

# Phosphorus release from farm yard slurry and MSW digestates by acid and base extraction

V. Oliveira<sup>1</sup>, L. M. Ottosen<sup>2</sup>, J. Labrincha<sup>3</sup>, C. Dias-Ferreira<sup>1,3</sup>

<sup>1</sup> Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture, Polytechnic Institute of Coimbra, Bencanta, 3045-601 Coimbra, Portugal

<sup>2</sup> Department of Civil Engineering, Building 118, Technical University of Denmark, 2800 Lyngby, Denmark

<sup>3</sup> Materials and Ceramic Engineering Department, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Keywords: Livestock, Municipal Solid Wastes, Phosphorous Recovery  
Presenting author email: veronica.oliveira@esac.pt

## Abstract

Farm yard slurry and digestates from anaerobic digestion of municipal solid wastes (MSW) are organic wastes containing phosphorus which can potentially be used as a secondary source of this nutrient. The present study investigated the effect of pH in the phosphorus release from these wastes. Results showed that when using HNO<sub>3</sub>, 100% of P content was extracted from farm yard slurry (2.0 < pH < 3.3) and 65% from MSW digestates (2.0 < pH < 4.2). The maximum extraction was obtained after 2.5 hours. The extraction efficiencies using NaOH were only 22% for farm yard slurry (12.9 < pH < 13.4) and 9% for MWS digestates (13.0 < pH < 13.4). Phosphorus concentration is higher in the sample of MSW digestate, but it is in a form not as easily extractable as with far yard slurry.

## Introduction

Currently there is a growing demand for phosphorus (P) at global level. This resource is obtained from phosphate deposits, which are controlled mostly by Morocco, United States of America and China, being Europe dependent on phosphorus imports to meet its needs (Smit *et al*, 2009). The existing reserves of phosphate will reach a peak by 2030 and will be exhausted in the next 50-100 years (Cordell *et al*, 2009). Thus, it is very important the development of new strategies for P recovery from secondary sources.

Phosphorus is present in various wastes, including livestock manure and municipal solid wastes which may cause major downstream environmental problems (Ye *et al*, 2014) (Hargreaves *et al*, 2008). Recently, Kalmykova and Fedje (2013) published a method for phosphorus extraction from Municipal Solid Wastes Incineration (MSWI) fly ash using acid and base leaching and precipitation procedures. Animal manure is rich in P but there are storage problems and the cost of transportation between the production and application sites becomes less economical with increase of distance (Keplinger and Hauck 2006). Acid extraction of P from sewage sludge ashes has been reported by Ottosen *et al* (2013) and both acid and alkaline leaching from the same material have been referred by Petzet *et al* (2012). Stark *et al* (2006) studied the influence of acid or base extraction of P from sludge ash, dried sludge and sludge residue from supercritical water oxidation.

The present work compares the extraction of phosphorus from two wastes: (i) farm yard slurry; and (ii) sludge from anaerobic digestion of mechanically-separated Organic Fraction of Municipal Solid Waste

(MSW digestate). The purpose is to investigate the influence of pH on phosphorus release overtime and to identify the conditions that optimise extraction.

## Material and Methods

A sample of sludge from anaerobic digestion of mechanically-separated Organic Fraction of Municipal Solid Waste MSW digestates were collected in April 2015 from a facility for the treatment and valorisation of municipal solid wastes (Portugal), specifically from the anaerobic digester fed by mechanically-separated OFMSW.

A sample of farm yard slurry was collected in April 2015 from a local dairy farm. The materials were dried in a forced draft at a temperature of 105°C. Both samples were prepared by grinding and passing through a sieve of about 1 mm and stored in closed glass containers at room temperature. For both samples water content, ash content, organic matter, pH, electric conductivity, total P, Ca, Mg, K and heavy metals (Cu, Zn, Cd and Pb) were measured.

The phosphorus extraction experiments were performed using two extractants: nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH). Extraction experiments were made using 40.0 g of dry sample and 1000 mL of HNO<sub>3</sub> and NaOH at liquid to solid ratio (L/S) of 25 during 48 hours (in duplicate). The experimental conditions are shown in Table 1. Extractions with distilled water were made as reference. To assess the P release over time samples were collected at 0, 2.5, 24 and 48 hours, and the electric conductivity, pH and soluble P were measured. At the end of experiment Ca, Mg, K, Cu, Zn, Cd and Pb in solution were measured. P-extraction efficiencies were defined as the ratio of P in solution, taking into account the volume and mass of the sample added to the trial, at the end of experiment, to the total mass of P present in the sample added to the experiment.

