

ELECTRO-OXIDATION AS AN ALTERNATIVE IN THE REMOVAL OF AMMONIA FROM SWINE WASTEWATER PRETREATED BY ELECTROCOAGULATION

Mores, R.^{*1}; Kunz, A.^{2,3}; Chini, A.³; Steffens, J.¹; Dallago, R. M.^{4,1}

¹Erechim, Erechim, RS – Brazil, rubiamores@yahoo.com.br

²Embrapa Suínos e Aves, Concórdia, SC - Brazil

³UNIOESTE, Cascavel, PR - Brazil

RESUMO: O presente estudo trata da aplicação da eletro-oxidação como uma alternativa de remoção da amônia que permanece no efluente da suinocultura pré-tratada por eletrocoagulação. O efluente utilizado nos testes de eletro-oxidação foi gerado pelo sistema de eletrocoagulação em fluxo contínuo, utilizando eletrodos de ferro. O reator de eletro-oxidação foi em sistema descontínuo utilizando eletrodos DSA[®] Ti/Ru₂. Um planejamento fatorial 2² foi utilizado para avaliar os efeitos da densidade de corrente (28-50 mA.cm⁻²) e a concentração de NaCl (0 a 10 g.L⁻¹) no processo de remoção da amônia e a produção de nitrato e nitrito. A condição de 39 mA.cm⁻² e a concentração de 5 g.L⁻¹ de NaCl removeu 1,435 mg L⁻¹ (76%) de amônia e gerou 61 mg L⁻¹ de nitrato em um tempo de operação de 6 horas. O consumo de energia nesta melhor condição foi de 150 kWh.L⁻¹.

Palavras-chave: planejamento fatorial, densidade de corrente, eletroquímica.

ABSTRACT: The present study addresses the application of electro-oxidation as an alternative to removal of ammonia that remains in swine effluent pre-treated by electrocoagulation. The effluent used in the electro-oxidation tests was generated in a continuous flow electrocoagulation system using iron electrodes. The electro-oxidation reactor was in a batch system and Ti/Ru₂ DSA[®] electrodes. A 2² factorial design was used to evaluate the effects of current density (28-50 mA.cm⁻²) and concentration of NaCl (0 to 10 g.L⁻¹) in the process of removal of ammonia and production of nitrate and nitrite. The condition of 39 mA.cm⁻² and concentration of 5 g.L⁻¹ NaCl removed 1435 mg.L⁻¹ (76%) ammonia and generated 61 mg.L⁻¹ nitrate in an operating time of 6 hours. The energy consumption in this best condition was 150 kWh.L⁻¹.

Keywords: Factorial design, current density, electrochemical

INTRODUCTION

Among the biological processes, anaerobic digestion is predominantly applied as an alternative to minimize the contamination of soil, water and air by the swine wastewater, for being a simple and convenient method of stabilization of organic matter and generation of biogas. However, the anaerobic treatment does not provide a solution for the removal of ammonia, this system increases the concentration of ammonia dissolved due to degradation of organic matter containing nitrogen (both soluble and suspended), which after its digestion releases NH₃ into wastewater (Lahav et al., 2013).

Recent studies show that electrocoagulation is an alternative in the removal of turbidity, phosphorus, total organic carbon using metals such as Al and Fe as electrode material (Mores et al., 2016 a,b). However, these electrode materials are not capable of carrying out the oxidation of ammonia, so the use of the electro-oxidation system is an electrochemical alternative of oxidation of ammonia (Mahvi et al., 2011).

During electro-oxidation, two oxidation mechanisms can occur: direct anodic oxidation and indirect oxidation (Anglada et al., 2009). Direct anodic oxidation occurs at the anode surface and its transformation reactions of ammonia into other forms by direct oxidation of nitrogen during the electrochemical process (He et al., 2015). The indirect oxidation occurs via a mediator oxidizing agent electrochemically generated to effect oxidation (Anglada et al., 2009). Free chlorine is a strong oxidizing agent that reacts with many compounds present in the wastewater (Zhenhai et al., 2011; Kim et al., 2005).

The present study evaluated the process of ammonia electro-oxidation as a wastewater ammonia removal alternative of swine effluent, pre-treated by electrocoagulation, evaluating the variables current density and concentration of sodium chloride.

MATERIAL AND METHODS

Swine wastewater: Samples was collected from the output of the upflow anaerobic sludge blanket (UASB), the swine manure treatment system was located at Embrapa Swine and Poultry, Concordia, Santa Catarina, Brazil and pretreated an electrocoagulation reactor in continuous flow (Mores, 2016b).

