

Application of natural adsorbents to remove nutrients from swine facility effluent

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Abstract

Confined swine facilities create great environmental concern due to the generation of highly concentrated effluents. Technologies applied for the treatment of such residues were adapted from domestic wastewater treatment systems. However, as swine wastewater has an initial concentration which is much higher than ordinary wastewater, the quality standard established by Brazilian Legislation cannot be reached through usual treatment technologies, mainly for nutrients. This work evaluated the efficiency of a natural clinoptilolite-mordenite zeolite to remove nitrogen from synthetic swine effluent in pH = 5.0; 6.0 and 7.0.

It was demonstrated that in this pH range, there was no significant differences in the kinetic of adsorption for different pH levels. Additionally, an experiment was run using swine facilities wastewater previously treated in a compact unit. Results have shown that zeolite removed 89% of N-NH₃, 88% of potassium and 61% of phosphorus after 60 minutes.

Keywords: livestock wastewater, pollutant abatement, zeolite

Introduction

In Brazil, swine production is highly concentrated in the South of the country (Paraná, Santa Catarina and Rio Grande do Sul States). Although this region represents only 4.75% of the Brazilian territory, it is responsible for 43% of swine production. According to investigations conducted by Santa Catarina State Agricultural Research and Rural Extension Corporation - EPAGRI, in early the 1990s in west of Santa Catarina State, known as one of the Brazilian region with higher livestock density, about 92% of surface water was contaminated with manure (EPAGRI 1995). In spite of this, according to Shigaki et al (2006), between 1993 and 2003, the number of housed animals increased 33%, mainly in the South of Brazil. The intensification of livestock production is observed in the whole world as well as the problems caused by this kind of production model, most of them related to the surplus of nutrients in regions of high animal density.

The most common technology applied for swine manure treatment is the physical separation of the solid fraction (screens or gravitational) followed by anaerobic lagoons. However, Medri (1997) concluded that this kind of treatment usually requires hydraulic retention time of 100 days to remove about 90% of nutrients and organic content due to the high initial concentration of swine manure. Recently, the development of compact units allows a better control in the whole microbiological processes, and as demonstrated by Higarashi et al (2004) and Kunz (2006), it is possible to reach similar treatment performance in about 7 days.

The number of anaerobic digesters installed in swine operations has increased in Brazil since the signing of the Kyoto Protocol, which came into force on February 16, 2005. Liquid manure naturally produces methane through anaerobic digestion, but in the digesters these gases are stored and can be used as a source of energy or burned under controlled conditions, to convert methane into carbon dioxide. As methane has 21 times more greenhouse effect than carbon dioxide, it is possible to trade this conversion as carbon credit through Clean Development Mechanism (CDM) and get financial support to invest in effluent treatment.

All technologies mentioned (lagoon, anaerobic digester, compact treatment system) are very effective in reducing the organic content; however the remaining nutrients in the effluent still can pose as a threat to environment and human health.

The United States Environmental Protection Agency – USEPA considered diffuse sources of phosphorus the mainly responsible for the acceleration of eutrophication processes in surface water around the world (USEPA, 2004). Additionally, among these diffuse sources of nutrients, intensive animal agriculture is the one that has received the most research and public and regulatory attention (Sharpley, 2000).

Nitrate enrichment of drinking water sources is one of the current environmental issues associated with agriculture (Bockman et al, 1990). Ammonia from livestock effluents can be converted into nitrate in aerobic environments such as turbulent rivers. Ordinary water treatment does not eliminate nitrate from drinking water, and the human intake of this compound increases the risk of cancer. Nitrate itself is inert but it can be converted into nitrite by bacterial action and form carcinogenic compounds by nitrosation in the stomach (Alaburda and Nishihara, 1998).

Considering legal aspects, swine effluents resulting from efficient physical-chemical and biological treatment systems, usually present concentration of total phosphorus and total ammonia of 50-200 mg/L (Medri, 1997; Higarashi et al, 2004 and Kunz, 2006). These values are not in compliance with the Brazilian Legislation that requires concentrations of 20 mg/L of ammonia in effluents to be disposed in the environment (CONAMA, 2005).

