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Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash

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HIGHLIGHTS

- A new electrodialytic remediation method for a nutrient rich waste stream is investigated.
- Reduction of compartments in experimental setup increases overall efficiency.
- Removal of heavy metals was faster and increased significantly in the new setup.
- Mobilization of phosphorus was faster and increased significantly in new setup.

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ABSTRACT

With decreasing availability of phosphorus from primary resources its recovery from waste streams becomes increasingly more important. Sewage sludge ash is rich in phosphorus, but the direct use as fertilizer is limited because of inorganic contaminants such as heavy metals and strong bonding of phosphorous in the ash. Electrodialysis (ED) can be used to recover phosphorus and simultaneously remove heavy metals. The present work is an experimental screening of different options for ED in relation to experimental setup and combination with acid addition. Experiments for stirred ash suspensions utilizing a three compartment cell setup where the anode, cathode and stirred suspension are separated by ion exchange membranes are reported. Simplifying this experimental setup by removing the anion exchange membrane brings the anode in direct contact with the stirred ash suspension. Through this adjustment, half-reactions at the anode contribute to the acidity of the stirred suspension resulting in increased dissolution of both phosphorus and heavy metals (Cd, Cu, Cr, Pb, Zn, Ni) and better separation of most heavy metals from the stirred ash suspension. When the ash is suspended in an acidic solution, these effects increase significantly in early stages of the experiments. The combination of ED in a two compartment setup and initial acidification of the stirred suspension is most effective in dissolving of phosphorus and separation of heavy metals. In this setup, up to 96% of the phosphorus in the ash was dissolved after 7 d. Using the three compartment setup and initially suspending the ash in distilled water, resulted in 53% dissolution of the total recovered phosphorus after 7 d.

1. Introduction

With primary sources of phosphorus (P) estimated to deplete within a century and the quality of mined phosphorus rock decreasing, focus on recycling of P from secondary sources becomes increasingly important to sustain the future demand in agriculture (Cordell et al., 2009). Secondary sources, such as municipal wastewater sludge, generally contain both organic and inorganic contaminants, limiting its direct application in agriculture. While many organic contaminants can be removed through biological (Parkin and Owen, 1986) or thermal treatment (Adam et al., 2007), inorganic contaminants remain generally in the ash (ICON, 2001). Furthermore, addition of iron- or aluminum salts during wastewater treatment, inducing the formation of insoluble phosphate complexes, results in a lower P fertilization value of both the sludge (Krogstad et al., 2005) and, upon incineration, the sewage sludge ash (SSA) (Franz, 2008).

Several methods have been investigated in an attempt to successfully separate HM and P from sewage sludge and SSA. These methods include acid and base treatment (Oliver and Carey, 1976; Levlin et al., 2003; Donatello et al., 2010; Ottosen et al., 2013), thermo (chemical) treatments (Adam et al., 2009) and electrodialytic remediation (Sturm et al., 2010). Electrodialysis (ED) is a

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treatment method mostly applied for remediation of heavy metal polluted soils, industrial effluents and more recently stirred suspensions such as harbor sediments (Kirkelund et al., 2009) and suspensions of dried sewage sludge and bio-ash (Ottosen et al., 2007). Phosphorus recovery from secondary resources using ED has not been studied as extensively and requires further improvement. Sturm et al. (2010) applied ED remediation on packed beds of sewage sludge ash in an attempt to recover P, but recovery rates remained below 1%.

1.1. Electrodialytic remediation

Many reported electrodialytic remediation (EDR) experiments for stirred suspensions consist of a three (or more) compartments experimental setup (Fig. 1a) (Jakobsen et al., 2004; Ottosen et al., 2007, 2014; Ebbers et al., 2012). The electrodes are placed in separate compartments (I and III) where electrolyte solutions are circulated. The stirred suspension is located in the middle compartment (II). Ion exchange membranes (AN – anionic exchange membrane; CAT – cationic exchange membrane) separate the compartments to restrict electromigration through the cell out of the central compartment.

A direct current in the order of a few mA is applied to the electrodes. Electrolytic half-reactions at the electrodes (reactions 1 and 2) significantly decrease and increase pH near the anode and cathode, respectively.

Cathode:

$$\text{Cathode}: \quad 4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^- \qquad (1)$$

$$\text{Anode}: \quad 2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \qquad (2)$$

Ionic complexes from the stirred suspension are transported by electromigration to either electrode, depending on its charge. Positively charged (cationic) complexes, concentrate in the cathode compartment and can precipitate at the cathode while negatively charged (anionic) complexes such as phosphate, will concentrate in the anode compartment.

