

## Limitations of Orthophosphate Removal during Aerobic Batch Treatment of Piggery Slurry

Pius M. Ndegwa

Department of Biosystems & Agricultural Engineering, Oklahoma State University, 120 Agricultural Hall, Stillwater, OK 74078, USA;  
e-mail: ndegwa@okstate.edu

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Previous studies on removal of orthophosphates (ortho-P) from piggery slurry during aeration treatments show performances ranging between 30 and 91%. This study investigated three factors believed to be potentially responsible for the wide variations as well as limiting even higher removals of ortho-P from the slurry during aeration treatments: (i) levels of insoluble P, (ii) inadequate pH levels, and (iii) inadequate metal ions. Results indicated that, removal of insoluble P by prior aeration solids/liquid (PASL) separation and by mid-aeration solids/liquid (MASL) separation (4 days into aeration process) resulted in an additional removal of 3 and 8%, respectively. Removal of insoluble P by MASL separation, therefore, significantly improved soluble ortho-P removal more than removal by PASL separation most probably because more insoluble P is removed in the former process than in the latter process. Results also showed that upward adjustments of pH beyond that obtained from the aeration process did not significantly improve the removal of ortho-P suggesting that the pH level achieved during aeration process may not significantly limit further removal of soluble ortho-P during the aeration treatment of piggery slurry. Significant additional removals of 11, 9, and 5% were observed on the addition of a single dose of  $\text{Ca}^{2+}$  ions ( $80 \text{ mmol } [\text{Ca}^{2+}] l^{-1} \text{ [slurry]}$ ) to the piggery slurry, improving removal levels to 95, 96, and 97% for the control, PASL separation, and MASL separation, respectively. Subsequent double and triple doses did not significantly improve the removal of ortho-P in the control or in the PASL separation treatments. Based on the results of this study, depletion of  $\text{Ca}^{2+}$  ions (or/and other similarly acting metal ions) and accumulated insoluble P, are most probably the two main factors limiting further removal of soluble ortho-P during aeration treatments of piggery slurry. These two factors are also likely to be responsible for the wide variations observed in the removal efficiencies because their content will vary with both the feed mineral-supplementation and the manure management practices.

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### 1. Introduction

Recycling of pig excreta to fertilise soils for crop or pasture production has been used for decades as a way to sustain both pig and crop agriculture without import of additional nutrients into the respective ecosystems. However, economic incentives have led into an increase in size and a simultaneous reduction of units of production facilities as well as regional concentrations of pig production. These larger and concentrated facilities have improved economic returns because of improved economies of scale but the downside has been the huge amounts of liquid manure produced. The pig excreta collected as slurry though easier to handle in this

form invariably leads into increased problems in utilisation and recycling, and has been identified as probably the major cause of overloading and eventual accumulation of nutrients in the land adjacent to pig production sites (Ndegwa *et al.*, 2002a; Zhu *et al.*, 2001a, 2001b; Osada *et al.*, 1991).

Some of these nutrients overloading and accumulation problems, however, may also be attributed to the traditional recycle of pigs as well as other manures. The traditional land application of manures has in the past been on the basis of the crop or pasture need for nitrogen (N) ignoring all other nutrients including phosphorus (P). As N:P ratios common in piggery slurry are usually much smaller than the N:P ratios

Notation			
P	phosphorus, $\text{mg l}^{-1}$	$x$	independent variable
$P$	probability	$y$	dependent variable
$R$	correlation coefficient	$\alpha$	probability level of significance
$R^2$	coefficient of determination		

requirements of most crops/pastures (Sherman *et al.*, 2000; Worley & Das, 2000; Powers & Van Horn, 2001), this N-based land application of the slurry results in over-application of P and consequent accumulation of P in the receiving soils (Chang *et al.*, 1991; Paik *et al.*, 1996; Sims *et al.*, 1998; Whalen & Chang, 2001; Whalen, 2002). Currently, regulations are being revised to replace the traditional N-based land application of piggery slurry by the P content. However, adopting P-based application without pre-treatment of the slurry to reduce the levels of P in the them will require more land to apply the same volume and in many cases may results in under-application of N. Significant amounts of P need to be removed from the slurry to reduce P over-application, and at the same time, safely apply target amounts of N. Since the P available to plants during a growing season is measured by the extractable ortho-P rather than total P, it is quite apparent that more slurry could be safely applied to cropland if their quantity of extractable ortho-P was lowered. The removed P, which is concentrated in a small volume of the sludge, can then be exported to remote areas where it can be utilised without adversely impacting the environment.

