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Chemical phosphorus removal: a clean strategy for piggery wastewater management in Brazil

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The intensive production of animal protein is known to be an environmental polluting activity, especially if the wastewater produced is not managed properly. Swine production in Brazil is growing, and technologies to manage all pollutants present in the wastewater effluent are needed. This work presents a case of study of phosphorus (P) removal from piggery wastewater using $\text{Ca}(\text{OH})_2$, and demonstrates the feasibility of this strategy for P management. The effluent of a swine manure treatment plant was treated with $\text{Ca}(\text{OH})_2$. According to the addition of $\text{Ca}(\text{OH})_2$ the pH of the effluent ranged from 8.0 to 10.0. Different conditions of sludge dewatering were evaluated, and the chemical composition of sludge was investigated. Ion chromatography analysis of effluent samples showed that 92% of total P (TP) was present as soluble P (SP) whereas 75% of SP species were present as phosphate. The efficiency of P removal was typically 90% at pH 8.5 and higher than 98% at pH 10.5. The sludge was separated by sedimentation, centrifugation or filtration and dried. The TP content of dried sludge was 9.3% (w/w). X-ray diffraction analysis of the dry sludge showed the presence of amorphous compounds of Ca and P, which is an indication that the sludge obtained from the swine manure treatment has a potential for application as biofertilizer.

Keywords: phosphorus; calcium phosphate; swine wastewater effluent treatment; calcium hydroxide

1. Introduction

Intensive animal farming has resulted in overproduction of manure in parts of the industrialized world. Brazil is the fourth largest world producer of swine meat, with a trend of expansion for the next few years [1]. According to IBGE the national herd of pigs is more than 36.8 million heads, corresponding to 59% of the herd in South America, and about 45% of them are concentrated in the south of Brazil [2]. Therefore, there is a great necessity to develop and apply sustainable clean technologies for managing pig manure.

The most common and low-cost pig manure management practice adopted in Brazilian farms is the storage in reception pits or anaerobic lagoons, and subsequent use in agriculture as a biofertilizer [3]. This is a good management strategy for nutrient recycling if the agronomic nutrient balance is respected [4]. Nonetheless, when the soil capacity is exceeded, pollution caused by nutrient accumulation in the soil or run-off to surface waters may occur. Shigaki *et al.* [5] reported that the P produced in manure (1.08 million tons) was 2.6 times more than the P requirements (0.42 million tons) for crops in South Brazil in 2003. The excessive amounts of manure produced and applied to soil, and the run-off and leaching of nutrients, metals and other

compounds present in the manure are of environmental concern [6].

Over the last few decades many technologies have been investigated for phosphorus removal from different types of wastewater, but the real-scale application on livestock wastewater is still sporadic. For P removal and recovery from liquid manure, some processes were studied such as precipitation and/or flocculation with the addition of Fe, Al, Mg or Ca [7–10]. The main advantages of chemical methods are the possibility of P recovery in the solid state, reduction of the liquid nutrient concentration and recovery of useful inorganic P compounds (e.g. $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or $\text{Ca}_3(\text{PO}_4)_2$) that can be utilized as a P fertilizer source [11].

Most of the studies reported in the literature concerning P removal from animal waste are based on P precipitation as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) [12–14]. Besides P removal, struvite formation also promotes nitrogen removal. However, the formation of struvite requires special conditions such as a stoichiometric relation between soluble P, Mg and NH_4^+ , low concentration of suspended solids and a pH higher than 7.5. However, the ideal molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ (close to 1:1:1 and up to 2.5:1:1) is almost never naturally found. Therefore, addition of Mg^{2+}

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to reach the desired stoichiometric ratio [9,13,15] is usually necessary.

Phosphorus in manure can also be removed by precipitation with calcium oxide or calcium hydroxide, producing calcium phosphate. The production of calcium phosphate is pH dependent. In general, the efficiency of calcium phosphate production increases with increasing pH (usually ≥ 9.0). The reaction between Ca^{2+} and PO_4^{3-} can also lead to the formation of other compounds of low solubility such as hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), octacalcium phosphate ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$), dicalcium phosphate (CaHPO_4) and calcium hydrogen phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Besides the formation of these crystalline compounds, amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$) can also be formed [8,16,17].

