Technical and economical assessment of formic acid to recycle phosphorus from pig slurry by a combined acidification–precipitation process

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ABSTRACT

Dissolution by acidification followed by a liquid/solid separation and precipitation of phosphorus from the liquid phase is one possibility to recycle phosphorus from livestock effluents. To avoid increase of effluent salinity by using mineral acids in the recycling process, the efficiency of two organic acids, formic and acetic acid, in dissolving the mineral phosphorus from piggery wastewater was compared. The amount of formic acid needed to dissolve the phosphorus was reduced three fold, compared to acetic acid. The amount of magnesium oxide needed for further precipitation was decreased by two with formic acid. Neither the carbon load nor the effluent salinity was significantly increased by using formic acid. An economical comparison was performed for the chemical recycling process (mineral fertilizer) vs. centrifugation (organic fertilizer) considering the centrifugation and the mineral fertilizers sold in the market. After optimisation of the process, the product could be economically competitive with mineral fertilizer as superphosphate in less than 10 years.

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1. Introduction

In areas with intensive livestock production, effluents have been spread on a nitrogen basis for many years, leading to phosphorus accumulation in soils [1,2]. Due to run-off and erosion, this phosphorus continues to contribute to eutrophication of surface fresh water. To avoid this pollution, legislation tends to limit phosphorus inputs to the amount required by the crop. To comply with the new regulations, part of phosphorus must be extracted from livestock effluents and exported far from production areas. This is even more important in sensitive areas, when nitrogen is biologically removed to prevent nitrate pollution of the groundwater [3]. The cost of exporting phosphorus depends on the purity of the product and on its fertilizer effect.

Usually phosphate fertilizers are produced from phosphate rocks. Recycling phosphorus from livestock effluents as a "pure" mineral fertilizer could also help economize phosphate ore, which, at its present rate of usage, will not last more than a few centuries [4].

Most recycling processes have been developed to recycle dissolved phosphorus, which is the main form of phosphorus in industrial or urban wastewater, but also to decrease the nutrient content of effluents from livestock treatment plants [5]. The recycled product is either calcium or magnesium phosphate, depending on the precipitant used in the process. In livestock effluents, phosphorus is mainly present in solid mineral form [6,7]. Several mechanical separation techniques can efficiently remove the phosphorus from livestock effluents [8], but the phosphorus is concentrated in a solid product mainly containing organic matter. Consequently, the cost of transporting the phosphorus is increased and special equipment is required to spread the product.

Chemical dissolution by acidification combined with solid/liquid separation is an alternative way to separate the phosphorus from the organic matter. The mineral product obtained by precipitation of phosphorus from the enriched supernatant can then be used for agricultural purposes. This technique has been already been tested in previous studies on pig slurry [9], poultry litter [10] and ashes [11]. Because of the acidic pH of the supernatant, the solubility of the reactant is increased and magnesium oxide or hydrated lime can easily be used to increase the pH and to simultaneously supply cations. Magnesium oxide (MgO) induces struvite ($MgNH_4PO_4^{3-}$:$6H_2O$) crystallisation and precipitation. Hydrated lime $Ca(OH)_2$ induces the formation of an amorphous calcium phosphate that is of agricultural value [10]. The agricultural value of the struvite is usually the same or better than that of superphosphate.

The limiting factor of this recycling process is the cost of the acidification step [9]. Less reactant is needed when the buffer effect due to ammonia and carbonate is mitigated by biological nitrification/denitrification [12]. Many mineral and organic acids have

