



## Release Reductions of Gaseous Ammonia and Nitrogen Oxides from Electrochemical Treatment of Swine Wastewater

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### ABSTRACT

This study investigates the release of NH<sub>3</sub> and nitrogen oxides (NO<sub>x</sub>) from wastewater into the air in relation to the variations in NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, and chemical oxygen demand (COD) concentrations in the swine wastewater with/without electrolysis using boron-doped diamond (BDD), PbO<sub>2</sub>, and graphite anodes. The NH<sub>3</sub> concentration in the air right above the swine wastewater without electrolysis increased over time and this increase was greater when the wastewater NH<sub>3</sub>-N concentration was higher. Electrolysis could reduce the release of NH<sub>3</sub> from swine wastewater into the air. The NO concentration in the air was greater for the wastewater without electrolysis than for that with electrolysis but an opposite trend was observed for NO<sub>2</sub>, although the corresponding NO<sub>x</sub> concentrations for the wastewater with and without electrolysis were similar. Roughly, the air NH<sub>3</sub>, NO, NO<sub>2</sub>, or NO<sub>x</sub> concentrations for using the different anodes in wastewater electrolysis followed the order Nb/BDD >> graphite/BDD > graphite > graphite/PbO<sub>2</sub> ≈ Ti/PbO<sub>2</sub>. Although the BDD and graphite anodes showed less formation of nitrite or nitrate than the PbO<sub>2</sub> anodes, the graphite/BDD and graphite anodes had worse performance in NH<sub>3</sub>-N or COD electro-degradation than the other tested ones. When the initial concentration of NH<sub>3</sub>-N or COD was higher, its specific energy consumption in electrolysis was lower.

**Keywords:** Swine wastewater; Electrochemical degradation; Anode material; Ammonia reduction; Nitrogen oxides.

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### INTRODUCTION

Pig farming including intensive or large-scale raising and breeding operations is still necessary to meet the increasing pork demand in several countries (Osada *et al.*, 2017; Song *et al.*, 2017). Despite the recent spread of African swine fever to new areas or countries, China, the United States and the European Union held the first, second, and third positions, respectively, for the global pork production in 2018 (Deblitz *et al.*, 2018). This phenomenon causes the generation of considerable amounts of swine wastewater which needs to be well treated before discharge for the prevention of surface and underground water pollution, because several types of pollutants including high levels of organic and nitrogen compounds might be present in swine wastewater, which are

regulated by water quality parameter limits (U.S. EPA, 2013; Ding *et al.*, 2017; Osada *et al.*, 2017; Song *et al.*, 2017).

Another great environmental concern for pig farming is the emissions of ammonia (NH<sub>3</sub>) and greenhouse gases (e.g., CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O) from the wastewater in purification facilities or the slurry in storages at pig farms prior to land application (Viguria *et al.*, 2015; Osada *et al.*, 2017). According to the European Environment Agency (EEA, 2019), ammonia and nitrogen oxides (NO<sub>x</sub>) are two of four key air pollutants with emissions restricted by the EU legislation from 2010 onward, and emissions of ammonia from the agricultural sector continue to rise, posing a challenge for EU Member States in meeting EU air pollution limits. Guthrie *et al.* (2018) also indicates that the agricultural sector is the biggest contributor to ammonia pollution in the UK. Although the levels of other air pollutants have declined, ammonia is one of the main sources of nitrogen pollution, alongside nitrogen oxides, and ammonia emissions have been rising since 2013 in the UK, with significant implications for biodiversity and human health. NH<sub>3</sub> and NO<sub>x</sub> are two of most important pollutants that need more intensive monitoring for the air

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pollution at Kathmandu Valley in Nepal (Kiros *et al.*, 2016). These compounds are also two of N-containing acidifying pollutants which may deposit from the atmosphere to the ground (Wright *et al.*, 2018) and impacts species composition through soil acidification (Guthrie *et al.*, 2018). In addition to agricultural sources,  $\text{NH}_3$  (reduced N) may also be produced from biomass burning, while  $\text{NO}_x$  (oxidized N) can be contributed from different sources, such as vehicle emissions, industry, and domestic combustion, and electricity generation (Wright *et al.*, 2018).  $\text{NH}_3$  and  $\text{NO}_x$  are regarded as precursor gases which may influence the chemical compositions of  $\text{PM}_{2.5}$ , visibility, and air quality (Li *et al.*, 2018), so they are concerned for their spatio-temporal variations (Cai *et al.*, 2018; Cheng *et al.*, 2018) and long-range transport (Sadanaga *et al.*, 2017).

Ammonia and hydrogen sulfide are the main odor gases related to manure swine houses (usually causing a nuisance for surrounding communities), although odor from inside swine production facilities is a complex mixture of gases (~330 different compounds), primarily due to manure decomposition under anaerobic conditions (Rahman and Borhan, 2012; Ubeda *et al.*, 2013). Therefore, manure treatment systems are necessary for controlling the ammonia and odor emission from swine wastewater. Odor emission from liquid manure can be reduced by a three-step process: solid-liquid separation of manure, anaerobic digestion, and aerobic biological treatment (for the removal of organic and nitrogen compounds) (Rahman and Borhan, 2012; Montes *et al.*, 2015). This process is also adopted in Taiwan for swine wastewater treatment; however, it has the disadvantages of time-consuming, low ammonia removal, and poor odor control. Moreover, ammonia is one of air toxic pollutants regulated by Air Pollution Control Act Enforcement Rules in Taiwan.

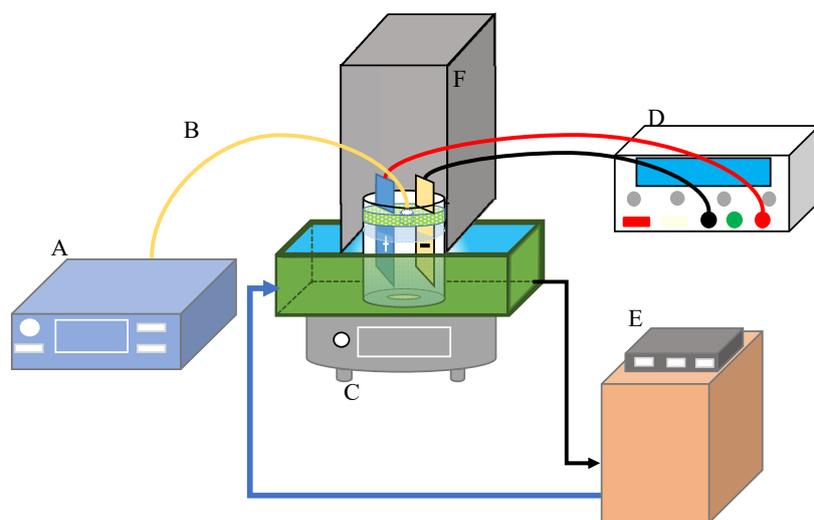
Electrochemical advanced oxidation process (EAOP) is a more efficient approach than the three-step one for swine wastewater treatment to alleviate the swine wastewater pollution along with its odor nuisance including ammonia emission. Generated in EAOP, hydroxyl radical ( $\bullet\text{OH}$ ) is a

powerful oxidant which is highly reactive for degrading organic pollutants in wastewater. In the presence of chloride, active chlorine can be electrochemically generated in the EAOP and it is very efficient for removing ammonia and other nitrogen-containing compounds in wastewater (Li and Liu, 2009; Sirés *et al.*, 2014; Radjenovic *et al.*, 2015; Moreira *et al.*, 2017). For this purpose and the effective production of  $\bullet\text{OH}$  for chemical oxygen demand (COD) degradation, EAOP highly relies on the use of non-active anode materials (e.g.,  $\text{PbO}_2$  and boron-doped diamond [BDD]) (Li and Liu, 2009; Sirés *et al.*, 2014; Radjenovic *et al.*, 2015; Moreira *et al.*, 2017). In our previous work, we explored the removal of COD and ammonia in swine wastewater at different operating parameters (Huang *et al.*, 2018, 2019). However, little attention has been paid to release of  $\text{NH}_3$  and nitrogen oxides ( $\text{NO}_x$ ) from wastewater into the air in association with the variations in  $\text{NH}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ , and COD concentrations in the swine wastewater with/without electrolysis. Therefore, this study focuses on the investigation of gaseous ammonia and nitrogen oxides emitted from electrochemical treatment of swine wastewater using different anode materials.