Considering the high concentration of P compounds in liquid swine manure and the associated environmental problems, this work was conducted to demonstrate the possibility of P removal from a swine manure treatment plant using $\text{Ca}(\text{OH})_2$. Physical and chemical parameters for efficient P removal were investigated. Sludge dewatering, submitted to different separation conditions, was studied. Analysis of the chemical constituents present in the sludge and identification of crystalline structures were carried out by inductively coupled plasma optical emission spectrometry (ICP OES) and X-Ray diffraction analysis, respectively. The data obtained in this work can serve as tools to evaluate the possibility of implementing the process at full scale in Brazilian farms.

2. Materials and methods

2.1. Wastewater sampling

The samples used in this study were collected from a swine manure treatment plant (SMTP), located at the Swine and Poultry National Centre of the Brazilian Agricultural Research Corporation (Embrapa) in Concórdia, Santa Catarina State, Brazil ($27^\circ 18' \text{S}$, $51^\circ 59' \text{W}$). The operational conditions of the SMTP are described elsewhere [3]. Wastewater was sampled from the SMTP after liquid–solid separation and biological treatment (anaerobic and active sludge processes) [3]. The collected samples were stored in high-density polyethylene (HDPE) flasks and kept at 4°C in the laboratory until analysis and phosphorus removal.

2.2. Analytical procedures

The determination of ortho-phosphate (PO_4^{3-}) concentration in the effluent was carried out by ion chromatography (IC) using a Modular IC System (Metrohm, Switzerland). For soluble phosphorus (SP) determination, the samples were filtered using a cellulose nitrate membrane (Sartorius, Germany) with a pore size of $0.45 \mu\text{m}$, according to the 4500-P method [18]. For total phosphorus (TP), Ca and Mg

determination, the samples were decomposed with acid in glass tubes in a heating block (model Dk 42 from Velp Scientifica, Italy). Aliquots of 2.5 mL of concentrated HNO_3 were added to 5 mL or 100 mg of dried sludge, and the mixture was heated for 2 h at 140°C . The sludge was previously dried at 105°C until constant weight. The determination of P, Mg and Ca was carried out by ICP OES using a Ciroc CCD spectrometer (Spectro Analytical Instruments, Germany). The X-ray diffraction analysis was carried out using an XD-7A diffractometer (Shimadzu, Japan). This analysis was made in order to verify the formation of crystalline compounds in the sludge.

Parameters such as chemical oxygen demand (COD), ammonium nitrogen ($\text{NH}_4\text{-N}$), alkalinity, oxidized nitrogen ($\text{NO}_3^- \text{-N}$ and $\text{NO}_2^- \text{-N}$), total Kjeldahl nitrogen (TKN), turbidity and pH were evaluated according to APHA [18].

2.3. Experimental

The experiments for P removal were carried out using 500 mL of the SMTP effluent. All experiments were conducted with three (or more) samples collected at different times. Aliquots of 5 mL of a 2% (w/v) suspension of $\text{Ca}(\text{OH})_2$ (Riedel de Haën, Germany) were slowly added to the effluent under constant mixing at 300 rpm. Then, the samples were left to stand for 30 min. This period of time was required to promote the best separation of the solid and liquid phases. The influence of pH on P removal was tested by varying the pH from 8.0 to 10.5. After the solid and liquid phase separation, the supernatant and solid (sludge) fractions were analysed.

An experiment was carried out to evaluate water loss from the sludge as a function of time at room temperature. For this experiment, three tests were carried out: 1) the sludge that settled after 30 min was separated from the supernatant, dried and weighed every day for a period of six days; 2) the separated sludge was filtered (filter Selecta, Carl Schleicher & Schüll, Nr. 589, Germany) and the solid fraction was dried and weighed every day for a period of six days; 3) the separated sludge was centrifuged (Excelsa II 206-BL, Fanem, Brazil) at 1500 rpm for five minutes; the solid fraction was dried and weighed everyday for a period of six days. In all experiments the sludge samples were placed on watch glasses for drying at room conditions (25°C and humidity around 65%). The material dried at room temperature was further dried in a furnace at 105°C in order to determine the residual water. It was further calcinated at 550°C prior to X-ray-analysis.