Removal of orthophosphate (ortho-P) in wastewater treatment has largely been accomplished by simultaneous adjustment of pH and addition of salts of Fe, Ca, or Al to form sparingly soluble phosphates, which are subsequently removed by solids/liquid separation (Maurer *et al.*, 1999; Kox, 1981; Fuhs & Chen, 1975). Chemical treatments, however, are not only expensive but also may lead into secondary environmental pollution by increasing chlorides and sulphates in the soil receiving the sludge product (Zhu *et al.*, 2001a; Kox, 1981). Substantial accumulation of phosphate in activated sludge has been observed on aeration without addition of such salts. Menar and Jenkins (1970), attributed this observation to calcium naturally found in hard water, which forms insoluble phosphates on the activated sludge floc during aeration because of a rise in pH resulting from purging of carbon dioxide from the activated sludge. According to this theory, ammonia in solution in settled slurry is neutralised by dissolved  $\text{CO}_2$  to form ammonium bicarbonate, which keeps the pH about neutral (Stevens & Cornforth, 1974). Passing an aeration gas mixture through the slurry purges  $\text{CO}_2$  out of solution, and therefore causes the pH to rise. Another

contributing factor to the pH elevation in pig slurry during aeration is from oxidation of volatile fatty acids (Paul & Beauchamp, 1989). Piggery slurry contains  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  ions due to mineral supplements in feeds (Campbell *et al.*, 1997) and, therefore, similar aeration treatments of the slurry even without additions of Ca or Fe salts, are likely to effect formation of insoluble ortho-P thus reducing the amounts of soluble ortho-P in the bulk of the manure liquid.

Several recent research studies on low-level aeration ( $0.067\text{--}0.33\text{ l [air] l}^{-1} [\text{manure}] \text{min}^{-1}$ ) of piggery slurry have, as a matter of fact, indicated significant reductions of soluble ortho-P ranging between 31 and 91% within fairly short periods of aeration (Ndegwa *et al.*, 2002a; Zhu *et al.*, 2001b; Luo *et al.*, 2001; Ndegwa *et al.*, 2001; Bicudo, 1996; Osada *et al.*, 1991). No information is available that explains either this wide range of variation in the removal efficiency, or why higher removal efficiencies are still elusive. Luo *et al.* (2001) observed a decrease in both soluble ortho-P and organic P and an increase in insoluble ortho-P during the first day of aeration. With prolonged aeration, insoluble inorganic P declined while organic P increased presumably because of microbial biomass growth. The level of soluble ortho-P from which the microbes obtain the P to synthesise organic P, however, did not appreciably change during this prolonged aeration treatment. It was concluded from this study that there is some form of equilibrium transformations between the various forms of P such that, once some soluble ortho-P is absorbed and immobilised in microbial biomass, an equal amount dissolves from the insoluble component into soluble component to maintain the level of the dissolved portion. Other observations were that, both the increase of pH and removal of soluble ortho-P leveled off a few days (2–5 days) after aeration was initiated. At the respective points where this levelling occurred, there were still substantial amounts of soluble ortho-P in the liquid manure (Ndegwa *et al.*, 2002b; Zhu *et al.*, 2001b; Luo *et al.*, 2001; Ndegwa *et al.*, 2001).

Based on the foregoing observations from previous work on removal of ortho-P the following hypotheses were drawn: (i) removal of all or some of the insoluble ortho-P by solids/liquid separation before aeration or after the first day of aeration could substantially enhance P removal in subsequent aeration treatments,

not only from increased microbial absorption and immobilisation of P because of increased microbial activity, but also from shifting the equilibrium in favour of ortho-P precipitation, and (ii) either the pH level was inadequate for further soluble ortho-P precipitation into insoluble ortho-P, or the metal ions (Fe, Ca, Al, Mg) necessary for the precipitation process were already depleted. The objectives of this study were to investigate the wide variations of removal of soluble ortho-P and the limitations of soluble ortho-P removal in piggery slurry during batch aeration treatment caused by: (i) accumulated insoluble ortho-P levels in the manure, (ii) depletion of metal ions in the manure, and (iii) inadequate level of pH achieved during aeration treatment.