**Table 1** Experimental conditions for P-extraction experiments.

| <b>Experiment</b> | <b>Extractant/Konc.</b> | <b>Sample</b>    |
|-------------------|-------------------------|------------------|
| <b>A1</b>         | Nitric Acid 0,075M      | Farm yard Slurry |
| <b>A2</b>         | Nitric Acid 0,05M       | Farm yard Slurry |
| <b>A3</b>         | Distilled Water         | Farm yard Slurry |
| <b>A4</b>         | Sodium Hydroxide<br>1M  | Farm yard Slurry |
| <b>B1</b>         | Nitric Acid 0,09M       | Digestate        |
| <b>B2</b>         | Nitric acid 0,05M       | Digestate        |
| <b>B3</b>         | Distilled Water         | Digestate        |
| <b>B4</b>         | Sodium Hydroxide<br>1M  | Digestate        |

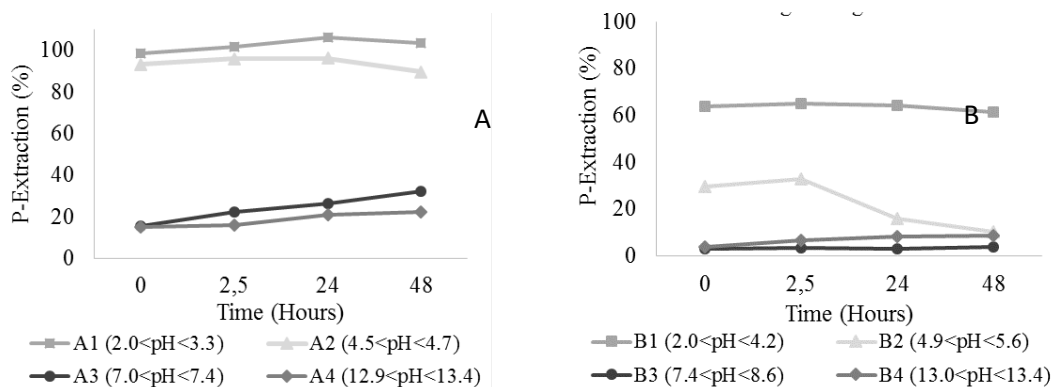
## Results and Discussion

Characteristics of the farm yard slurry and MSW digestates are shown in table 2. The pH of digestate is slightly higher than farm yard slurry, but nevertheless close to neutrality. The concentration of phosphorus is higher in the digestate than in farm yard slurry. These levels are low compared with ash residues from the incineration of sewage sludge, where concentrations of 8-10% have been reported (Ottosen, Kirkelund, and Jensen 2013). The content in heavy metals is much higher in digestate than in farm yard slurry, with lead (Pb) concentrations being more than 10 times higher in digestate.

**Table 2** Characteristics of the two waste samples (mean  $\pm$  standard deviation)

| Parameter                                | Farm yard slurry  | MSW digestates    |
|--|-------------------|-------------------|
| <b>pH (H<sub>2</sub>O)</b>               | 8.2 – 8.3         | 8.9 – 9.0         |
| <b>Conductivity (mS cm<sup>-1</sup>)</b> | 3.64 $\pm$ 0.02   | 3.38 $\pm$ 0.04   |
| <b>Water Content (%)</b>                 | 85.11 $\pm$ 0.08  | 63.40 $\pm$ 0.51  |
| <b>Ash Content (%)</b>                   | 4.49 $\pm$ 0.07   | 18.55 $\pm$ 0.88  |
| <b>Organic Matter (%)</b>                | 10.40 $\pm$ 0.14  | 18.05 $\pm$ 0.41  |
| <b>pH (H<sub>2</sub>O)</b>               | 6.6               | 7.8               |
| <b>Conductivity (mS cm<sup>-1</sup>)</b> | 8.60 $\pm$ 0.18   | 5.22 $\pm$ 0.04   |
| <b>Total P (mg g<sup>-1</sup> dw)</b>    | 4.04 $\pm$ 0.08   | 8.11 $\pm$ 0.25   |
| <b>Ca (mg g<sup>-1</sup> dw)</b>         | 142.82 $\pm$ 3.85 | 103.68 $\pm$ 3.64 |
| <b>Mg (mg g<sup>-1</sup> dw)</b>         | 4.04 $\pm$ 0.13   | 12.59 $\pm$ 0.39  |
| <b>K (mg g<sup>-1</sup> dw)</b>          | 13.70 $\pm$ 3.28  | 9.38 $\pm$ 0.19   |

The extraction of P from farm yard slurry and digestate into solution using nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH) over time is presented in Fig. 1. For both wastes, extractions were higher when HNO<sub>3</sub> was used than when NaOH or water, expressly indicating that base extraction was not as effective and that the release of P from both wastes was better at lower pH values.



