

ALKALINITY CHANGING DURING NITROGEN REMOVAL IN A MLE REACTOR AT HIGH TSS CONCENTRATION

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ABSTRACT: The current scenario requires wastewater treatment systems with high efficiency, easy operation and low cost. Several factors influence the choice of nitrogen removal through nitrification and denitrification, and these are not always well enlightened in the literature. In this sense, the aim of this study was to evaluate the effect of the increase in total suspended solids (TSS) concentration in the MLE system on the efficiency of nitrification/denitrification and the behavior of alkalinity through the process. For this purpose swine wastewater was used, which has undergone a solid liquid separation (SLS) performed with a brush-roller screen (2 mm mesh) followed by a settling unit. The nitrogen removal unit was composed of a MLE process, operated in three phases, according to different sedimentation times in the SLS process. The MLE system endured total suspends solids concentration higher than 14 g L⁻¹, reaching removal efficiency of 88.3% for nitrogen and 86.3 % for total organic carbon. Alkalinity consumption lower than the stoichiometry were verified for nitrification and denitrification. The nitrogen removal system presented high efficiencies in the removal of both carbon and nitrogen, however the consumption of alkalinity was lower than expected, being necessary further studies to elucidate this discrepancy.

Keywords: Denitrification, nitrification, settling, swine wastewater

INTRODUCTION

Nitrogen compounds can cause severe damage to the environment, such as oxygen depletion in water bodies, or eutrophication (HEWAWASAM et al., 2017). There are several sources of contamination, one of which is animal production. More specifically swine farming is one of the activities with the highest volume of effluents generation and with elevated concentration of this pollutant (CESTONARO DO AMARAL et al., 2016). The biological nitrogen removal, in particular nitrification and denitrification, performed in Modified Ludzack-Ettinger (MLE) system, is an interesting alternative to minimize the environmental impacts of these wastes (LIU et al., 2018).

The nitrification and denitrification occurs in specific conditions such as pH, dissolved oxygen, temperature, alkalinity, among others (ZHANG et al., 2014). Among these parameters, alkalinity is directly related to the nitrogen removal. Many residues that do not have enough natural alkalinity require an external source for the alkalinity requirement establishment (LI and IRVIN, 2007).

The requirement of alkalinity is calculated according to the quantity of bicarbonate required to neutralize the acidity generated in the nitrification. If denitrification is complete, there will be a compensation of 50% of the alkalinity consumed, due to the consumption of H^+ for denitrification process and consequently return of alkalinity to the system. Therefore, in the MLE system, for each gram of ammoniacal nitrogen supplied 3.57 g CaCO₃ L⁻¹ are needed. This relation is important for the maintenance of the pH in the system in values close to neutrality, so that it does not occur inhibition of the processes by other chemical forms (METCALF and EDDY, 2003).

In addition to these factors, pre-treatment of wastewater is an important step to have suitable conditions for the nitrogen removal. Conventionally, solid-liquid separation (SLS) is performed by means of flocculation, coagulation and sedimentation, with the use of chemical additives, which makes the treatment system more expensive (HJORTH et al., 2010).

Despite some studies dealing with the combination of SLS with nitrification and denitrification process, few is known about how much MLE system could withstand organic load increase by total suspended solids concentration. Also the combination of settling without chemical additives with the MLE system was not reported in the literature for swine effluents.



Therefore, the aim of this study was to evaluate the effect of TSS concentration increase in the MLE system on the efficiency on nitrification/denitrification process and the behavior of alkalinity in the system.

MATERIAL AND METHODS

For the development of this study, swine wastewater from experimental facilities of Embrapa Suínos e Aves (Concordia, Santa Catarina state, Brazil) was used (KUNZ et al., 2009). The samples were collected directly after the separation into static sieve of rotating brushes (2 mm mesh).

After the mechanical separation the effluent was submitted to solids separation in a conic settler (volume of 1 L) at retention times of 30 minutes (for phase I feeding), 10 minutes (for phase II feeding) and 5 minutes (for phase III feeding), aiming to increase total solids concentration in the effluent. Three separated aliquots (130 L) for each phase were collected and stored at 4 $^{\circ}$ C.

The nitrogen removal from the effluent resulting from solid-liquid separation as performed in a MLE system. The system was operated at a hydraulic retention time (HRT) of 4.6 days, of 1.5 mL min⁻¹ (Q_{in}), with a sludge recirculation rate of 1 Q_{in} and nitrate recirculation rate of 5.5 Q_{in} (BORTOLI, 2010). The solid retention time (SRT) was fixed at 25 days.