## MATERIALS AND METHODS

### *Electrolysis of Swine Wastewater*

The electrolysis of swine wastewater with the addition of 0.05 M NaCl was performed in an undivided electrochemical cell at room temperature ( $25^\circ\text{C}$ ) and  $0.25\text{ A cm}^{-2}$  (Fig. 1). A Ti plate was used as the cathode, while the anode material was BDD-I (Nb/BDD from Neocoat, Germany), lab-prepared substance (Ti/ $\text{PbO}_2$ , graphite/ $\text{PbO}_2$ , or graphite/BDD), or graphite. The fabrication method for the lab-prepared  $\text{PbO}_2$  was provided elsewhere (Chen *et al.*, 2012), whereas the fabrication of graphite/BDD referred to an approach of hot filament chemical vapor deposition (HFCVD) (Pinheiro *et al.*, 2012). A DC power supply (Twintex TP2H-20S, Taiwan,) was used to monitor the cell voltage and current over time in the electrolytic experiments.



**Fig. 1.** The scheme of experimental device (A: Ammonia analyzer, B: Sampling tube, C: Magnetic stirrer, D: DC power supply, E: thermostatic bath, F: Three-side rectangular box, +: Anode, and -: Cathode).

The degradation or removal efficiency of COD or NH<sub>3</sub>-N was calculated using the following equation:

$$\text{Degradation or removal efficiency} = (1 - C_t/C_0) \times 100\% \quad (1)$$

where  $C_t$  is the residual concentration of either COD or NH<sub>3</sub>-N at a given electrolysis time  $t$  and  $C_0$  is the initial concentration of COD or NH<sub>3</sub>-N.

The specific energy consumption ( $E_{SP}$ ) (kWh g-COD<sup>-1</sup> or kWh g-NH<sub>3</sub>-N<sup>-1</sup>) was determined using the following calculation (Martínez-Huitle and Ferro, 2006; Radjenovic *et al.*, 2015):

$$E_{SP} = E_{cv}It/(C_0 - C_t)V_{wv} \quad (2)$$

where  $E_{cv}$  is the average cell voltage (V);  $I$  is the applied current (A);  $V_{wv}$  is the wastewater volume (L).

#### **Analysis of Ammonia and Nitrogen Oxides in the Air**

An ammonia analyzer (Ecoech Serinus-44) was used to directly collect air samples and quantify the concentrations of NH<sub>3</sub>, NO, NO<sub>2</sub>, and NO<sub>x</sub> in the air right above the electrolytic cell holding swine wastewater with or without electrolysis (Fig. 1). In experiments, the swine wastewater was well mixed using a magnetic stirrer (stir bar, length = 4 cm and diameter = 0.8 cm) operated at 320 rpm, which proceeded the thorough mixing of swine wastewater without vortex formation in the electrochemical reactor (diameter = 6 cm). The air entrance of sampling tube was placed at 4 cm right above the swine wastewater and the sampling space was three-side surrounded by a paper holder to reduce interference of air flow and provide temporary accumulation of species of interest for sampling. The method detection limits of these nitrogen compounds are all 0.4 ppb, while their upper limits of quantitation are the same (20 ppm). The reported concentrations of these four species in the air were all background (blank) corrected. These data were obtained in laboratories A and B, and the former had higher background air ammonia concentrations than the latter (~100 ppb).

#### **Chemical Analysis of Swine Wastewater**

The swine wastewater samples, obtained from two pig farms in southern Taiwan, were stored at 4°C before use. Prior to testing, each sample was filtered using a 0.45 μm filter to remove suspended solids. The methods set forth in the National Institute of Environmental Analysis (NIEA) (Taiwan) W517.52B, W203.51B, W448.51B, W418.53C, W419.51B, and W424.52A were used for the analyses of COD, conductivity (EC), ammonium nitrogen (NH<sub>3</sub>-N), nitrite nitrogen (NO<sub>2</sub><sup>-</sup>-N), nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N), and pH respectively.

A COD analyzer (COD Reactor CR25, Rocker) coupled with a colorimeter (Hach-DR900) was used to analyze the COD concentrations of samples. The required digestion for the ammonia measurements was conducted by a Gerhardt VAP-200 Kjeldahl Nitrogen Distillation System. The NH<sub>3</sub>-N in wastewater was spectrophotometrically measured at 640 nm (Hanna HI 96715) based on the reaction of ammonia

with phenol and hypochlorite catalyzed with nitroprusside to form intensively blue indophenol in an alkaline medium (Berthelot reaction). Some ammonia measurements were also performed using a Hach-DR900 analyzer.

Sulfanilamide was used to diazotize the nitrite nitrogen of a sample followed by coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED), and the concentration of nitrite was then photometrically analyzed at 543 nm. Nitrate was also spectrophotometrically determined at 220 nm through deduction of the double absorbance at 275 nm for each sample. The chloride concentration was quantitatively determined using a redox potential titrator (Metrohm 702 SM Titrino), while the EC and pH were measured using an SC-170 conductivity meter (Suntex, Taiwan) and a TS-100 pH meter, respectively.

## **RESULTS AND DISCUSSION**

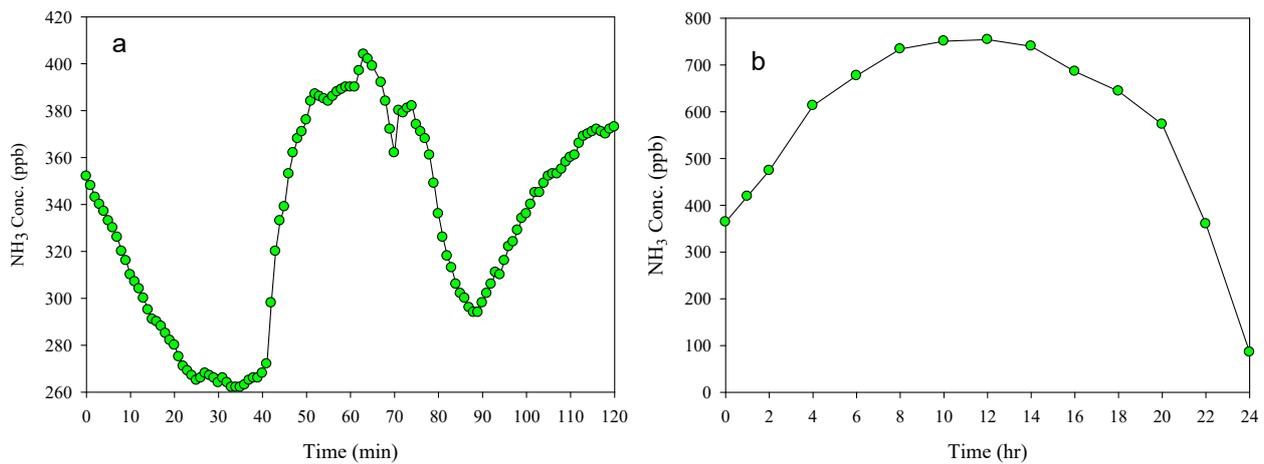
#### **Concentrations of NH<sub>3</sub> in the Air and NH<sub>3</sub>-N in the Wastewater without Electrolysis**

The air NH<sub>3</sub> samples were collected in two laboratories (A and B), so the background NH<sub>3</sub> concentrations in the air in the laboratories need to be measured before the tests of swine wastewater. In fact, the background NH<sub>3</sub> concentrations in the air in the laboratories varied with time. Figs. 2(a)–2(b) show two examples of the time-dependent concentration profiles of background air NH<sub>3</sub> collected in laboratory A. The air NH<sub>3</sub> concentrations fluctuated within the range of 262–404 ppb for a minute-based measurement (Fig. 2(a)), while those for an hour-based measurement ranged from 86–754 ppb (Fig. 2(b)). The latter had an increase in air NH<sub>3</sub> concentration during daytime, mainly due to the increase in worker activity during office hours in the laboratory, because the chemical composition of human perspiration includes urea and the ammonia nitrogen can be detected in human perspiration (Thurmon and Ottenstein, 1952).