3. Results and discussion

3.1. Characterization of swine wastewater samples

The swine wastewater after treatment at SMTP (liquid fraction after solid–liquid separation and biological treatment) has a very high P content [3]. The concentrations

Table 1. Physical and chemical characteristics for raw swine manure and SMTP effluent (n = 3).

Parameter	Raw manure*	SMTP effluent
pH	7.05 ± 0.25	6.70 ± 0.01
Turbidity (NTU)	>1000	382 ± 43
COD (mg L ⁻¹)	11605 ± 440	389 ± 12
Alkalinity (mg L ⁻¹ CaCO ₃)	5150 ± 320	569 ± 6
TP (mg L ⁻¹ P)	430 ± 52	129 ± 2
SP (mg L ⁻¹ P)	–	119 ± 1
PO ₄ ³⁻ (mg L ⁻¹ P)	–	91 ± 1
TKN (mg L ⁻¹)	1845 ± 391	905 ± 178
NH ₄ -N (mg L ⁻¹)	1014 ± 237	133 ± 3
Oxidized nitrogen (mg L ⁻¹)	<0.1	267 ± 5

*Influent of SMTP.

(≥400 mg L⁻¹ P) are above the maximum allowed for P disposal in the environment according to the Brazilian water regulation [19]. The chemical treatment for P removal is influenced by the chemical composition of the wastewater. Therefore, it is necessary to know critical parameters such as COD, NH₄-N, alkalinity, NO₂⁻-N and NO₃⁻-N, TP, SP, TKN and pH. The chemical and physical characteristics of the wastewater before and after being submitted to treatment at SMTP are shown in Table 1.

Alkalinity and NH₃-N can interfere with P removal. The interference occurs due to the reaction between Ca(OH)₂ and HCO₃⁻, CO₃²⁻ or NH₄⁺, producing CaCO₃ and NH₃ [20]. This buffering problem (high alkalinity and ammonia concentration), typical in livestock effluents (Table 1), can be substantially reduced by a biological nitrification pretreatment. As consequence, the system reduces buffering capacity, which promotes P removal using smaller amounts of Ca(OH)₂.

By comparing TP and SP in SMTP samples it was observed that 92% of the total phosphorus was present as soluble species. Ion chromatography analysis of the filtrate effluent, carried out to determine the concentration of P species prior to treatment with Ca(OH)₂, showed that about 75% of soluble P is present as PO₄³⁻. Another part (about 25%) could be present as soluble organic P species and/or polyphosphates [21].

After biological treatment at the SMTP, most of the organic matter is removed whereas organic P and polyphosphates are partially converted to soluble phosphorus species, mainly PO₄³⁻. Formation of PO₄³⁻ is of great importance because this P species reacts preferentially with Ca. In this case, P removal is based on the formation of insoluble P compounds, which depends mainly on the effluent composition and pH [22,23].

3.2. Phosphorus removal

Experiments with Ca(OH)₂ were performed to compare the efficiency of TP and SP removal from the SMTP effluent.

