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Research article

Efficiency of basalt zeolite and Cuban zeolite to adsorb ammonia released from poultry litter

Giselle B. Nuernberg^{*}, Marcelo A. Moreira, Paulo R. Ernani, Jaime A. Almeida, Tais M. Maciel

Santa Catarina State University, 88520-000, Lages, SC, Brazil

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ABSTRACT

Confined poultry production is an important livestock activity, which generates large amounts of waste associated with the potential for environmental pollution and ammonia (NH₃) emissions. The release of ammonia negatively affects poultry production and decreases the N content of wastes that could be used as soil fertilizers. The objective of this study was to evaluate a low-cost, simple and rapid method to simulate ammonia emissions from poultry litter as well as to quantify the reduction in the ammonia emissions to the environment employing two adsorbent zeolites, a commercial Cuban zeolite (CZ) and a ground basalt Brazilian rock containing zeolite (BZ). The experiments were conducted in a laboratory, in 2012–2013. The zeolites were characterized by X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), physical adsorption of N₂ (BET) and scanning electron microscopy (SEM). Ammonia released from poultry litter and its simulation from NH₄OH solution presented similar capture rates of 7.99×10^{-5} and 7.35×10^{-5} mg/h, respectively. Both zeolites contain SiO₂ and Al₂O₃ as major constituents, with contents of 84% and 12% in the CZ, and 51% and 12% in the BZ, respectively, besides heulandite groups. Their BET surface areas were 89.4 and 11.3 m² g⁻¹, respectively, and the two zeolites had similar surface morphologies. The zeolites successfully adsorbed the ammonia released, but CZ was more efficient than BZ, since to capture all of the ammonia 5 g of CZ and 20 g of BZ were required. This difference is due to higher values for the superficial area, porosity, CEC and acid site strength of CZ relatively to BZ. The proposed methodology was shown to be an efficient method to simulate and quantify the ammonia released from poultry litter.

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1. Introduction

Brazilian exports of chicken meat have been the largest in the world since 2004 and in terms of production this country is third, after the USA and China (UBABEF, 2014). Santa Catarina State is one of the most important poultry producing areas in Brazil and the birds are raised mainly in confinement systems. Hence, large amounts of wastes are generated in small areas and these can have a negative impact on the environment, in addition to resulting in elevated rates of ammonia emissions (Hernandes and Cazetta, 2001; Sales et al., 2013; Ji-Qin et al., 2012).

Ammonia (NH₃) is a colorless, water-soluble gas by-product of the microbiological decomposition of organic nitrogen compounds present in poultry manure (Soares et al., 2012; Busca and Pistarino,

2003). It does not have an ionic charge, making it readily released into the atmosphere in a gaseous form. The protonation of NH₃ into nonvolatile ammonium (NH₄⁺) requires an acidic environment. Factors that contribute to the formation of NH₃ include the temperature, moisture, pH and nitrogen content of the litter or manure (Ritz et al., 2004; Soares et al., 2012).

Ammonia is the predominant polluting gas in poultry barns. Both the concentration and exposure time of birds to ammonia may influence the effect that NH₃ can have on the health of birds and workers, such as tracheal irritation, eye damage, decreased feed efficiency and mortality. In humans, acute inhalation is associated with respiratory-related problems (Sinha et al., 2012; Cockburn et al., 2013; Webb et al., 2014).

Thus, reduction in ammonia emissions from poultry litter is important and in this regard some materials able to capture the ammonia released have been tested, including zeolites. Higarashi et al. (2008) studied the removal of ammonia from pig holding

^{*} Corresponding author.

E-mail address: gi_qmc@hotmail.com (G.B. Nuernberg).

wastewater using natural zeolite and observed that the adsorption was increased as the zeolite particle size range decreased from 3.0–8.0 to 0.6–1.3 mm. Li et al. (2010) investigated the adsorption of ammonia at a pig farm using different clinoptilolite moisture contents. The authors noted that the optimum effect was obtained when the moisture content of the clinoptilolite was 40%. The adsorption of ammonia with the use of natural clinoptilolite was considered to occur through a physical mechanism rather than via an ion exchange reaction. Although many research studies have shown that zeolites are able to trap ammonia, this material must be associated with low cost in order to be economically viable.

There are more than 50 types of natural zeolites and clinoptilolite (along with laumontite and mordenite) belongs to the family heulandite and has the simplified ideal formula of $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72} \cdot n\text{H}_2\text{O}$ (Charkhi et al., 2010). It has several important properties including adsorption potential, porosity and polarity. Also, clinoptilolite has a high affinity for NH_3 , H_2S and CO_2 and it can be used for the removal of NH_4^+ and heavy cations from contaminated water and wastewater, acts as a soil fertilizer and conditioner, and reduces bad odors in animal barns (Moussavi et al., 2011; Halim et al., 2010; Marco-Lozar et al., 2012). The loss of ammonia from poultry barns can not only negatively affect the environment but also cause respiration problems in the birds. In addition, the N content of the litter, which can be used as a soil fertilizer, is reduced. In this context, we hypothesized that both Cuban zeolite and basalt zeolite are able to trap ammonia volatilized from poultry litter and this process can be simulated with a system using a solution of ammonium hydroxide.