## 2. Methods and materials

### 2.1. Equipment and instrumentation

This study was conducted in six clear Plexiglas reactors; 91 cm tall, 15 cm diameter, and an operating volume of 14 l of liquid manure leaving approximately 15 cm headspace to facilitate mixing and to provide room for frothing created by aeration (Ndegwa *et al.*, 2002b). To aerate the slurry, a positive pressure air pump (Model DOA-P104-AA, Gast MFG Corp.) was used to introduce air into the slurry through a flexible rubber air diffuser (Catalogue No. W107A, Won Brothers Inc.) placed at the bottom of each reactor. A variable area flow meter (Model P-32461-64, Cole-Parmer Instrument Company) was used to regulate and maintain the flow of aeration air in each unit. An airflow rate of  $0.067 \text{ l [air]} \text{ l}^{-1} [\text{slurry}] \text{ min}^{-1}$  was maintained throughout the study period. The oxidation–reduction potential (ORP or Redox, these two terms have been used interchangeably in this article) of the liquid manure was determined using a platinum band ORP probe and a voltmeter (Accumet 1003, Fisher Scientific). A handheld pH meter (Accumet 1003, Fisher Scientific) equipped with a temperature compensating probe was used to monitor the pH and the temperature in each reactor on a daily basis just prior to daily sampling of slurry. The reactors were operated in an environmentally controlled room, where the ambient temperature was maintained at between 19 and 21°C.

### 2.2. Piggery slurry collection, loading, and sampling

Piggery slurry from a nursery barn located at the Oklahoma State University Swine Research Facility was collected in plastic containers. The manure collection

**Table 1**  
Some pertinent characteristics of the manure used in this study

Parameter	Quantity
Total solids (TS), $\text{g l}^{-1}$	$15.59 \pm 0.81$
Total volatile solids (TVS), $\text{g l}^{-1}$	$10.28 \pm 0.64$
Total phosphorus (TP), $\text{mg l}^{-1}$	$493.17 \pm 9.94$
Soluble orthophosphate, $\text{mg l}^{-1}$	$424.97 \pm 16.16$
pH	$5.5 \pm 0.0$
Oxidation–reduction potential, mV	$-264 \pm 8$

system in this Research Facility is a pit recharge system operated either once or twice a week. The 8-week old piglets in this barn were fed a maize and soya bean diet. Pertinent characteristics of the slurry used in this study are given in Table 1.

Prior to filling the reactors, the slurry was thoroughly mixed. Each reactor was then filled with 14 l of this well-mixed slurry. To facilitate solids/liquid separation in two of the reactors for the pre-aeration solids/liquid (PASL) separation treatment, the slurry was allowed to quiescently settle for 5 h. The liquid portion in two of the reactors was then decanted out into separate containers. The two reactors were cleaned thoroughly of the solids before pouring back the separated liquid manure. A pair of the remaining four reactors with unseparated manure was chosen for the mid-aeration solids/liquid (MASL) separation treatment after 4 days of aeration. A similar preparation to that of PASL separation treatment pair of reactors was repeated for this pair of MASL separation treatment.

Before starting the aeration in each case, the slurry in each reactor was again thoroughly stirred using a recirculation pump (Little Giant Model 2E-38N) for about 10 min and a sample was drawn from approximately 30 cm from the bottom of each reactor for further laboratory analyses. For the rest of duration of the study, samples were taken every day. Analyses were done immediately after the sampling whenever possible and if not, samples were deep frozen for future analyses. The frozen samples were thawed and allowed to reach the room temperature prior to analyses.

### 2.3. The pH and $\text{Ca}^{2+}$ adjustments

The removal of ortho-P in the two treatments (PASL and MASL separations) and in the control had completely stabilised by day nine when the aeration treatment was terminated. Two sets of samples, each of approximately 200 ml of the slurry were drawn from each of the six reactors after a thorough mixing of the reactors contents. Using a pH meter to monitor pH of

manure, 4 N sodium hydroxide was gradually added to one set of samples from each treatment to bring the pH from the approximate levels of 8.7 attained at the end of the aeration treatment to 10, then to 12, and eventually to 12.7 (maximum achievable pH). After each level of pH was attained, 50 ml samples were taken out for the analyses of soluble ortho-P. In the other set of samples and based on the known stoichiometry of calcium ions ( $\text{Ca}^{2+}$ ) and known forms of ortho-P ( $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ),  $\text{Ca}^{2+}$  was added in three steps so as to give  $\text{Ca}^{2+}$  ions levels of 80, 160, and 240  $\text{mmol} [\text{Ca}^{2+}] \text{ l}^{-1}$  [slurry], referred to as single dose, double dose, and triple dose, respectively, in this study. Again after each level was achieved, 50 ml samples were taken for determination of soluble ortho-P.

