



Research article

Extraction of hazardous metals from green liquor dregs by ethylenediaminetetraacetic acid



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ABSTRACT

Green liquor dregs are the major inorganic solid side stream of kraft pulp mills which contain environmentally hazardous metals. The presence of hazardous metals in this industrial residue brings statutory limits for its landfilling, although they are not easily mobilized from the solid phase. In this study, the chelating agent ethylenediaminetetraacetic acid (EDTA) is utilized to extract hazardous metals such as Cd, Pb and Zn from green liquor dregs. Furthermore, the influence of EDTA on the removal of Ca as the main mineral nutrient present in the green liquor dregs is studied. The effect of parameters such as EDTA dosage, L/S ratio and contact time on the removal rate of the elements is investigated. In addition, the experimental data are fitted to the Elovich model and the pseudo-first-order model to describe the desorption kinetics. The results show that 59 wt% of Cd, 13 wt% of Co, 62 wt% of Cu, 3 wt% of Mn, 12 wt% of Ni, 43 wt% of Pb, 16 wt% of Zn, and less than 1 wt% of Ca were extracted from green liquor dregs with EDTA dosage of 0.035 g_{EDTA salt}/g_{dregs} and the L/S ratio of 6.25 ml/g. The current study opens up new possibilities to use the green liquor dregs for improving the soil fertility instead of landfilling.

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1. Introduction

Green liquor dregs (GLD) are the main inorganic solid side stream of kraft pulp mills originating from the chemical recovery cycle (Pöykiö et al., 2006; Mäkitalo et al., 2012). This cycle is mainly responsible for the recovery of cooking chemicals such as sodium hydroxide (NaOH) and sulfide (Na₂S), which are utilized in lignin removal from wood chips (Sixta, 2006; Tran and Vakkilainen, 2007). The operation of the recovery cycle comprises the main stages of weak black liquor concentration in evaporators, combustion of black liquor in a recovery boiler, converting the Na₂CO₃ content of the smelt to NaOH in a recausticizing plant, and regeneration of reactive lime (CaO) by a lime cycle. GLD sludge is generated after dissolving the molten smelt of the recovery boiler, which contains mostly Na₂CO₃ and Na₂S in weak white liquor in a dissolving tank (Cardoso et al., 2009; Klugman et al., 2007; Sanchez, 2007; Tikka, 2008; Tran and Vakkilainen, 2007). Then the green liquor of GLD sludge is purified from suspended solids which are so called dregs by various methods, such as sedimentation, cross-flow filtration, cake filtration, and centrifugation (Golmaei et al., 2017).

The purified green liquor is circulated back to the chemical recovery process, while the dregs are disposed at landfill after treatment in a series of washing and deliquoring stages (Tikka, 2008; Tran and Vakkilainen, 2007).

Dregs contain usually sodium hydroxide, carbonates of sodium and calcium, sulfides, and unburned carbon (Jia et al., 2013). In addition, this alkaline (pH > 10) inorganic solid residue contains non-process elements (NPEs) such as Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, and Zn (Kinnarinen et al., 2016; Nurmesniemi et al., 2005). Owing to the presence of NPEs in GLD, its disposal is a way to remove these elements from the chemical recovery cycle (Sedin and Theliander, 2004). NPEs such as As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, and Zn are present in the GLD as low water-soluble compounds, e.g. hydroxides and carbonates. Of these elements, considerable amounts of As, Ba, Cd, Cu, Cr, Mn, Ni, Pb and Zn are present in the form of oxidizable minerals, e.g. metal sulfides. It is supposed that the oxides of Fe and Mn are the most common forms of these elements in the GLD which are able to coat other elements, especially Ba, Co, Ni, V and Zn (Nurmesniemi et al., 2005). The recognized compounds of Al and Fe in dregs are silicate diopside (CaMgSi₂O₆), aluminosilicates pargasite (NaCa₂Mg₃Fe²⁺Si₆Al₃O₂₂(OH)₂) and vermiculite (Mg_{1.8}Fe²⁺_{0.9}Al_{4.3}Si₁₀(OH)₂·4(H₂O)) (Taylor and McGuffie, 2007). In addition, calcium is accumulated in the dregs in the form of calcite

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(CaCO₃), calcite containing a small amount of magnesium (Ca_(1-x)Mg_xCO₃), calcium oxide (CaO), portlandite (Ca(OH)₂), anhydrite (CaSO₄), and dihydrate (CaSO₄·2H₂O) (Jia et al., 2013; Martins et al., 2007; Taylor and McGuffie, 2007).

Previous research by Nurmesniemi et al. (2005) on the extractability of NPEs from dregs by sequential leaching indicates that heavy metals are mostly available in the easily reduced fraction (extracted by HONH₃Cl) and oxidizable fraction (extracted by H₂O₂ + CH₃COONH₄). In the other study done by Mäkelä et al. (2016), the cyclone processing has been introduced as a potential method to reduce heavy metal content in green liquor dregs. It is also possible to extract the heavy metals from solids by using the chelating agents. One of the most commonly utilized chelating agents for the extraction of several divalent metals is ethylenediaminetetraacetic acid (EDTA) because of its strong ability to chelate (Di Palma and Mecozzi, 2007; Garrabrants and Kosson, 2000; Giannis et al., 2010; Nörtemann, 1992). Also, the relatively low price of EDTA (1.3 €/kg for technical grade) makes it an economically feasible choice for treatment processes (Leštan et al., 2008).