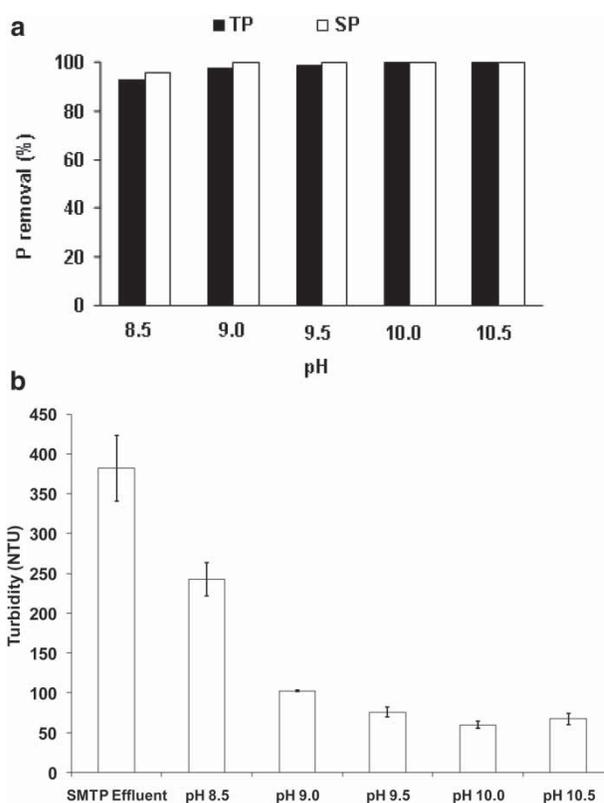


Figure 1. (a) Effect of pH on TP and SP removal efficiency with a 2% (w/v) suspension of Ca(OH)₂. (b) Residual turbidity of SMTP effluent samples before and after treatment with Ca(OH)₂ at different pH values.

Reagent consumption, phosphorus removal and clarification of the effluent were the parameters used to evaluate the effectiveness in P removal. Figure 1a shows the effect of pH on TP and SP removal using different volumes of 2% (w/v) Ca(OH)₂ suspension. As expected, addition of Ca(OH)₂ increased the pH. The SP removal efficiency was higher than 90% and increased with increasing pH. At higher pH more insoluble species of Ca²⁺ and PO₄³⁻ are produced.

Figure 1b shows the results obtained for residual turbidity of SMTP effluent with different pH treated with a 2% (w/v) suspension of Ca(OH)₂. The turbidity was measured after the suspension had been allowed to stand for 30 min. According to Figure 1b, turbidity decreased at higher pH: 37% was removed at pH 8.5, 73% at pH 9.0 and more than 80% at pH ≥ 9.5. The initial turbidity (382 ± 43 NTU) of the effluent was reduced to 102.5 ± 0.7 NTU, which represents 73% of turbidity reduction after Ca(OH)₂ treatment at pH 9.0.

According to the results shown in Table 2, the maximum TP and SP removal efficiency was close to 96%. The TP removal was higher than 90% at pH 8.5 and higher than 96% at pH above 9.0. However, to reach 98% of TP removal at pH 9.5 it was necessary to increase the volume of 2% (m/v) Ca(OH)₂ suspension to 30%. In this case, the small increase (2%) in removal efficiency does not justify the use of more

Table 2. Relevant parameters of the phosphorus removal treatment with $\text{Ca}(\text{OH})_2$ at pH 9.0 and 9.5 from SMTP effluent samples ($n = 3$).

Parameters	Results	
	pH 9.0	pH 9.5
TP after separation (mg L^{-1})	4.2 ± 0.1	1.3 ± 0.1
SP after separation (mg L^{-1})	1.2 ± 0.1	0.4 ± 0.1
Total phosphorus removal (%)	96	98
Soluble phosphorus removal (%)	98	99
Suspension volume of $\text{Ca}(\text{OH})_2$ (mL L^{-1} of sample)	33 ± 1	46 ± 1
Concentration of $\text{Ca}(\text{OH})_2$ (mg L^{-1} of sample)	664 ± 44	920 ± 20
Residual concentration of Ca^* (mg L^{-1} of sample)	69 ± 2	75 ± 2
Molar ratio Ca:P	2.1	2.8
Sludge volume after 30 min (mL L^{-1} of sample)	196 ± 5	194 ± 9
Dry sludge mass (g L^{-1} of sample)	5.5 ± 0.2	6.7 ± 0.2
COD (mg L^{-1})	337 ± 18	258 ± 37
$\text{NH}_3\text{-N}$ (mg L^{-1})	128 ± 2	118 ± 3
Oxidized nitrogen (mg L^{-1})	260 ± 3	261 ± 2

*Initial Ca concentration: $106 \pm 4 \text{ mg L}^{-1}$.

