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ANIMAL PRODUCTION

Zeolites in poultry and swine production

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ABSTRACT: *Zeolites are minerals that have intriguing properties such as water absorption, ion adsorption and cation exchange capacity. There are approximately 80 species of natural zeolites recognized and hundreds of artificial zeolites, which have been researched in several fields. Due to their chemical characteristics, zeolites have great potential for use in animal production, especially in poultry and swine farms, as food additives, litter amendment and treatment of residues, with direct and indirect effects on performance, yield and quality of carcass, ambience of farm sheds and reduction of environmental pollution.*
Key words: *ammonia, moisture, pollution, poultry, swine.*

Zeólitas na produção de aves e suínos

RESUMO: *Zeólitas* são minerais *que possuem propriedades peculiares como absorção de água, adsorção de íons e capacidade de troca catiônica. Existem aproximadamente 80 espécies de zeólitas naturais reconhecidas e centenas de zeólitas artificiais, as quais vêm sendo pesquisadas nas mais diversas áreas do conhecimento. Frente às suas características químicas, as zeólitas apresentam grande potencial de utilização na produção animal, principalmente nas criações de aves e suínos, como aditivos alimentares, condicionadores de cama e no tratamento de resíduos, com efeitos diretos e indiretos sobre desempenho zootécnico, rendimento e qualidade de carcaça, ambiência dos galpões de criação e na redução da poluição ambiental.*
Palavras-chave: *amônia, avicultura, poluição, suinocultura, umidade.*

INTRODUCTION

Zeolites are defined as a mineral group characterized by a three-dimensional linked tetrahedral framework, each composed of four oxygen atoms surrounding a cation, conferring particular characteristics (COOMBS et al., 1997). This mineral was first described by Swedish mineralogist Freiherr Axel Fredrick Cronstedt in 1756, who gave the name "zeolite", which originates from the Greek words "stones that boils" (Greek zeo = boil; lithos = stone) in reference to their behavior of bubbling when heated (MUMPTON, 1999).

Nowadays, there are more than 80 described species of natural zeolites and hundreds of artificial zeolites. The great stimulus for zeolite synthesis in the lab is a result of their economic importance and many technological applications (RESENDE et al., 2008). Mineral deposits are explored commercially in many countries. China is the biggest producer and consumer of zeolites around the world (MONTE & RESENDE, 2005).

Due to their molecular characteristics, natural zeolites have been tested and utilized for removal of undesired molecules (JIMENEZ et al., 2004) in several sectors. ARMBRUSTER (2001) notes properties and applications of zeolites in ion exchange and adsorption, pollution abatement, catalysis, gas separation, animal hygiene and bedding products. The zeolite characteristics arouse interest for research and use in several fields and are studied worldwide.

The use of zeolites in swine farming is mainly related to animal nutrition. The properties of zeolites allow the retention of nitrogen and confer the ability

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to improve the efficiency in the digestion of proteins (SHURSON et al., 1984; MUMPTON, 1999; LEUNG et al., 2007). New studies also related zeolites to the preservation of the environment due to their capacity to retain pollutants of animal production, especially ammonia (LEUNG et al., 2007; ISLAM et al., 2014; ZIMMERMANN, 2014; BUJŇÁK et al., 2015).

In poultry, zeolites were tested in the diet of laying hens and the effects on egg quality, pH of excreta and nitrogen digestibility (ROMERO et al., 2012) showed positive results. For broilers, inclusion of zeolites as a feed additive showed a beneficial effect on broiler performance and led to the improvement of their litter quality (NIKOLAKAKIS et al., 2013). The inclusion of 10% zeolite in litter reduced litter moisture and ammonia volatilization (SCHNEIDER et al., 2016). In addition, the health of the intestine was improved by inclusion of zeolites in diet (WU et al., 2013a). This review aimed to gather and introduce relevant information about chemical structure and zeolite properties, as well as its use in poultry and swine production.

DEVELOPMENT

This review will first address the chemical structure of zeolites and their three main chemical properties: ion adsorption, water absorption and ion exchange. Then, the use of zeolites in poultry and swine production, with zootechnical and sanitary results will be discussed.

Chemical structure

The primary zeolite structure is characterized by a framework of linked tetrahedrals composed of oxygen atoms surrounding a central cation (COOMBS et al., 1997), highlighting AlO_4 and SiO_4. Negatives charges of these molecules are balanced by cations, that can be replaced through ion exchange (CORREIA, 2003).

