Feasibility of Phosphorus Chemical Recycling from Piggery Wastewater. A combined Experimental and Modeling approach

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Introduction

In intensive animal production areas, phosphorus (P) brought to the soils by livestock wastes is higher than crop requirements. P is fixed by the soils but rainfall runoff and erosion lead to the transfer of soil particles in surface water. After solubilisation of P in water, eutrophication can occur. To regulate the overloading of P on soils, an alternative way is to export the P in excess from the sensible zones by recycling it as calcium and magnesium phosphate. In fact, these products could be used later as mineral fertilisers in intensive cropping areas. Moreover, this is in compliance with the fact that P is a limited resource which has to be save.

Some successful attempts to recycle P as struvite (Ammonium magnesium phosphate) from the liquid phase of piggery wastewater have been performed at laboratory and pilot scales (Burns et al, 2003 ; Kim et al., 2004; Nelson et al., 2003 ;Suzuki et al., 2007). However, the recycling potential was low and must be increased by recycling also the mineral P from the solid phase representing up to 80% of the P in piggery wastewater. Enrichment of the liquid phase in dissolved P before a decantation and a side-stream recycling process could be obtained by solubilisation of the solid P. For that, Greaves et Haygarth.(2001) have proposed to use the enhanced biological P removal metabolism to act as a "phosphate pump". Accumulating P in cells during alternate aerobic/anaerobic steps was performed while releasing P was obtained by adding a high amount of carbon as acetic acid at the beginning of the anaerobic step. These experiments were done using a centrifuged and diluted piggery wastewater and more recent works have shown the limited effect of biological treatment on dissolved P using raw piggery wastewater (Daumer at al., 2007 b and c). Indeed, in this case, the biological effect is concealed by the chemical changes occurring during the biological treatment. Then, chemical solubilisation of the P seems to be necessary in order to obtain a high dissolved P concentration needed to increase the recycling rate as chemical fertiliser. Further precipitation of P could be obtained by combining the addition of calcium or magnesium salts and pH increase. Due to the process and the product complexity, chemical-equilibrium modeling could be an interesting way to evaluate the effects of a chemical or physical change and, then, to simulate the changes induced by a treatment process (Celen et al, 2007). In a previous work, the PHREEQCI software (Parkhust and Appelo; 1999) and the MINTEQ database (Allison and Brown, 1995) had been assessed and implemented successfully to describe forms of P in piggery wastewaters (Daumer, 2007). Struvite, brushite and calcite were the main phases predicted and initially observed in the mineral solid fraction of piggery wastewaters. Bril and Salomons (1990) have also predicted whitlockite ($Ca_3(PO_4)_2$) and monetite ($CaHPO_4$) but identification of these compounds was not confirmed by the experimental observations.

The aim of this study was to assess experimentally the feasibility of a chemical recycling process on different piggery wastewaters and then, to investigate the usefulness of chemical modeling for describing the process and choosing the best wastewater/reactant combination to recycle P from piggery wastewater. Experiments were performed on four different piggery wastewaters. The results of modeling P precipitation and solubilisation were compared with experimental results.

Material and methods

Piggery wastewater. Three raw piggery wastewaters (D1, D2 and D3) issued from an experimental program testing different diets for their impact on pH and P forms in piggery wastewaters were used (Table 1). They have been stored 10 months outside at ambient temperature and out of rainfall before the experiments. The other piggery wastewater (AS) was sampled in the biological reactor of a commercial piggery wastewater treatment plant.

Cold PCA extraction. Concentration of the mineral forms in the solid and liquid phase was measured after a cold PCA extraction (30 min, 4°C) (Daumer et al., 2007 a). The analysis was repeated three times for each wastewater.

Biochemical analyses. Total solids (TS) and volatile solids (VS) were measured by the APHA method (2540B and E). Total P was measured by a flow injection analyser (Lachat Instruments, Milwaukee, Wisc., USA) with a blue molybdate method after mineralisation (digestion with peroxodisulfate and sulfuric + nitric acid at 120°C under pressure 1 bar). Dissolved ortho-phosphate in slurry and PCA extract (colored samples) were analysed by ionic chromatography after centrifugation and filtration. All the samples were analysed for cations by ionic chromatography (DIONEX, Sunnyvale, Cal.) except for Fe, Cu, Al and Zn which were analysed by inductive coupled plasma (ICP) and ammonium measured by steam distillation (Bremner and Keeney, 1965).