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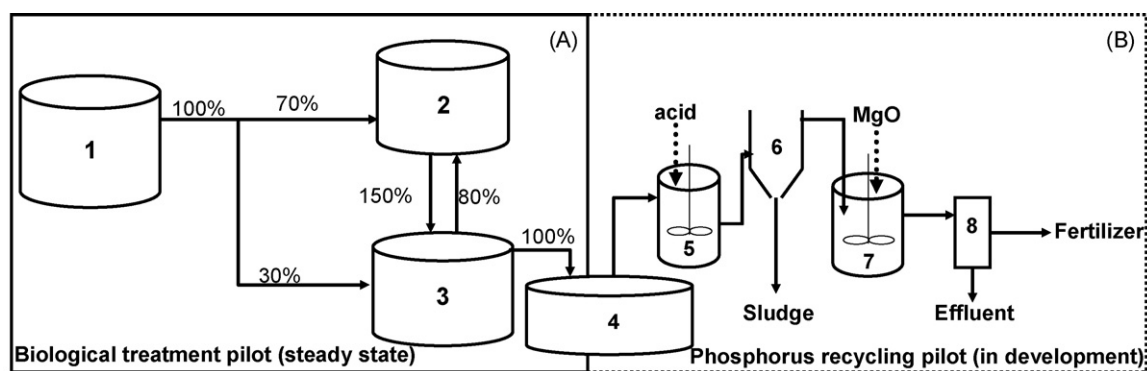 E-mail address: marie-line.daumer@cemagref.fr (M.-L. Daumer).

Fig. 1. Technical schematic of the combined biological and phosphorus recycling treatment unit. (A) Biological treatment for nitrogen removal and methane production: 1: raw pig slurry storage pit; 2: anaerobic digester; 3: aerobic/anoxic reactor; 4: treated slurry storage pit. Figures are in percent of input mass treated in one cycle. (B) Phosphorus recycling process: 5:acidification reactor; 6: decantor; 7: precipitation tank; 8: filter bags.

been tested. Szögi et al. [10] showed that citric acid is more efficient than hydrochloric or acetic acid to extract phosphorus from poultry litter. However, for economic reasons, these authors chose sulphuric acid to evaluate the production cost at a large pilot scale. Mineral acids supply anions (chloride or sulphate) at high concentrations ($>2\,g\,L^{-1}$). These soluble anions increase the salinity of the final effluent. On the other hand, organic acids increase the easily degradable carbon content of the effluent. Formic acid, which is the only strong organic acid with only one carbon, has never been tested as a phosphorus recycling technique.

The aim of this study was to assess the technical and economic interest of using formic acid compared to acetic acid to recycle the mineral phosphorus from biologically treated pig slurry. We evaluated its impact on the acidification step but also on the further precipitation step with and without a polymer.

2. Material and methods

2.1. Biologically treated pig slurry

Treated slurry was collected in the storage pit of a Cemagref pilot treatment plant located in Rennes (France). The pilot plant was designed to combine biological aerobic/anoxic nitrogen removal and anaerobic digestion for methane production from slurry from a commercial pig farm (Fig. 1).

The anaerobic digester is a 100 L plastic pit with agitation, the aerobic/anoxic reactor is a 125 L plastic pit equipped with a fine bubbles diffuser. The hydraulic retention time in both of the pits was 40 days. The pilot was fed two times a day with 2.5 kg of raw slurry just after the discharge of the same amount. Aeration began seven hours after the feeding and was running during two hours after that the redox reached its maximum level.

The characteristics of the biologically treated pig slurry are depicted in Table 1.

2.2. Acidification

Formic acid (HCOOH, 85%, 405832, Carlo Erba) or acetic acid (CH$_3$COOH, 80%, 20-119-368, VWR) was added, under mixing, to 2 L beakers containing 1 L of pig slurry. Experiments were per-

formed in triplicate. Beakers were covered to avoid evaporation. After decantation (72 h at room temperature), the supernatants were pumped gently with a peristaltic pump (Ecoline VC, Ismatec®, Switzerland). After sampling for analysis, the supernatants from the three replicates of formic acid tests (SFA) or acetic acid tests (SAA) were combined.

2.3. Precipitation

Because the ammonium required for struvite crystallisation had been completely removed in the preceding biological process, supernatant from untreated pig slurry was added to each of the supernatants to provide ammonium (4%, v/v). The SFA and SAA were both split into $9 \times 100\,g$ fractions in 250 ml beakers. Three beakers were used as controls.