Experimental procedure

Reactor electro-oxidation: The experiments were performed in a cylindrical shape batch reactor with working volume of 1L. The system was equipped with a magnetic stirrer, in order to maintain the system homogeneous. The current density applied in the reactor was controlled by DC power supply FA-3005 Instrutherm. The Ti/Ru₂ DSA® anode and the cathode (130 mm x 70 mm) were provided by De Nora Brazil. Electrodes were installed vertically with 2 cm distance between electrodes. Samples were collected at 0, 2, 4 and 6 hours, to analysis the ammonia, nitrate, nitrite and pH.

Analytical techniques: The concentrations of ammonia, nitrite and nitrate were analyzed by flow injection analysis system (FIA lab 2500 Bellevue, WA, USA) equipped with an auto sampler following the equipment manufacturer recommendations and according to the official methods APHA 4500-NH₃ H nitrogen (ammonia), 4500-Nitrite nitrogen (Nitrite) and APHA 4500-Nitrate nitrogen (Nitrate) described by the American Public Health Association (APHA, 2012). The pH was directly determined using a glass combined electrode connected to a pH meter, Marconi PA200. The conductivity was determined by direct measurement of conductivity Hanna HI 255.

RESULTS AND DISCUSSION

The EC presented removal efficiencies only 1% of ammonia. Thus, additional techniques are needed to improve the quality of the wastewater, and therefore electro-oxidation is the alternative proposed in this work. Table 1 shows the matrix of the 2² factorial design where the independent variables were current density (CD) and the concentration of NaCl and the results of the dependent variables (responses) final ammonium concentration, nitrate and nitrite and energy consumption values are presented.

The relative significance of the main effects and their interactions are shown on the Pareto diagram (Figure 1). The values that exceed a reference line, that is, those that correspond to 95% confidence interval, are significant values. According to Figure 1, the current density (CD) variable exerted effect on the ammonia removal process and in nitrate generation process, while the variable NaCl concentration and the interaction between the CD x NaCl represent a significant effect on the ammonia removal only.

The condition of 39 mA.cm⁻² and concentration of 5 g.L⁻¹ NaCl (Table 1) showed the best removal of ammonia with about 76% and also increased production of nitrate, with approximately 61 mg.L⁻¹. In relation to nitrite production the amounts were insignificant. Figure 2 shows the evolution of the removal of ammonia and nitrate production for different current densities (28 to 39 mA.cm⁻²) and different doses of sodium chloride (0 to 10 g.L⁻¹) as a function of operating time. Regarding the power consumption, this increased with the increase in CD from 28 to 39 mA.cm⁻². The power consumption values ranged from 116 to 155 kWh.L⁻¹.

The ammonia removal occurred steadily for assays with 5 and 10 g.L⁻¹ NaCl, whereas for the assays without NaCl, ammonia removal did not occur. The concentration of nitrate increased from 0 to 63 mg.L⁻¹ with the operating time, and the largest increase was the assay with the CD of 39 mA.cm⁻² and NaCl concentration of 5g.L⁻¹. The ammonia present in the solution is converted to different forms of nitrogen, as represented in Equations 1-6, which shows the set of reactions that occur in the electrochemical process of ammonia removal (Kim et al., 2006).





Overall reaction:



In the assay without NaCl, ammonia removal did not occur, this indicates that the Ti/Ru2 DSA® electrodes are not suited for direct electrochemical oxidation, due to the dependence of the oxidation rate of ammonia on the catalytic activity of the anode (Chen et al., 2011). The assays with a concentration of 5 g.L⁻¹ and 10 g.L⁻¹ resulted in the removal of 76% and 67%, respectively.

These results indicate that removal of ammonia by electro-oxidation process takes place through the indirect oxidation mechanism and the NaCl concentration plays a vital role during the electrochemical oxidation of ammonia using the Ti/Ru2 DSA® electrodes. In the indirect oxidation mechanism, the generated molecular chlorine is hydrolyzed to form hypochlorous acid (HOCl) as shown in Equation 4 which is sequentially changed to the hypochlorous ion (OCl⁻), this reaction is pH dependent. The hypochlorous acid and hypochlorous ion can decompose ammonia to nitrogen gas (Equations 3-7) due to its high oxidative potential (Gendel et al., 2012; Zhenhai et al., 2011; Kim et al., 2005).

The pH decreases to approximately 3.85 after 6 hours treatment, only for the assays with NaCl concentrations 5 and 10 g.L⁻¹ independent of the current density. The change of basic pH to acidic pH states that the ammonia removal reaction is the indirect oxidation (Eq. 6 and 7). The low pH allows to control the production of nitrate during the process of electro-oxidation of ammonia (Yao et al., 2016), this control can be seen by comparing the assay of CD 28 mA.cm⁻² and NaCl concentration of 0 g.L⁻¹ where the final pH was 7.7 and during the oxidation of ammonia under this condition, nitrate production was 32 mg.L⁻¹ compared to CD 28 mA.cm⁻² and NaCl 10g.L⁻¹, where the final pH was 3.91, producing 26 mg.L⁻¹ nitrate.

