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Electrodialytic extraction of phosphorus from ash of low-temperature gasification of sewage sludge

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ABSTRACT

Low-temperature gasification allows the production of energy from biomass with high contents of low melting point compounds, like sewage sludge, and the recycling of the nutrients as P from the resulting ashes as renewable fertiliser. Major drawbacks are, however, the presence of heavy metals and the low plant-availability of Al- and Fe- phosphate compounds in the gasification ashes. In the present research, the feasibility of a 2-compartment electrodialytic (ED) setup for P separation from Al, Fe and heavy metals in two different low-temperature gasification ashes was investigated. One ash was from gasification of sewage sludge where P was precipitated with Fe and Al salts, from which it was possible to extract up to 26% of the P. The other ash was from co-gasification of a mixture of biologically precipitated sewage sludge and wheat straw pellets. More promising results were obtained with this ash, as up to 90% of the P was extracted from the ashes. For both ashes, P was extracted by ED in acidic aqueous solutions with ratios of Fe, Al and each heavy metal to P considerably below the values found in the initial ashes. Therefore, the 2-compartment ED cell technology was proved as possible method to separate Al, Fe and heavy metals from P for low-temperature gasification ashes.

1. Introduction

Phosphorus is an essential element for life which has no biological or technological substitutes [1]. Current P supply for agriculture is dominated by phosphate rock (P-rock) fertilisers. However, the reserves of this mineral are estimated to be depleted in a period ranging from 50 to 400 years, depending on the study [2,3] and both the production and reserves are concentrated in Morocco, China and USA [4]. Thus, scarcity is likely to increase phosphate production costs by factor 3 to 5 in this century [5] and geopolitical issues might also influence both the cost and availability. In 2013, the European Union countries imported around 86% of the consumed P-rock, a dynamic observed at least over the last decade [6]. Today, only about one fourth of the P applied to agricultural fields is actually recycled [1]. Moreover, P-rock fertilisers have been a major contributor to the addition of heavy metals like Cd to soils over the last decades [7,8]. For all these reasons, innovative recycling and re-use technologies need to be developed and implemented.

Paradoxically, while the global reserves of P-rock rapidly decline, urban and industrial regions generate increasing amounts of waste rich in organic phosphate that is currently not appropriately recycled and utilised [1]: P is usually immobilised and precipitated in sewage sludge during wastewater treatment by phosphate accumulating organisms [9] and/or by Fe/Al salts addition [10].

Low-temperature gasification allows an energy production from biomass resources like sewage sludge with high contents of low melting point ash compounds [11] – which are often shown to be a source of boiler operational problems in more traditional incineration [12]. The resulting sewage sludge ashes (SSA), with a high P content, could potentially be recycled back to agricultural soils after this thermal gasification process securing a safe renewable P fertiliser without the risk of applying organic contaminants like pharmaceuticals, detergent metabolites and others. Major drawbacks of using gasified SSA directly as fertiliser, however, are its heavy metal content and the presence of low plant available Al- and Fe- phosphates [13–15]. Hence, a mobilisation of

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P from the bulk gasification ashes and a simultaneous separation from heavy metals would be beneficial.

P separation from incinerated SSA can be achieved by acid leaching; but, heavy metals are also released [16–18]. Electrodialysis (ED) has been investigated as a technology to recover P from incineration SSA, from Al- and Fe- precipitation, and separate it from heavy metals, with a 3-cell compartment (Fig. 1a) [19,20]. In this set up, the ashes are placed in the middle compartment together with an acid solution and stirred constantly, so as to extract both P and heavy metals from incinerated SSA [19,20]. Released heavy metals are expected to be found as positively charged species and therefore migrating towards the catholyte during the ED treatment. In contrast, solubilised P is likely to be found in negatively charged or neutral species at acidic pH (H_3PO_4, $H_2PO_4^{2-}$), except for Al-P and Fe-P complexes formation, so P ions would stay in the middle compartment and/or migrate towards the anolyte. In one of the studies, P separation into the middle compartment liquid and the anode compartment ranged around 15-85% for Al-precipitated incinerated SSA, a lower recovery than for Fe-precipitated ones which was around 45-95% [19]. In the other research, up to 70% of the P was recovered in the anode compartment [20].

