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Extraction and precipitation of phosphorus from sewage sludge

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ABSTRACT

Raw sewage sludge from East Rand Water Care Association (ERWAT) had high phosphorus (P) content, approximately 15.2% (w/w) P_2O_5, which indicates a potential resource for the limiting nutrient. Leaching sewage sludge with 1 M sulphuric acid at 5% solid loading for 2 h resulted in an 82% phosphorus extraction. However, the phosphorus was recovered as iron phosphates, thus a further purification step using ion exchange to remove iron was required to increase the degree of P release. Magnesium oxide and ammonium hydroxide were used as magnesium and nitrogen sources, respectively, as well as pH regulators to precipitate P as struvite. 57% struvite was precipitated and the total phosphorus content of the precipitate was 25.9%. Kinetic studies showed that the leaching of phosphorus follows the Dickinson model for the first 100 min with a rate of reaction of about $2 \times 10^{-5}\ s^{-1}$. The rate limiting step is controlled by diffusion. Phosphorus solubility in 2% critic acid was almost 96%, which is the amount of phosphorus available to plants if the precipitate is applied as a fertiliser. Environmental, gram-positive *Bacillus subtilis* were found in the precipitate, which are harmless to the environment since they already exist in the soil where the precipitate can be applied as a fertiliser.

1. Introduction

The East Rand Water Care Association reported that about 103,295 ton of sewage sludge is produced yearly in Johannesburg, South Africa. The sewage sludge is normally stockpiled and dried before being either applied on land as a fertiliser, used to produce compost or disposed in landfills or dedicated land disposal sites. In some instances liquid sludge is directly applied to soils or digested in an anaerobic digester to produce biogas for electricity generation. Land application appears to be the most beneficial and environmentally sustainable method for sewage sludge management in South Africa. However, problems such as land shortage, eutrophication, and accumulation of heavy metals in the soil inhibit its use. These problems have intensified as a result of rapid urbanization leading to an increase in sewage sludge production (Mastau, 2005). This has resulted in an increased interest in developing new effective methods to manage or utilise sewage sludge by removing the metals and the nutrients present in the sludge (Stark, 2004).

Sewage sludge has a high phosphorus content, approximately 8% (w/w), which makes it a potential source of the P nutrient (Biswas et al., 2009). Phosphorus recovery from sewage sludge will become increasingly important within the next decades due to the depletion of apatite minerals (Biswas et al., 2009). Phosphorus is the eleventh most abundant element in the Earth's crust and is an essential element in DNA, RNA lipids, proteins, enzymes, energy carrier ATP, as well as an important factor in the development of teeth and bones. Phosphorus together with potassium and nitrogen are the three primary nutrients for plants (Tunnicliffe et al., 2014).

Incineration of sewage sludge is commonly practised in most European countries as a result of the banning of landfilling of sewage sludge in line with the EU Landfill Directive (99/31/EC). Thus, most studies on phosphorus extraction from sewage sludge were conducted using sewage sludge ash. Methods aimed at extracting and recovering phosphorus from sewage sludge ash have been widely reported by Gao (2012) and Marti et al. (2010) and many more. The effect of acid concentration, liquid/solid (L/S) ratio, temperature and the rate of reaction on phosphorus recovery was also studied for each method (Alamdari and Rohani, 2007). However, the high energy associated with ashing of sewage sludge and co-leaching of heavy metals necessitates the need to research an alternative method to recover phosphorus by direct leaching of sewage sludge without ashing (Xu and Lancaster, 2009). Since there are no extensive published work on the extraction of phosphorus from sewage sludge, a comparison of the results obtained from this approach will be compared to those obtained using sewage sludge ash.

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Leaching is a process of extracting minerals from a solid by dissolving them in a liquid. Leaching with acidic or alkaline solutions has been used to recover phosphorus from sewage sludge ash and has been reported by Biswas et al. (2009), Stark (2004) and Levlin (2005). However, leaching generates a heavy metal laden solution thus there is need for solution purification to remove the heavy metals before precipitating phosphorus. Common heavy metal removal techniques involve adsorption (Ali et al., 2012) and ion exchange (Levlin, 2005). In this paper both approaches were evaluated as a means of solution purification before precipitation of P. Phosphorus can be precipitated in many phases, one of them being struvite. Struvite is the most precipitated form of phosphorus worldwide. It is a white crystalline substance containing magnesium, ammonium and phosphorus (Zaixing et al., 2012). The precipitation of struvite from the phosphorus leach solution will also be addressed in this paper.