Table 1: Diets tested for their different acidifying impact. In the 13% protein diets, synthetic essential amino-acids were added (lysine : 8.2g.kg^{-1}; methionine and cysteine : 4.9 g.kg^{-1}; tryptophane : 1.5g.kg^{-1})

	D1	D3	D6
Protein Fraction	13%	18%	13%
Benzoic acid (1% mass)	-	+	-
Phytase (750UI)	+	+	-

Table 2 : Modifications to the Minteq database

Phase	Equilibrium equation	Ksp
Struvite	$MgNH_4PO_4:6H_2O = 6H_2O + Mg^{2+} + NH_4^+ + PO_4^{3-}$	-12.72
Brushite	$CaHPO_4:2H_2O = Ca^{+2} + 2H_2O + HPO_4^{2-}$	- 6.73
Monetite	$CaHPO_4 = Ca^{+2} + HPO_4^{-2}$	- 7.04

Table 3 : main characteristics of piggery wastewaters. Dissolved and total mineral concentrations, S : dissolved ; TM : total mineral =dissolved + mineral in solids.TS : total solids, MM : mineral solids, VS : volatile solids. Figures in bracket are for the standard deviation

	pH	TS	MM	VS	P total	P-PO$_4^{3-}$	Mg^{2+}		Ca^{2+}		N-NH$_4^+$	
		g.kg^{-1}				mmoles.kg^{-1}						
						S	TM	S	TM	S	TM	S
AS	7.78	29(1)	16(1)	13(1)	(29(1)	3.5	22	4.2	19	1.9	43	45
D1	8.66	36(1)	16(1)	21(1)	35(1)	1.8	28	0.2	23	0.8	81	194
D2	7.43	35(1)	13(1)	22(1)	29(1)	0.7	18	5.8	18	3.7	62	123
D3	7.96	44(1)	17(1)	27(1)	37(1)	1.8	29	0.7	30	1.9	47	221

Volatile fatty acid were analysed by HPLC (Peu et al., 2004).

Results for each sample are the mean of 3 analyses.

Table 4: Amount of reactant needed to precipitate all the P in acidified supernatant of piggery wastewaters (mmoles.kg^{-1})

	NaOH	Na$_2$CO$_3$	MgO
AS	50	50	45
D2	75-100	75	45

Table 5: Solid phase composition (mmoles.kg-1)

	Struvite MgNH$_4$PO$_4$:6H$_2$O	Calcium carbonate hydrated CaCO$_3$: H$_2$O
AS	18	42
D1	22	81
D2	16	60
D3	29	46

Solubilisation runs. The experiments have been performed in 500 ml Erlenmeyer flasks. About 100 g of the same wastewater were weighted precisely. Different amounts of hydrochloric acid were added in flasks to obtain a pH value between the initial pH (7-8) and 2. Flasks have been kept under a slow mixing for a 3 hours equilibration time. Then, the samples were centrifuged and the supernatant were analysed for their ionic composition.

Precipitation runs. The supernatants of acidified slurries (pH=4) have been divided in 100 ml fractions in Erlenmeyer flasks. Increasing amounts of reactants (NaOH, MgO and Na$_2$CO$_3$) were added in each flask to reach pH values between 4 and 9. The flasks were slowly mixed for 3 hours and centrifuged. The supernatant was analysed for its ionic concentrations and the pellet was kept for solid analysis. Chemical reactants were laboratory pure reactant obtained from Sigma-Aldrich Chemical (Saint-Louis, Missouri, USA).

Solid analyses. Samples were centrifuged (10510G, 20 min, 20°C). Optical analyses were performed, at once, on the wet pellet. Scanning electronic spectroscopy coupled with energy dispersive X-ray analysis (SEM-EDS) (Philips XL 30 SFEG) and X-ray diffraction analysis (XRD) (Power X-ray diffractometer D 5005 Siemens) were performed after drying at room temperature.