In the past, zeolites were limited to tectosilicates and tetrahedrons containing aluminum and silicon. However, it was observed that some minerals comply with traditional criteria for zeolites in all respects, but they contain other elements in the tetrahedral. Currently, the Subcommittee on Zeolites of the International Mineralogical Association (IMA), Commission on New Minerals and Mineral Names outlined that zeolites can be composed of other elements in addition to aluminum and silicon (COOMBS et al., 1997). Although, the concept of zeolites has been expanded according to the IMA, hydrated aluminum silicates of alkali metals or alkali earth metals are the most frequent (MONTE & RESENDE, 2005).

The framework tetrahedral of zeolite structure is interconnected and forms open cavities and channels, conferring porosity to the mineral and resulting in the term “molecular sieves” proposed in 1932 by McBain (LUNA & SCHUCHARDT, 2001). Porosity of zeolites makes the internal surface bigger than the external surface. The micropore diameter of these minerals differs between varieties and allows molecules smaller than the diameter to pass through (LUZ, 1995).

There are many species of zeolites, such as Analcime, Chabazite, Clinoptilolite, Faujasite, Ferrierite, Heulandite, Laumontite, Mordenite. Zeolite species differ in chemical formula, void volume (%), pore size, thermic stability, and ion exchange (BERNARDI et al., 2008).

Properties

Zeolites show a high degree of hydration, low density, great void volume when dehydrated, stability of the crystalline structure when dehydrated, ion exchange, dehydrated uniform channels, electric conductivity, adsorption of gases, and catalytic properties (CLIFTON, 1987).

Zeolites has three essential properties: ion adsorption, water absorption and ion exchange capacity. Adsorption can be defined as an adherence of one solute to the surface of a solid material surface. The adsorption processes have been studied and used in purification systems and pollutant treatment (RUTHVEN, 1984). This property is directly related to the molecular sieve concept, attributed to the micropore structure of zeolites (pore around 5 Å diameter), and the selective adsorption capacity of molecules and ions, retaining only the lower pore size (BRAGA & MORGAN, 2007). The internal surface of the clinoptilolite zeolite is 300m²/g, and is responsible for its adsorptive efficiency (LUZ, 1995). Adsorptive capacity of zeolites is useful for removal of impurities or separation of molecules (AGUIAR & NOVAES, 2002). LY et al. (1996) showed adsorption of ammonium by zeolites in vitro, and highlighted its beneficial effects on digestive processes as a result of preventing ammonia intestinal absorption.

Hygroscopy can be defined as the ability of a material to hold water molecules. Water absorption occurs through osmotic balance and the hydration of cations to compensate for the surface charge (CASTAING, 1998). COOMBS et al. (1997) affirmed that zeolite channels are often occupied by water molecules and cations.

Ion exchange capacity is defined as the amount of cations that one mineral can adsorb or exchange as a result of electrical charge imbalance. The ion exchange capacity of one mineral can influence its physical and chemical characteristics (BERTELLA, 2008). Currently, it is accepted that cations can replace each other freely in zeolites, provided that the charge balance is unchanged. For example, $2Na^+$ can replace $1Ca^{2+}$, since they have the same positive charges (MONTE & RESENDE, 2005).

According to LUZ (1995), the high ion exchange capacity of zeolites is due to an imbalance of charges, which attracts the closer cation to maintain neutrality. This process depends on the nature, chemical composition, pH, temperature, as well as the characteristics of the cation exchanged (RAMOS et al., 2004).

Utilization in poultry

Research on zeolites in the poultry industry has focused on performance, ambience, and pollutant reduction, and using zeolites as a feed additive and litter and excreta amendment. Zeolites were tested as inorganic additives by inclusion of 0.0% and 0.2% zeolite into the diet, and 0.0kg m^{-2} and 2.0kg m^{-2} into the litter of broilers (factorial array). This resulted in greater weight gain in broilers receiving the diet with zeolites and/or litter with zeolites without affecting mortality and feed conversion (KARAMANLIS et al., 2008). Inclusion of 15g kg^{-1} or 25g kg^{-1} in the diet of broilers reduced broiler weight gain; however, poultry house ammonia levels were also reduced from 21.15ppm (control) to 17.25ppm and 17.75ppm with use of 15g kg^{-1} and 25g kg^{-1} zeolite, respectively (ÇABUK et al., 2004). The addition of 5 g/kg zeolite to the diet or 100g kg^{-1} zeolite to the litter of broilers did not affect feed intake, live body weight, feed conversion and average daily gain up to 42 days old (SCHNEIDER et al., 2016). Data generated from metabolism testing showed reductions in pH and moisture of excreta when poultry received a diet with 0.5% clinoptilolite zeolite (SCHNEIDER, 2017). Higher doses can present different results. Diets containing 2% and 3% zeolite showed increases in body weight gain and the feed conversion ratio in broilers raised up to six weeks (NIKOLAKAKIS et al., 2013).