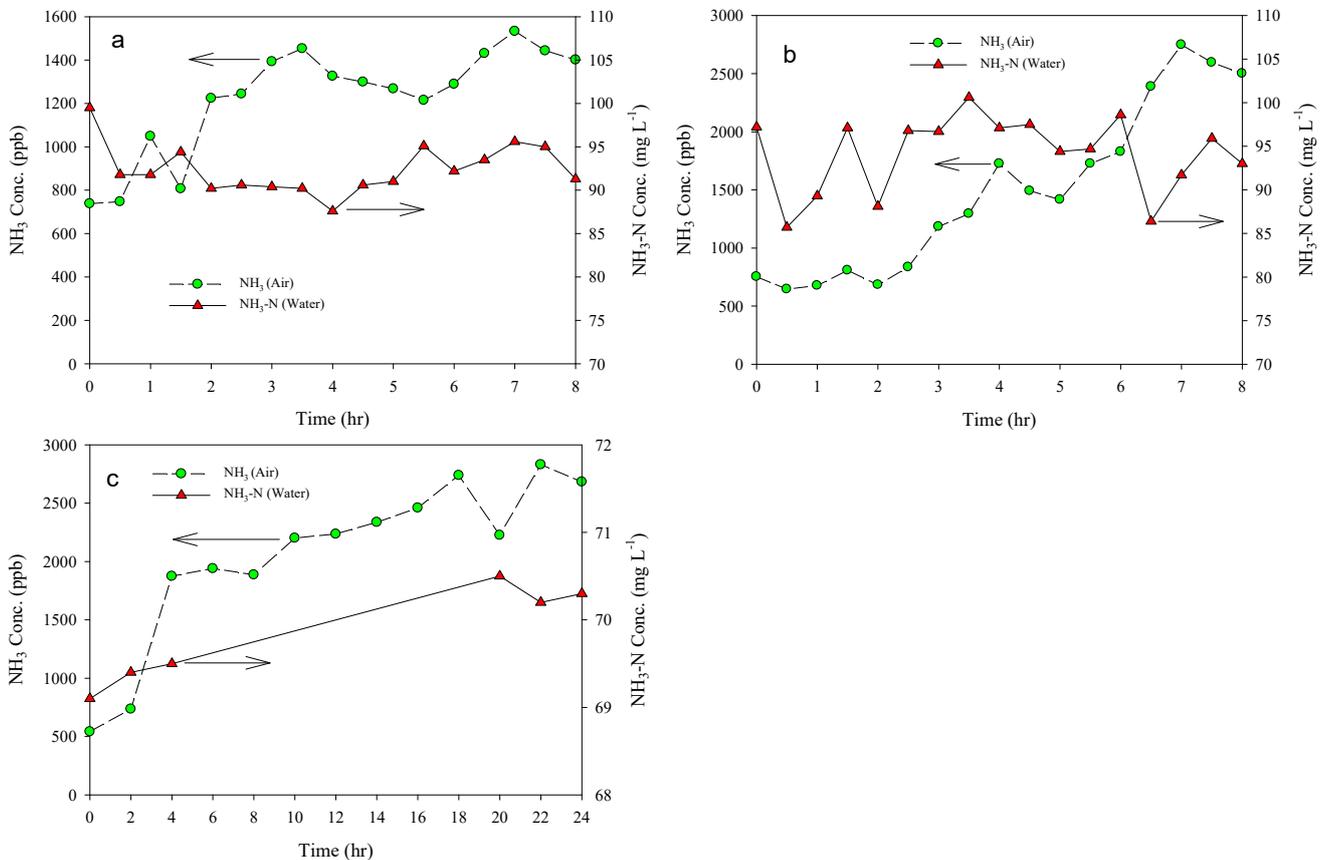
Figs. 3(a)–3(b) show the variation air NH<sub>3</sub> concentrations along with that of wastewater NH<sub>3</sub>-N over time at similar initial wastewater NH<sub>3</sub>-N concentrations (99.5 and 97.2 mg L<sup>-1</sup>, respectively) in laboratory A. As can be seen from these two figures, the NH<sub>3</sub> concentrations in the air right above the electrolytic cell without operation were significantly higher than that of background air. This phenomenon is associated with the release of NH<sub>3</sub> from the swine wastewater into the air, because ammonia is a volatile compound which may partition itself between the liquid and the gas above the liquid (Arogo *et al.*, 1999). According to Arogo *et al.* (1999), the mass transfer rate of NH<sub>3</sub> from the swine wastewater into the air is proportional to the product of a mass transfer rate constant, the interfacial surface area, and a concentration driving force:

$$\frac{dm}{dt} = kA_s(C_w - C_{air}) \quad (3)$$

where  $m$  is the mass of ammonia,  $k$  is the overall mass transfer coefficient of ammonia,  $A_s$  is the interfacial surface area,  $C_w$  is the ammonia concentration in wastewater,  $C_{air}$  is the ammonia concentration in the air, and  $t$  is time.



**Fig. 2.** Air  $\text{NH}_3$  concentration variations over time ((a) 2 and (b) 24 hrs) in laboratory A.



**Fig. 3.** Air  $\text{NH}_3$  and wastewater  $\text{NH}_3\text{-N}$  concentration variations over time at different initial wastewater  $\text{NH}_3\text{-N}$  concentrations or sampling durations ((a) 99.5 (8-hr), (b) 97.2 (8-hr), and (c) 69.1 (24-hr)  $\text{mg L}^{-1}$ ) (laboratory A).

Moreover, the ammonia volatilization might be influenced by other factors such as air velocity, air temperature, liquid temperature, and system geometry. Although the fluctuation of  $\text{NH}_3\text{-N}$  concentrations in the swine wastewater was observed, it was almost negligible in comparison to that of  $\text{NH}_3$  concentrations in the air. This trend was also found when increasing the hourly sampling from 8 to 24 hrs for the wastewater with a lower initial  $\text{NH}_3\text{-N}$  concentration (Fig. 3(c)). The gradual rise of ammonia concentration in the

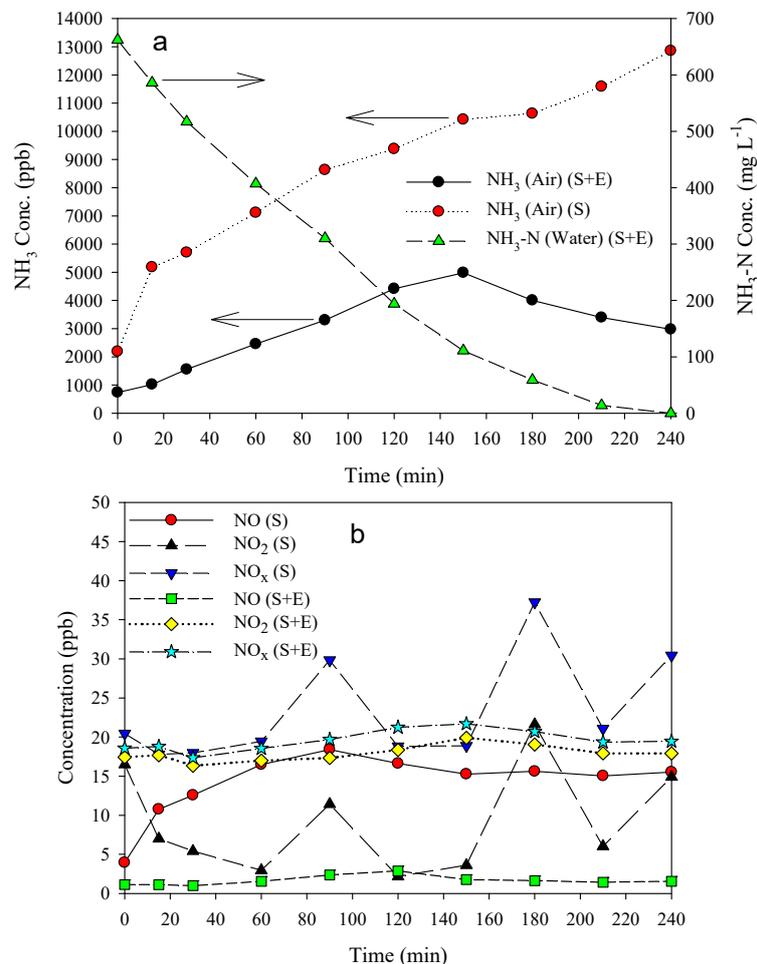
air above the swine wastewater with the increase of time is attributed to the continuing release of ammonia with an increasing time and its temporary accumulation in the sampling space.

