



Effect of partial oxidation of organic matter on cadmium leaching from phosphate



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ABSTRACT

Phosphate rocks are the main phosphorus source, a key nutrient for crop production in the tropics. Besides phosphorus and calcium, phosphate rocks may contain organic matter and heavy metals, such as cadmium and lead, depending on their geological origin. In general, phosphate rocks from sedimentary origin present higher content of heavy metal than igneous phosphate rocks. The world phosphate rock consumption of sedimentary and igneous origin is around 75 and 20%, respectively. The use of cadmium containing phosphate rocks as fertilizers can bring risks to the environment. The objective of this work was to investigate the influence of partial oxidation of organic matter with H₂O₂ as a pre-treatment to improve cadmium leaching from sedimentary phosphate with high organic matter content. As leaching agents, MgCl₂, KCl, Na₂-EDTA and citric acid solutions were tested. When cadmium removal was carried out with a 0.1 mol L⁻¹ Na₂-EDTA solution without partial oxidation of organic matter, its content in the sample was reduced from 49.5 to 38.5 mg kg⁻¹, after 5 h, corresponding to a removal of only 23%. On the other hand, when cadmium leaching was carried out after organic matter oxidation with a 40 mg L⁻¹ H₂O₂ solution, the cadmium content in the sample was reduced from 49.5 to 22.5 mg kg⁻¹, corresponding to a removal of 54.5%, turning it more adequate to be used as fertilizer.

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1. Introduction

Phosphorus is a key nutrient for crop production. According to United Nations' Food and Agriculture Organization (FAO/UN, 2012) the world phosphate consumption is forecast to grow annually 2 percent during the period from 2012 to 2016 and about 14 and 25% of this growth are expected to occur in Brazil and India, respectively (FAO/UN, 2012), due to the expansion of agriculture production into highly weathered tropical soils that present a high phosphate retention capacity.

Various minerals contain more than 1% P₂O₅ and several of them contain a P₂O₅ grade higher than that of apatite, which is around 41.8%P₂O₅, according to the Mineralogy Database (2013). However, the most important minerals for the fertilizer industry belong to the apatite group that present a general formula Ca₁₀(PO₄)₆X₂, where X⁻ can be F⁻, Cl⁻ or OH⁻.

Besides phosphorus and calcium, phosphate rocks may contain organic matter and heavy metals, such as cadmium (Cd) and lead

(Pb). The heavy metals and organic matter contents depend on the rock geological origin, which can also change even within the same deposit (Al-Shawi and Dahl, 1999; Mar and Okazaki, 2012; Batarseh and El-Hasan, 2009; Bech et al., 2010). In general, phosphate rocks from sedimentary origin present a higher heavy metal content than igneous phosphate rocks. The world phosphate rock consumption of sedimentary and igneous origin is around 75 and 20%, respectively (Mar and Okazaki, 2012; Aydin et al., 2010, 2009). Cadmium is one of the most toxic elements found in nature and phosphate rocks are the main source of this element in agricultural soils. Its content in those rocks can range from 1 to 243 mg kg⁻¹ (Aydin et al., 2010; Roberts, 2014; Mar and Okazaki, 2012; Benredjem and Delimi, 2009; Bech et al., 2010). This has been a major concern and a worldwide issue for cadmium containing phosphate rocks used in fertilizer production. The maximum accepted values for cadmium concentration in fertilizers were established by several countries, as shown in Table 1.

Several methods, *in situ* or *ex situ*, can be used for heavy metal removal from different types of samples, such as sediments, soils and phosphate rocks (Safarzadeh et al., 2007; Bennedsen et al., 2012; Zheng et al., 2013; Borra et al., 2015; Zhao et al., 2014;

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Table 1

Maximum limiting value for cadmium concentration in manufactured fertilizers and/or rock established by several countries.

Country	Limit
Brazil ^a	4 mg Cd/% P ₂ O ₅
Australia ^{b,f}	300 mg Cd/kg P
New Zealand ^c	26 mg Cd/ kg superphosphate fertilizer
Finland ^d	50 mg Cd/kg P
Belgium ^{e-h}	90 mg Cd/kg P ₂ O ₅
Germany ^{e-h}	40–90 mg Cd/kg P ₂ O ₅
Portugal ^{e-h}	40–70 mg Cd/kg P ₂ O ₅
USA/Oregon ^{e-h}	7.5 mg Cd/% P ₂ O ₅
USA/California ^{e-h}	4 mg Cd/% P ₂ O ₅
USA/Washington ^{f,h}	889 mg Cd/kg P ₂ O ₅
European Union ⁱ	20 mg Cd/kg P ₂ O ₅ by 2015

^a Ministry of Agriculture, Livestock and Food Supply (abbreviated MAPA/Brazil, 2006).

^b Al-Shawi and Dahl (1999).

^c Considering a SSP fertilizer with P₂O₅ content range between 16 and 20%. Fertiliser Matter (2005) in: Schipper et al. (2011).

^d Study report for the Finnish Ministry of Agriculture and Forestry/Finnish Environmental Institute (2000).

^e Oosterhuis et al. (2000), Cupit et al. (2002) and European Commission – Enterprise DG (2001).

^f Roberts (2014).

^g Van Balken (2004).

^h Chaney (2012).

ⁱ Jiao et al. (2012).