#### 2.4. Laboratory analyses

The following parameters were determined using standard laboratory methods (APHA, 1998): total solids (TS), total volatile solids (TVS), soluble ortho-P, total phosphorus (TP), and total Kjeldahl nitrogen (TKN). To determine the soluble ortho-P, a well-mixed sample was diluted and vigorously shaken for 5 min. The diluted sample was then filtered using GF/A (1.6  $\mu\text{m}$ ) Whatman filter papers. The soluble ortho-P in the filtrate was determined colorimetrically as the phosphomolybdate complex after reaction with ascorbic acid (APHA, 1998). The TP was determined using the persulphate digestion method, by which all the forms of P in a sample are first converted to soluble ortho-P. The samples are then filtered and the TP measured calorimetrically using the ascorbic acid method. The volatile fatty acids (VFAs) in the filtrates were determined using an esterification method. This method is based on esterification of the carboxylic acids present in the sample followed by colorimetric determination of the esters produced by the ferric hydroxamate reaction. All VFAs are reported as their equivalent  $\text{mg l}^{-1}$  acetic acid (Hach, 1993).

### 3. Results and discussion

#### 3.1. Effect of removal of insoluble P

The changes in both the pH of slurry and soluble ortho-P in the slurry under the two treatments and the control are shown in Fig. 1. The general trends of soluble ortho-P are exactly the reverse of the trends of the pH profiles. Significant changes in both pH and soluble ortho-P occurred between day 1 and 3 and slowed down at approximately day 4, except for the

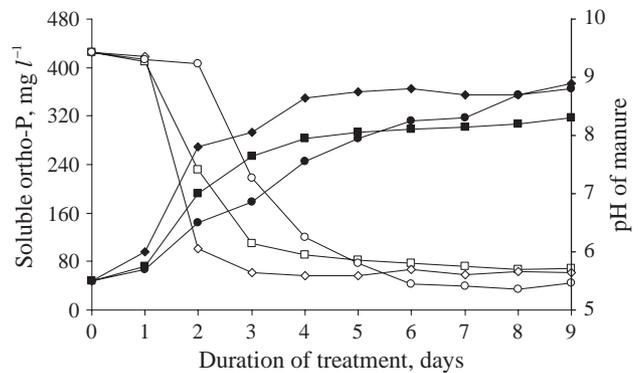


Fig. 1. An overview of the change in both pH ( $\blacklozenge$ , pre-aeration solids/liquid separation;  $\bullet$ , mid-aeration solids/liquid separation;  $\blacksquare$ , control) and soluble ortho-P reduction ( $\diamond$ , pre-aeration solids/liquid separation;  $\circ$ , mid-aeration solids/liquid separation;  $\square$ , control) in the manure during aeration

mid-aeration solids–liquid separation treatment. In the latter treatment the changes in pH and soluble ortho-P seemed to rapidly pick up after the solids–liquid separation on day 4. In the first 2 days of aeration, the pH rose by a less than 0.5 units in both treatments and the control. Previous studies by Zhu *et al.* (2001a, 2001b) and Ndegwa *et al.* (2001) indicated higher pH changes in the first 1.0 and 1.5 days of aeration of 1.0 and 1.5 units, respectively. The manure from these two studies all came from deep pits in under-slat-floor for finishing pig-barns while the manure for this study came from a nursery facility with pull-plug manure management system. While it is quite likely that, the rapid pH change observed in Zhu *et al.* (2001a, 2001b) and Ndegwa *et al.* (2001) studies occurred from purging of carbon dioxide from the piggery slurry, it may not be the only mechanism of raising the pH in this study. The authors believe that, the rise in pH observed in this study could also have been caused by oxidation and volatilisation of fatty acids. This postulation is well supported by the volatile fatty acids (VFAs) data obtained in this study and presented in Fig. 2. The strong correlation of determination of 0.98 of the regression equation of the pH as a function of VFAs suggest that 98% of the increase in pH can be explained by the decrease in VFAs content in the manure. Moreover, the relationship between pH and VFAs depicts a typical weak acid titration curve if the VFAs values on the abscissa are replaced by molar equivalents of a strong base. This type of pH change is usually caused by change in the contents of weak acids in aqueous environments similar to the degradation of VFAs in piggery slurry during an aeration treatment.