Recently, a patent has been applied for a new set-up developed at the Technical University of Denmark, consisting of 2 compartments (Fig. 1a), which simplifies the experimental procedures in relation to the 3-compartment cell (Fig. 1b). The principle idea is that there is an acidification of the ash suspension by protons generated from electrolysis at the anode, and thus no acid addition is needed. The P remains in the filtrate of the ash suspension, instead of potentially dividing it between the anolyte and the middle compartment liquid. A study compared the performance of the two setups used in the P-recovery from incinerated SSA, and observed a lower voltage in the 2-compartment than in the 3-compartment ED cells by several orders of magnitude, when the ash was stirred only with water [21]. This can be due to a higher presence of ions in the suspension in the former than in the latter, as well as the use of one membrane and one electrolyte liquid instead of two. Thus, there is a potential saving on electricity and chemical costs with this new setup. Furthermore, with the 2-compartment setup it was possible to mobilise up to 90% of the P in the anode compartment [21]. No investigation has been made to recover P from gasification SSA by either acid or ED extraction, although the viability of low-temperature sewage sludge gasification depends partly on nutrient recycling. The aim of the present study was to test the technical feasibility of the 2-compartment ED cell to extract P, and separate it from Al, Fe and heavy metals, from SSA produced by low-temperature gasification of dried sewage sludge from two different plants.

2. Experimental

2.1. Gasification ashes

Two gasification ashes were collected from the second cyclone of a 100 kW experimental Low Temperature Circulating Fluid Bed gasifier (Fig. 2) at the Department of Chemical and Biochemical Engineering, Roskilde campus of the Technical University of Denmark [11]. The process is based on separate pyrolysis and gasification fluid bed reactors with a suitable circulating heating medium to transfer the heat from the gasification process to the pyrolysis. The temperature is kept below the melting point of the ash components (700 - 750 °C) avoiding sintering of the ash and subsequent fouling (from e.g. potassium) or corrosion (from e.g. chlorine) of the plant unit operations. The char conversion in the experimental Low Temperature Circulating Fluid Bed gasifier is a combination of sub stoichiometric oxidation of the char and steam gasification [22]. The ash particles are circulated in the process until they are too small/light to be separated by the primary cyclone. Most of the ashes are separated out of the hot gas by the secondary cyclone [11], where they were sampled for this research. The original feedstocks of the two gasification ashes were:

- Randers ash: Dried sludge collected at the wastewater treatment plant in the municipality of Randers, Denmark, where P was captured 50% biologically and 50% chemically (with Fe and Al chlorides), approximately. The gasification took place in July 2013.
- Stegholdt ash: Wheat straw pellets (70% in weight) and dewatered sewage sludge (30% in weight) from Stegholdt wastewater treatment plant, Denmark, where P was mainly removed biologically with a minor amount of Fe salts. The co-gasification of both materials took place in June 2013.

2.2. Analytical methods and sampling

For both gasification ashes, small batches of around 200 grams were sampled from the total mass collected. Each ash was thereafter dried at 105 °C overnight, cooled in the fume hood, homogenised with a steel spatula and immediately stored in plastic bags and under dry conditions.

The concentration of elements was investigated for all untreated and treated gasification ashes. The targeted elements were: Al, Ca, Cd, Cu, Cr, Fe, K, Ni, P, Pb and Zn. The element content was measured by Varian 720-ES inductively coupled plasma optical emission spectrometry (ICP-OES) in six samples for the untreated ashes and in triplicates for the ED treated ashes after pre-treatment by Danish Standard DS259 [23]: 1 g ash and 20 mL 7.3 M HNO_3 were heated at 200 kPa (120 °C) for 30 min. The liquid

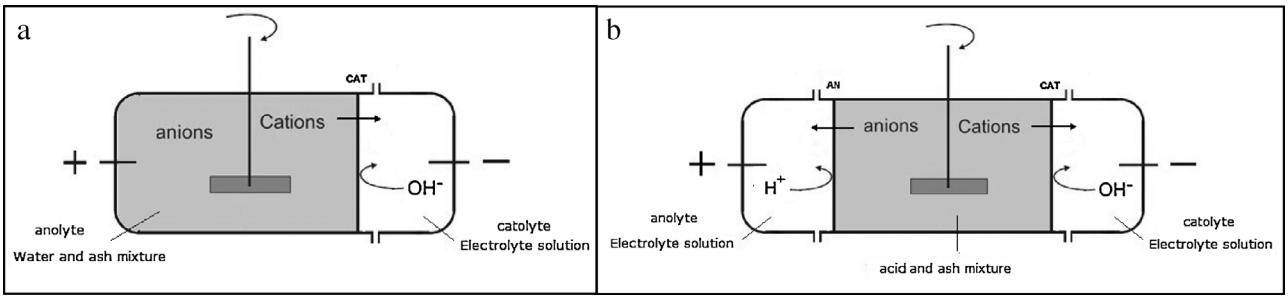

Fig. 1. Schematic view of a 2-compartment (a) and a 3-compartment (b) ED cell. CAT: cationexchange membrane. AN: anion-exchange membrane.