Arabian Journal of Chemistry (2016) 9, S446–S450

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Cadmium extraction from phosphate ore. Effect of microwave

Zahia Benredjem, Rachid Delimi *, Assia Khelalfa

Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, Badji-Mokhtar University, BP 12, Annaba 23000, Algeria

Received 13 February 2011; accepted 28 May 2011
Available online 6 June 2011

KEYWORDS
Cadmium;
Phosphate ore;
Extraction;
Microwave;
Environment;
Treatment

Abstract This study discusses the operating variables for removal of cadmium from phosphate ore using Na_2EDTA. These variables include the reaction time, Na_2EDTA concentration, liquid/phosphate ore ratio, number of extractions and microwave extraction. Na_2EDTA induced a two-step extraction process including a rapid extraction within the first hour, and a subsequent gradual release that occurred over the following hours. The cadmium extraction efficiency increased progressively with the increasing of Na_2EDTA concentration. The extraction efficiency of cadmium increased with increasing liquid/phosphate ratio in the 5–200 range. Consecutive extractions using low concentrations were more effective than a single soil extraction with concentrated Na_2EDTA. Microwave was beneficial to improve the removal in soil washing, and using microwave could partly substitute for agitation.

1. Introduction

Phosphate fertilizers contain traces of cadmium that can be accumulated in soil with repeated application of phosphate fertilizer. Cadmium can cause adverse animal and human health impacts at high levels or at lower levels if exposure occurs over a prolonged period. To prevent soil from cadmium contamination of phosphate fertilizer, it is primordial to remove cadmium from phosphate ore. Two techniques are proposed to eliminate cadmium from phosphate ores: calcinations and leaching, but leaching technique is economical, better than calcinations (Keith Syers, 2001a,b). Several studies have focused on cadmium removal using various extracting agent. One of the most suitable and successfully used techniques for the treatment of soils contaminated with heavy metals on-site ex situ is soil washing technique. Soil washing often needs the use of different extracting agents for heavy metals decontamination. These agents include acids, bases, chelating agents, electrolytes, oxidizing agents and surfactants (Hong et al., 1995; Schramel et al., 2000; Reddy and Chinthamreddy, 2000; Sun et al., 2001). Acid washing leads to a decrease of soil productivity and a number of changes in the chemical and physical structures of soils due to mineral dissolution (Reed

* Corresponding author. Tel./fax: +213 38 87 27 50.
E-mail addresses: r.delimi@labltevdi-univ-annaba.org, ltevdi@yahoo.fr (R. Delimi).
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.05.016
1878-5352 © 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.

et al., 1996). Chelating agents, such as ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and S,S-ethylene-diaminedisuccinic acid (EDDS) are considered as the most attractive alternative because they can form strong metal–ligand complexes and are thus highly effective in remediating heavy metal-contaminated soils (Norvell, 1984; Elliott and Brown, 1989; Kim and Ong, 1998). EDTA is also extensively used for soil remediation because of its ability to mobilize metal cations efficiently coupled with only a minor impact on the physical and chemical properties of the soil matrix (Lee and Marshall, 2002). Studies focused on the cadmium extraction from phosphate ore, which would be reduced to lower rates, were rarely investigated by researchers so far. Our study was carried out to discuss a scheme in order to assess the suitability of Na_2EDTA operating variables and compare cadmium extraction efficiencies in different washing conditions. The influence of some parameters was taken into consideration, such as liquid/phosphate ratio (L/P), reaction time, concentration of Na_2EDTA, number of extractions and microwave extraction.

2. Experimental

2.1. Materials

The phosphate samples were collected from Djebel El Onk, Tebessa north east Algeria. The samples are ground to less than 2 mm particle size. All the chemicals used in the experiments were in pure form (Merck and Sigma brand). Bidistilled water was also used in all experiments.

2.2. Analytical procedures

2.2.1. Mineralization

Before the determination of the phosphate ore chemical composition, the acid digestion ($HF/HClO_4/HNO_3$) was added to 1.00 g of the phosphate samples, the suspension was then centrifuged at 3000 rpm for 15 min in EBA 20 Hettich centrifuge; the supernatant was filtered through Whatman filter paper (45 μm) and then analyzed.