The system was monitored by physical-chemical analysis, performed in the Laboratory of Studies and Environmental Analyzes at Embrapa Suínos e Aves. The evaluated parameters were total ammoniacal nitrogen (TAN as NH_3-N), pH, total organic carbon (TOC), total solids (TS), total suspend solids and alkalinity according to methodology described by Rice et al. (2017).

RESULTS AND DISCUSSION

The MLE system was operated for 52 days during phase I and II, and 61 days in phase III. The characteristics of effluent used in feeding each phase are presented in the table 1. The removal efficiency obtained for inorganic nitrogen species (TAN, NO₂-N and NO₃-N) was 91% in phase I and II and 88% in phase III. Results of MLE system effluent analysis showed TAN of 1.3 (\pm 1.5) mg L⁻¹ in phase I, 6.4 (\pm 2.8) mg L⁻¹ in phase II and 10.5 (\pm 4.9) mg L⁻¹ in phase III. Additionally the efficiency of TOC removal was 74% in phase I and 86 % in phases II and III. These removal efficiencies are related mainly to the carbon consumption by denitrification process, since the presence of organic matter and NOx (nitrite and nitrate) electrons acceptor favors the denitrifying bacteria growth (LIU et al., 2010).

The TOC addition in the system resulted in a TSS concentration increase in the reactors. In phase I, TSS in nitrifying reactor was 9.7 ± 0.9 g L⁻¹, 13.5 ± 1.4 g L⁻¹ in the phase II and 14.4 ± 2.1 g L⁻¹ in the phase III. The TSS in the denitrifying reactor in the phase I was 9.4 ± 0.32 g L⁻¹, 14.3 ± 1.9 g L⁻¹ in the phase II and 15.1 ± 0.8 g L⁻¹ in phase III. As a comparison, conventional activated sludge systems operate at concentrations of TSS around 4 to 6 g L⁻¹. (VON SPERLING, 2007). Despite the elevated TSS concentration in the system, the nitrogen removal was not impaired, which highlights the robustness of the employed MLE system.

The pH and temperature remained stable throughout all the experimental phases. The average pH was $8.15(\pm 0.23)$ in both reactors (nitrifying and denitrifying reactor) along the three experimental phases. These values do not cause inhibitory effects over the nitrogen removal processes studied (ZANG et al, 2014).

Although the pH in the three studied phases was high, loss of ammonia by volatilization was negligible. The calculated concentration of free ammonia (FA) was very low: 0.02 ± 0.01 mg L⁻¹ and 0.13 ± 0.03 mg L⁻¹ in nitrifying and denitrifying reactors respectively.

The effluent alkalinity used to fed MLE system changed according the different effluent characteristics collected for the different phases: $2907 \pm 225 \text{ mg L}^{-1}$, $5119 \pm 384 \text{ mg L}^{-1}$ and $3001 \pm 293 \text{ mg L}^{-1}$ in phases I, II and III, respectively (Figure 1). This variability of effluent characteristic is inherent to swine production systems (CESTONARO DO AMARAL et al., 2016).

The alkalinity consumption in the effluent was $34 \pm 12\%$ lower than the requirement calculated to nitrification and denitrification processes in the phase I and up to the fortieth day of phase II (Figure 1). From the fortieth day onwards, the system presented crowding depletion in dissolved oxygen due to high concentration of solids and consequently incomplete nitrification, although the total nitrogen removal has not being affected. Although the system consumed less alkalinity than the theoretical requirement to nitrification and denitrification the process remains stable with no reductions of nitrogen removal efficiencies.



One of the hypotheses that could justify this surplus of alkalinity in the process is that besides the alkalinity formed in the denitrification by the generation of hydroxide ions, a fraction could be formed by dissociation of carbon dioxide in bicarbonate ion. As a consequence, higher alkalinity is returning to the system (GERARDI et al., 2006).

Another hypothesis for the higher alkalinity concentration as expected according to the literature is that the alkalinity may has been supplemented by the solubilization of carbon dioxide formed due to organic matter degradation, in addition to the compensation caused by denitrification. Due to the alkaline pH, CO₂ chemical equilibrium is shifted to bicarbonate increasing the system alkalinity (Equation 1 and 2) (DUBLEN e STEINHAUSER, 2011; KUNZ e MUKHTAR, 2016).

$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_{3(aq)}$	(1)
$H_2CO_{3(aq)} \rightleftharpoons HCO_{3(aq)} + H^+_{(aq)}$	(2)

The high concentrations of solids could favor the incorporation of CO_2 into the solution instead of volatizing it to the atmosphere, this aspect could justify the fact that in this study the system had lower alkalinity consumption when compared to the theoretical values expected in nitrification and denitrification stoichiometry.

