L.; Hodge, I. D.; Riordan, P.; Macdonald, D. W. Does organic farming reduce environmental impacts? A meta-analysis of European research. *J. Environ. Manage.* **2012**, *112*, 309.

(11) Ndegwa, P. M.; Hristov, A. N.; Arogo, J.; Sheffield, R. E. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. *Biosyst. Eng.* **2008**, *100*, 453.

(12) Harper, L. A.; Flesch, T. K.; Wilson, J. D. Ammonia emissions from broiler production in the San Joaquin Valley. *Poultry Sci.* **2010**, *89*, 1802.

(13) Sheppard, S. C.; Bittman, S.; Tait, J. Monthly NH_3 emissions from poultry in 12 ecoregions of Canada. *Can. J. Anim. Sci.* **2009**, *89*, 21.

(14) Choudhury, M. G.; Saha, N. Influence of environmental ammonia on the production of nitric oxide and expression of inducible nitric oxide synthase in the freshwater air-breathing catfish. *Aquat. Toxicol.* **2012**, *116–117*, 43.

(15) Ip, Y. K.; Chew, S. F. Ammonia production, excretion, toxicity, and defense in fish: A review. *Front. Physiol./Aquat. Physiol.* **2010**, *1*, 134.

(16) Wlasow, T.; Demska-Zakes, K.; Gomulka, P.; Jarmolowicz, S. Various aspects of piscine toxicology. *Interdiscip. Toxicol.* **2010**, *3*, 100.

(17) Eshchar, M.; Lahav, O.; Mozes, N.; Peduel, A.; Ron, B. Intensive fish culture at high ammonium and low pH. *Aquaculture* **2006**, *255*, 301.

(18) Eddy, F. B. Ammonia in estuaries and effects on fish. *J. Fish Biol.* **2005**, *67*, 1495.

(19) Calvet, S.; Cambra-Lopez, M.; Estelles, F.; Torres, A. G. Characterization of gas emissions from a Mediterranean broiler farm. *Poultry Sci.* **2011**, *90*, 534.

(20) Liang, Y.; Xin, H.; Wheeler, E. F.; Gates, R. S.; Li, H.; Zajaczkowski, J. S.; Topper, P. A.; Casey, K. D.; Behrends, B. R.; Burnham, D. J.; Zajaczkowski, F. J. Ammonia emissions from U.S. laying hen houses in Iowa and Pennsylvania. *Trans. ASAE* **2005**, *48*, 1927.

(21) Nicholson, F. A.; Chambers, B. J.; Walker, A. W. Ammonia emissions from broiler litter and laying hen manure management systems. *Biosyst. Eng.* **2004**, *89*, 175.

(22) Estellés, F.; Melse, R. W.; Ogink, N. W. M.; Calvet, S. Evaluation of the NH_3 removal efficiency of an acid packed bed scrubber using two methods: A case study in a pig facility. *Trans. ASABE* **2011**, *54*, 1905.

(23) Melse, R. W.; Ogink, N. W. M.; Rulkens, W. H. Air treatment techniques for abatement of emissions from intensive livestock production. *Open Agric. J.* **2009**, *3*, 6.

(24) Melse, R. W.; Ogink, N. W. M. Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands. *Trans. ASABE* **2005**, *48*, 2303.

(25) Foti, G.; Comninellis, C. Electrochemical oxidation of organics on iridium oxide and synthetic diamond based electrodes. In *Modern Aspects of Electrochemistry, No. 37*; White, R. E., Conway, B. E., Vayenas, C. G., Eds.; Kluwer Academic/Plenum Publishers: New York, 2004.

(26) Panizza, M.; Cerisola, G. Direct and mediated anodic oxidation of organic pollutants. *Chem. Rev.* **2009**, *109*, 6541.

(27) Bejan D.; Bunce N. J. Oxidation of organic pollutants on active and non active anodes. In *Encyclopedia of Applied Electrochemistry*; Savinell R. F., Ota K., Kreysa G., Eds.; accepted for publication.