$\text{Ca}(\text{OH})_2$. Table 2 shows the volume of sludge produced, mass of dry sludge and molar ratio of Ca:P after treatment at pH 9.0 and 9.5. By increasing pH from 9.0 to 9.5, $\text{Ca}(\text{OH})_2$ consumption was increased by 30%, suggesting that $\text{NH}_3\text{-N}$ and mainly CO_3^{2-} were also consumed.

Despite the high Ca concentration initially present in the sample ($106 \pm 4 \text{ mg L}^{-1}$) it was necessary to add more $\text{Ca}(\text{OH})_2$ (360 mg L^{-1} of Ca) to reach an effluent with a pH of 9.5. The final concentration of Ca in the treated effluent decreased considerably (70 mg L^{-1} Ca), for both pH 9.0 and 9.5. In this case, the molar ratio of Ca:P did not change significantly at both pH conditions.

The high TP and SP removal efficiency as well as the $\text{Ca}(\text{OH})_2$ consumption was consistent with other reported values for similar treatments (after buffer reduction with biological treatment) applied to livestock effluents [21,24, 25]. Variations in $\text{Ca}(\text{OH})_2$ consumption and phosphorus removal efficiency are caused by the presence of NH_4^+ and CO_3^{2-} in the effluent [20,26]. Szogi and Vanotti [26] reported that effluents from swine farms required 352 mg L^{-1} of $\text{Ca}(\text{OH})_2$ to raise pH from 6.4 to 9.0 after a nitrification process (alkalinity = 91 mg L^{-1} and $\text{NH}_3\text{-N} = 42 \text{ mg L}^{-1}$). In contrast, the pH increased only 0.2 units (with slight effect on P removal) when the same $\text{Ca}(\text{OH})_2$ concentration was used (i.e. 352 mg L^{-1}) in a control effluent without prenitration (alkalinity = 2279 mg L^{-1} and $\text{NH}_3\text{-N} = 380 \text{ mg L}^{-1}$). Nitrification reduces NH_4^+ and alkalinity, which are known to interfere positively in the process, promoting P removal by reaction with $\text{Ca}(\text{OH})_2$ [25]. In the present work, by consuming 664 mg L^{-1} of lime, as $\text{Ca}(\text{OH})_2$, P removal was 96% (from 129 to 4.2 mg L^{-1} ; Table 2), increasing the pH from 6.7 to 9.0

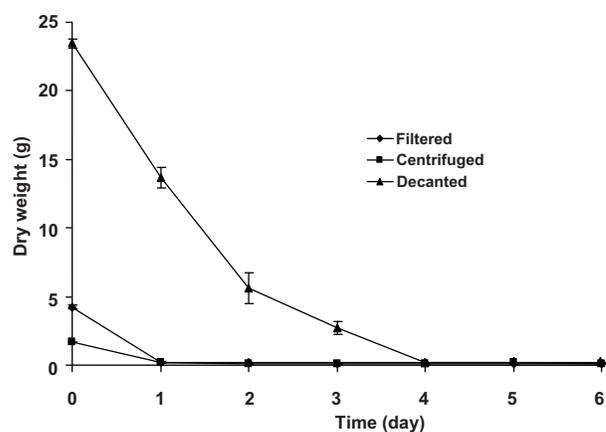


Figure 2. Sludge drying tests obtained after SMTP effluent treatment with $\text{Ca}(\text{OH})_2$ at pH 9.0 ($n = 3$).

after biological nitrogen removal in the SMTP effluent (alkalinity = 569 mg L^{-1} , $\text{NH}_3\text{-N} = 133 \text{ mg L}^{-1}$).

At pH 9.0 and 9.5 the COD decreased by 13% and 33%, respectively, and no significant changes in the concentrations of oxidized nitrogen were observed after treatment. At pH 9.0 and 9.5 $\text{NH}_3\text{-N}$ removal was 4% and 11%, respectively. At this pH it is supposed that NH_4^+ converted to NH_3 and volatilized [27].

According to Brazilian regulations, the treated effluent can be properly disposed of without pH adjustment (effluent with pH ranging from 6.0 and 9.0). In addition, the effluent can be used as treated water, minimizing the overall water demands on activities like washing and manure flush [28,29].