**Variations of  $\text{NH}_3$  and Nitrogen Oxides Concentrations in the Air and of  $\text{NH}_3\text{-N}$  in the Wastewater with/without Electrolysis**

Increasing over time like the trend shown in Figs. 3(a)–3(b),

the air  $\text{NH}_3$  concentrations (2186–12858 ppb) in Fig. 4(a) were significantly higher than those in Figs. 3(a)–3(b), because the swine wastewater (stirring [S] only) had a significantly higher initial  $\text{NH}_3\text{-N}$  concentration ( $661 \text{ mg L}^{-1}$ ). During the electrolysis (E) of this swine wastewater (S+E), the air  $\text{NH}_3$  concentrations, also increasing over time at  $t \leq 150 \text{ min}$ , were significantly smaller (738–4985 ppb) than those without

electrolysis; additionally, the decrease in air  $\text{NH}_3$  concentration was observed at  $t > 150 \text{ min}$ . This result is attributed to the decrease in driving force for ammonia volatilization (Eq. (3)) because of the decrease in wastewater  $\text{NH}_3\text{-N}$  concentration (from  $661 \text{ mg L}^{-1}$  at  $t = 0 \text{ min}$  to  $< 0.01 \text{ mg L}^{-1}$  at  $t = 240 \text{ min}$ ) (pseudo first order rate constant of  $\text{NH}_3\text{-N}$  removal  $k_{\text{NH}_3\text{-N}} = 1.33 \times 10^{-4} \text{ s}^{-1}$ ) (Table 1).



**Fig. 4.** (a) Air  $\text{NH}_3$  and wastewater  $\text{NH}_3\text{-N}$  concentration variations and (b) air nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$ ) concentration variations over time (E: electrolysis and S: stirring for wastewater) (laboratory B).

**Table 1.** Initial concentrations ( $\text{mg L}^{-1}$ ) of COD,  $\text{NH}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ , and  $\text{NO}_3\text{-N}$  of tested wastewater (volume = 200 mL); pseudo first order rate constants ( $\text{s}^{-1}$ ) of COD and  $\text{NH}_3\text{-N}$  removal ( $k_{\text{COD}}$  and  $k_{\text{NH}_3\text{-N}}$ , respectively); specific energy consumptions of COD degradation (2-hr  $E_{\text{SP-C}}$ ,  $\text{kWh g-COD}^{-1}$ ) and  $\text{NH}_3\text{-N}$  removal (0.5-hr  $E_{\text{SP-N}}$ ,  $\text{kWh g-NH}_3\text{-N}^{-1}$ ); and  $\Delta N_T$  (2-hr, mg) (G: graphite and NA: not available).

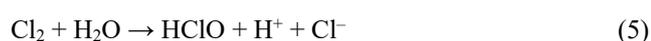
Batch	Electrode	COD	$\text{NH}_3\text{-N}$	$\text{NO}_2\text{-N}$	$\text{NO}_3\text{-N}$	$k_{\text{COD}}$	$k_{\text{NH}_3\text{-N}}$	$E_{\text{SP-C}}$	$E_{\text{SP-N}}$	$\Delta N_T$
I	BDD-I	6266	661	1.58	88.5	$1.21 \times 10^{-4}$	$1.33 \times 10^{-4}$	0.052	0.316	89.8
II-01	Ti/PbO <sub>2</sub>	NA	98.2	NA	NA	NA	$4.63 \times 10^{-4}$	NA	1.250	17.4
II-02	BDD-I	NA	82.0	NA	NA	NA	$4.83 \times 10^{-4}$	NA	0.899	16.0
II-1	BDD-I	542	76.3	0.26	0.57	$5.13 \times 10^{-4}$	$5.13 \times 10^{-4}$	0.408	1.043	12.5
II-2	Ti/PbO <sub>2</sub>	360	87.0	0.48	5.50	$9.90 \times 10^{-4}$	$5.38 \times 10^{-4}$	0.805	0.825	16.3
II-3	G/PbO <sub>2</sub>	480	82.1	0.80	2.63	$1.19 \times 10^{-3}$	$6.35 \times 10^{-4}$	0.658	0.963	14.4
II-4	G	484	90.0	0.32	5.96	$4.50 \times 10^{-5}$	$2.98 \times 10^{-4}$	0.593	6.703	10.1
II-5	G/BDD	388	84.0	0.15	5.96	$1.55 \times 10^{-4}$	$3.68 \times 10^{-4}$	0.853	5.174	9.97

Batch I: initial conductivity =  $12.45 \text{ ms cm}^{-1}$ ,  $\text{Cl}^- = 1737 \text{ mg L}^{-1}$ , and  $\text{pH} = 7.86$ .

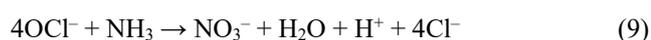
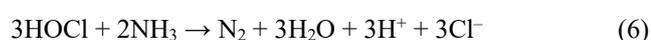
Batch II: initial conductivity =  $7.40 \text{ ms cm}^{-1}$ ,  $\text{Cl}^- = 1895 \text{ mg L}^{-1}$ , and  $\text{pH} = 7.34\text{--}7.80$ .

It is interesting to note that the NO concentration in the air was greater for the wastewater without electrolysis than for that with electrolysis, but an opposite tendency was observed for NO<sub>2</sub> in the air (Fig. 4(b)). However, their corresponding NO<sub>x</sub> concentrations were similar at most of sampling intervals, although the NO concentrations were significantly higher at t = 90, 180, and 240 min for the wastewater with electrolysis than for that without electrolysis. This finding is related to the conversion of ammonia into other nitrogen compounds. Without electrolysis, it is known that two groups of bacteria, *Nitrosomonas* and *Nitrobacter* may cause the oxic conversion of ammonia to nitrite and nitrate, respectively. However, ammonia oxidizers are able to oxidize ammonia under anoxic conditions (Schmidt and Bock, 1997). According to Stuenkel and Bock (2001), significant NO and NO<sub>2</sub> production was observed during biological N-elimination from synthetic wastewater and sludge liquor from the municipal wastewater treatment plant wastewater with high ammonium concentration (about 700 mg N L<sup>-1</sup>); moreover, *Nitrosomonas* was an efficient NO producer and significant NO<sub>2</sub> formed during simultaneous nitrification/denitrification. Nevertheless, various disinfecting oxidants such as chlorine, ozone, and hydroxyl radicals can be generated at BDD electrodes in NaCl solution (Yano *et al.*, 1998). The free chlorine, active chlorine, or chloramines might involve in the inactivation of *Nitrosomonas (europaea)* (Chauret *et al.*, 1998), which affected the production of NO and NO<sub>2</sub> from nitrification in the wastewater and thus the release of nitrogen oxides from wastewater into the air, leading to the variations of nitrogen oxides in the air.

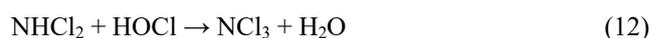
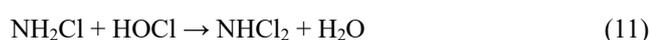
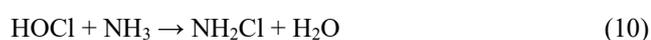
During the electrolysis of swine wastewater containing 0.05 M NaCl in this study, the electrochemical production of active chlorine (Cl<sub>2</sub>, HOCl, and OCl<sup>-</sup>) could be achieved through the following two reactions (Kapałka *et al.*, 2010).



Based on reactions 6–9, the HOCl from the above reaction could oxidize NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> to produce nitrogen gas or nitrate (Li and Liu, 2009).



Or HOCl might react with NH<sub>3</sub> to form chloramines via reactions 10–12 (Kapałka *et al.*, 2010; Pérez *et al.*, 2012), while the formation of chloramines was indicated to be insignificant at pH > 8 (Pérez *et al.*, 2012).

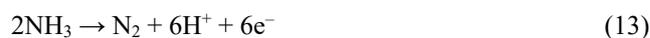


It was reported that ammonia can be electrochemically oxidized through several complicated steps to various nitrogen compounds such as N<sub>2</sub> and NO<sub>x</sub> gases, although the former is more dominant than the latter (Wasmus *et al.*, 1994; Kim *et al.*, 2006). According to Kim *et al.* (2005), the ammonia was oxidized mainly to nitrogen gas through a direct electrolytic reaction in the basic solution, while ammonia could be partly decomposed to nitrogen by the hydroxyl radicals in the neutral and acid solution; besides, the ammonium ion could be oxidized to NO<sub>x</sub> and nitrogen by electrochemically generated hypochlorite plus hydroxyl radicals in the neutral condition. This explanation is also appropriate for the finding of NO<sub>x</sub> production from the electrochemical oxidation of ammonia in swine wastewater in this study. However, the evolution of oxygen on anode and that of hydrogen on cathode leading to an effect of ammonia stripping might also influence the rate of NO<sub>x</sub> release from wastewater into the air.