Adsorption has been related as an efficient technology to remove nutrients and heavy metals from wastewater, mainly industrial effluents. Nevertheless, ion exchange and adsorbent resins usually applied to perform these treatments are still considered expensive to treat livestock effluents. On the other hand, there are some natural minerals such as zeolite and clay which have high adsorption capacity and can remove nutrients from effluents at reasonable costs.

Zeolites are described as aluminosilicate frameworks of SiO_4 and AlO_4 forming cage-like structures with high surface area and cation-exchange capacities of several equivalents per kilogram (Haggerly and Bowman, 1994). Some natural zeolites have high affinity with NH_4^+ and have been successfully employed as adsorbents in filters for treatment of industrial and domestic effluents.

This paper presents results from two batch experiments performed in bench scale in order to:

- (1) study the efficiency of zeolite to remove ammonia from synthetic swine effluents in the range of pH commonly found in field conditions (6.0 – 7.0) and evaluate if adsorption efficiency increases in acid media (pH 5.0) as described in previous work (Kithome et al, 1998);
- (2) study the performance of zeolite in the abatement of macronutrients (ammonia, phosphorus and potassium) from a real effluent collected in a compact biological treatment system installed in a swine facility.

These studies intend to assess the potential of using natural zeolite in adsorbents filters to remove nutrients from livestock wastewater.

Materials and methods

Influence of pH in N-NH₃ adsorption

Synthetic effluent (100 mg/L of N-NH₃) was prepared using deionised water (*Millipore*) and NH₄Cl (*Ecibra P.A.*). The pH was adjusted with acetate buffer in 5.0, 6.0 and 7.0 (Kithome et al, 1998).

The adsorbent used was the natural zeolite clinoptilolite-mordenite 70-85% (Figure 1) purchased from Celta Brasil - particle size = 0.6-1.3 mm, specific density; $d_{\text{specific}} = 2.1\text{-}2.24 \text{ g/cm}^3$ and surface area BET (Brunauer, Emmet e Teller method) = $38.05 \text{ m}^2/\text{g}$.

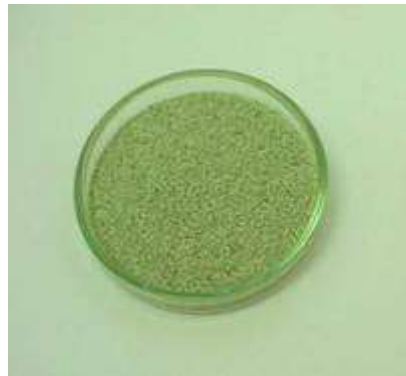


Figure 1. Sample of adsorbent mineral (zeolite) used in the experiments

The experiments were run in a batch process in laboratory. The adsorbent (5% - w/w) was added to 9 L of synthetic effluent under magnetic stirring. Samples of 10.0 mL were collected in triplicate from the supernatant in intervals from 0.5 to 30 minutes (0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 30 and 60 minutes) and N-NH_3 analysed by Kjeldahl micro-distillation according to official methodology (AOAC, 1994).

Macronutrients removal from swine facility effluent

Piggery waste manure from swine facilities of Embrapa Swine and Poultry (capacity of 4,000 heads) was used in this experiment. The compact unit installed to treat the manure is shown in Figure 2 and 3. The effluent used for the adsorption experiment was collected in the discharge pipe of the biological aerobic reactor (final effluent).