From the results presented in Fig. 1 and detailed in Table 2, it is evident that, the solids or more specific the

content of the insoluble P had a significant limitation on the effectiveness of the removal of soluble ortho-P. Removal of insoluble P before aeration treatment resulted in an additional 3% removal of soluble ortho-P, while removal of insoluble P 4 days after the start of aeration treatment resulted in a significant additional removal of 8%. The solids/liquid separation 4 days after the start of the aeration process definitely means that more of the insoluble P will be removed with the solids because there is more insoluble P component at this point in the aeration process than before the aeration process. Solids/liquid separation prior to the aeration process did not significantly improve soluble ortho-P removal for the manure used in this study. A careful analysis of the information presented in Table 1 provides an explanation. The manure used in this study had a huge component of TP as soluble ortho-P at approximately 86% with only 14% making up for the insoluble P and soluble organic P. The implication here is that, even a 100% removal of solids would not remove this entire 14% because the soluble organic P component will not settle. Further evidence that, it is more likely the removal of insoluble P and not removal of solids *per se* that was responsible for the improved removal of soluble ortho-P can be seen in Fig. 3, since the two treatments had approximately the same levels of

TS after the solids/liquid separation. However, although a good 8% additional removal of soluble ortho-P was realised upon removal of insoluble P after 4 days of aeration, more research is needed to determine the most optimal separation point (*i.e.* day 2, day 3, day 5, day 6, or day 7).

From this author's experience working with piggery slurry (Ndegwa *et al.*, 2001, 2002a; Luo *et al.*, 2001; Zhu *et al.*, 2001a, 2001b) the proportions of the soluble P and insoluble P in the piggery slurry used in this study is by no means typical. In most cases, piggery slurry usually has more insoluble P than the soluble P and separation of solids prior to aeration treatment can, therefore, remove substantial quantities of this insoluble P, which may lead into improved ortho-P removal efficiency during subsequent aeration. Due to the practical appeal of solids/separation prior to aeration rather than in the middle of aeration, research work is definitely needed to verify this stipulation.

### 3.2. Effect of pH adjustment

It is evident from Fig. 1 that, there is an inverse relationship between pH and content of soluble ortho-P in the manure liquid. For better understanding of the

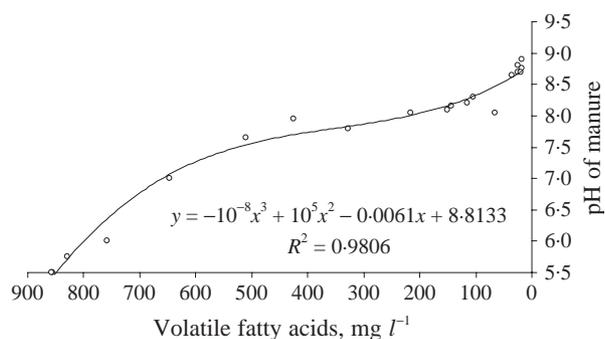


Fig. 2. The pH of manure as a function of volatile fatty acids during the aeration treatment process;  $R^2$ , coefficient of determination

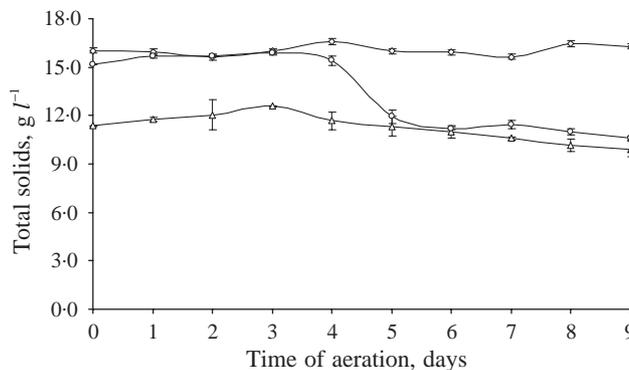


Fig. 3. Changes in the total solids (TS) of respective piggery slurry with time during the aeration treatment process: ( $\Delta$ , pre-aeration solids/liquid separation;  $\circ$ , mid-aeration solids/liquid separation;  $\diamond$ , control)