2.2.2. Extraction procedure

The extraction tests were conducted in 25 mL beaker. 1.00 g of the sample and a measured volume of EDTA was agitated using an end-over-end shaker at a speed of 400 rpm at room temperature (25 °C) for a given time. The suspensions were centrifuged at 3000 rpm for 15 min and the supernatants were then filtered through a 45 μm membrane for heavy metal analysis.

The washing solution was prepared from analytical grade reagents. All tests were performed in triplicates and the results were presented as averages of the triplicate extracts. As a typical experimental procedure, the mixture of 1.00 g phosphate ores and volume of Na_2EDTA was treated by microwave irradiation in a domestic microwave oven for pre-set time. During the test processes, the samples were obtained at a predetermined time, and the solution samples were analyzed for cadmium.

2.2.3. Analysis methods

Cd, Pb, Cr concentrations were measured by absorption atomic spectrometry (spectrometer Shimadzu AA 6200). A UV–visible (Jenway) spectrophotometer was used for phosphate analysis according to the standard methods (vanadomolybdophosphoric acid colorometric method) (Olsen and Sommers, 1982). Ca, Mg, and Fe were measured by fluorescence X spectrometry.

3. Results and discussion

3.1. Composition of phosphate ore

The analytical results of some elements in the phosphate ore are presented in Table 1. The content of cadmium in phosphate is 16.5 ppm. This level exceeds the recommended value (10 ppm). In this work, we will study the possibility of reducing the cadmium content by simple extraction and microwave assisted extraction.

3.2. Conventional cadmium extraction

3.2.1. Influence of consecutive extractions

Although Na_2EDTA could remove cadmium from the phosphate ore, it is not adequate to completely decontaminate the mineralization. To remove more cadmium, three consecutive extractions with 0.25 M Na_2EDTA (L/S = 25, 2 h) were carried out on the same sample. The results are illustrated in Fig. 1.

Renewing the extracting solution greatly increased the dissolution of cadmium; the cumulative removals of cadmium from phosphate after 1st and 3rd extraction cycles were 38.9% and 55.9% respectively. Three reasons that explain the greater removal of cadmium with the increasing renewal of the solution: (1) the removal of some residual metal chelates which may be trapped in the soil pores (Sun et al., 2001) or re-adsorbed onto the sediment particles during the first step of the sequential extraction procedure; (2) the reduction the interference in metal–chelant complex formation after removing the major content of the competition cations in the first steps (Polettini et al., 2007); and (3) the reduction of readsorption of the desorbed metals and increase of the dissolution rate of metal-containing particles by maintaining undersaturated conditions (Strawn and Sparks, 2000). As the number of consecutive extractions increased, only a small percentage of the total cadmium was extracted. After the previous extractions where the mobile forms were extracted, the Metal was released from the less mobile forms (i.e., bound to organic matter, bound to Fe/Mn oxides or residual fraction). This is presumably related to the dissolution of mineral constituents of sediment (including oxides and silicates) initially retaining the contaminants (Polettini et al., 2007).

3.2.2. Influence of concentration

The effect of Na_2EDTA concentration on the rate of cadmium extraction was tested using a concentration range of 0.01–0.25 M. It was noticed that the extraction of cadmium increased with increasing Na_2EDTA concentration and reached 36.6% (Fig. 2). From Fig. 2, it can be seen that when the concentration of Na_2EDTA varies from 0.01 to 0.125 M, the concentration of the extracted cadmium increases accordingly and becomes

Table 1 Phosphate ore composition.