Zeolite effects on nutrient absorption was tested by WU et al. (2013b) through dietary supplementation by natural clinoptilolite (2.0%) and modified clinoptilolite (2.0%). The authors did not observe differences in weight gain, feed conversion and mortality; however, they reported beneficial changes to intestinal morphology, such as higher heights of intestinal villi, and increases in digestive enzyme activity including chymotrypsin, trypsin and amylase in the small intestine. The authors recommend future studies that clarify the mechanism of action of zeolites in the intestine. Altogether, the effect of zeolite inclusion in the diet on ileal digestibility of energy and protein for broilers was evaluated, and the inclusion of 3.0% zeolite in the diet significantly increased protein digestibility (SAFAEIKATOULI et al., 2012).

Effects of zeolites are not only tested for changes in poultry performance, but also in relation to carcass yield and quality. Two broiler diets were tested containing 3.0 or 10.0% linseed and 2.0% zeolite and it was observed that the addition of the natural zeolite resulted in a significant increase in thigh meat weight and decrease of abdominal fat (CHRISTAKI et al., 2006). In contrast, the inclusion of 0.5% zeolite in the diet and 10% zeolite in litter did not lead to differences of total carcass yield, or breast, leg and thigh meat of broilers (SCHNEIDER et al., 2016). Also, the inclusion of 2% and 4% zeolite in broiler diets slaughtered at 42 days old did not change the carcass weight, breast meat, thigh meat, distal back and drumsticks and abdominal fat relative to the weight percentage (TATAR et al., 2012).

In nutritional studies, 35% of the limestone in the diet of laying hens was replaced with a mixture of $CaSO_4$ and zeolite (6.94% of diet), which resulted in increased proportions of yolk, total solid content, and egg weight, with no reduction in egg production and shell quality or apparent nitrogen retention, but a reduction in excreta pH (ROMERO et al., 2012).

The beneficial effects of zeolites on animal sanitation were also investigated. The inclusion of 2.0% zeolite in the diet of broilers during winter and summer reduced *Salmonella* count in carcasses and caeca in more than 50% of animals compared to the control group without zeolites (AL-NASSER et al., 2011). The same authors affirmed that inclusion of 2.0% zeolite in the diet can increase the cost of production by 5.0%; however, this value is much lower than what is lost as a result of *Salmonella* contamination. Supplementation with natural clinoptilolite and modified clinoptilolite was associated with greater villi height in the jejunal and ileal mucosa of broilers, from day 1 to 42. Total viable counts of *Escherichia coli* decreased with natural clinoptilolite and modified clinoptilolite supplementation from day 1 to 21 and day 22 to 42, respectively (WU et al., 2013a). The authors recommend natural clinoptilolite and modified clinoptilolite as a feed additive for broilers because of its improvement to intestinal health. They affirmed that natural clinoptilolite can adsorb bacteria selectively and bind certain toxins. In support of this finding, WANG et al. (2012) demonstrated that addition of 0.2% zinc-bearing clinoptilolite in the feed of broilers exerted protective effects on the performance and gut health of broilers with *Salmonella pullorum* infection.

There are many zeolites that are aluminosilicates and affect mycotoxins. BATINA et al. (2005) observed serum biochemical levels of broilers receiving a diet with 5ppm aflatoxin, and with inclusion of 0.25 and 0.5% sodium montmorilonite. A level of 0.5% was able to adsorb mycotoxins and these broilers were similar to those that did not receive mycotoxins.

The possible adverse effects of zeolites administered as a feed additive have been questioned, and because of that, experiments that evaluate physiological parameters are necessary. Inclusion of 15g kg^{-1} and 30g kg^{-1} zeolite in the feed of male broilers did not change levels of serum biochemical parameters, or T4 (tiroxin), TSH (thyroid stimulating hormone) and GH (growth hormone). The authors affirmed that zeolites have beneficial effects as a feed additive for broilers (SAFAEIKATOULI, 2011).

Due to the cost of litter in poultry houses, it is necessary to reuse the material for some flocks. Reused litter has a greater amount of excreta, and leads to high humidity and increased ammonia levels inside poultry houses ranging from 60ppm up to 100ppm, which is harmful for broilers health (CARVALHO et al., 2011). Therefore, zeolites are incorporated into litter to reduce ammonia and moisture levels, through its ability to adsorb ions and absorb water. Litter chemical amendments are substances that improve the physical, chemical and microbiological integrity of litter and; therefore, can enhance ambience, performance and hygiene of poultry (OLIVEIRA et al., 2004).