Modeling. The PHREEQCI software (Parkhust and Appelo, 1999) and the joined Minteq database (Allison and Brown, 1995), were used. Input are, to one side, the mineral compounds and organic acids concentrations in the media and characteristics of the solution (pH, redox and conductivity) and, to the other side, equilibrium equations and corresponding thermodynamic data in the database. The modelling run starts with an initial activity assessment of components present in the system and, then, calculates the activities of possible aqueous species and the amount of precipitated phase by solving equilibrium and mass balances equations. Struvite, brushite and monetite, previously found in piggery wastewater, were added to the database (Bril and Salomons, 1990; Daumer, 2007) (Table 2). The thermodynamic constants were taken from the NIST database (2001). The Ksp for struvite (-12.72) was taken from Abbona et al.(1986). The fit between calculated and measured data was expressed by the slope of the linear regression between the calculated data and the measured data. The dispersion of the data was calculated by the determination coefficient of this linear regression. Calculation was performed with the linear regression function of the Microsoft Excel® software.

Results and discussion

Piggery wastewater characteristics. The characteristics of the piggery wastewater are described in table 3. Even for the most acidic piggery wastewater, less than 5% of P was initially as mineral dissolved P. The ratio between the total mineral P and the total P, which represents the P recycling potential by a chemical process, varied from 62% (D2) to 80% (D1). Calcium was the main cation in the mineral solid form in all the samples but the Ca/Mg molar ratio varied from 1.6 (D3) to 3.4 (D2). The ammonium concentration varied

from 45 to 221 mM . The minimum was observed for AS which was previously treated for nitrogen removal by nitrification /denitrification.

Calcium carbonate, calcium phosphate and magnesium phosphate were observed either by optical microscopy analysis or SEM-EDS in the solid phase of all the piggery wastewater. Magnesium phosphate crystals had the same shape than those described as struvite by Doyle and Parsons (2002). However struvite were not clearly identified by X-ray diffraction probably because of interferences with others crystals and the high organic matter in the solid phase.

Solubilisation runs. Between 70% and 80% of the total mineral P were dissolved between pH 6 and pH 7 in AS, between pH6 and pH 5 for D1, D2 and D3 (figure 1). Then, a plate was observed, no more increase of dissolved P was observed in AS and very strong acidic conditions (pH<2) are needed to dissolve the remaining P in D1 and D2.

Figure 1: Dissolved P as pH function during piggery wastewaters acidification tests
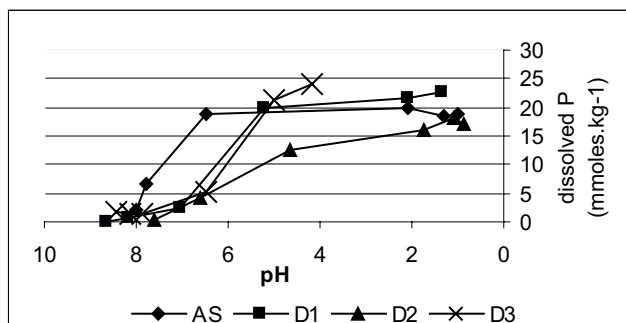
A noticeable difference in buffer effect was observed for the different wastewaters. For instance, 0.13, 0.18, 0.29 and 0.48 moles HCl .kg^{-1}, were needed to reach pH 5.5 and dissolve most of the P for AS, D2, D1 and D3 respectively (figure 2).

Figure 2: pH as function of hydrochloric acid added during piggery wastewaters solubilisation runs
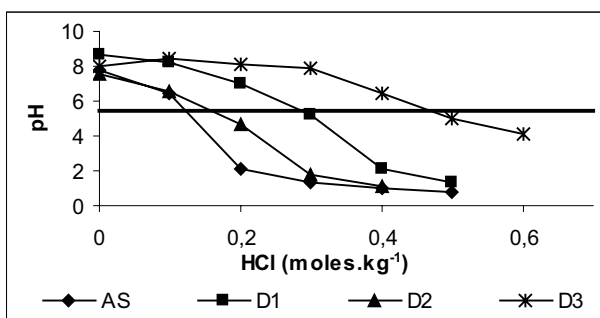
In piggery wastewater, the buffer effect is driven mostly by the ammoniacal nitrogen and carbonate systems (Sommer and Husted, 1995). It was lowered in AS because nitrogen was removed by the biological treatment by nitrification/denitrification. In D2, the amount of ammoniacal nitrogen was also decreased by decreasing the protein ratio in the diet.

No more struvite crystals were observed by optical microscopy for pH 7 and below.