Magnesium oxide (25054-367, VWR) was added under mixing (magnetic stirring) to reach a pH close to 8 in six of the nine beakers. After three hours contact time the mixing was slowed down and $30\,mg\,kg^{-1}$ of polymer (Magnafloc 120L®, CIBA, Germany) were added to three of the six beakers containing MgO and to the controls. The concentration was adapted from Szogi et al. [13].

The solid was separated form the liquid by filtration on 100 μm porous bags made of the same material as those used by Szogi et al. [13] (Teknobag®).

2.4. Biochemical analyses

Total solids (TS) and volatile solids (VS) were measured using the APHA method (2540B and E) [14]. Mineral solids (MS) were calculated as the difference between TS and VS. Total chemical oxygen demand (TCOD) was measured using the French standard NF T 90-101. Total phosphorus was measured with a flow injection analyser (Lachat Instruments®, Milwaukee, WI, USA) using a blue molybdate method after mineralisation (ashes were digested with peroxodisulphate and sulphuric + nitric acid at 120 °C under pressure of 1 bar). Total cations from the digestate were measured by ionic chromatography (DIONEX®, Sunnyvale, CA, USA). Dissolved orthophosphate and cations were analysed by ionic chromatography after centrifugation (20 min at 18000 g) and filtration. Volatile fatty acids (VFA), namely acetic acid, propionic acid, butyric acid,

Table 1
Characteristics of raw slurry (RS) and biologically treated slurry (BTS).

	pH	TCOD	VFA	P total	Mg total	Ca total	N-NH$_4^+$
		$gO_2\,kg^{-1}$	$g\,kg^{-1}$				
RS	8.0	37 ± 1	4.6 ± 0.1	1.0 ± 0.1	0.62 ± 0.1	3.4 ± 0.1	2.4 ± 0.1
BTS	8.4	26 ± 1	0.2 ± 0.1	1.2 ± 0.1	0.62 ± 0.1	3.0 ± 0.2	0.05 ± 0.01

isobutyric acid, valeric and isovaleric acid were analysed using high-pressure liquid chromatography (HPLC) [15]. Ammonium was analysed by steam distillation [16]. Results for each sample are the mean of three analyses.

2.5. Economic simulation

The prices of the chemicals were obtained from local suppliers and were based on a representative pig farm located in "Côtes d'Armor", which is the main pig production area in France. This farm produces 15–20 m^3 of pig slurry per day. The cost of transport was included. The process is not yet sufficiently developed to obtain data about investment costs, which were estimated to be about €80.000 for the configuration described in Fig. 1, with an 8-year write-off. Annual maintenance and other running cost (mainly energy) were considered to be 10% of the investment. For the purpose of comparison, the data on the organic fertilizer currently produced by centrifugation were obtained from the managers of existing farm-scale equipment. They included investments, maintenance and all running costs. Finally a comparison, including the transport cost of the product on a phosphorus unit basis, was performed for the two products. The distribution between liquid effluent and sludge was similar for the two treatment techniques. So the management cost of these products was considered to be the same and was not included in the comparison.

3. Results and discussion

3.1. Acidification step

The amount of formic acid required to reach a pH of between 4.5 and 5 was only 7 g kg^{-1} with formic acid compared to 20 g kg^{-1} with acetic acid. Previous works showed that more than 80% of the total phosphorus in piggery wastewater was dissolved at this pH [6]. The performance of the liquid/solid separation by decantation step was the same, about 50/50 (w/w).

There was no difference between the two treatments in terms of sludge characteristics. TS was 64 ± 3 g kg^{-1}, mainly as volatile solids (43 ± 4 kg^{-1}). The composition of the supernatants after acetic or formic acidification was also the same except for TCOD and VFA (Table 2).

Even though sulphuric acid is cheaper [10], we chose an organic (formic or acetic) acid to dissolve the mineral phosphorus in pig slurry. Our objective was to avoid enriching the effluent with undesirable compounds (chloride or sulphate), which increase salinity or can be reduced to foul-smelling or toxic compounds during anaerobic storage [19].