Clinoptilolite is used in products of animal hygiene and litter poultry, due to its capacity to absorb odors and exchange NH_4 (ARMBRUSTER, 2001). Addition of 0, 25, 50 and 75% natural zeolite in relation to total weight of sawdust litter in broilers at densities of 15 poultry/m² decreased moisture levels 36.2, 25.2, 23.6, and 21.8%, respectively. In this study, 25% zeolite is recommended in litter (ELEROGLU & YALCIN, 2005).

The doses of zeolites included in the diet or litter are extremely variable in the literature. Inclusion of 5% zeolite in the litter composed of elephant grass in five consecutive flocks did not change the moisture of the material (LOCH et al., 2011). The same author affirmed that litter amendment can reduce ammonia emissions inside poultry houses because decreases of pH and water activity directly affect microorganism survival. Zeolite and kaolin utilization in broiler diets (inclusion of 30g kg^{-1}) resulted in moisture, calcium, and nitrogen decreases in litter after 42 days, but had no effect on pH, ash or phosphorous (SAFAEIKATOULI et al., 2014). The unique addition and initial addition of 10% natural zeolite (clinoptilolite) in relation to total weight of sawdust litter in three consecutive flocks raised on the same litter reduced litter moisture and ammonia volatilization by up to 32%. Thus, effects were observed until the third flock, which means that zeolites do not need to be added for every new flock (SCHNEIDER et al., 2016).

Zeolites can be effective in reduction of ammonia emissions from stored poultry manure. LI et al. (2008), using zeolites on laying hen manure in low (2.5%), medium (5.0%) and high (10%) doses of the manure weight, reduced NH_3 emissions by 36%, 62% and 92%, respectively, within seven days of storage. According to CASTING (1998), the capacity to absorb ammonia by zeolites is mainly because of ammonium ion exchange (NH_4^+), which makes the use of the additive possible.

Utilization in swine

Zeolites are usually used in pig diets at concentrations from 0.5% up to 8.0%. Clinoptilolite concentrations of 0.5, 1.0, 1.5, 2.0 and 3.0%, in the diets of growing and finishing pigs do not lead to any differences in feed intake, daily weight gain, feed conversion, blood parameters and carcass characteristics (ROCHA et al., 2012). These results corroborated those obtained by SHURSON et al. (1984), who did not find any significant effects on weight gain and feed intake as a result of diets containing 0.3% zeolite (artificially produced) and 0.5% clinoptilolite (natural zeolite) during the growth stage. These authors also compared the concentration of 1% zeolite A with 5% clinoptilolite in finishing swine diets. They did not observe differences in weight gain and feed intake, but did observe the effects of destruction of zeolite A in the acidic environment of the pig stomach, where the pH values are lower than 2.0. In very acidic solutions, the structure of the zeolite is destroyed, releasing aluminum ions (Al) that are part of its structure. A greater release of Al can interfere with the absorption of calcium and phosphorus. In the same study, a linear reduction in phosphorus retention was observed. However, the various levels of clinoptilolite used in this study did not affect the retention of Ca, Mg, Na, K, Fe and Zn. The level of 0.5% clinoptilolite, in growing and finishing pigs diets did not affect feed intake, daily weight gain, feed conversion, carcass quality, hot carcass weight, back-fat thickness, loin depth and lean percentage, compared to a diet without addition of zeolites (ZIMMERMANN, 2014). The same result was reported by ISLAM et al. (2014), where the use of 0.5% artificial zeolites had no effect on growth performance and carcass quality. In contrast, ALEXOPOULOS et al. (2007) reported that weight and feed conversion increased using 2% clinoptilolite in growing and finishing pigs. Although, the feed intake, serum biochemical parameters, hematological and serum concentrations of minerals (K^+, Na^+, Ca and PO_4^{2+}) were not affected by the addition of zeolite. LEUNG (2004) also did not observe significant effects on the daily weight gain, feed conversion and feed intake, with the addition of 2% zeolite in the growing and finishing pig diet. PEARSON, SMITH & FOX (1985) worked with the inclusion of 4% and 8% zeolite in growing and finishing diets, but did not find any effects on weight gain and feed conversion. The inclusion of 0% and 2% clinoptilolite in pregnancy and lactation diets showed that serum levels of vitamins and minerals were not affected, indicating a proper status in both treatments during the reproductive cycle; although, the level of vitamin E was slightly lower in animals fed the clinoptilolite diet (KYRIAKIS et al., 2002). This study also demonstrated that the serum potassium was not affected by dietary use of zeolites. The number of piglets born alive, the number of weaned piglets, the live weight at birth, the weaning live weight, and the live weight gain during lactation were significantly higher in animals fed diets containing 2% clinoptilolite. This result was attributed to the improved feed efficiency of animals receiving diets supplemented with clinoptilolite, which can be caused by better delivery of energy and nutrients, a better performance during lactation and a protective effect of clinoptilolite in diets containing mycotoxins. In another study, the addition of 2% clinoptilolite to the diet of piglets did not affect the serum concentrations of vitamin A and E, phosphorus, magnesium, calcium, copper and zinc as well as the levels of these elements in the liver (PAPAIOANNOU et al., 2002).