(28) Bunce, N. J.; Bejan, D. Mechanism of electrochemical oxidation of ammonia. *Electrochim. Acta* **2011**, *56*, 8085.

(29) Haas, C. H. Chemical disinfection. In *Water Quality and Treatment: A Handbook on Drinking Water*; Edzwald, J. K., Ed.; AWWA McGraw Hill: New York, 2011.

(30) Randtke, S. J. Chemistry of Aqueous Chlorine. In *White's Handbook of Chlorination and Alternative Disinfectants*; Wallis-Lage, C., Ed.; John Wiley & Sons, Inc., Hoboken, NJ, 2010.

(31) Schreiber, I. M.; Mitch, W. A. Enhanced nitrogenous disinfection byproduct formation near the breakpoint: Implications for nitrification control. *Environ. Sci. Technol.* **2007**, *41*, 7039.

(32) Charrois, J. W. A.; Hrudey, S. E. Breakpoint chlorination and free-chlorine contact time: Implication for drinking water *N*-nitrosodimethylamine concentrations. *Water Res.* **2007**, *41*, 674.

(33) Jafvert, C. T.; Valentine, R. L. Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.* **1992**, *26*, 577.

(34) Pressley, T. A.; Bishop, D. F.; Roan, S. G. Ammonia−nitrogen removal by breakpoint chlorination. *Environ. Sci. Technol.* **1972**, *6*, 622.

(35) Rueffer, M.; Bejan, D.; Bunce, N. J. Graphite: An active or an inactive anode? *Electrochim. Acta* **2011**, *56*, 2246.

(36) Brochet, A.; Boiteau, G. Electrolytic oxidation of ammonia. *Bull. Soc. Chim. France* **1910**, *5*, 667.

(37) Hine, F.; Yasuda, M. Studies on the mechanism of the chlorine electrode process. *J. Electrochem. Soc.* **1974**, *121*, 1289.

(38) Seed, L. P.; Shelp, G. S. Wastewater ammonium extraction and electrolytic conversion to nitrogen gas. U.S. Patent 2008/0277289 A1, 2008.

(39) Shelp, G. S.; Seed, L. P. Electrochemical treatment of ammonia in waste-water. U.S. Patent 7,160,430 B2, 2007.

(40) Melse, R. W.; Ogink, N. W. M.; Rulkens, W. H. Overview of European and Netherlands' regulations on airborne emissions from intensive livestock production with a focus on the application of air scrubbers. *Biosyst. Eng.* **2009**, *104*, 289.

(41) Clesceri, L. S., Greenberg, A. E., Eaton, A. D., Eds. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, 1998.

(42) Ji, X.; Banks, C. E.; Compton, R. G. The electrochemical oxidation of ammonia at boron-doped diamond electrodes exhibits

analytically useful signals in aqueous solutions. *Analyst* **2005**, *130*, 1345.

(43) Gendel, Y.; Lahav, O. Revealing the mechanism of indirect ammonia electrooxidation. *Electrochim. Acta* **2012**, *63*, 209.

(44) Kapalka, A.; Katsaounis, A.; Michels, N.-L.; Leonidova, A.; Souentie, S.; Comninellis, C.; Udert, K. M. Ammonia oxidation to nitrogen mediated by electrogenerated active chlorine on Ti/PtO_x–IrO_2. *Electrochem. Commun.* **2010**, *12*, 1203.

(45) Kapalka, A.; Joss, L.; Anglada, A.; Comninellis, C.; Udert, K. M. Direct and mediated electrochemical oxidation of ammonia on boron-doped diamond electrode. *Electrochem. Commun.* **2010**, *12*, 1714.

(46) *Total Organic Carbon Analyzer TOC-V CPH/CPN User Manual*; Shimadzu Corporation, Analytical & Measuring Instruments Division: Kyoto, Japan; p 300.

(47) Hsieh, B.-C.; Cheng, T.-J.; Shih, S.-H.; Chen, R. L. C. Pencil lead microelectrode a the application on cell dielectrophoresis. *Electrochim. Acta* **2011**, *56*, 9916.