The current density (CD) determines the ammonia removal rate in the electro-oxidation process by speeding up the oxidation reaction (Diaz et al., 2011). The ammonia removal and nitrate production was influenced by the CD increase from 28 mA.cm⁻² to 39 mA.cm⁻², due to increased electrochemical generation of chlorine, there was an increase in the production of hypochlorite acid (Eq. 1-9) which is responsible for the oxidation and ammonia removal (Deng & Englehardt, 2007).

However, when increasing the CD to 50 mA.cm⁻², heating of the system occurred (51°C) in only 1 h 33 min. The same happened to the two assays performed in this CD, regardless of the NaCl concentration (Conductivity test 2 - 19.21mS and Conductivity test 4 - 25.02mS). This heating occurred due to high conductivity (11.5 mS), characteristic of wastewater swine. In this context, in the present study, CD increase negatively affected the process of electro-oxidation.

CONCLUSION

The present study proposed electro-oxidation as the ammonia oxidation alternative from the electrocoagulation effluent of wastewater from swine farming and the system obtained a removal of 76% during an operating time of 6 hours. The factorial design showed that the extreme conditions of current density and NaCl concentration do not favor the process of electro-oxidation and that with these variables, the current density ranges should be 28-39 mA.cm⁻² and NaCl concentration next to 5 g.L⁻¹. The process of electro-oxidation proved to be a good alternative to the removal of ammonia from swine wastewater pre-treated by electrocoagulation.

ACKNOWLEDGEMENTS

The authors acknowledge URI-Erechim, CAPES, Embrapa Swine and Poultry, CNPq and De Nora of Brazil for donation of the Ti/Ru2 DSA® electrode.

REFERENCES

- AMERICAN PUBLIC HEALTH ASSOCIATION. Standard Methods for the Examination of Water and Wastewaters. 22nd ed. 2012. Nitrogen (Nitrite) (APHA 4500-Nitrite), 4-120.
- ANGLADA, A.; URTIAGA, A.; ORTIZ, I. Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, *Journal of Chemical Technology and Biotechnology*. v. 84, p.1747–1755, 2009.
- CHEN, J.; SHI, H.; LU, J. 2007. Electrochemical treatment of ammonia in wastewater by RuO₂–IrO₂–TiO₂/Ti electrodes. *Journal of Applied Electrochemistry*, v. 37, p. 1137–1144, 2011.
- DENG, Y.; ENGLEHARDT, J.D. Electrochemical Oxidation for Landfill Leachate Treatment. *Waste Management*. v. 27, p. 380-388, 2007.
- GENDEL, Y.; LAHAV, O. Revealing the mechanism of indirect ammonia electrooxidation, *Electrochimica Acta*. v. 63, p. 209– 219, 2012.
- KIM, K.; KIM, Y.; KIM, I.; PARK, G.; LEE, E. Electrochemical conversion characteristics of ammonia to nitrogen. *Water Research*, v. 40, p. 1431 – 1441, 2006.
- KIM, K.W.; KIM, Y.J.; KIM, I.T.; PARK, G.I.; LEE, E.H. The electrolytic decomposition mechanism of ammonia to nitrogen at an IrO₂ anode. *Electrochimica Acta*, v. 50, p. 4356-4364, 2005.
- LAHAV, O.; SCHWARTZ, Y.; NATIV, P.; GENDEL, Y. Sustainable removal of ammonia from anaerobic-lagoon swine waste effluents using an electrochemically-regenerated ion exchange process. *Chemical Engineering Journal*, v. 218, p. 214–222, 2013.
- MAHVI, A.H.; EBRAHIMI, S.J.A.; MESDAGHINIA, A.; GHARIBI, H.; SOWLAT, M.H. Performance evaluation of a continuous bipolar electrocoagulation/electrooxidation–electroflotation (ECEO–EF) reactor designed for simultaneous removal of ammonia and phosphate from wastewater effluent. *Journal of Hazardous Materials*, v. 192, p. 1267–1274, 2011.
- MORES, R.; KUNZ, A.; STEFFENS, J.; DALLAGO, R.M.; BENAZZI, T. L.; , AMARAL, A. C. DO. Swine manure digestate treatment using electrocoagulation. *Scientia agricola*, v.73, p. 439-443, 2016a.
- MORES, R.; TREICHEL, H.; ZAKRZEWSKI, C.A.; KUNZ, A.; STEFFENS, J.; DALLAGO, R.M. Remove of phosphorous and turbidity of swine wastewater using electrocoagulation under continuous flow. *Separation and Purification Technology*, v. 171, p. 112–117, 2016b.
- YAO, J.; ZHOU, M.; WEN, D.; XUE, Q.; WANG, J. Electrochemical conversion of ammonia to nitrogen in non-chlorinated aqueous solution by controlling pH value. *Journal of Electroanalytical Chemistry*, v. 776, p. 53–58, 2016.
- ZHENHAI, L.; SU, L.; WENQIAN, G.; CAIMEI, F. The kinetics for electrochemical removal of ammonia in coking wastewater. *Chinese Journal of Chemical Engineering*, v. 19, p. 570–574, 2011.

