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COPPER AND ZINC DISTRIBUTION IN SWINE EFFLUENT DURING ANAEROBIC TREATMENT

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ABSTRACT: Swine effluents can have high levels of metals as cooper and zinc that are used during animal rearing. In this way, the present study evaluated the influence of anaerobic biodigestion on the bioavailability of copper and zinc by sequential extraction scheme (SES) in raw (RM) and digested (DM) swine manure. The most representative fractionation of Cu and Zn in all samples was the oxidizable fraction, indicating that the metals are bonded mainly to organic matter and sulfide.

Keywords: Swine manure, metals, bioavailability, biodigestion

INTRODUCTION

The swine intensive production generates large amount of effluent. Treatment alternatives as anaerobic digestion, appears as a tool for organic matter removal, which generates by-products such as biogas and biofertilizer. Biogas can be used to obtain heat, electricity or carbon credits. Biofertilizer can be directly used in agriculture or subjected to subsequent treatment stages (Kunz et al. 2009).

The raw and anaerobic digested manure, when disposed in the soil without an agronomic recommendation, can exceed the soil absorption capacity and cause the accumulation of many elements like nutrients, metals, and pathogens (Vanotti et al., 2002).

Among the metals present in swine manure, copper (Cu) and zinc (Zn) are found in greater concentrations due to its use as feed supplements Zn to avoid diarrhea and Cu to improve swine growth, and low animal absorption capacity (Jondreville et al., 2003; Bolan et al., 2004; Steinmetz et al., 2007). In recent years it has been shown an increasing on Cu and Zn levels in soil when manure is spread on arable land for long time (Nicholson et al., 2003; Ceretta and Girotto, 2009).

In this way, metal bioavailability is an important parameter and has effect on toxicity over soil and water organisms and is dependent on liability of chemical bonds between the metal and inorganic or organic species (Ure et al., 2001). For Cu and Zn, the extraction of metals with different solvents can generate consistent information about metal biovailability

In order to determine the forms of metals in the manure, speciation studies has been conducted using different procedures to extract Cu and Zn from swine effluent when it was submitted to anaerobic biodigestion.

MATERIAL AND METHODS

Sampling

The swine manure samples, raw manure (RM) and digested manure (DM), were collected in a biodegestor of 10 m^3, operated at mesophilic conditions, located at Embrapa Swine and Poultry – Concordia/SC.

Sequential extraction BCR

Sequential extraction scheme developed by Community Bureau of Reference (BCR) (Ure et al., 1993) was used with some modifications (included steps 1 and 5), presented in Figure 1.

Analytical analysis

Volatile solids were analyzed according APHA, (2012).

Total Cu and Zn concentration were obtained by nitric acid/hydrogen peroxide mixture digestion. 5mL of HNO_3 were added to 5 mL of sample. The mixture was heated under reflux for 5 h. After cooling, 500 µL of H_2O_2 8.8 mol.L^{-1} was added and the solution was heated again under reflux for 1 h or until the solution became transparent.

A flame atomic absorption spectrometer (VarianSpectr AA 220) was used in this study for metal analysis. All measurements were carried out in an air/acetylene flame at 324.75 nm (Cu) and 213.86 nm (Zn).

RESULTS AND DISCUSSION

Table 1 shows the volatile solids (VS) during the process of anaerobic biodigestion, achieving a reduction of 55%, and the total concentration of the studied metals for RM and DM.

Cu concentration in RM and DM, were lower than the established by Brazilian regulation (1.5 mg.g^{-1}). One the other hand, Zn concentrations exceeded the allowed maximum concentration (2.8 mg.g^{-1}) (CONAMA 2006).

The values found at each stage of metals fractionation are presented in Table 2. An internal check was performed on the results of the sequential extraction by comparing the total amount of metals removed in all steps with the results of total digestion. The recovery of the sequential extraction procedure was obtained as follows:

$$\text{RECOVERY (\%)} = \{(\text{Step 1} + \text{Step 2} + \text{Step 3} + \text{Step 4} + \text{Step 5}) / \text{Total}\} \times 100$$

As can be seen in Tab.2, the sum of contained metals in the five fractions is similar to the total contents obtained. Recoveries of 81–91% were reached. These values were very similar to those recorded in the literature for the same extraction scheme (Fuentes et al., 2004).

The percentage in all steps of total Cu and Zn was presented in Figure 2.

Cu water soluble fraction (step 1) decreased after anaerobic biodigestion. The presence of hydrogen sulfide (H_2S), generated by sulfate reduction, may results in free ions Cu precipitation and formation of hardly soluble sulfide species (Ks_{CuS} = 8.0 10^{-37}) (Vivan et al., 2010).

The decrease in the amount of Zn in the step 3 after anaerobic biodigestion, may be due to changes in manure redox potential (Eh) (Marin et al., 1997). In anaerobic digester, Eh values reached near -300 mV characterizing a reducing environment. The Zn dissolution should be more effective than Cu, because it is a less noble metal, with higher tendency to donor electrons (Eh = -760 mV). The Cu is less reactive than Zn (Eh = + 340 mV). The released Zn ions by reducible fraction, may be precipitated by H_2S (generatied by sulfato reduction in anaerobic conditions), justifying the increase of metal in the oxidizable fraction (Ks_{ZnS} = 1.2 10^{-23}).