Contrary to the redox agents and strong acids which release metals by decomposition of the solid matrix, the chelating agents extract metals from the coordination sites (Manskinen et al., 2011). In general, the chelating agents donate their nitrogen and oxygen atoms for metal complexation, and their chelating strength is probably also determined by the number of these atoms (Kocialkowski et al., 1999). The chemical properties of the solid phase, such as pH and the presence of competing ions influence the extraction of metals. Also, the extraction efficiency of metals by chelating agents depends on the specific metal compound involved in the solid phase (Kim et al., 2003; Peters, 1999; Sun et al., 2001). In addition to chemical factors, physical factors like particle size, specific surface area, porosity, and the liquid-to-solid ratio influence the mobility of constituents from the solids (Sabbas et al., 2003; Virolainen et al., 2013). EDTA reacts with all present cationic metals in the solid phase, and consequently there is always a competition between these ions for complexation with EDTA (Kim et al., 2003).

Unfortunately, there is not much information about the influence of other present metals on the extractability of the target metal (Kim et al., 2003). Therefore, the order of metal mobility by the use of chelating agents needs to be studied case by case (Peters, 1999). Due to this and other incomparable conditions, the choice of the suitable chelating agent for the extraction of a specific metal is extremely difficult (Kocialkowski et al., 1999). The environmental risk in using EDTA for industrial residue treatment is the accumulation of its low biodegradable complexes with heavy metals in the aquatic environment like ground waters, rivers and lakes. The main complexed species of this chelating agent existing in natural waters are Ca-EDTA, Zn-EDTA, and Fe(III)-EDTA (Nowack and Sigg, 1996).

The utilization of GLD as a forest soil improving material is a way to return the nutrients lost through the harvesting of trees to the ecosystem (Mahmoudkhani et al., 2004). Only in Finland, 64200 metric tons of GLD solids were landfilled in 2012 (Kinnarinen et al., 2016). This high figure indicates that the reuse of this industrial residue as a fertilizer would be a considerable achievement towards circular economy. GLD contains macronutrients, such as less soluble salts of Ca and Mg, and easily soluble salts of Na and K (Mahmoudkhani et al., 2004; Nurmesniemi et al., 2005; Pöykiö et al., 2006). However, the presence of heavy metal elements, such as Cd, Cr, Cu, Ni, Pb and Zn in GLD would probably contaminate the soil (Alloway and Ayres, 1997; Kasassi et al., 2008). Of these pollutant metals, Pb is mostly present in the non-mobile fraction, and it can only be released to water resources as a result of weathering as a very long-term effect (Nurmesniemi et al., 2005).

The present study is the first one in which a chelating agent has been used to extract hazardous metals from GLD. The sample of GLD for the experimental part of the study was provided by a kraft pulp mill located in Finland. In this research, Cd, Pb and Zn represent the target pollutants. Moreover, the extractability of Ca as the main mineral nutrient of GLD and other metals such as Co, Cr, Cu, Mn and Ni are investigated. The removal of hazardous metals from GLD is still an unresolved issue for the industry. Using conventional acids for leaching from GLD at its highly alkaline pH is not feasible for industrial scale. The current research proposes a practical method for hazardous metals removal from green liquor dregs, while keeping their main nutrients. With this method, GLD could be utilized to improve soil fertility instead of landfilling, and consequently minimize the waste production in kraft pulp mills.

2. Materials and methods

2.1. Preparation and characterization of dregs

The sample of GLD sludge was collected from the reject side of X-Filter at a Finnish kraft pulp mill. The X-Filter is a falling film cross-flow filter that consists of a pressure vessel and vertically mounted filter elements (Keskinen et al., 1995). The required solid sample of dregs for extraction tests was prepared through GLD sludge filtration, dregs drying and crushing. In the first step, the GLD sludge was filtered by a laboratory scale press filter, PF 0.1 (manufactured by Outotec Oy, Finland) to separate the solid phase of dregs from the green liquor. The filtration was followed by pressing at the same equipment, but the resulted cake was not washed with water. Then, the cake of dregs with the moisture content of 33 wt% was dried in an electrical oven, after which the dried cake was crushed by a laboratory planetary ball mill to produce a homogeneous solid mixture for extraction experiments. The approximate volumetric particle size distribution (PSD) of the prepared dregs was measured with a Mastersizer 3000 particle size analyzer (manufactured by Malvern Co, UK). The PSD of the solids was calculated according to the Fraunhofer model.

The total concentrations of the elements in the dregs were measured with a Fisher Scientific ICAP6500 Duo (Thermo Fisher Scientific Inc., Cambridge, UK) inductively coupled plasma optical emission spectrometer (ICP-OES). The solids were digested completely prior to the analysis by using the method 3051 introduced by the US Environmental Protection Agency (1995). The SEM images were taken and energy-dispersive X-ray spectroscopy (EDS) mapping of the samples performed with a Hitachi SU 3500 scanning electron microscope, with a carbon tape background.

2.2. Preparation of extractant solutions

The extractant solutions were prepared by dissolving the ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA·2Na·2H₂O) as the chelating agent in Millipore water. After the complete dissolution of the chelating agent, the pH of the solution was adjusted to 4.5. The desired pH of the solution was obtained by adding hydrochloric acid solution (HCl 0.1 M). In the experiments, various amounts (Table 1) of the chelating agent were dissolved in water, and the pH was in all cases slightly higher than 4.5. Therefore, only some droplets of the acidic solution were enough to adjust the pH of the extractant solution to 4.5.

2.3. Batch extraction

The pH-adjusted extractant solution containing a specified dosage of the chelating agent was added to 4 g of the dregs in plastic bottles. The extractant solutions were prepared in a higher

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