3.2.1. Phosphorus sludge dewatering and composition

The volume of sludge generated by the treatment was taken into account for chemical treatment for P removal. A high water content could make sludge transport and disposal prohibitively expensive [3]. For all tested pH values, it was observed that the volume of sludge and its concentration did not exceed 20% (v/v) and 7 g L^{-1} , respectively.

The sludge produced from the chemically treated effluent using $\text{Ca}(\text{OH})_2$ at pH 9.0 was submitted to drying tests in order to characterize its composition and potential for use as fertilizer [11]. The sludge separated by decantation for 30 min was submitted to three different dewatering processes: a) air drying, b) air drying after filtration, and c) air drying after centrifugation. The obtained results are shown in Figure 2. Nearly dry sludge was obtained for all processes used. As expected, the most efficient dewatering process was centrifugation and filtration, whereby less than two days was necessary for drying. In contrast, approximately four days were necessary for drying the sludge not previously separated from the liquid phase by decantation. Although not tested in this work, it is worth citing that in full-scale applications sedimentation could be attractive

Table 3. Concentrations of TP, extractable P, Ca and Mg in the dried sludge after effluent treatment with $\text{Ca}(\text{OH})_2$ (pH 9.0 and dried at 105°C) in comparison with the results obtained in the literature ($n = 3$).

Constituents	This work, g (100 g)^{-1}			Vanotti <i>et al.</i> [20], g (100 g)^{-1}		
	Digestion ¹	Extraction ²	Molar ratio ³	Digestion ¹	Extraction ²	Molar ratio ³
TP	10.6 ± 0.1	—	1.14	7.2 ± 0.3	—	1.05
Extractable P	—	9.3 ± 0.1	1.00	—	6.9 ± 0.2	1.00
Ca	28.9 ± 0.2	27.1 ± 0.6	2.90	—	24.6 ± 1.3	2.74
Mg	1.82 ± 0.02	0.88 ± 0.01	0.09	—	1.21 ± 0.01	0.22

¹Sample digestion with concentrated HNO_3 .

²Phosphorus extraction with 1 mol L^{-1} HCl solution.

³Molar ratio P-PO_4 .