Because of their low buffer effect, AS and D2 were the most suitable effluent to chemically recycle P. Then, these 2 piggery wastewaters were used for the precipitation runs. A larger amount of these two piggery wastewaters were acidified to obtain a pH about <4 in supernatant and let to settle for 72 hours. However, after the settlement time, the pH was 5.32 and 4.1 for AS and D2, respectively.

Precipitation runs.

The pH needed to precipitate all the dissolved P was about 7 for D2 and 8 for AS.

About 50 mmoles.kg^{-1} of reactant were needed to precipitate all the P from AS supernatant whatever the reactant tested. Even if a lower pH was needed to precipitate the P in D2, a larger amount of reactant was required excepted when MgO was used (table 4).
The lower buffer effect of AS previously discussed could explain that less reactant was needed to increase the pH in AS. The effect of MgO addition was both to increase the pH and to supply magnesium. An initial Mg/P molar ratio between 2 and 3 was needed to precipitate all the P from the acidified supernatant. This is in accordance with Celen et al (2007) who obtained a 98% precipitation rate by adding $MgCl_2$ with a Mg/P molar ratio of 2 in supernatant from an anaerobic treated piggery wastewater. Usually, because of its higher solubility, $MgCl_2$ is used instead of MgO, to supply magnesium. However $MgCl_2$ has an acidifying effect and NaOH addition is required to increase the pH for P precipitation (Türker and Celen, 2007; Suzuki et al., 2007). In our study, the supernatant was already acid, increasing the solubility of the MgO which could supply magnesium while increasing the pH without NaOH addition. The crystals of calcium phosphate, observed in all the samples by optical microscopy and SEM-EDS between pH 5 and pH 8, were clearly identified as brushite by X-ray diffraction. A mixture of struvite and calcite were identified at higher pH in MgO and Na_2CO_3 samples. No more brushite was observed. A very few crystals were observed in NaOH samples when pH was higher than 6. They had a non regular shape and no clear spectra were obtained by X-ray diffraction.

The succession of brushite and struvite precipitation with Na_2CO_3 and MgO addition was in compliance with dissolved calcium and magnesium changes. Calcium started to precipitate between pH 5 and 7 while precipitation of magnesium occurred only from pH 7. No magnesium decrease was observed with NaOH addition in D2 and only 5 mmoles were precipitated with NaOH addition in AS. An amorphous calcium phosphate was probably the main mineral phosphate in NaOH samples where a very few amount of crystals were observed. In contrast to MgO or Na_2CO_3, NaOH was added on a liquid form. Crystallisation is increased by suspended particles (Valsami-Jones, 2004). When NaoH was added, nucleation without crystallisation could occur. In MgO and Na_2CO_3 samples, dissolved calcium did not increase after brushite dissolution (pH above 7) partly because of the formation of calcite observed in the samples. Another explanation is the formation of an amorphous calcium phosphate even in the samples where struvite were formed. Brushite is the most stable form of calcium phosphate in acidic conditions (Valsami-Jones, 2001) but amorphous forms of octocalcium phosphate, tricalcium phosphate and monetite have been identified at neutral or basic pH in sewage sludge (Frossard et al, 1994; Angel, 1999). This is confirmed by the precipitated Mg/P ratio in Na_2CO_3 precipitated samples, which was 0.58 for AS and 0.85 for D3, while Mg/P ratio in struvite is 1. With MgO, magnesium in solution was in excess and the ratio Mg/P in solid was up to 2. Formation of magnesium carbonate or adsorption of magnesium on mineral particles could occur. The same succession of solid phases, brushite, struvite and amorphous calcium phosphate, with pH evolution has been described by Abbona et al. (1986,1988) in synthetic solution containing calcium magnesium and phosphate.The size and the amount of the struvite crystals were different from a sample to another. A lot of small crystals were observed in AS supernatant when Na_2CO_3 was used. They had a stick shape, 20-30µm length and width<10µm. Bigger and wider ones with the characteristic shape of struvite were

observed with D2, but crystal density was low. When MgO was used a large amount of medium size crystals was observed for AS and D2 (length=50µm, width=20µm). Struvite cristallisation depends on several factors and the size and the shape of crystals can be modified by ionic strength, foreign ions among which calcium (Le Corre et al., 2005) or organic matter (Valsami-Jones, 2004). Moreover a very low amount of samples was taken for solid analysis and the conclusions about crystals size and shape have to be confirmed.