**Table 2**  
Soluble ortho-P (SOP) in swine manure before and after aeration treatments

Treatment	SOP in raw manure ( $PO_4^{3-}$ , $mg\ l^{-1}$ )	SOP in separated liquid after treatment ( $PO_4^{3-}$ , $mg\ l^{-1}$ )	Maximum reduction achieved, %
Control	$425.0 \pm 16.2^\dagger$	$67.0 \pm 14.0$	$84^{a\dagger}$
Pre-aeration	$425.0 \pm 16.2$	$57.6 \pm 2.3$	$87^{a,b}$
Mid-aeration*	$425.0 \pm 16.2$	$34.8 \pm 0.5$	$92^b$

\* Four days after solids-liquid separation.

† The symbol '±' refers to one standard deviation from the mean ( $n = 6$  for raw manure,  $n = 2$  after treatment).

‡ Values with the same letter are not significantly different at  $\alpha = 0.05$ .

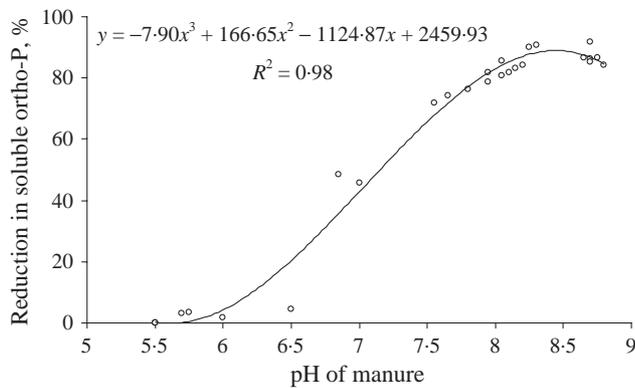


Fig. 4. Relationship between pH and reduction in soluble ortho-P in swine manure based on pooled data;  $R^2$ , coefficient of determination

relationship between pH changes and removal of soluble ortho-P from the liquid, the data from the three treatments were pooled together. Figure 4 shows the relationship between pH and removal of soluble ortho-P (%) from the liquid. The best and simplest regression fitted was a third-order polynomial equation with a correlation coefficient  $R$  of 0.99. From this regression equation, it is evident that the rate of removal of soluble ortho-P is low at either ends of the pH regime (5.5–8.8) and higher in between these two extremes. The removal of soluble ortho-P seems to completely cease at approximately the removal level of 90% even though the pH continued to increase. This observation is in agreement with those of previous research work reported in the literature on aeration treatment processes for removal of ortho-P from piggery slurry (Zhu *et al.*, 2001a; Luo *et al.*, 2001; Ndegwa *et al.*, 2001).

The effects of pH adjustments beyond the values obtained through the aeration processes are shown in Fig. 5, while more detailed results are presented in Table 3. Based on probability  $P$  of ANOVA performed on ortho-P removal data after the adjustment of pH: 0.1345, 0.4032, and 0.0512 for the control, PASL and MASL treatments, respectively, there was no significant ( $\alpha = 0.05$ ) improvement in the removal of ortho-P because of pH adjustment. This is further confirmed by failure to separate the means by the LSD method (down the column values). From these observations, it can be inferred that higher pH levels not reached during aeration treatment are not factors limiting higher removal efficiencies of soluble ortho-P in piggery slurry.