Compared to acetic acid, formic acid allowed the amount of reactant required to dissolve the phosphorus to be reduced 3-fold, and minimised the increase in chemical oxygen demand in the liquid effluent. The amount of formic acid needed to dissolve 1 kg of phosphorus in pig slurry was similar to the amount of sulphuric acid required to extract 1 kg of phosphorus from poultry litter: 7 kg kgP^{-1} [20]. This is much more than the amount cited by Dockorn et al. [21] (0.9 kg kgP^{-1} of hydrochloric acid) required to dissolve phosphorus from wastewater sludge ash.

3.2. Precipitation step

Four percent of untreated pig slurry supernatant was added to the acidified supernatant to provide the ammonium required to increase phosphorus crystallisation as struvite as shown in a previous study [9]. After this addition, the ammoniacal nitrogen content was respectively 120 ± 20 mg kg^{-1} and 149 ± 1 mg kg^{-1} in the SAA and SFA. No precipitation was observed when raw piggery supernatant was added without MgO. The amount of MgO required to reach a pH > 8 and to precipitate nearly all the dissolved phosphorus was 0.2 and 0.4 g kg^{-1} in the SFA and SAA samples respectively. The amount of magnesium oxide added in this study was also less than the amount of hydrated lime used by Szögi et al. [20] to precipitate phosphorus from acidic extract of poultry litter. The difference could be explained by reactant activity but also the low buffer effect of formic acid compared to the citric acid used by these authors.

The total phosphorus in the liquid after 100 μm filtration was 25 ± 5 mg kg^{-1} in the SFA and 120 ± 30 mg kg^{-1} SAA samples. A lot of small particles were observed, mainly in the SAA samples. There was no significant difference in dissolved P-PO$_4^{3-}$. When about 30 mg kg^{-1} of anionic polymer were added before filtration, as recommended by Szogi et al. [13], the total phosphorus concentration in the liquid decreased to 14 mg kg^{-1} in all samples (Table 3). In addition, separation was faster.

Finally, three products were obtained from the complete recycling process: The decanted sludge from acidification, and the liquid from the precipitation step, which are spread locally, and the solid dried product, which can be exported as mineral fertilizer. The solid dried product represented less than 2% and the liquid product about 85–90% of the initial mass of acidified supernatant. Loss due to evaporation during the solid drying step was 10–15%. The final distribution of mass, phosphorus and calcium in the products of the complete recycling process (including the acidification step) is summarized in Fig. 2., Magnesium in liquid was increased two-fold by the process using formic acid and 2/3 of the added magnesium ended up in the solid product. Magnesium in liquid was increased 4-fold using acetic acid and only 1/3 of the added magnesium ended up in the solid product. Recovery calculated from

Table 2
Characteristics of supernatants from decantation after acidification. Control means decantation without acidification.

	pH	TCOD	VFA	P total	Mg total	Ca total	N-NH$_4^+$	Mg^{2+}	Ca^{2+}	P-PO$_4^{3-}$
		gO$_2$ kg^{-1}	mg kg^{-1}							
Control	8.4	3 ± 1	220 ± 6	267 ± 12	115 ± 20	100 ± 3	40 ± 1	111 ± 12	104 ± 1	226 ± 1
SFA	4.92 ± 0.04	6 ± 1	7087 ± 0112	922 ± 4	616 ± 25	2090 ± 55	66 ± 2	516 ± 6	1885 ± 08	821 ± 80
SAA	4.75 ± 0.02	18 ± 1	19000 ± 2000	832 ± 6	596 ± 13	1980 ± 49	71 ± 4	526 ± 6	2034 ± 50	791 ± 09

Table 3
Composition of the liquid effluent from the precipitation step, mg kg^{-1}.*Only one of the three replicates was available for analysis.