The oxidizable fraction after the anaerobic biodigestion, was 86% - 67% of total Cu and Zn, respectively. These results are supported by other studies performed on manure stabilized under anaerobic conditions (Lasheen and Ammar 2009).

CONCLUSION

The process of anaerobic biodigestion has an influence on the distribution of Cu and Zn in swine manure, suggesting that anaerobic conditions favored the formation of stable chemical forms of metals. This was indicated by increasing of fraction of metals bound to organic-sulfide, which is less bioavailable than the three fractions before.

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Table 1. Average volatile solids (VS) and concentration of Cu and Zn during of the study.

Sample	VS ($gVS.L^{-1}$)	[Cu] ($mg.gVS^{-1}$)	[Zn] ($mg.gVS^{-1}$)
RM	0.95±0.12*	0.793±0.024*	6.209±0.108*
DM	0.41±0.12*	0.759±0.008*	5.658±0.115*

* Standard deviation

Table 2 Study the recovery of fractioned metals.

Sample	Step 1	Step 2	Step 3	Step 4	Step 5	Sum	Total	Recovery (%)
Cu (RM) ($mg.gVS^{-1}$)	0.091 ±0.067	0.083 ±0.004	0.030 ±0.004	0.883 ±0.003	0.026 ±0.002	1.114 ±0.078	1.276 ±0.039	87.69
Cu (DM) ($mg.gVS^{-1}$)	0.025 ±0.003	0.082 ±0.006	0.036 ±0.002	1.017 ±0.005	0.019 ±0.001	1.180 ±0.133	1.447 ±0.016	81.60
Zn (RM) ($mg.gVS^{-1}$)	0.172 ±0.029	0.704 ±0.027	2.911 ±0.035	5.198 ±0.068	0.158 ±0.006	9.143 ±0.423	9,990 ±0.175	91.52
Zn (DM) ($mg.gVS^{-1}$)	0.144 ±0.004	0.569 ±0.011	2.299 ±0.060	6.435 ±0.286	0.083 ±0.003	9.531 ±0.624	10.781 ±0.220	88.40

Value ± standard deviation

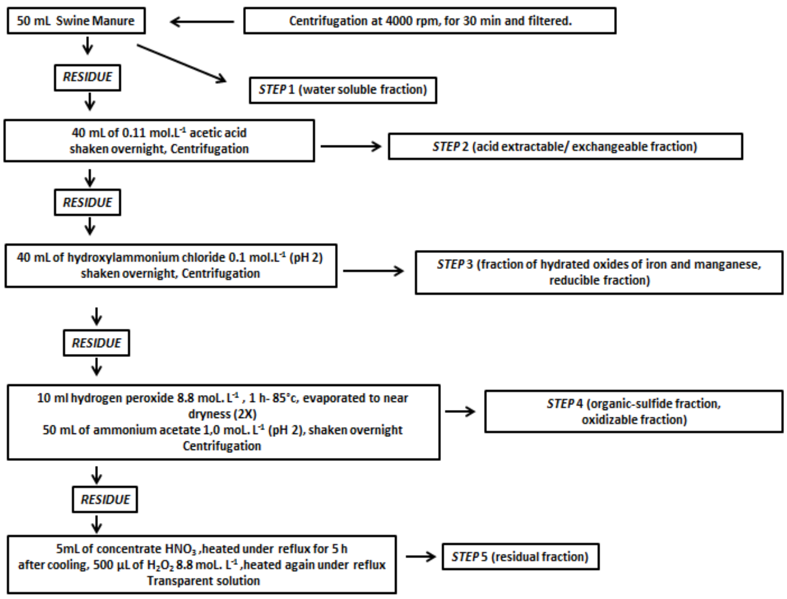

Figure 1 Sequential extraction scheme.

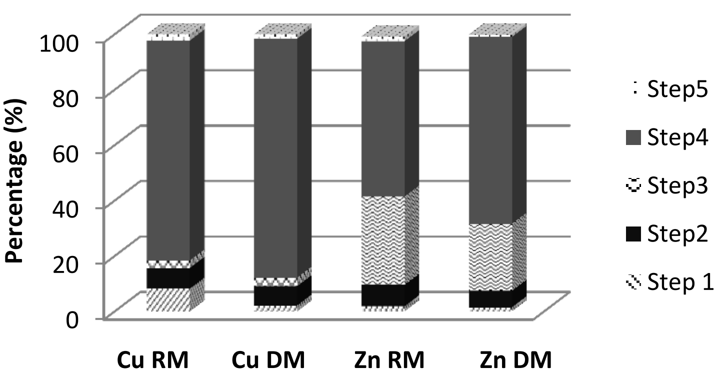

Figure 2 Percentage of Cu and Zn in DM and RM.