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Phosphorus recovery from sewage sludge ash through an electrodialytic process

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ABSTRACT

The electrodialytic separation process (ED) was applied to sewage sludge ash (SSA) aiming at phosphorus (P) recovery. As the SSA may have high heavy metals contents, their removal was also assessed. Two SSA were sampled, one immediately after incineration (SA) and the other from an open deposit (SB). Both samples were ED treated as stirred suspensions in sulphuric acid for 3, 7 and 14 days. After 14 days, phosphorus was mainly mobilized towards the anode end (approx. 60% in the SA and 70% in the SB), whereas heavy metals mainly electromigrated towards the cathode end. The anolyte presented a composition of 98% of P, mainly as orthophosphate, and 2% of heavy metals. The highest heavy metal removal was achieved for Cu (*ca.* 80%) and the lowest for Pb and Fe (between 4% and 6%). The ED showed to be a viable method for phosphorus recovery from SSA, as it promotes the separation of P from the heavy metals.

1. Introduction

Phosphorus (P) has no substitute in food production and the European Union is almost entirely dependent upon imports, with China, Jordan, Morocco, South Africa and USA controlling 85% of global phosphate reserves (Smit et al., 2009). As EU is a phosphate importer it is vulnerable to geopolitical tensions in the countries that export phosphate and to its volatile prices (as demonstrated during the recent 800% spike in the price of phosphate rock in 2008) (Schröder et al., 2010. Phosphorus peak has been estimated to occur by 2035 (Cordell et al., 2009) and published data on the lifetime of the exploitable high quality reserves of phosphate rock vary to a great extent, between one hundred and several hundreds of years (EFMA, 2000; IFDC, 2010; United States Geological Survey, 2012). This makes the development new strategies for P recovery from secondary resources one of the new world challenges.

One potential P resource is sewage sludge from municipal and industrial wastewater treatment plants (WWTP) (Schaum et al., 2009) which potential substitution for primary phosphate imports has been estimated, e.g. 40% for Germany (Cornel and Schaum, 2003). Incineration of sewage sludge is increasing as it presents several advantages when compared to other available disposal routes as it reduces the volume and mass generated by 90% and 70%, respectively (Chen and Yan, 2012; Hjelmar, 1996; Kirby and Rimstidt, 1993; Medici et al., 2000). Also it destroys pathogenic agents, oxidizes organic compounds and generates thermal energy that can be reused (Marani et al., 2003; Porteous, 2005). The obtained SSA can be rich in P but they do not have a direct value as fertilizer, as P is not in a plant available form (Ottosen et al., 2013). In addition, due to the presence of leachable heavy metals, SSA must be treated before the P resource can be reused.

1.1. Electrodialytic process

The electrodialytic process (ED) was developed at the Technical University of Denmark in 1992 and was patented in 1995 (PCT/DK95/00209). This method applies a low level direct current (DC) and proved to be efficient in removing contaminants from soils and other porous matrices (Virkutyte et al., 2002). A basic ED cell can be divided in three compartments. The electrodes are placed in opposite sites where electrolyte solutions circulate and the contaminants are concentrated at the end of the process. To separate the central compartment (with the contaminated matrix) from the electrode ends, ion exchange membranes are used. An anion and cation exchange membranes are used only allowing the passage of anions and cations, respectively.

Electrodialytic treatment relies on several interacting mechanisms but the dominant and most important electron transfer reactions that occur at electrodes during the process is the electrolysis of water (Eqs. (1.1) and (1.2)):

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$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- \quad \text{(anode)} \tag{1.1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \quad \text{(cathode)} \tag{1.2}$$

As the anion exchange membrane is not a 100% perfect rectifier some hydrogen ions are still transported from the anode end towards the cathode end, passing through the middle compartment and consequently lowering the pH.

When ED is applied to ashes in stationary cells, there is a decrease of mass and subsequently volume during the process (Hansen et al., 2004; Pedersen, 2003), due to their high percentage of easily soluble particles. This decrease can be a problem during ED in a stationary setup, but it is overcome when a stirrer is introduced in the ED cell (Fig. 1), improving the process efficiency when compared to an unstirred cell (Ottosen et al., 2000).

Several authors studied the ED remediation of fine-grained materials in suspension, using non-stationary set-ups, such as municipal solid waste incineration (MSWI) fly ash (Ferreira et al., 2005; Pedersen, 2002), wood combustion fly ash (Pedersen, 2003), wastewater sludge (Jakobsen et al., 2004), contaminated harbor sediments (Nystroem et al., 2005) and SSA (Pazos et al., 2010).