Figure 2. Compact unit designed for swine manure treatment installed at Embrapa Swine and Poultry, in Concordia City, Santa Catarina State

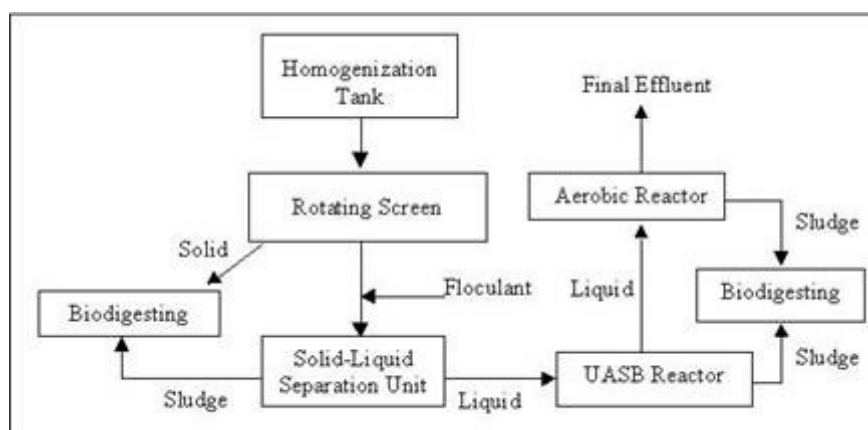


Figure 3. Schematic description of the compact unit for swine manure treatment

At the laboratory, the effluent was filtered in Millipore glass microfiber filters 0.7 mm to remove suspended particles of activated sludge, and analyzed using official methodologies (AOAC, 1990; APHA/AWWA/WEF 1994). Analysis of potassium (K) was done using flame photometry, ammonium (N-NH₃) was analyzed using distillation followed by titration and phosphorus (P_{Total}) were analysed by UV-Vis absorption.

The experiment was run as described for “Influence of pH”, although samples were collected only after 30 and 60 minutes. The results were expressed as C_t/C_0 (C_t = nutrient concentration after t minutes - 30 and 60 minutes; C_0 = initial concentration of nutrient).

Results and discussion

Influence of pH in N-NH₃ adsorption

Figure 4 shows the results of ammonium adsorption in pH 5, 6 and 7. The graphic represents the rate of decrease of ammonium concentration in 60 minutes

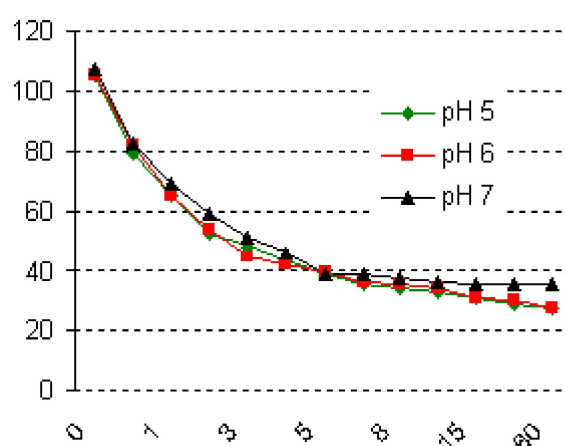


Figure 4. Kinetic behavior of ammoniacal nitrogen adsorption according to effluent pH

As it can be seen in the range of pH evaluated, no significant change was observed in the kinetic behavior of N-NH₃ adsorption into zeolite.

According to Figure 4, it was possible to remove 50% of N-NH₃ from the effluent in about 2 minutes and the equilibrium is reached in approximately 20 minutes. In the range of pH evaluated (between 5.0 and 7.0),

the parameter did not affect the adsorption behavior significantly, but the efficiency of N-NH₃ removal at equilibrium seems to be slightly higher in lower pH (74.3% in pH=5.0, 73.7% in pH=6.0 and 66.8% in pH=7.0).

At equilibrium, the amount of N-NH₃ adsorbed was 1.37, 1.41 and 1.32 mg per gram of zeolite in pH 5.0, 6.0 and 7.0, respectively.

Macronutrients removal from swine wastewater

The initial concentration of nutrients evaluated in the filtered effluent used in the experiment was: $[P_{\text{Total}}]_0 = 58.7 \text{ mg/L}$; $[K]_0 = 221 \text{ mg/L}$ and $[N\text{-NH}_3]_0 = 147 \text{ mg/L}$.