Pecina et al., 2008). Leaching is a process widely employed for heavy metals removal from contaminated solid samples and presents the possibility of reagent recycling, permitting its reuse in the process (Voglar and Lestan, 2013; Sun et al., 2001; Pocięcha and Lestan, 2010). However, this process depends on several factors, such as the way metals are bounded to the other constituents (oxides, silicates and organic matter) present in the sample; and also the experimental conditions, such as pH, soil/water ratio, number of leaching cycles, temperature, reaction time and leaching agent concentration (Zheng et al., 2013; Udovic and Lestan, 2009; Zhao et al., 2014; Chen et al., 2006; Peters, 1999).

Benredjem and Delimi (2009) used different chemicals, such as HCl, ammonium acetate and disodium ethylenediaminetetraacetate (Na₂-EDTA) for cadmium removal from phosphate rock. These authors reported a 70% cadmium removal with HCl leaching; however, this may cause the phosphate dissolution. This undesirable behavior does not occur with EDTA leaching, despite the lower cadmium removal. Sun et al. (2001) investigated the Cd, Pb, Zn and Cu extraction from contaminated soils using Na₂-EDTA as extracting agent. Results from batch experiments shown that the extraction efficiency was similar independently of the metals. Nevertheless, when the leaching test was carried out in columns, the extracting response was different for each contaminant metal.

Makino et al. (2006) used different chemicals for *in situ* Cd removal from paddy soils. They observed that the cadmium extraction with calcium chloride (CaCl₂) was higher than with others chemicals tested (acetic acid, citric acid, EDTA, nitric acid, MgCl₂, etc.). They attributed, this behavior, partly, to the high affinity of the soil adsorption sites for Ca²⁺ ions and to the good ability of Cd²⁺ ions to form complexes with several anions, such as Cl⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻, fulvic and other organic acids (Traina, 1999; Makino et al., 2006). They also observed that, cadmium removal increased with number of leaching cycles. Similar results were found by Benredjem et al. (in press) using Na₂-EDTA.

Zhao et al. (2014) and Zheng et al. (2013) showed that cadmium retention in soils is increased by the presence of organic matter, but this behavior depends on the soil types and pH (Zheng et al., 2013; Egli et al., 2010). Cadmium in the soil is distributed throughout different fractions, such as exchangeable, carbonate, organic

matter, oxides (Fe and Mn) and the residual ones. Cadmium distribution in different soils was investigated by Quezada-Hinojosa et al. (2009). They observed that more than 50% cadmium was bound to carbonates, around 30% was associated with Fe-oxihydroxides and only 10% was bound to organic matter. Additionally, a small fraction can be bound to Mn-oxides and clay minerals. For these researchers, cadmium mobility in soils depends on pH and on the cadmium content bound to exchangeable fraction; if the cadmium content in this fraction is low, the probability of cadmium becoming immobilized by plants will be low, assuming that the soil pH remains neutral.

This way, the objective of this work was to investigate the influence of partial oxidation of organic matter as a pre-treatment to improve cadmium leaching from sedimentary phosphate with high organic matter content, in order to improve its quality and safety to be employed as raw material for fertilizers production.

2. Materials and methods

2.1. Sample

A phosphate concentrate sample from Bayóvar Mine/Peru was used for the tests. According to Bayovar rock phosphate specification sheet (Union Harvest, 2015) the cadmium content ranges from 10 to 60 mg kg⁻¹ (Bech et al., 2010). For this work, the sample with a medium particle size, around 150 μm, was used.

2.2. Cadmium removal tests from the phosphate sample

Cadmium leaching tests were carried out in two steps: (1) oxidation with 40 mg L⁻¹ H₂O₂ (based on exploratory tests) for organic matter removal; (2) leaching with different leaching agents, such as MgCl₂, KCl, Na₂-EDTA and citric acid for cadmium removal. In order to check the benefits of partial oxidation of organic matter, some leaching tests were carried out without previous oxidation for comparison purposes. A simplified flowsheet of the cadmium removal process by organic matter oxidation with hydrogen peroxide followed by leaching with MgCl₂, KCl, Na₂-EDTA or citric acid solution is presented in Fig. 1.

2.2.1. Organic matter oxidation tests

The partial oxidation of organic matter tests were carried out in a 0.5 L reactor with a liquid/solid ratio of 3:1 (Lu et al., 2010; Usman et al., 2012; Xin-De et al., 2012). The sample was mixed with 40 mg L⁻¹ H₂O₂ and stirred with a magnetic bar (250–300 rpm, measured with a strobe light) from 1 to 7 h, at temperatures ranging from 25 to 45 °C. Then, the pulp was filtered, washed with distilled water, dried at 120 °C for 3 h and the solid residue was analyzed to quantify the amount of organic matter removed from the sample.

2.2.2. Cadmium leaching and sequential extraction tests

Cadmium leaching tests (with and without previous organic matter oxidation) were carried out in a 200 mL-flask with a liquid/solid ratio of 4:1 (Lu et al., 2010; Zheng et al., 2013; Benredjem et al., in press). Five grams of the sample were mixed with 20 mL of solution, prepared with different reagents, within a concentration range of 1 × 10⁻⁴ to 0.1 mol L⁻¹, and stirred with a magnetic bar (250–300 rpm, measured with a strobe light) during 1–5 h at room temperature. Then, the pulp was filtered, washed with distilled water, dried at 120 °C for 3 h and the solid residue was analyzed to quantify the amount of cadmium removed from the sample.

The sequential extraction procedure to quantify the cadmium content associated with the different phases present in the sample

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