The advantage of treating SSA is their exclusively inorganic formation, a fact which (in contrast to sewage sludge) facilitates phosphorus recovery (Cornel and Schaum, 2009). During ED the part of P presented in negatively charged species (orthophosphates) will be transported out of the ash suspension towards the anode. Still, during the ED process, other elements present in the ash may also move towards the anode end (e.g., metals of negative standard reduction potential).

This works aims to evaluate the possibility to recover P and separate it from the heavy metals from SSA using the ED process. For this, two SSA samples were collected at a sewage sludge incineration facility and laboratory experiments with ED treatment of the SSAs as stirred suspensions were conducted.

2. Materials and methods

2.1. Sewage sludge ash

Sewage sludge ashes were collected at Lynettefællesskabet, Copenhagen, Denmark, in June 2012. This plant mono-incinerates sewage sludge from about 500,000 PE. In this WWTP, the process of P precipitation is initially done in a Bio-P tank followed by the addition of iron salt. The sludge is incinerated in a fluid bed oven at about 800 °C. The incinerator has an installed capacity of 2.35 t DM h^{-1} and an outgoing flue of 17,000 N m^3 h^{-1} at 59 °C. It produces 1 t DW ash h^{-1} and for that it consumes 3.8 MW h^{-1} in kettle and 2.9 MW h^{-1} in flue gas condensation. After incineration the SSA is stored (until it finds use) in an open air deposit at the site of Lynettefællesskabet close to the sea.

Two SSAs were sampled for this investigation: one immediately after the incineration process (SA) and the other from the deposit (SB). The exact residence time of SB is not known. The samples were stored in closed 5 L plastic containers, at room temperature.

2.2. Analytical

2.2.1. Ash characterization

The water content of the ash was measured as weight loss after 24 h at 105 °C. Ash pH and conductivity were measured in a 1:2.5 (mass:volume) suspension in deionized water, using Radiometer pH and conductivity electrodes. The solubility in water was evaluated by a four times washing procedure in a 1:10 suspension in deionized water, followed by ash drying and weighting at the end of the procedure. Loss on ignition was found after 30 min at 550 °C. Gas production was measured with a volumetric calcimeter flask in a 10% HNO_3 suspension. For pH, conductivity, loss on ignition and gas production five replicates were made, three replicates for water content and two replicates for solubility in water.

2.2.2. Heavy metal and phosphorus content

The concentration of Al, Cd, Cu, Cr, Fe, Ni, P, Pb, and Zn were determined after a pre-treatment of the ash in accordance to DS259 (DS259, 2003): 1.0 g dry ash and 20 mL of HNO_3 (1:1) was heated until 120 °C and 200 kPa for 30 min. The samples were filtered through a 0.45 μm filter and the element contents measured in an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES), Varian 720-ES. All metal concentrations are given on a dry weight basis. Five replicates were made for the initial SSA determinations.

In terms of Fe, the DS259 standard does not give its total concentration and the reason is that there is a small mineral residue that contains insoluble Fe compounds, which is removed before the ICP analysis (Ottosen et al., 2013).

Three replicates of the anolyte solutions collected after 14 days of ED treatment of each SSA sample were analysed by standard colorimetric methods (Standard Methods, 1998) for total phosphorus, inorganic phosphorus and orthophosphate content. Polyphosphates were determined by indirect method (polyphosphates = inorganic P − orthophosphates).

2.2.3. Electrodialytic experiments

The ED laboratory cell (Fig. 1) is divided in three compartments, with a stirrer in the central one to maintain the matrix suspended. The cell was made from Plexiglas with an internal diameter of 8 cm. The ion exchange membranes separating the central compartment from the electrode compartments were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes from Permascand were

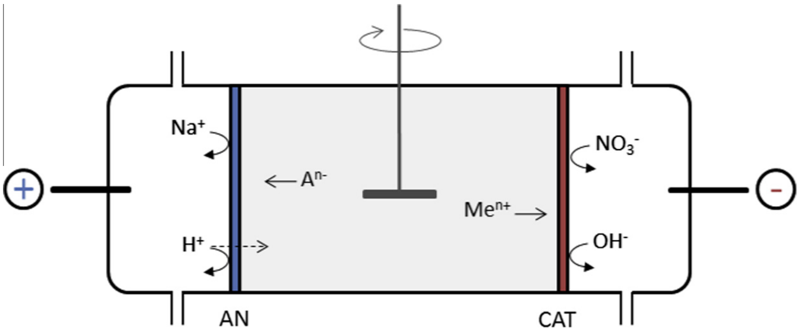

Fig. 1. Schematic electrodialytic stirred cell (AN: anion exchange membrane, CAT: cation exchange membrane).