The aim of this study was to evaluate a low-cost, simple and rapid method to simulate ammonia emissions from poultry litter using a solution of ammonium hydroxide. The reduction in ammonia emissions to the environment achieved through the trapping of ammonia volatilized from poultry litter using two adsorbent zeolites (Cuban zeolite and basalt zeolite) was then quantified.

2. Materials and methods

2.1. Simulation of ammonia emissions from poultry litter

The methodology used for the simulation and quantification of ammonia emissions from both NH_4OH and poultry litter was an adapted version of the method described by Hernandez and Cazetta (2001). In summary, 100 mL of 0.0050 N $\cdot \text{NH}_4\text{OH}$ solution or 100 g of poultry litter were placed into a 1.0 L graduated cylinder used as an incubator. A 50 mL beaker containing 10 mL of 2% (m/v) boric

acid solution (H_3BO_3) (Tedesco et al., 1995) was placed 10 cm above the surface of the alkaline solution or the poultry litter in order to collect the ammonia released. After incubation for 24–144 h, the H_3BO_3 solution was titrated with a standard sulfuric acid solution ($\text{H}_2\text{SO}_4 - 0.0050 \text{ N}$) in order to quantify the ammonia captured from NH_4OH and from the poultry litter. The experiment was conducted in a laboratory, at room temperature. The period of evaluation was based on the fact that almost all studies show that ammonia released from poultry litter occurs mainly in the first week after soil application. The experiment was conducted in a completely randomized design with three replications.

Ammonia released from the NH_4OH solution was quantified considering the difference in the results for its titration with a standard hydrochloric acid solution ($\text{HCl} - 0.0050 \text{ N}$) before and after the incubation period using methyl red as an indicator. The results were expressed as milligrams of ammonia captured, which was obtained by multiplying the volume (mL) of HCl spent in the titration by its normality and by 17, which is the molar mass of NH_3 . Ammonia emission curves were obtained by nonlinear curve fitting with appropriate software.

2.2. Characterization of the adsorbent materials

All reagents used were of analytical grade. The Cuban zeolite was donated by Celta Brasil and the basalt containing zeolite was extracted from a site in São Joaquim, Santa Catarina State, southern Brazil (latitude $28^\circ 17'38''$ South and longitude $49^\circ 55'54''$ West). Both zeolites were characterized by X-ray diffraction (XRD) on a Philips Xpert System with a PW 3710 MPD control module and graphite monochromator. The chemical composition and Si/Al ratio were determined by X-ray fluorescence spectrometry (XRF, Panalytical - Epsilon 3). The N_2 adsorption-desorption isotherm measurements were carried out at 77 K using an Autosorb 1C (Quantachrome) apparatus. The specific surface area and pore volume were determined at the equilibrium points P/P_0 in the ranges of 0.05 and 0.99 respectively, by the BET method. The morphology of the materials was examined by field emission scanning electron microscopy (FE-SEM) using a JEOL - JSM 6701F microscope.

2.3. Minimization of ammonia released from poultry litter using zeolites

In order to capture the ammonia released from poultry litter, two adsorbent materials were tested: a commercial Cuban zeolite (CZ) and a basaltic saprolite containing zeolite (BZ) extracted from rocks in Santa Catarina, southern Brazil. Both materials were

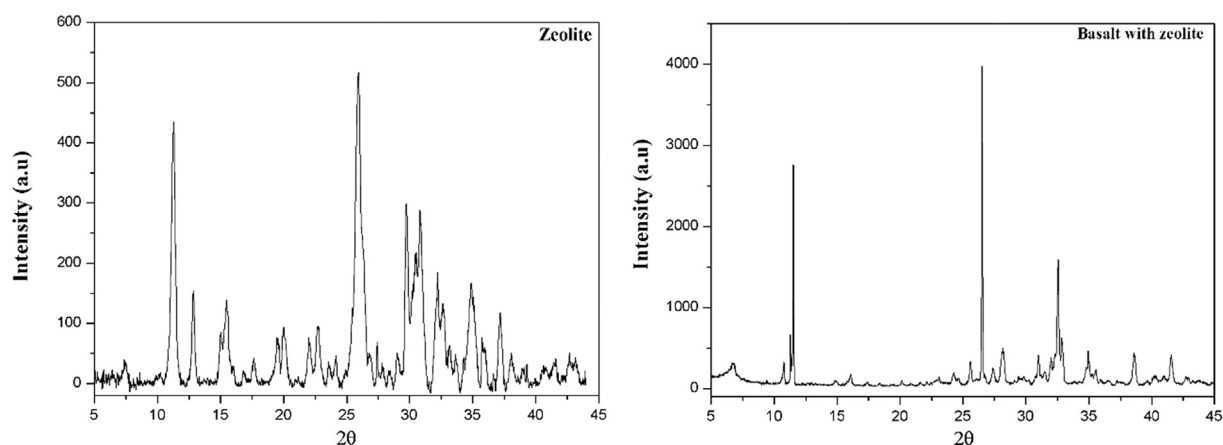


Fig. 1. X-ray diffractograms for Cuban zeolite (pH 7.5, CEC 424 meq/100 g) and basalt zeolite (pH 7.2, CEC 85 meq/100 g).

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