Table 1. 2² factorial design matrix with coded values (real) and the responses of the final ammonia concentration, nitrate and nitrite and energy consumption values.

Test	CD (mA.cm ⁻²)	NaCl (g)	Responses			
			Final concentration (mgN.L ⁻¹)			Energy consumption kWh.L ⁻¹
			Ammonia	Nitrate	Nitrite	
1	-1 (28)	-1 (0)	1857	32	2	116
*2	+1 (50)	-1 (0)	1991	0	0	0
3	-1 (28)	1 (10)	641	26	1	84
*4	+1 (50)	1 (10)	1944	0	0	0
5	0 (39)	0 (5)	437	60	1	155
6	0 (39)	0 (5)	425	63	0	145
7	0 (39)	0 (5)	458	59	0	151

* The system was shut down after 1 h and 33 min due to temperature increase (51 °C) and the emergence of the boiling process of the residual water present in the system was observed.

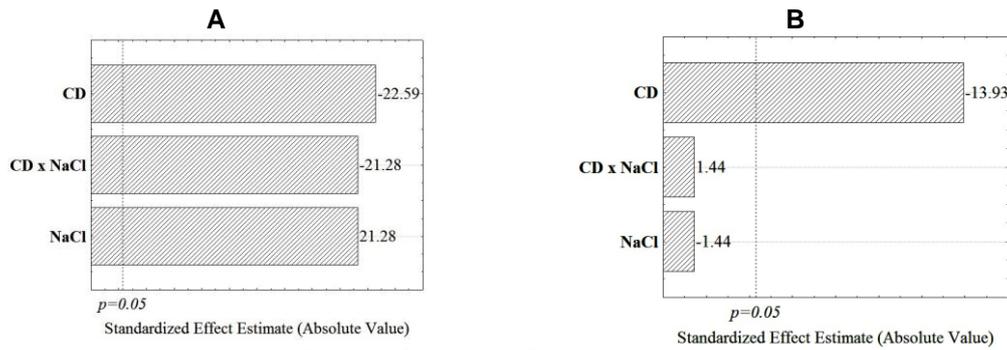


Figure 1. Pareto diagrams for the effects of CD and NaCl concentration for the removal of ammonia (A) and nitrate generation (B).

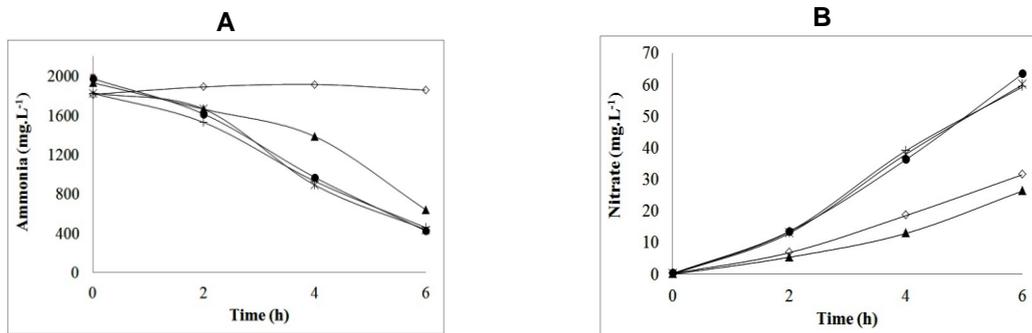


Figure 2. Evolution of ammonia concentration (a) and nitrate concentration (b) in the solution during electro-oxidation; where (◇) $28 \text{ mA.cm}^{-2} + 0 \text{ g.L}^{-1} \text{ NaCl}$, (▲) $28 \text{ mA.cm}^{-2} + 10 \text{ g.L}^{-1} \text{ NaCl}$ and (□, ●, -) $39 \text{ mA.cm}^{-2} + 5 \text{ g.L}^{-1} \text{ NaCl}$.