(48) King, D.; Friend, J.; Kariuki, J. Measuring vitamin C content of commercial orange juice using a pencil lead electrode. *J. Chem. Educ.* **2010**, *87*, 507.

(49) Tavares, P. H. C. P.; Barbeira, P. J. S. Influence of pencil lead harness on voltammetric response of graphite reinforcement carbon electrodes. *J. Appl. Electrochem.* **2008**, *38*, 827.

(50) Goldcamp, M. J.; Underwood, M. N.; Cloud, J. L.; Harshman, S.; Ashley, K. An environmentally friendly, cost-effective determination of lead in environmental samples using anodic stripping voltammetry. *J. Chem. Educ.* **2008**, *85*, 976.

(51) Bendikov, T. A.; Harmon, T. C. A sensitive nitrate ion-selective electrode from a pencil lead. *J. Chem. Educ.* **2005**, *83*, 439.

(52) Huang, L.; Li, L.; Dong, W.; Liu, Y.; Hou, H. Removal of ammonia by OH radical in aqueous phase. *Environ. Sci. Technol.* **2008**, *42*, 8070.

(53) Neta, P.; Maruthamuthu, P.; Carton, P. M.; Fessenden, R. W. Formation and reactivity of the amino radical. *J. Phys. Chem.* **1978**, *82*, 1875.

(54) March, J. G.; Gual, M. Breakpoint chlorination curves of greywater. *Water Environ. Res.* **2007**, *79*, 828.

(55) Qiang, Z.; Macauley, J. J.; Mormile, M. R.; Surampalli, R.; Adams, C. D. Treatment of antibiotics and antibiotic resistant bacteria in swine wastewater with free chlorine. *J. Agric. Food Chem.* **2006**, *54*, 8145.

(56) Kim, H.; Kwon, S.; Han, S.; Yu, M.; Gong, S.; Colosimo, M. F. New process control strategy for wastewater chlorination and dechlorination using ORP/pH. *Water Sci. Technol.* **2006**, *53*, 431.

(57) Yang, X.; Shang, C.; Huang, J.-C. DBP formation in breakpoint chlorination of wastewater. *Water Res.* **2005**, *39*, 4755.

(58) Melse, R. W.; Ogink, N. W. M. Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands. *Trans. ASAE* **2005**, *48*, 2303.

(59) Aarnink, A. J. A.; Landman, W. J. M.; Melse, R. W.; Zhao, Y.; Ploegaert, J. P. M.; Huynh, T. T. T. Scrubber capabilities to remove airborne microorganisms and other aerial pollutants from the exhaust air of animal houses. *Trans. ASAE* **2011**, *54*, 1921.

(60) Kuo, C.-H.; Yuan, F.; Hill, D. O. Kinetics of oxidation of ammonia in solutions containing ozone with or without hydrogen peroxide. *Ind. Eng. Chem. Res.* **1997**, *36*, 4108.

(61) Hoigné, J.; Bader, H. Ozonation of water: Kinetics of oxidation of ammonia by ozone and hydroxyl radicals. *Environ. Sci. Technol.* **1978**, *12*, 79.

(62) Singer, P. C.; Zilli, W. B. Ozonation of ammonia in wastewater. *Water Res.* **1975**, *9*, 127.

(63) Sharma, V. K. Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review. *J. Environ. Sci. Health, A* **2010**, *45*, 645.

(64) Ruffino, B.; Zanetti, M. C. Bicarbonate and ammonia depletion on ozonized systems with bromide ion. *Ozone Sci. Eng.* **2011**, *33*, 425.

(65) Yang, M.; Uesugi, K.; Myoga, H. Study on by-products of ozonation during ammonia removal under the existence of bromide: Factors affecting formation and removal of the by-products. *Ozone Sci. Eng.* **2000**, *22*, 23.

(66) Haag, W. R.; Hoigné, J.; Bader, H. Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment. *Water Res.* **1984**, *18*, 1125.