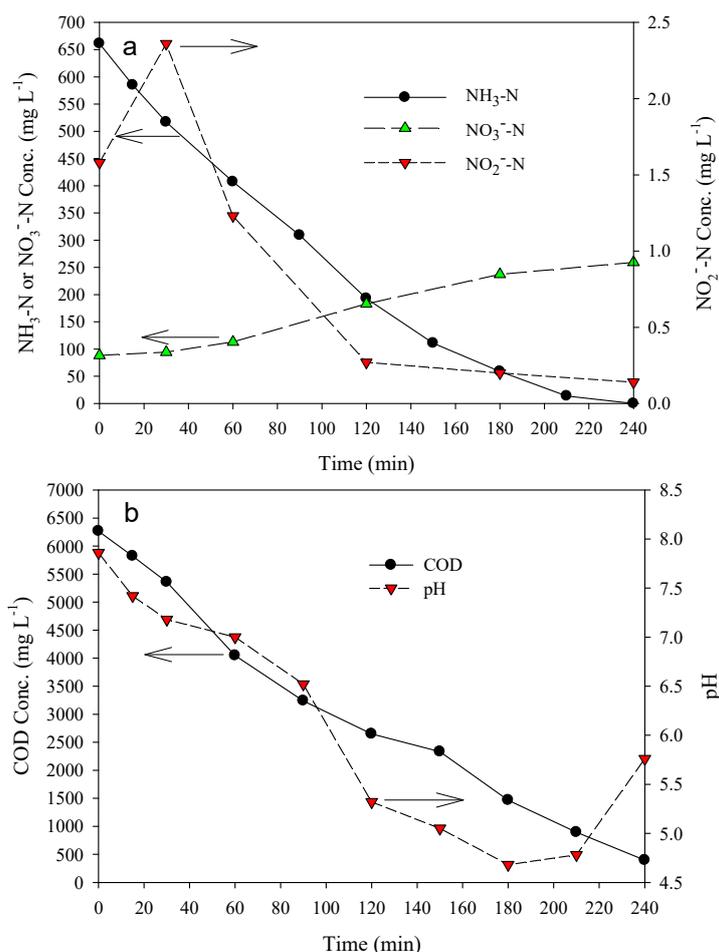
#### Variations of Nitrite, Nitrate, and COD Concentrations over Time in Wastewater

The reactions on both anode and cathode might influence the production and decomposition of ammonia, nitrite, nitrate, and COD, which then resulted in the variations of NH<sub>3</sub> and NO<sub>x</sub> concentration over time in the air. Fig. 5(a) shows the variations of nitrite and nitrate concentrations over time in wastewater. For comparison, the data of NH<sub>3</sub>-N taken from Fig. 4(a) is also presented in Fig. 5(a). The concentration of NH<sub>3</sub>-N decreased over time from 661 to ND, that of NO<sub>2</sub><sup>-</sup>-N slightly increased initially and then decreased over time (0.14–2.36 mg L<sup>-1</sup>), and that of NO<sub>3</sub><sup>-</sup>-N significantly increased with an increasing time (88.5–259 mg L<sup>-1</sup>) during the electrolysis of swine wastewater.

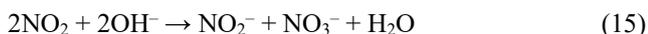
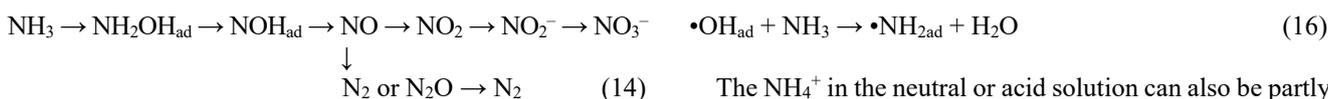
As discussed in the previous section, the decrease in NH<sub>3</sub>-N concentration over time was chiefly resulted from the reactions of free (or un-ionized) ammonia (NH<sub>3</sub>) or ionized one (NH<sub>4</sub><sup>+</sup>) (pK<sub>a</sub> of NH<sub>4</sub><sup>+</sup> ↔ NH<sub>3</sub> = ~9.24 (Huang *et al.*, 2008)) with electrochemically generated active chlorine, which led to the formation of NO<sub>3</sub><sup>-</sup> or chloramines. Kapałka *et al.* (2010) concluded that the oxidation of ammonia at pH < 8 was mostly mediated by electro-generated *in situ* active free chlorine to enhance ammonia oxidation using BDD in the presence of chloride, because the dominant ammonia species was NH<sub>4</sub><sup>+</sup> based on the pK<sub>a</sub> = 7.50 for HOCl → OCl<sup>-</sup> + H<sup>+</sup> (Pérez *et al.*, 2012). Nevertheless, they also indicated that direct (non-mediated) electrochemical oxidation of ammonia on BDD electrode proceeded mainly at pH > 8 via NH<sub>3</sub> oxidation.



In addition to N<sub>2</sub>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> might also be produced on the anode via the further oxidation of NH<sub>2</sub>OH or NO formed from electrochemical oxidation of ammonia (Kim *et al.*, 2005) or by dissolution of nitrogen oxides, e.g., Eq. (15) in the aqueous phase (Bunce and Bejan, 2011).



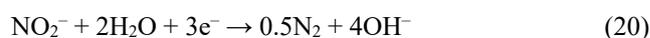
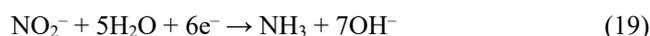
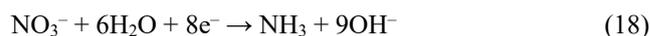
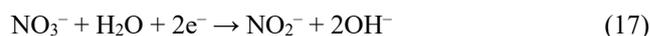
**Fig. 5.** Concentration variations in nitrogen compounds (NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, and NO<sub>3</sub><sup>-</sup>-N) (a) and COD and pH (b) over time in wastewater (Batch I, laboratory B).



In fact, these reactions are known to occur through more complicated steps. According to Bunce and Bejan (2011), the one-electron oxidation of water at the anode surface MO<sub>n</sub> initially yields an adsorbed hydroxyl radical MO<sub>n</sub>OH• (physisorbed active oxygen), which can be further oxidized to MO<sub>n+1</sub> (chemisorbed active oxygen) at noble metal oxides, such as Ti/IrO<sub>2</sub>, Ti/RuO<sub>2</sub>, and PtO<sub>x</sub>. The MO<sub>n+1</sub> can initiate oxidation of a substrate by a two electron, one oxygen atom transfer mechanism. In the case of ammonia, this can form H<sub>3</sub>N<sup>+</sup>-O<sup>-</sup>, tautomeric to NH<sub>2</sub>OH; however, at anodes where MO<sub>n</sub>OH• cannot be oxidized further, such as PbO<sub>2</sub>, Ti/SnO<sub>2</sub>, and BDD, the anode acts as a source of hydroxyl species in its reactions with external substrates (including ammonia). Nevertheless, N<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub> may be formed from ammonia electrochemical oxidation on BDD in basic solution, and •OH might react with NH<sub>3</sub> to form NH<sub>2</sub>•<sub>ad</sub> (Eq. (16)), although the usual mechanism for oxidation of an extrinsic substrate at BDD is not yet clear (Bunce and Bejan, 2011).

The NH<sub>4</sub><sup>+</sup> in the neutral or acid solution can also be partly decomposed to nitrogen by •OH (with a decomposition rate much lower than that in the basic condition), not by a direct electrode reaction (Kim *et al.*, 2005).

The nitrite and nitrate could be reduced on cathode via the following reactions (Pérez *et al.*, 2012), which should also participate in the variation in NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, and NO<sub>3</sub><sup>-</sup>-N concentrations shown in Fig. 5(a).



The small nitrite concentration detected in our experiments was related to its almost instantaneous oxidation by OCl<sup>-</sup> in the presence of chloride during electrolysis (Pérez *et al.*, 2012).