Acidification of the ash suspension is important for mobilization of phosphorus, but will simultaneously release heavy metals (Oliver and Carey, 1976; Levlin et al., 2003; Franz, 2008; Donatello et al., 2010; Ottosen et al., 2013). The ash suspension in a three compartment setup can be acidified through water splitting at the anion membrane, proton leakage from the anode compartment or the ion exchange from the cathode compartment (Nystroem et al., 2005). Under conditions similar to those in this study, the acidification of the suspension can take several days to weeks before reaching sufficiently low pH for release of phosphorus, and is therefore considered relatively slow. Suspension of the ash in mineral acid will rapidly increase mobilization of both phosphorus and heavy metals, in particular when using sulfuric acid (H_2SO_4) as opposed to nitric (HNO_3) or phosphoric acid (H_3PO_4) (Oliver and Carey, 1976; Levlin et al., 2003).

Moreover, Ottosen et al. (2013) pointed out that usage of H_2SO_4 for the extraction of phosphorous and heavy metals can limit the reuse options of SSA in construction materials due to formation of gypsum, significantly increasing the volume of the remaining ash. Development of a means to extract phosphorus and separate both phosphorus and heavy metals without impairing the chances to reuse the bulk material is a necessity when considering disposal of large volumes of (treated) ash in the future.

In this study, adjustments are made to the earlier established electrodialytic cell setup by reducing the number of compartments and introducing the anode directly into the ash suspension (Fig. 1b). This new approach utilizes the acid production by electrolysis at the anode and combines this with initial acidification of the suspension by H_2SO_4 in order to mobilize phosphorus and heavy metals faster. Mobilized heavy metal complexes will electromigrate from the suspension liquid and concentrate in the cathode compartment. The objectives of this study are twofold; (1) to compare a two-compartment (2C) and three-compartment (3C) electrodialytic cell setup regarding the efficiency of mobilizing and separating heavy metals and phosphorus and (2) to study the influence of pH and experimental duration on the efficiency of the experiments.

2. Experimental

2.1. Ashes for the experiments

The sewage sludge ash used in these experiments is from mono-incinerated sewage sludge in a fluidized bed combustor, Avedøre Wastewater Service, Denmark. The wastewater treatment plant annually treats 25–30 million m^3 of wastewater. During the waste water treatment the chemical compound Kemira PIX-118, containing ironchloridesulphate, is added to precipitate phosphates into the sludge and prevent their release into the environment through effluents.

2.2. Analytical methods

Heavy metal and phosphorus concentrations in the ash before and after the experiments were determined according to Danish Standard (DS 259). 20 mL of 1:1 HNO_3 was added to 1 g dry ash and heated at 200 kPa (120 °C) for 30 min. The suspension was vacuum filtered through a 45 μm filter and diluted to 100 mL. Phosphate and heavy metal concentrations of all samples were measured in aqueous phase by inductively coupled plasma optical emission spectrometry (ICP-OES). The pH and conductivity of the ash were measured after agitating 5 g of oven dried ash in 12.5 mL 1 M KCl and distilled water for 1 h, respectively. Organic matter content was determined through loss by ignition, exposing dry ash for 1 h to a temperature of 550 °C. To determine solubility, 50 g of ash was agitated three times for 1 min using 500 mL distilled water. Through filtration, remaining ash was collected, dried

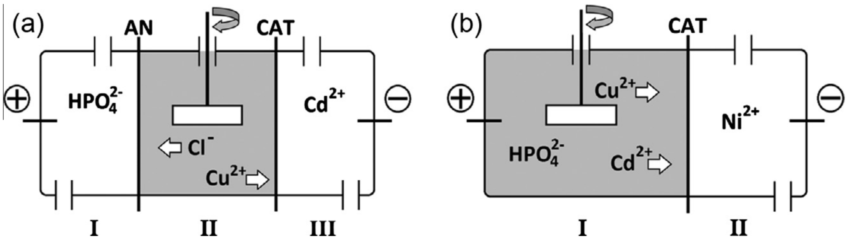

Fig. 1. The (a) three and (b) two compartment cell setup, 3C and 2C, respectively, for electrodialytic (ED) remediation of the ash suspension. In the 3C-ED cell setup, the anode (+) is separated from the ash suspension by an anion exchange membrane (AN) whereas in the 2C-ED cell setup, the anion exchange membrane is removed and the anode is placed in direct contact with the ash suspension.