As it can be seen in Figure 5, after 30 minutes of treatment about 84% of N-NH₃, 58% of P_{total} and 86% of K were removed from the effluent and after 60 minutes these values increased to 89%, 61% and 88%, respectively.

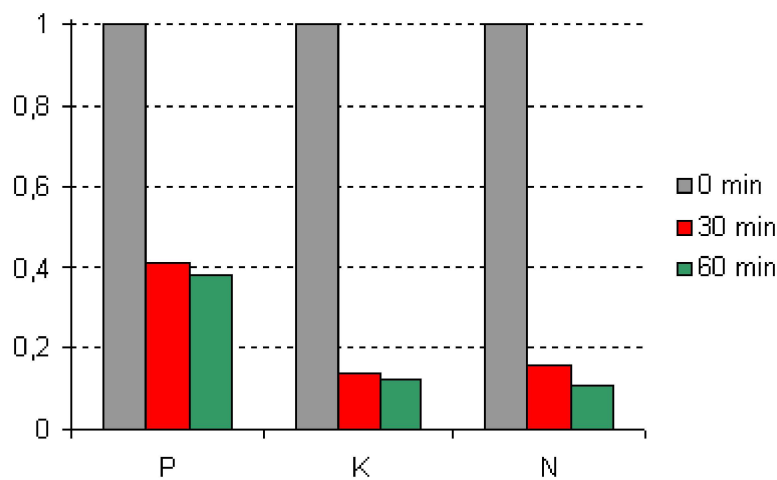


Figure 5. Nutrient removal efficiency from swine facility effluent after 0, 30 and 60 minutes in contact with natural adsorbent under magnetic stirring (5% - w/w)

The results for N-NH₃ and K are in agreement with Miladinovic et al (2004) who reported that natural zeolite clinoptilolite mordenite presents similar adsorption behavior for these both cations; however it has generally slightly higher selectivity for K⁺ than NH₄⁺.

As expected, the removal of P_{Total} from the effluent was lower if compared to K and N-NH₃ because phosphorus is present in manure mainly as phosphate (PO₄³⁻) and natural zeolite usually has little affinity for inorganic anions due to its net negative charges.

The efficiency of natural zeolites in the removal of PO₄³⁻ can vary widely according to data from literature; while Sánchez et al (1995) reported removal rates of 70-80% of PO₄³⁻ from swine effluents using packed column, Hrenović et al (2003) obtained removal rates of only 20% from synthetic wastewater. These can be explained by differences in the characteristics of the zeolites employed in the experiments (purity, CTC, size of pores and particles, etc). Also it is possible that another kind of interactions occurs in parallel with adsorption such as physical entrapment or precipitation with cations released during adsorption processes.

Considering the legal aspects, in Brazil, ammonium is the only macronutrient whose concentration in effluent is regulated by Federal Law (N-NH₃ < 20 mg/L), as each State has its own Environmental Law. In Santa Catarina State, for instance (Santa Catarina, 1991), the requirements for effluent emission are stricter than Federal Law for total nitrogen (<10 mg/L) as well as for phosphorus (<1.0 mg/L).

According to Federal Legislation, effluent submitted to 60 minutes of treatment became suitable to be released into the environment because N-NH₃ concentration dropped from 147 to 15.9 mg/L. Otherwise, if Santa Catarina State Legislation is taken as reference, neither nitrogen nor phosphorus satisfy legal requirement.

Conclusions

- Effluents from livestock facilities have high nutrient content which are not removed through ordinary treatment technologies.
- The natural zeolite clinoptilolite-mordenite has similar kinetic behavior in the adsorption of N-NH₃ in the pH range commonly found in swine facilities effluent. Load of 5% (w/w) of zeolite in pre-treated real effluent removes up to 80% of N-NH₃ and K and about 60% of P in less than 60 minutes of contact.

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