2. Materials and methods

2.1. Materials

Sewage sludge was collected from a local waste water treatment plant, East Rand Water Care Association (ERWAT), and was used as a source of P. The plant from which the sewage sludge was collected treats wastewater from domestic and industrial premises. The wastewater goes through primary treatment, which involves both screening and passing the waste stream through large settling tanks. It is at this point that about 70% of the materials in the water sinks to the bottom, becoming sewage sludge. The sludge is pulled from the tank, thickened by dewatering and further treated by anaerobic digestion. The digested sludge is pump from the digester and air dried in sludge drying beds. The dried sewage sludge was then used as a source of P in this study. All chemical reagents such as sulphuric acid, hydrochloric acid and nitric acid were supplied by Rochelle Chemicals. Bentonite was supplied by the G & W Mineral Resources and was used as an adsorbent. Ion exchange resin (Lewatit Monoplus S 108) was supplied by Protea Chemicals.

2.2. Equipment

A reflux apparatus was used to leach out phosphorus from sewage sludge. X-ray fluorescence (Rigaku ZSX primus II) and XRD (X-ray Diffraction 40 kV) were used to determine the elemental composition of sewage sludge and the mineralogy of the precipitate respectively. Metal analysis was achieved by using an Atomic Absorption Spectrometer (Thermo scientific ICE 3000 series). A UV–vis spectrophotometer (PG Instruments T60) was used to measure the phosphorus content in both purified and unpurified leachate. FTIR (Fourier transform infrared spectroscopy) Thermoscientific Nicket IS10 was used to characterize the sewage sludge before and after precipitation. The morphology of the sewage sludge before and after precipitation was analysed using a Scanning Electron Microscope (SEM model Tescan Vega 3 XMU). pH was measured using a Mettler Toledo dual meter (Sevenduo pH meter with a Mettler Toledo InLab Pro ISM pH electrode). The zeta potential was measured using a Laser Doppler Micro-electrophoresis method with water as a dispersant (Malvern Zetasizer Nanoseries).

2.3. Leaching of P from sewage sludge

The effect of the type of acid, acid concentration, solid loading (g of sewage sludge/100 ml of leaching solution) and reaction time was investigated. 1 g of ground sewage sludge was mixed with 100 ml of each acid namely; HNO_3, HCl and H_2SO_4 at a concentration of 1 M for each acid. The solutions were then refluxed for 120 s. After the reaction, the samples were allowed to cool and were filtered. The filtrates/leachates were then analysed for phosphates using the EPA method 365. This procedure was followed for the screening of all other parameters. All leaching experiments were performed at 100 °C. The solid/liquid ratio (solid loading) was determined by keeping sulphuric acid volume fixed at 100 ml while varying the sewage sludge mass from 1 to 10 g. A summary of the experiments conducted and leaching conditions used are shown in Table 1. The optimal leaching parameters [1 M sulphuric acid, 5% solid loading, 2 h] were used to leach out phosphorus from the sludge and the solutions generated were purified by either ion exchange or adsorption before P precipitation.

2.4. Removal of heavy metal from P rich solution

Removal of heavy metals from the P rich solution was achieved using either adsorption onto bentonite or ion exchange using a cationic resin. 10 g of bentonite was mixed with 50 mL of the leachate and agitated using the thermostatic shaker for 4 h at 200 rpm and room temperature. The solution was then filtered using vacuum filtration after agitation was stopped and the pH was measured. AAS was then used to analyse for the metal content in solution.

Incremental amounts of the ion exchange resin (1–5 g) was mixed with 50 mL of leachate to determine the most suitable solid loading that could remove the metals present in the leachate. The mixture was agitated at 200 rpm for 2 h. AAS was used to obtain the metal content from the filtrate after agitation. 10% solid loading (g of resin/100 mL solution) was used for further experiments as it gave the highest metal removal levels.

2.5. Recovery of P as struvite precipitate and its bioavailability

50 ml of the sample purified by ion exchange in order to remove heavy metal impurities in the leachate was mixed with magnesium hydroxide, as a source of magnesium and ammonium hydroxide as a source of nitrogen and to adjust the pH. The samples were kept for 24 h and the composition of the precipitate was analysed using XRF and XRD after filtration. The precipitation procedure was repeated for different samples with pH ranging from 5 to 9 to establish the pH that gave a higher P recovery with lower metal content in the precipitate. After the pH was established, the same procedure was repeated with different Mg:N:P ratios. 10 g of precipitated P was dissolved in 100 ml of distilled water and in 100 ml of 2% citric acid to determine its bioavailability to plants.

Table 1
Experimental variables for the determination of the optimal conditions to leach out phosphorus from sewage sludge.

Experiment description	Experimental conditions
Screening for the type of acid used	1 N [H_2SO_4 or HCl or HNO_3], S/L ratio = 1 g/100 ml, 100 °C, time = 2 h
Effect of acid concentration on P extraction	H_2SO_4 [0.01–2 M], S/L ratio = 1 g/100 ml, 100 °C, time = 2 h
Effect of leaching time on P extraction	1 M H_2SO_4 [0.5–3 h], S/L ratio = 1 g/100 ml, 100 °C
Effect of the solid/loading ratio on P extraction	1 M H_2SO_4, S/L = [1–10 g/100 mL] 100 °C, time = 2 h

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