**Fig. 1** P-extraction efficiency for farm yard slurry (A1-A4) and digestate (B1-B4) by acid and base treatment during 48 hours

In the case of farm yard slurry, the phosphorus extracted with acid reached between 90-100% of total phosphorus (A1 and A2), with the differences between the two experiments being relatively small. On the opposite, for digestate the best extraction was only about 65% (B1, pH between 2.0 and 4.2), so for this waste it might be necessary to go below pH 2 to achieve extraction percentages close to 100%. The phosphorus extracted with NaOH was very low and did not exceed 22% for farm yard slurry and 9% for digestate.

## Conclusion

In this work two different wastes were evaluated for the recovery of phosphorus: digestate, arising from the anaerobic digestion of municipal solid wastes and farm yard slurry. The concentration of phosphorus in the samples was 0.8% (dry weight) and in the farm yard slurry 0.4% (dry weight). These levels are low compared with values reported for ash residues (8 -10%).

When trying to extract P from the wastes using nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH), 100% of the P contained in farm yard slurry could be extracted into solution after only 2.5 hours at a pH of 4.5. For MSW digestates the maximum extraction was only 65 %, indicating that even though P concentration is higher in this residue, phosphorus is in a form not so easily extracted and therefore the extraction process needs to be optimised. One of the possible options might be to carry out the extraction at a pH below 2. For both wastes, extractions were higher with HNO<sub>3</sub> than with NaOH or water, expressly indicating that phosphorus is released better under acidic conditions.

## Acknowledgments

C. Dias-Ferreira gratefully acknowledges the FCT – Fundação para a Ciência e a Tecnologia for the financial support (SFRH/BPD/100717/2014). This work was also funded by CERNAS (UID/AMB/00681/2013).

## References

- Cordell, Dana, Jan Olof Drangert, and Stuart White. 2009. "The Story of Phosphorus: Global Food Security and Food for Thought." *Global Environmental Change*. Vol. 19.x
- Hargreaves, J. C., M. S. Adl, and P. R. Warman. 2008. "A Review of the Use of Composted Municipal Solid Waste in Agriculture." *Agriculture, Ecosystems and Environment* 123 (1-3): 1–14.
- K. Stark, E. Plaza, B. Hultman. 2006. "Phosphorus Release from Ash, Dried Sludge and Sludge Residue from Supercritical Water Oxidation by Acid or Base." *Chemosphere* 62: 827–32.
- Kalmykova, Yuliya, and K Karlfeldt Fedje. 2013. "Phosphorus Recovery from Municipal Solid Waste Incineration Fly Ash." *Waste Management (New York, N.Y.)* 33 (6).
- Keplinger, Keith O., and Larry M. Hauck. 2006. "The Economics of Manure Utilization: Model and Application." *Journal of Agricultural and Resource Economics* 31 (2): 414–40.
- Ottosen, Lisbeth M., Gunvor M. Kirkelund, and Pernille E. Jensen. 2013. "Extracting Phosphorous from Incinerated Sewage Sludge Ash Rich in Iron or Aluminum." *Chemosphere* 91 (7).
- Petzet, Sebastian, Burkhard Peplinski, and Peter Cornel. 2012. "On Wet Chemical Phosphorus Recovery from Sewage Sludge Ash by Acidic or Alkaline Leaching and an Optimized Combination of Both." *Water Research* 46 (12).
- Smit, A.L., P.S. Bindraban, J.J. Schröder, J.G. Conjin, and H.G.v.d. Meer. 2009. "Phosphorus in Agriculture: Global Resources, Trends and Developments". *Plant Research International B.V., Wageningen Report* 282.

Ye, Zhilong, Yin Shen, Xin Ye, Zhaoji Zhang, Shaohua Chen, and Jianwen Shi. 2014. "Phosphorus Recovery from Wastewater by Struvite Crystallization: Property of Aggregates." *Journal of Environmental Sciences (China)* 26 (5).