On the other hand, the concentration of COD decreased from 6266 to 397 mg L<sup>-1</sup> over time in wastewater electrolysis

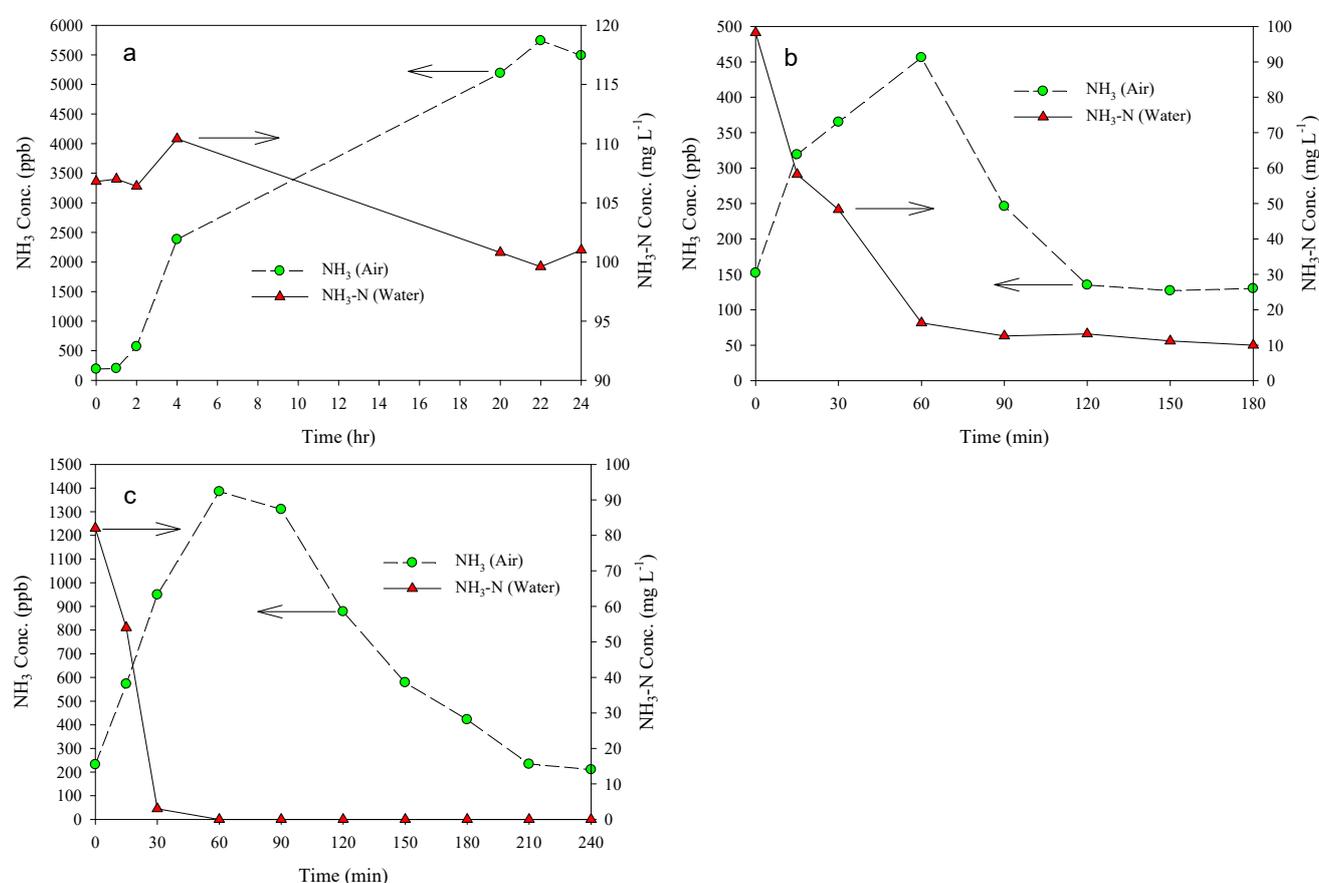
(Fig. 5(b)) (pseudo first order rate constant of COD removal  $k_{\text{COD}} = 1.21 \times 10^{-4} \text{ s}^{-1}$  in Table 1). The electro-generated  $\bullet\text{OH}$  was principally responsible for the degradation and mineralization of COD (Li and Liu, 2009; Sirés et al., 2014; Radjenovic et al., 2015; Moreira et al., 2017). Moreover, the solution pH also decreased from 7.86 to 4.68 with time at  $t \leq 180$  min but it began to rise for the electrolysis after 180 min (Fig. 5(b)). The reactions 4–9 and 13–17 may cause the variation of pH in solution; furthermore, the electrochemical reactions for the evolution of oxygen on anode and that of hydrogen on cathode also involve in the pH change in solution. It was reported that the electrochemical production of  $\bullet\text{OH}$  were not favored in solution at  $\text{pH} > 9$  [25].  $\text{Cl}^-$  may react with  $\bullet\text{OH}$  to generate  $\text{OCl}^-$ , which can be further oxidized by  $\bullet\text{OH}$  to form  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$  stepwise (Kapařka et al., 2010).

### Effect of Anode Material on $\text{NH}_3$ and Nitrogen Oxides Concentration Variations in the Air

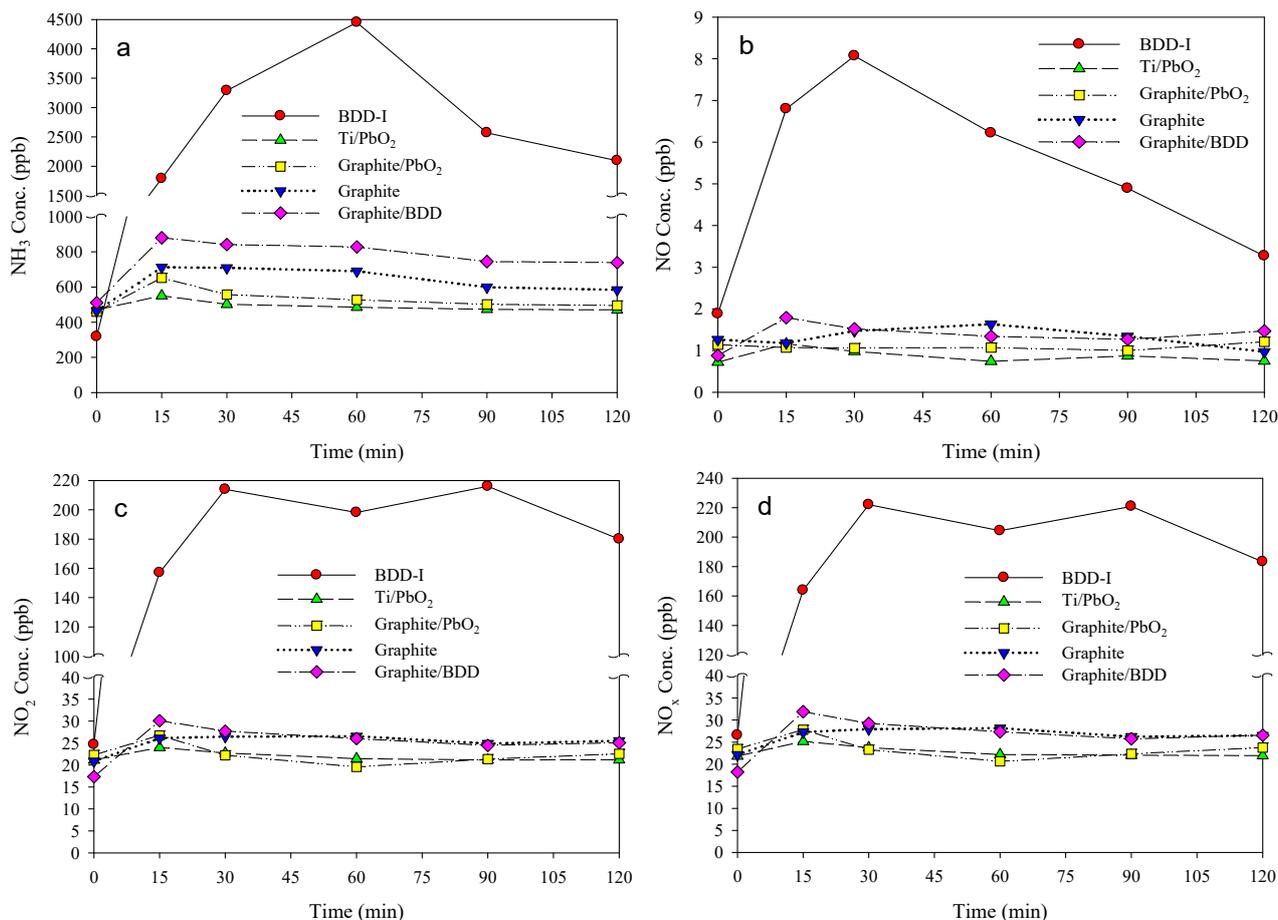
Fig. 6(a) shows the increase in air  $\text{NH}_3$  concentration over time for the non-electrolyzed swine wastewater with an initial  $\text{NH}_3\text{-N}$  concentration of  $107 \text{ mg L}^{-1}$ , similar to the trend depicted in Fig. 4(a). However, the air  $\text{NH}_3$  concentration was greater in Fig. 4(a) than in Fig. 6(a), because the initial  $\text{NH}_3\text{-N}$  concentration in wastewater was higher for the former than for the latter. The electrolysis of swine wastewater