### 3.3. Effect of calcium ( $\text{Ca}^{2+}$ ) ions addition

The effect of addition of  $\text{Ca}^{2+}$  ions after the removal levels of soluble ortho-P had stabilised at the end of the aeration process in day nine are shown in Fig. 6, while

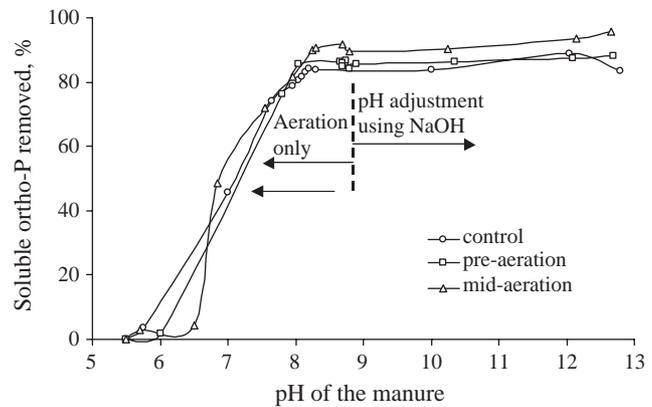


Fig. 5. Effect of adjustment pH with sodium hydroxide on removal of soluble ortho-P after the aeration treatment process: ( $\square$ , pre-aeration solids/liquid separation;  $\Delta$ , mid-aeration solids/liquid separation;  $\circ$ , control)

**Table 3**  
Mean percentage removal of soluble ortho-P (SOP) in swine manure in the treatment and control at each pH adjustment level\*

pH level	Control	Pre-aeration	Mid-aeration
8.8	83.8 <sup>a</sup>	86.7 <sup>a</sup>	91.8 <sup>a</sup>
10.0	83.7 <sup>a</sup>	86.2 <sup>a</sup>	90.1 <sup>a</sup>
12.0	88.8 <sup>a</sup>	87.6 <sup>a</sup>	93.4 <sup>a,b</sup>
12.7	88.3 <sup>a</sup>	88.0 <sup>a</sup>	95.6 <sup>b</sup>
$P^\dagger$	0.1345	0.4032	0.0512

\* Means with the same letters in the same column are not significantly different at  $\alpha = 0.05$ .

<sup>†</sup> Refers to probability  $P$  values from the analysis of variance (ANOVA) performed on the control and the treatment after pH adjustment.

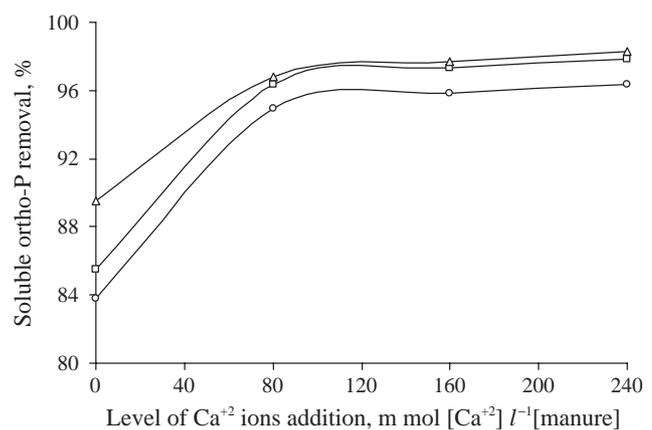


Fig. 6. Effect of addition of  $\text{Ca}^{2+}$  on the removal of soluble ortho-P in the swine manure after the aeration treatment process: ( $\square$ , pre-aeration solids/liquid separation;  $\Delta$ , mid-aeration solids/liquid separation;  $\circ$ , control)

**Table 4**  
**Mean percentage removal of soluble ortho-P (SOP) in swine manure at various stages of calcium ions addition\***

Calcium dose	Removal of soluble ortho-P, %		
	Control	Pre-aeration	Mid-aeration
Zero	83.8 <sup>a</sup>	86.7 <sup>a</sup>	91.8 <sup>a</sup>
Single <sup>†</sup>	94.9 <sup>b</sup>	96.4 <sup>b</sup>	96.8 <sup>b</sup>
Double	95.9 <sup>b</sup>	97.3 <sup>b</sup>	97.7 <sup>c</sup>
Triple	96.4 <sup>b</sup>	97.9 <sup>b</sup>	98.3 <sup>d</sup>
<i>P</i> <sup>‡</sup>	0.0114	0.0010	<0.0001

\* Means with the same letters in the same column are not significantly different at  $\alpha = 0.05$ .

<sup>†</sup> Single dose = 80 mmol  $[\text{Ca}^{2+}] \text{ l}^{-1}$  [manure].