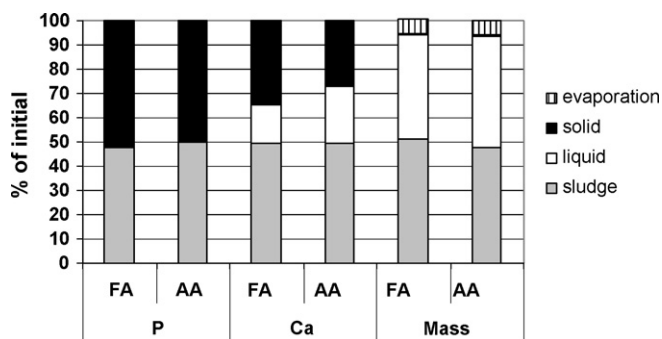|	pH	P total	Mg total	Ca total	N-NH$_4^+$	Mg^{2+}	Ca^{2+}	P-PO$_4^{3-}$
SFA + MgO	8.88	25 ± 5	1405 ± 22	1129 ± 12	115 ± 18	961 ± 120	609 ± 99	8 ± 3
SAA + MgO	8.98	120 ± 30	2450 ± 70	986 ± 58	55 ± 6	1930 ± 13	1007 ± 9	12 ± 2
SFA + MgO + Pol*	8.23	14	1394	915	114	984	681	14
SAA + MgO + Pol	8.9	14 ± 4	2491 ± 56	1049 ± 24	nd	1573 ± 10	272 ± 19	nd

Fig. 2. Mass, phosphorus and calcium distribution in products from the recycling process. FA: formic acid; AA: acetic acid; P: phosphorus; Ca: calcium.

Table 4
Composition of solid after two weeks drying at room temperature, $g\,kg^{-1}$.

	SFA + MgO + polymer	SAA + MgO + polymer
TS	838 ± 1	866 ± 35
VS	238 ± 2	303 ± 12
P	96 ± 2	83 ± 2
NTK	4 ± 1	7 ± 1
Ca	142 ± 26	118 ± 24
Mg	70 ± 10	59 ± 11
K	50 ± 4	30 ± 3
Na	17 ± 1	10 ± 1

the concentrations and mass in the liquid, sludge and solid products ranged between 90% and 110% of the total amount in the initial treated pig slurry for all the components.

3.3. Composition of the solids

Table 4 shows the concentrations of solids after two weeks of drying at room temperature. The dry matter content of the products obtained using formic and acetic acid was respectively 834 and 866 g kg^{-1} including 28% and 35% of organic matter. The total percentage of calcium, magnesium and phosphate in the mineral dry matter was 84% in products made using formic and 77% in products using acetic acid. Potassium and sodium remaining after evaporation of the liquid phase were 7% and 4%, respectively.

To be sold as fertilizer, the product must comply with regulations. The normalized NPK (N–P$_2$O$_5$–K$_2$O) composition of the product of formic acidification was 0–22–6 including 19% of CaO and 12% of MgO, while for the product of acetic acidification, it was 1–19–4 including 16% of CaO and 10% of MgO. The N–P–K levels were in compliance with the minimum contents required for class II PK fertilizers as described in the French standard NF U42-001/A8 (>18% of P$_2$O$_5$ + K$_2$O). The CaO and MgO concentration were close to the limits for class III products (fertilizers supplying calcium and magnesium). The neutralizing value of the products was not analysed in the present study.
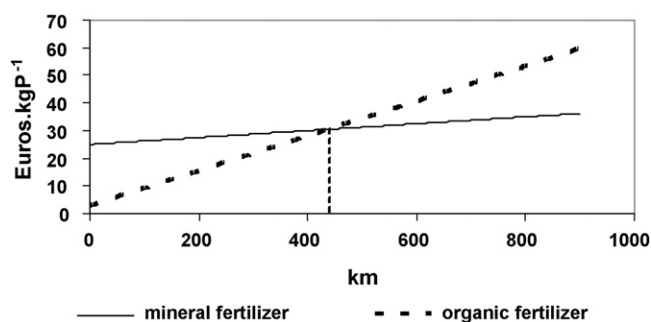

Fig. 3. Comparison between the production and transport cost of the product from the chemical recycling process (mineral fertilizer) and from centrifugation (organic fertilizer) on a phosphorus unit basis.

3.4. Economic considerations

The above results were used to calculate the cost of chemicals for phosphorus recycling (Table 5). Polymer is added in such small quantities, that the price was not included (less than 1 cent m^{-3}).