Modeling Process

A good fit between measured and calculated elements distribution in solid and liquid phase was observed. Also, the composition of the solid phase of the initial piggery wastewater was calculated (table 5). This is in compliance with the optical and electronical microscopic observations except for calcium phosphate which was observed by SEM-EDS and not predicted. The succession of solid phases predicted for the precipitation tests were the same as those identified by microscopy and X-ray diffraction analysis. Moreover, the limits of pH intervals in which the phase were predicted were consistent with the observation. Brushite was predicted between pH 5.2 and 8.2, struvite between 7.4 and 9.2, and hydrated calcite between 7 and 9.2. Only a few amount of struvite was predicted in NaOH precipitated samples but brushite and hydrated calcite were predicted instead, while only a few crystals were observed experimentally. The fit between measured and calculated pH during the acidification tests was good except for the last acidification point for D3. The slope of the linear regression was 0.99 and the determination coefficient was 0.987 and 0.995 with and without the last D3 acidification point respectively. The pH was slighty underestimated by the calculation in the precipitation tests (slope = 0.96). The slope of the linear regression curve between calculated and measured dissolved P for all the samples was 1,0 and 0.98 for the solubilisation and precipitation runs/precipitation tests respectively. However, the dispersion of the data was higher than for pH, the determination coefficient was 0.98 and 0.92, respectively. This dispersion was mainly due to the underestimation of calculated dissolved P linked to the overestimation of brushite formation at pH about 6, either during the solubilisation or precipitation runs. The fit was good, in precipitation tests, for calculated dissolved magnesium but calcium was overestimated. The slope of the linear regression was 1.1 and 1.22 and the determination coefficient 0.92 and 0.96 respectively. Brushite is the first solid phase formed during the precipitation process. In acidification tests, brushite precipitation depends on dissolved phosphate released by struvite dissolution and dissolved calcium released by calcite dissolution. The determination of the constants and the role of adsorption mainly in organic containing wastewater are the main limits in geochemical modelling in environment (Dudal and Gerard, 2004). More often, the solubility constant in the database are measured with pure phase in water. In complex media like piggery wastewater, foreign ions could be substituted and impurities included during the crystallisation process modifying the solubility of the solid phase. Mixed phase could also formed (Valsami-Jones 2001). Further works are needed to precise the constants and their variability in our context experimentally and then to better evaluate the role of ionic interactions and of the organic matter in the process. On a technical point of view, PHREEQCI was tested for its ability to determine the amount of reactant needed either to decrease the pH between 5 and 6 to dissolve all the P in the acidification test and to increase it between7 and 8 to precipitate all the phosphate from the supernatant. Measured amount of HCl needed to reach a pH close to 5.5 in the solubilisation runs was inside or close to the calculated interval except for D3. The measured of reactant needed to precipitate all the P was always in the interval calculated to obtain a pH between 7 and 8. According to Celen et al. (2007) geochemical modelling gave a good estimation of the magnitude order of reactants needed and was useful to compare wastewater on one side and reactants which could enter in the recycling process in the other side. However, some improvements are required to refine the amount and to better understand the evolution of dissolved compounds and solid phases in the intermediate step of the solubilisation and precipitation processes.

Conclusion

This work have shown that the feasibility of chemical P recycling from piggery wastewater will strongly depend on the buffer effect/capacity of the effluent and, consequently, on the pig diets but also on previous treatment which could reduce the ammoniacal nitrogen content. Indeed, the amount of acidifying reactant could be reduced by four using an optimised diet or by biologically nitrogen removal compared to a standard diet. The amount of reactant was minimal with the acidified supernatant from biologically treated piggery wastewater precipitated by magnesium oxide or sodium hydroxide. The crystallisation and so further separation of the solid was better with magnesium oxide. Brushite, struvite and calcite were identified as the solid phases involved in the acidification/precipitation process both in experimental and simulated results. Another form of calcium phosphate and complex mixed calcium/magnesium phases and adsorption mechanisms could explain the quantitative differences between calculated and experimental data. Even if some improvement are needed to describe more precisely the process, the PHREEQCI geochemical modelling software is a useful tool to predict the ability of an effluent to enter the process and the amount of reactant required.

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