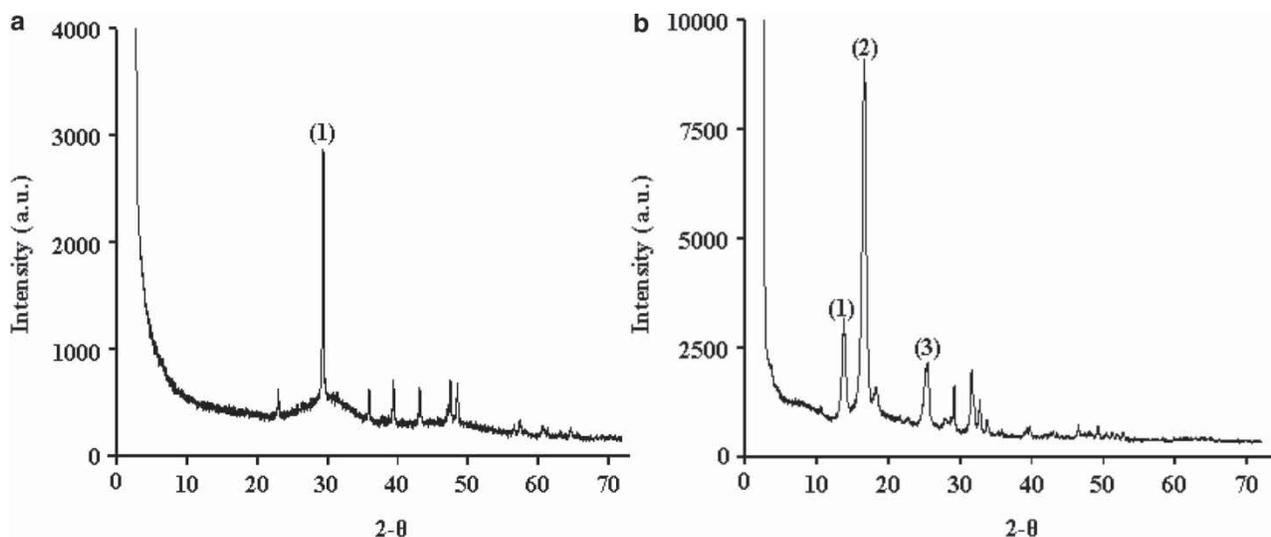


Figure 3. X-ray diffraction spectrum of sludge residue dried at (a) 105°C and (b) 550°C , after effluent treatment with 2% (w/v) $\text{Ca}(\text{OH})_2$ suspension at pH 9.0. Spectrum (a): peak 1 = CaCO_3 . Spectrum (b): peak 1 = CaCO_3 ; peak 2 = $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and/or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; peak 3 = $(\text{Ca,Mg})_3(\text{PO}_4)_2$ and/or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

because of the low costs involved. Thus, drying the sludge after sedimentation, using passive drying beds, could be a feasible strategy for an SMTP at field scale.

The TP, extractable P, Ca and Mg concentrations found in the dried sludge are shown in Table 3. Phosphorous removal efficiency and $\text{Ca}(\text{OH})_2$ consumption were higher than those reported by Vanotti *et al.* [20]. According to the mass balance for P in dried sludge, 95% and 94% of P was removed when the treatment was carried out at pH 9.0 and pH 9.5, respectively. This agrees with the amount of P removed from the liquid fraction.

The X-ray diffraction spectrum of the dried solid residue is shown in Figure 3a. Seven peaks were compared with the expected values for the interatomic distances and the probable compounds present in the sludge [30]. The analysis showed that a mixture of minerals (e.g. crystalline microstructures) and amorphous substances were produced in the sludge. An intense peak (number 2 in Figure 3a) indicates the presence of CaCO_3 , while the small peaks observed do not correlate to any known P mineral species. Therefore, P compounds in the dry sludge

were of an amorphous nature. More peaks are observed in Figure 3b. From the interatomic distances, peak 1 is related to aragonite (CaCO_3) and peak 2 is related to carbonate-hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) or struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Formation of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is less probable because of the low concentration of NH_4^+ in the liquid fraction. Peak 3 suggests the presence of calcium-magnesium phosphate ($(\text{Ca,Mg})_3(\text{PO}_4)_2$) and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

The results obtained by X-ray diffraction analysis point out that amorphous P was present in the sludge. Amorphous P compounds are more soluble than crystalline ones and more available as nutrient for plants. Moreover, they can be recovered from the sludge by drying naturally in the environment [31]. Thus it is possible to affirm that SMTP effluent is a candidate for use as fertilizer, as similarly observed by Bauer *et al.* [11].

By using drying beds, 5.5 kg of sludge per m^3 of SMTP effluent was obtained at pH 9.0 when left to stand for 30 min. Approximately 396 g of P per m^3 was recovered by adding 664 g of $\text{Ca}(\text{OH})_2$ per m^3 . Without considering initial

costs regarding the system implementation, it would cost US\$0.14 to treat 1 m³ of SMTP effluent (the cost of Ca(OH)₂ in Brazil is approximately US\$0.22 per kg). Therefore, the cost for obtaining 1 kg of phosphorus from swine manure would be US\$0.37. This cost is quite satisfactory if compared with phosphorus-based mineral fertilizers commercially available in Brazil (US\$0.42 to US\$1.50 per kg).

4. Conclusions

The results obtained in this work showed that the use of Ca(OH)₂ was effective for P removal in wastewater effluent from a swine manure treatment plant. The removal efficiencies for TP and SP were higher than 96% at pH 9.0. The effluent treated with Ca(OH)₂ had a low amount of suspended solids and was clear. Therefore, treatment at pH 9.0 was considered the best option.

Regarding the sludge produced, it was observed that drying after centrifugation and filtration was faster than simple sedimentation and drying. X-ray diffraction analysis indicated the presence of Ca and P compounds of an amorphous nature, which suggests potential for utilization of the sludge as fertilizer.

The results obtained demonstrated that the use of hydrate lime to remove P from wastewater is a clean strategy for treatment of STMP effluent in Brazil and has potential for reducing environmental impact.

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