The cost of the acetic acid was more than double that of formic acid and had no technical advantages. Consequently, we only retained the formic acid technique for comparison with organic fertilizer obtained by centrifugation. If we consider this process as a treatment process it is far from being competitive with centrifugation, 12.3 € m^{-3} of slurry treated vs. 1.6–2.5 € m^{-3} for centrifugation. The difference is even bigger when production costs are considered on the basis of a phosphorus unit: about 25 € kgP^{-1} using the chemical recycling process and 2.6 € kgP^{-1} using centrifugation. The transport cost for organic fertilizer is about 1.2 € t^{-1} km^{-1}. On this basis, the cost of P in the mineral fertilizer obtained by formic acid recycling is competitive with that in organic fertilizer when it is transported more than 450 km (Fig. 3)

More than 98% of the dissolved phosphorus from the acidified supernatant was precipitated by the addition of magnesium oxide. So, the limiting step of the process is the solid/liquid separation after acidification, which retains only 50% of the initial total phosphorus. We selected static decantation because of its low running cost, but simple mechanical separation using vibrating screens, draining or a belt filter, could increase the recycling rate with the same amount of acid. If the performances are the same as for raw slurry, the recycling rate could be up to 80% [17,18]. In this case, the final increase in the cost of the treatment would be about 2.7 € m^{-3} because of the initial investment and magnesium oxide, but the production cost of the recycled product would be reduced to 15 € kgP^{-1}. In this case, the new estimation of the distance above which the recycled mineral product will be competitive with the organic one is reduced to 250 km. However, the production cost of phosphorus using this process was still much higher than that of a standard mineral fertilizer with a similar P content as superphosphate, which is sold for 10 € kgP^{-1} including transport (public price).

If the increase in the price of standard mineral fertilizer keeps up with the increase in the price of mined phosphate as stated

Table 5
Treatment cost estimation.

	Amount kg m^{-3} of pig slurry		P.U. € kg^{-1}	Price € m^{-3} of pig slurry	
	Formic	Acetic		Formic	Acetic
Acid	8	20	1	8	20
MgO	1	2	1.5	1.5	3
Invest				1.4	1.4
Energy & Maintenance				1.4	1.4
Total				12.3	26.1

by Van Horn and Sartorius [22], recycled products could become competitive with mineral fertilizers made from phosphate rock in ten years. Moreover thanks to its high magnesium and calcium content, the recycled product could replace several mineral fertilizers. A recent study showed a higher fertilizing value of recycled phosphorus from wastewater sludge than that of superphosphate, probably because of the synergy between magnesium and phosphorus on lettuce [23]. In this case, the sales price would be higher than that of simple phosphate fertilizers, increasing its economic feasibility.

In this study, estimated production cost was based on the cost of the chemical reactants used in the technique. Substituting these reactants by industrial by-products could be another way to reduce the cost of the recycling process. However, further work is required to determine if such products are suitable for use with livestock effluents.

4. Conclusions

As the phosphorus in livestock effluent is mainly in solid mineral form mixed with organic matter, an initial chemical dissolution step is required to dissolve the phosphorus so that, after separating from the organic matter, it can be recovered into mineral fertilizer. This study showed that formic acid allows phosphorus to be dissolved without increasing the salinity or the carbon load of the effluent or resulting in undesirable components like sulphate. The amount of formic acid required is three times lower than that of acetic acid. By reducing the buffer effect, using formic acid also means the amount of precipitation reactant can be reduced. The decantation step after acidification is the limiting step in increasing the recycling rate and decreasing the production cost of recycled fertilizer. Better performances could be obtained using a mechanical separation technique instead of simple decantation. But, even in these conditions, the costs of the chemical phosphorus recycling process are about ten times higher than using a centrifuge decanter. This process would be competitive only if phosphorus has to be exported long distances from the treatment plant or for a specific agricultural use. The product from recycling could be classified as Type II or III fertilizer (French standards). However, its production cost is above the public sales price of superphosphate even including transport. But from an economic point of view, given the price of mined phosphate rock and even without public incentives, it could become competitive in less than ten years.

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