Zeolites have also been studied in diarrhea control in weanling piglets. A similar result wasreported using a conventional treatment with erythromycin the addition of 100g/day to the diet for three days resulted in 33% more efficient diarrhea control, (MARTÍNEZ et al., 2004). In waste management and control of toxic gases and odors produced by animals, zeolites have been tested continuously. The use of 5% zeolite as a food additive to the pig diet resulted in reduced ammonia volatilization of waste by 21% compared to animals that did not receive zeolites. This is due to the selectivity of ammonium ions by clinoptilolite. The clinoptilolite may act as a reservoir of nitrogen in the animal's digestive system, allowing for slower release and more efficient use of ammonium ions (BAIDOO, 2000). ALUWÉ et al. (2009) in order to reduce boar taint in male pig carcasses. The use of natural zeolites at this concentration was not effective at reducing the characteristic odor.

Pigs diets with increasing levels of zeolite A and clinoptilolite indicated that the daily intake of nitrogen was not affected, but the daily fecal excretion increased, resulting in a linear decrease in nitrogen digestibility. Zeolite A and clinoptilolite were effective in reducing ammonia produced by the deamination of proteins in the gastrointestinal tract during digestion, preventing their absorption and resulting in increased fecal nitrogen, while the total nitrogen content in urine decreased. The biological value of protein was not affected linearly in the pigs' diets with increasing levels of clinoptilolite, but it did obtain a linear reduction in the use of total protein (SHURSON et al., 1984).

Clinoptilolite with 90% purity and more than 25 micrometers, at pH 7.0 has an adsorbing capacity of 158+Cmol kg^{-1} of ammonium (NH_4+). However, at pH 2.0, it adsorbs 123+Cmol kg^{-1}. Thus, clinoptilolite retains 20% more of its ammonia adsorption capacity when exposed to pH 7.0 compared to pH 2.0. This indicated that zeolites have a higher capacity to adsorb ammonia from the manure than in the pigs stomach (LEUNG et al., 2007). The inclusion of 0.5% clinoptilolite in growing and finishing pig diets reduced the ammonia concentration (ppm) within the facility with a slatted floor. This was shown by ISLAM et al. (2014), who reported that the use of 0.5% artificial zeolite in the diet of pigs led to a significant reduction in the emission of ammonia, sulfur dioxide and hydrogen sulfide from feces. Likewise, BUJŇÁK et al. (2015), using 2% zeolite in the diet of growing pigs, obtained similar results, where the addition of zeolites showed a tendency to increase the ammonia content in feces, decreasing their volatilization to the environment.

Zeolite accumulation in the stored waste and its physicochemical properties allowed adsorption of both ammonium ions (NH_3) and ammonia gas (NH_4), decreasing their volatilization and; therefore, decreasing its concentration within the facility (ZIMMERMANN, 2014). The concentration of adsorbed ammonia increases with increasing doses of zeolite. This was shown by t MILÁN et al. (2001) using natural zeolite doses (0.0 to 10.0g) in anaerobic digestion of manure for 30 days. The presence of zeolites reduced the concentration of ammonia and ammonium in solution, thereby reducing the inhibitory effects of these compounds in the anaerobic digestion of waste.

CONCLUSION

Zeolites have unique physical and chemical characteristics that may be used in the production of poultry and pigs as a food additive, and litter, excreta and waste amendment. Results regarding zootechnical performance is variable and can be related to the different doses, kinds of zeolites, and experimental conditions used in each study. Regarding the improvement to the ambience of the farms and the reduction of greenhouse gases, the results are consistent and promising. The zeolites have great potential for the mitigation of pollution and waste control processes produced by the poultry and swine industries.

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