<sup>‡</sup> Refers to probability *P* from the analysis of variance (ANOVA) performed on the control and the treatment after addition of respective additions of calcium.

detailed results are presented in Table 4. The ANOVA indicates significant difference ( $\alpha = 0.05$ ) in the removal of ortho-P with addition of calcium ions, with *P* of 0.0114, 0.0010, and <0.0001 for the control, PASL separation and MASL separation treatments, respectively. The addition of 80 mmol  $[\text{Ca}^{2+}] \text{ l}^{-1}$  [slurry] (single dose) resulted in a tremendous increase in the removal of soluble ortho-P without any adjustment of pH in the control and in the treatments. Double and triple doses did not significantly improve the removal of ortho-P over the single dosage in both the control and the PASL separation treatment. However, double and triple doses also statistically significantly improved removal of ortho-P in the MASL separation treatment. For the control, additional removals of ortho-P of 11.17, 12.08, and 12.59% were achieved by use of single, double, and triple dosages, respectively. Samples drawn from the pre-aeration solids/liquid separation treatment registered 9.63, 10.56, and 11.12% improvement in removal of ortho-P upon addition of single, double, and triple dosages, respectively. The scenario was not any different for the samples drawn from the mid-aeration solids/liquid separation treatment which registered 5.03, 5.89, and 6.47% improvement, respectively, in going from single, to double, and to triple dosages, respectively.

It is, however, self-evident from the foregoing results that  $\text{Ca}^{2+}$  ions and probably other similarly acting ions ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ) were already depleted by the time the higher end of the pH range was reached. It appears that depletion of these ions was a major factor limiting further removal of ortho-P by precipitation of soluble ortho-P into insoluble ortho-P. Addition of small quantities of such ions at the end of the aeration process is therefore recommended in situations where additional soluble ortho-P removal is necessary. Because of economics and the potential secondary environmental

pollution posed by the addition of salts of Ca, Fe, Al, or Mg, the stoichiometry of these treatments will need to be adequately established. More research work is, therefore, necessary to help understand or recommend the extra dosages of metal ions needed to supplement the amounts already in the manure.

#### 4. Conclusions

- (1) Solids/liquid separation prior to aeration treatment resulted in an insignificant 3% additional removal of soluble ortho-P removal while solids/liquid separation 4 days after the start of aeration treatment resulted in a significant 8% additional removal of ortho-P. Solids/liquid separation midway into the aeration process, therefore, was more effective in the removal of soluble ortho-P than pre-aeration solids/liquid separation. This extra-removal of ortho-P in the mid-aeration solids/liquid separation over the pre-aeration solids/liquid separation is attributed to higher removal of insoluble P with solids in former process compared to the latter process.
- (2) Adjustments of pH upward beyond that obtained from the aeration process did not significantly improve the removal of ortho-P from piggery slurry solution. The pH level achieved during aeration process may not be a significant factor limiting further removal of soluble ortho-P during aeration treatment of piggery slurry.
- (3) Significant additional removals of 11, 9, and 5% were observed on the addition of a single dose of  $\text{Ca}^{2+}$  ions (80 mmol  $[\text{Ca}^{2+}] \text{ l}^{-1}$  [slurry]) to the slurry improving removal levels to 95, 96, and 97% for the control, pre-aeration insoluble P removal, and mid-aeration soluble P removal, respectively. No significant additional removal of ortho-P was achieved by double and triple dosages in the control and in the pre-aeration solids/liquid separation. However, a statistically significant additional ortho-P removal was observed in subsequent double and triple dose-treatment in the mid-aeration solids/liquid separation treatment. It can be inferred that depletion of  $\text{Ca}^{2+}$  ions and other similar metal ions necessary for chemical precipitation in the slurry was a major factor limiting even higher removal efficiencies.
- (4) Based on the results of this study, depletion of  $\text{Ca}^{2+}$  ions (and other similarly acting metal ions) and accumulated insoluble P are, most probably, the two main factors limiting the soluble ortho-P removal during aeration treatments of piggery

slurry. These two factors are also likely to be responsible for the wide variations observed in the removal efficiencies because their content will vary with feed rations and manure management practices.

- (5) As high as 98% removal of soluble ortho-P in piggery slurry can be achieved by combining removal of insoluble P (with solids), either prior to aeration treatment or mid-way in the aeration process and addition of limited amounts of  $\text{Ca}^{2+}$  ions during or after completion of batch aeration processes. More research work is needed for more thorough quantification of precise dosages of  $\text{Ca}^{2+}$  needed to most economically realise these high removal efficiencies.

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