CONCLUSION

The MLE system fed with swine effluent subjected to a low cost SLS presented high efficiency in the nitrogen and carbon removal. It was verified that the alkalinity consumption in the system was lower than the calculated requirement. Authors believe that the dissolution of CO_2 and the chemical equilibria involved are responsible by this behavior. However further studies are needed to confirm this hypothesis.

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REFERENCES

BORTOLI, M. **Partida, operação e otimização de um sistema de nitrificação/desnitrificação visando a remoção de nitrogênio de efluente da suinocultura pelo processo Ludzack-Ettinger modificado**. 2010. 155 p. Dissertação (Mestrado em Engenharia Química) - Centro tecnológico, Universidade Federal de Santa Catarina, Florianópolis, 2010.

BUHA, D. M. E ATALIA, K. R. E SHAH, N. K. Continuous process study on simultaneous nitrification– denitrification of high ammoniacal nitrogen load wastewater in aerobic–anoxic sequencing bioreactors. **International journal of environmental science and technology**, v. 14, n. 11, p. 2451–2458, 2017.

CESTONARO DO AMARAL, A., et al. Influence of solid-liquid separation strategy on biogas yield from a stratified swine production system. **Journal of environmental management**, v. 168, p. 229–235, 2016.

DUBLEN, D; STEINHAUSER, A. **Biogas from waste and renewable resources**: an introduction. 2^a ed. Wiley-VCH Verlag GmbH & Co. KGa, 2011.

HEWAWASAM, C.; MATSUURA, N.; MAHARJAN, N.; et al. Oxygen transfer dynamics and nitrification in a novel rotational sponge reactor. **Biochem. Eng. J.**, v. 128, p.162–167, 2017.

HJORTH, M.; CHRISTENSEN, K. V.; CHRISTENSEN, M.L.; SOMMER, S.G. Solid-liquid separation of animal slurry in therory and practice. A review. **Agron. Sustain. Dev.**, v.30, p.153–180, 2010.

KUNZ, A.; MIELE, M.; STEINMETZ, R. L. R. Advanced swine manure treatment and utilization in Brazil. Bioresour Technol 100:5485–5489, 2009.

LI, B.; IRVIN, S. The comparison of alkalinity and ORP as indicators for nitrification and denitrification in a sequencing batch reactor (SBR). **Biochemical Engineering Journal**, v. 34, n. 3, p. 248-255, 2007.

LIU, F.; HU, X.; ZHAO, X.; ET AL. Rapid nitrification process upgrade coupled with succession of the microbial community in a full-scale municipal wastewater treatment plant (WWTP). **Bioresource Technology**, v. 249, p.1062–1065, 2018.



LIU, Y.; SHI, H.; XIA, L.; SHI, H.; SHEN, T.; WANG, Z.; WANG, G.; WANG, Y. Study of operational conditions of simultaneous nitrification and denitrification in a Carrousel oxidation ditch for domestic wastewater treatment. **Bioresource Technology**, v. 101, n.3, p. 901-906, 2010.

RICE, E.W.; BAIRD, R.B.; EATON, A.D. (org.). **Standard methods for the examination of water and wastewater**. 23^a ed. Washington dc: american water works association and water environment federatio, 2017. KUNZ, A.; MUKHTAR, S. Hydrophobic membrane technology for ammonia extraction from wastewaters. **Engenharia agrícola**, v. 36, n. 2, p. 377–386, 2016.

METCALF, L.; EDDY, H. Wastewater engineering treatment and reuse. 5 ed. McGraw-Hill Education, 2003.

GERARDI, M.H. (org.). Wastewater bacteria. A john wiley & sons, inc, 2006.

VON SPERLING, M. Activated sludge and aerobic biofilm reactors. IWA publishing, 2007.

ZHANG, S., WANG, Y., HE, W., WU, M., XING, M., YANG, J., ET AL. Impacts of temperature and nitrifying community on nitrification kinetics in a moving-bed biofilm reactor treating polluted raw water. **Chem. Eng. J.**, v. 236, p. 242–250, 2014.

Table 1. Characteristics of effluent in each phase.

	TAN (mg _N L ⁻¹)	TOC mg L ⁻¹	TS (g L ⁻¹)
Phase I	831 (±139)	2023 (±378)	7.8 (±1.3)
Phase II	1386 (± 217)	3208 (±279)	12.55 (± 0.74)
Phase III	875 (±138)	3047 (±317)	18.45 (±1.83)



Figure 1. Alkalinity monitoring during the experimental phases of MLE system (nitrification and denitrification). (I, II and III in the figure corresponds to phases I, II and III respectively).