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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.

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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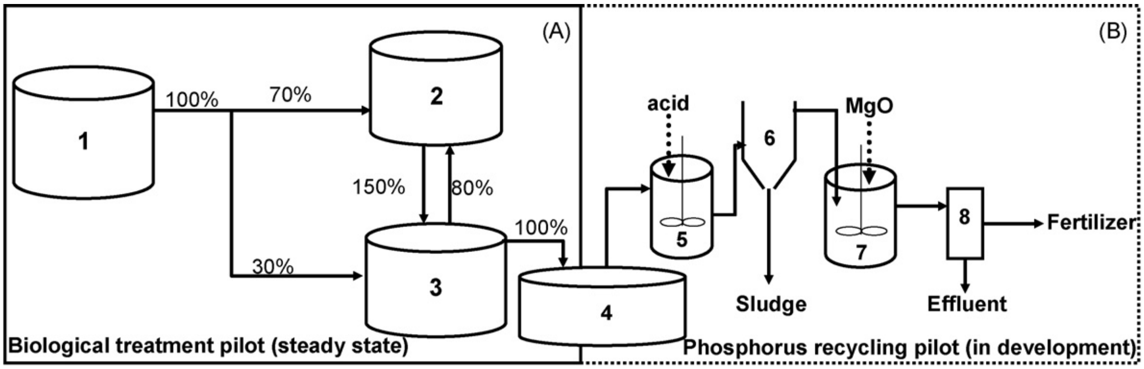

Fig. 1. Technical schematic of the combined biological and phosphorus recycling treatment unit. (A) Biological treatment for nitrogen removal and methane production: 1: raw pig slurry storage pit; 2: anaerobic digester; 3: aearobic/anoxic reactor; 4: treated slurry storage pit. Figures are in percent 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_3COOH, 80%, 20-119-368, VWR) was added, under mixing, to 2 L beakers containing 1 L of pig slurry. Experiments were performed 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 × 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	$N\text{-}NH_4^+$
		$gO_2\ kg^{-1}$	$g\ kg^{-1}$				
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