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## Combined application of induced MAP (Magnesium Ammonium Phosphate) precipitation and adsorption through natural zeolites for reducing $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ in swine wastewaters

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Modern agriculture, in response to the constantly increasing need of high crop production, requires application of high levels of N and P fertilizers to soil. These substances are mainly composed by nutrients such as  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  and are often applied in strong excess in order to assure high crop yield. The nutrients applied through fertilizers and not exploited by crops (estimated on average around 50%) can considerably impair environmental quality through nitrogen losses in atmosphere ( $\text{N}_2\text{O}$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ) and eutrophication of water bodies.

In this work, a new method for reducing  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  in swine wastewaters (commonly used as organic fertilizer) was studied. The aim is to reduce their environmental impact and concomitantly create a new slow-release fertilizer.

Two techniques have been combined: the induced MAP precipitation (magnesium ammonium phosphate) and natural zeolite ammonium adsorption for removing the  $\text{NH}_4^+$  excess that generally remains in solution after MAP precipitation. Given the complexity of working with real wastewaters, in this preliminary phase a synthetic analogue was used in order to better evaluate the efficiency of this method. Two synthetic wastewaters with different  $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$  molar ratio were tested: MR1 (1:1,5:1) and MR2 (2:1:1), which according to the literature give the best reductions of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . Since swine wastewater are naturally rich of both  $\text{NH}_4^+$  and  $\text{K}^+$ , isotherm studies were conducted on natural zeolites for evaluating their adsorption capacity of

$\text{NH}_4^+$  under different levels of  $\text{K}^+$  competition. Results showed that the potential in  $\text{NH}_4^+$  adsorption decreased while competition with  $\text{K}^+$  increased. The combination of MAP precipitation and  $\text{NH}_4^+$  adsorption by natural zeolite has been tested in 2 ways: 1) zeolite was added before inducing MAP precipitation 2) zeolite was added after inducing MAP precipitation. These two treatments were compared to a blank in which only MAP precipitation technique was used.

The amount of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  was monitored in various steps during the experiments as well as SEM observations were conducted on precipitated obtained. Results showed that adding zeolites before MAP precipitation induce a variation in the  $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$  ratio due to cation exchange processes before MAP precipitation which introduce interfering ions such as  $\text{Ca}^{2+}$  favoring calcium phosphates precipitation instead of MAP. The best test conditions, which produced the 75,1% of  $\text{NH}_4^+$  and 99,9% of  $\text{PO}_4^{3-}$  reductions, occurred when zeolites have been added after MAP precipitation using the MR2. This new material obtained combines good N and P concentration and have therefore potentialities to be a high-quality slow-release fertilizer.