(initial  $\text{NH}_3\text{-N}$  concentration =  $98.2 \text{ mg L}^{-1}$ ) using a  $\text{Ti/PbO}_2$  anode exhibited an increase in air  $\text{NH}_3$  concentration at  $t \leq 60$  min and then decreased at  $t > 60$  min (Fig. 6(b)), while the  $\text{NH}_3\text{-N}$  concentration in wastewater decreased over time, also similar to the tendency shown in Fig. 4(a). This trend was also observed when replacing  $\text{Ti/PbO}_2$  with BDD-I as the anode for the electrolysis of wine wastewater with an initial  $\text{NH}_3\text{-N}$  concentration of  $82.0 \text{ mg L}^{-1}$  (Fig. 6(c)). However, the  $\text{NH}_3\text{-N}$  concentration reached ND at 60 min for using the BDD-I anode, but the  $\text{NH}_3\text{-N}$  concentration decreased smaller after 60 min and was only close to  $10 \text{ mg L}^{-1}$  for using the  $\text{Ti/PbO}_2$  one. The removal rate of  $\text{NH}_3\text{-N}$  was faster using the BDD-I than using the  $\text{Ti/PbO}_2$  ( $k_{\text{NH}_3\text{-N}} = 4.83 \times 10^{-4}$  and  $4.63 \times 10^{-4} \text{ s}^{-1}$ , respectively) (Table 1); hence, the increase in air  $\text{NH}_3$  concentration was faster when using the BDD-I.

More anodes were tested to further explore the variations of air  $\text{NH}_3$  and nitrogen oxides concentrations during the electrolysis of swine wastewater. When using BDD-I as the anode, the air  $\text{NH}_3$  concentration increased with increase in electrolysis time, reached a maximum (4450 ppb) at 60 min, and then decreased over time (Fig. 7(a)). It was noticed that the air  $\text{NH}_3$  concentrations for using different anodes in wastewater electrolysis followed the order BDD-I (Nb/BDD)  $\gg$  graphite/BDD  $>$  graphite  $>$  graphite/ $\text{PbO}_2 \approx$   $\text{Ti/PbO}_2$  (Fig. 7(a)). Therefore, using BDD anodes resulted



**Fig. 6.** Air  $\text{NH}_3$  and wastewater  $\text{NH}_3\text{-N}$  concentration variations over time for the (a) wastewater without and (b) with electrolysis on  $\text{Ti/PbO}_2$  (Batch II-01), and (c) BDD-I (Batch II-02) (laboratory A).



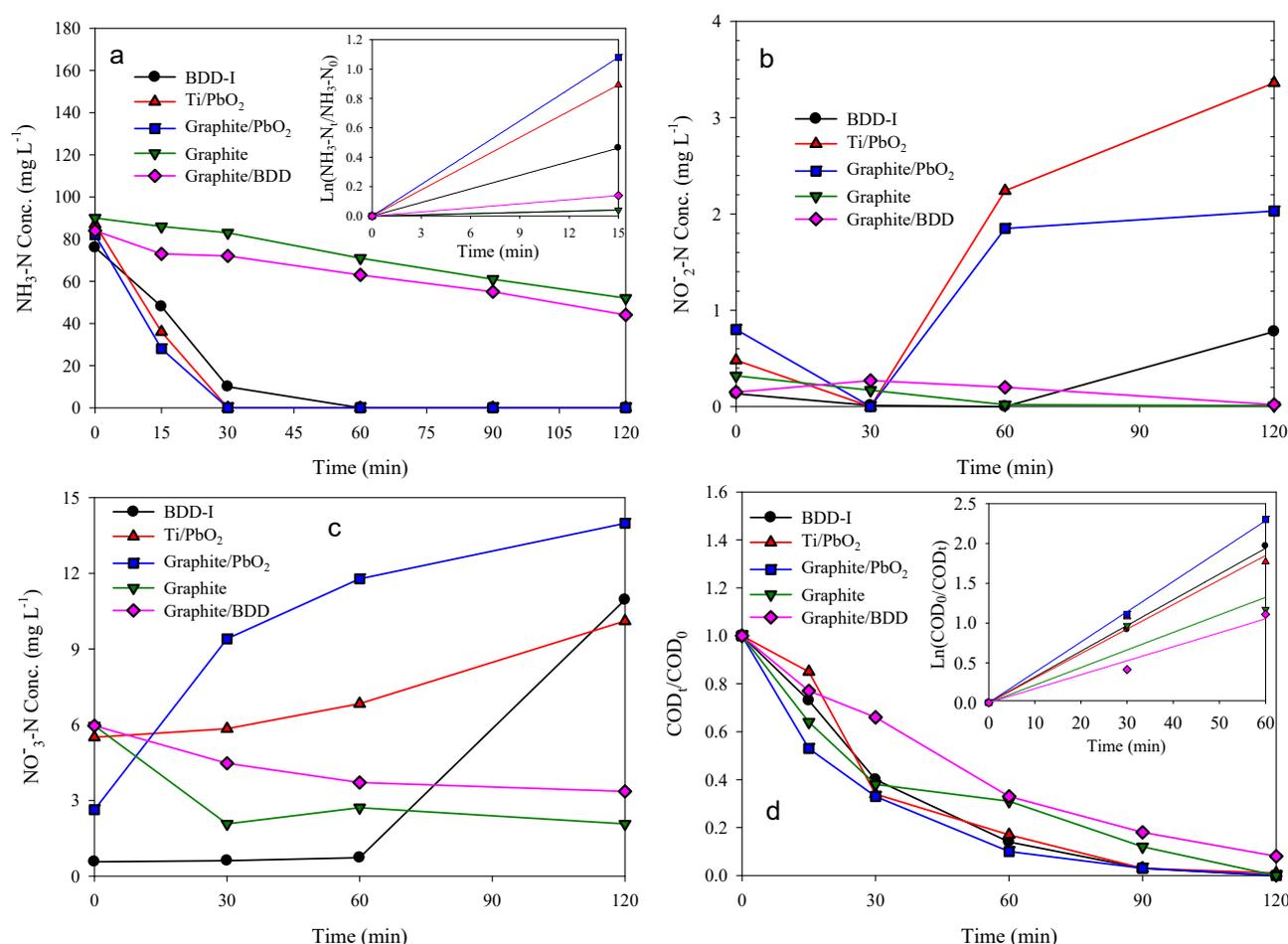
**Fig. 7.** Concentration variations in (a) NH<sub>3</sub>, (b) NO, (c) NO<sub>2</sub>, and (d) NO<sub>x</sub> over time in the air (Batch II-1 to Batch II-5, laboratory A).

in more release of NH<sub>3</sub> from wastewater into the air than using PbO<sub>2</sub> or graphite, regardless of the difference in electrode substrate material. Similarly, the BDD-I anode still exhibited a significantly greater release of NO (maximum = 8.1 ppb) from wastewater into the air than the other tested anodes (Fig. 7(b)). However, the air NH<sub>3</sub> concentrations for using graphite/BDD and graphite anodes were similar, and this tendency was also true for using graphite/PbO<sub>2</sub> ≈ Ti/PbO<sub>2</sub> ones. Like the trend of NO release from wastewater into the air, the air NO<sub>2</sub> concentrations for using these anodes were in the order BDD-I (Nb/BDD) (maximum = 216 ppb) >> graphite/BDD ≈ graphite > graphite/PbO<sub>2</sub> ≈ Ti/PbO<sub>2</sub> (Fig. 7(c)). Consequently, this trend was also true for the air NO<sub>x</sub> concentrations (BDD-I, maximum = 222 ppb) when using these anodes. The significant deviation in air NO<sub>x</sub> concentration resulted from using BDD-I (Nb/BDD) and graphite/BDD is probably attributed to the BDD crystalline structure was significantly better for the former than for the latter, and the graphite/BDD should significantly had more graphite structure than the BDD-I. Further study on electrode surface analysis is necessary to verify this point. Accordingly, NO<sub>x</sub> formation was more favorable on BDD than on PbO<sub>2</sub> or graphite. More study is necessary to explore the reaction mechanisms related to this issue (see more discussion in the next section).

#### **Effect of Anode Material on NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, and COD Concentration Variations in the Wastewater**

The performance of NH<sub>3</sub>-N degradation in wastewater for using the five tested anodes was in the order graphite/PbO<sub>2</sub> ≈ Ti/PbO<sub>2</sub> > BDD-I >> graphite/BDD > graphite (Fig. 8(a)), consistent with their pseudo first order rate constants of NH<sub>3</sub>-N removal ( $k_{\text{NH}_3\text{-N}} = 2.98 \times 10^{-4} \text{--} 6.35 \times 10^{-4} \text{ s}^{-1}$ ) (Table 1). This result is similar to another study which used swine wastewater with comparable NH<sub>3</sub>-N and higher COD concentrations (Huang *et al.*, 2019). The better removal rate of NH<sub>3</sub>-N on PbO<sub>2</sub> than on BDD and graphite in wastewater was associated with the inherently different nature in electrode material and the mechanisms for ammonia removal. The difference in initial NH<sub>3</sub>-N concentration (76.3–90.0 mg L<sup>-1</sup>) was small (Table 1), so its influence on the NH<sub>3</sub>-N removal should be minor in comparison to that of anode material.

As discussed earlier, the dominant ammonia species is NH<sub>4</sub><sup>+</sup> in neutral or acidic aqueous solution, which is not favored for the direct (non-mediated) oxidation of ammonia on anode (Pérez *et al.*, 2012), while NH<sub>3</sub> can be directly oxidized on BDD in basic solution (Kapařka *et al.*, 2010), and both NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> can be oxidized by •OH (Kim *et al.*, 2005; Bunce and Bejan, 2011). The oxidation rate of ammonia was also slow by the •OH generated from using H<sub>2</sub>O<sub>2</sub> plus UV irradiation (Huang *et al.*, 2008). However, for the swine



**Fig. 8.** Concentration variations in (a) NH<sub>3</sub>-N, (b) NO<sub>2</sub><sup>-</sup>-N, (c) NO<sub>3</sub><sup>-</sup>-N, and (d) COD<sub>t</sub>/COD<sub>0</sub> over time in wastewater (Batch II-1 to Batch II-5, laboratory A).

wastewater with the addition of 0.05 M NaCl in this study, the electro-generated active chlorine was more useful for mediated oxidation of ammonia than electro-produced •OH (Kapařka *et al.*, 2010; Pérez *et al.*, 2012). On the other hand, the BDD or graphite anode exhibited less formation of nitrite (Fig. 8(b)) or nitrate (Fig. 8(c)) than the PbO<sub>2</sub> one during the electrolysis of wastewater, also supporting that the electro-generated active chlorine dominated for the ammonia removal in wastewater, although the Ti cathode was also responsible for the variations of nitrite and nitrate concentrations.

Fig. 8(d) shows that the graphite/BDD and graphite anodes exhibited worse performance in COD removal ( $k_{\text{COD}} = 4.50 \times 10^{-5}$ – $1.55 \times 10^{-4} \text{ s}^{-1}$ ) than the other tested anodes ( $k_{\text{COD}} = 5.13 \times 10^{-5}$ – $1.19 \times 10^{-3} \text{ s}^{-1}$ ) (Table 1). This phenomenon is associated with the fact that the performance in electrochemical production of •OH in water solution is better on non-active electrodes (e.g., BDD and PbO<sub>2</sub>) than on active electrodes (e.g., graphite and Pt); moreover, the electro-generated •OH is powerful for the degradation and mineralization of organic pollutants in solution (Comninellis, 1994; Sirés *et al.*, 2014; Radjenovic *et al.*, 2015; Moreira *et al.*, 2017). According to Table 1, the initial COD concentration also affected the COD removal in wastewater. For example, the initial COD concentration in Batch I wastewater (6266 mg L<sup>-1</sup>) was

significantly higher than that in Batch II-1 (542 mg L<sup>-1</sup>), so the former had a smaller  $k_{\text{COD}}$  ( $1.21 \times 10^{-4} \text{ s}^{-1}$ ) than the latter ( $5.13 \times 10^{-4} \text{ s}^{-1}$ ) when using the same BDD-I anode. In addition to anode material, the initial concentration of COD or NH<sub>3</sub>-N also influenced its specific energy consumption in electrolytic removal ( $E_{\text{SP-C}}$  and  $E_{\text{SP-N}}$ , respectively). For comparison and consistency, the NH<sub>3</sub>-N and COD reached ND at 0.5 (Fig. 8(a)) and 2 hrs (Fig. 8(d)), respectively, so the data of 0.5-hr  $E_{\text{SP-N}}$  and 2-hr  $E_{\text{SP-C}}$  are provided in Table 1. The  $E_{\text{SP-C}}$  (0.052–0.853 kWh g-COD<sup>-1</sup>) or  $E_{\text{SP-N}}$  (0.316–6.703 kWh g-NH<sub>3</sub>-N<sup>-1</sup>) was lower as its initial concentration was higher. Therefore, the  $E_{\text{SP-C}}$  (0.052 kWh g-COD<sup>-1</sup>) and  $E_{\text{SP-N}}$  (0.316 kWh g-NH<sub>3</sub>-N<sup>-1</sup>) of this study for BDD-I were lower than those in another our study (0.323 kWh g-COD<sup>-1</sup> and 1.398 kWh g-NH<sub>3</sub>-N<sup>-1</sup>, respectively) which had lower initial COD and NH<sub>3</sub>-N concentrations (1025 and 86 mg L<sup>-1</sup>), respectively (Huang *et al.*, 2019). According to mass balance and using 1 L (10 cm × 10 cm × 10 cm) for the space volume above the wastewater, the total nitrogen mass (the mass of NH<sub>3</sub>-N and NO<sub>x</sub>-N in air plus that of NH<sub>3</sub>-N, NO<sub>2</sub><sup>-</sup>-N, and NO<sub>3</sub><sup>-</sup>-N in wastewater) at 0-hr deducts that at 2-hr is denoted as  $\Delta N_{\text{T}}$  and the data of  $\Delta N_{\text{T}}$  for different runs are also given in Table 1. The  $\Delta N_{\text{T}}$  value of Batch I wastewater was 89.8 mg, significantly greater those of Batch II wastewater

(9.97–17.4 mg), because the former had significantly higher ammonia concentration than the latter. The  $\Delta N_T$  should be present as the other forms of nitrogen compounds (e.g.,  $N_2$  and  $N_2O$ ), and the change in organic nitrogen concentration in the wastewater should also involve in the change of  $\Delta N_T$ .

## CONCLUSIONS

In this study, the  $NH_3$  concentration in the air right above the swine wastewater without electrolysis was found to increase over time and this increase of air  $NH_3$  concentration was greater when the wastewater  $NH_3-N$  concentration was higher. During the electrolysis of this swine wastewater using each of five tested anodes, the air  $NH_3$  concentrations, increasing to a maximum and then decreasing over time, were smaller than those without electrolysis, mainly because the decrease in driving force for ammonia volatilization resulted from the decrease of wastewater  $NH_3-N$  concentration over time. The  $NO$  concentration in the air was greater for the wastewater without electrolysis than for that with electrolysis but an opposite tendency was observed for  $NO_2$  in the air, while their corresponding  $NO_x$  concentrations were similar at most of sampling intervals.

Both anode material and initial pollutant concentration influenced the release of  $NH_3$  and nitrogen oxides from wastewater into the air and the variations in  $NH_3-N$ ,  $NO_2-N$ ,  $NO_3-N$ , and COD concentrations in the wastewater. The air  $NH_3$  concentrations for using different anodes in wastewater electrolysis followed the order BDD-I (Nb/BDD)  $\gg$  graphite/BDD  $>$  graphite  $>$  graphite/ $PbO_2 \approx Ti/PbO_2$ , while for air  $NO$ ,  $NO_2$ , or  $NO_x$  concentrations the order slightly shifted to: Nb/BDD  $\gg$  graphite/BDD  $\approx$  graphite  $>$  graphite/ $PbO_2 \approx Ti/PbO_2$ . The graphite/BDD and graphite anodes exhibited worse performance in  $NH_3-N$  ( $k_{NH_3-N} = 2.98 \times 10^{-4}$ – $6.35 \times 10^{-4} s^{-1}$ ) or COD electro-degradation ( $k_{COD} = 4.50 \times 10^{-5}$ – $1.19 \times 10^{-3} s^{-1}$ ) than the other tested ones, but they exhibited less formation of nitrite or nitrate than the  $PbO_2$  anodes. The specific energy consumption of  $NH_3-N$  or COD was lower as its initial concentration was higher.

## ACKNOWLEDGEMENT

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