Element	P (%)	Ca (%)	Mg (%)	Fe (%)	Mn (%)	Cd (ppm)	Pb (ppm)	Cr (ppm)	Zn (ppm)
Content	13.0	35.3	0.90	1.2	0.0012	16.5	39	146	170

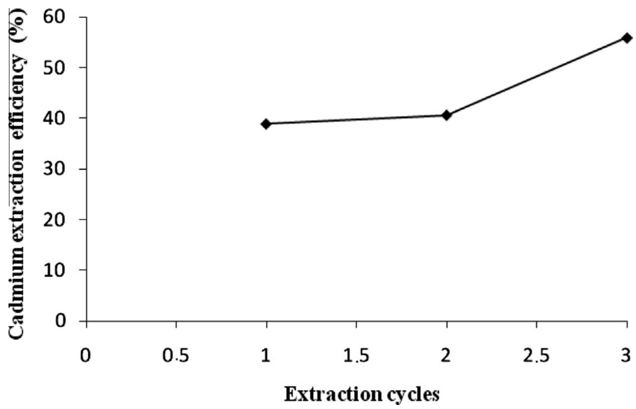

Figure 1 Cumulative result of three cycles of consecutive 2 h extractions with 0.25 M Na_2EDTA (L/P = 25).

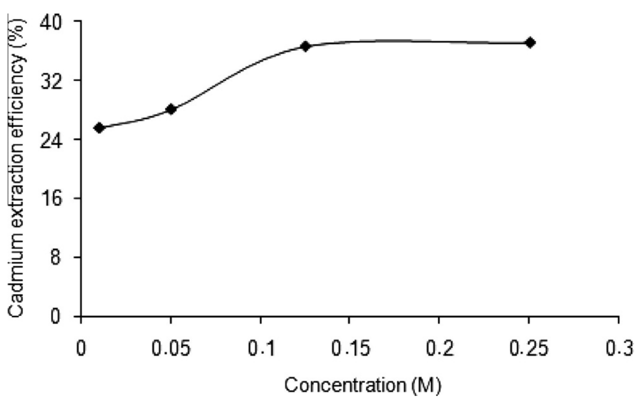

Figure 2 Effect of Na_2EDTA concentration on extraction efficiency of cadmium (L/P = 25, 400 rpm, 25 °C, 2 h).

constant after 0.125 M. Therefore, the optimal concentration of Na_2EDTA is 0.125 M.

3.2.3. Kinetic of cadmium extraction

The extraction of metals from phosphate ore is a kinetic equilibrium process. Therefore, the extraction time plays a very important role in the phosphate ore washing. In order to comprehend the washing process and determine the optimum contact time for cadmium extraction, a kinetic study was undertaken by washing phosphate ore with 0.125 M Na_2EDTA. The kinetic experiment (Fig. 3) shows that Na_2EDTA induced a two-step extraction process, in which a rapid extraction within the first hours was followed by a subsequent gradual release that occurred over the following hours. Effectively, the major part of cadmium (86.9%) was extracted within the first hour. With further mixing, the removal approached a plateau after 30 h and remained almost constant. Therefore, the concentration obtained after 30 h extraction can be considered as the equilibrium concentration. This corresponds to 48% removal efficiency of cadmium from phosphate ore. Cadmium concentration obtained after two hours represents 96% of its equilibrium concentration (Table 2). Therefore, an extraction time of 2 h was chosen for the study of the influence of other parameters.

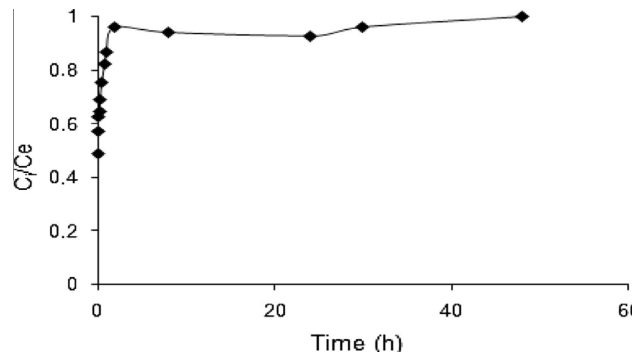

Figure 3 Kinetics of cadmium extraction with 0.125 M Na_2EDTA. C_t: cadmium concentration in washing solution at time t, C_e: cadmium concentration in extraction solution at equilibrium. (L/P = 25, 400 rpm, 25 °C, 48 h.)

3.2.4. Influence of liquid/phosphate ratio

In order to investigate the effect of liquid/phosphate ratio (L/P) on cadmium extraction, a series of extractions were carried out maintaining the concentration of Na_2EDTA at 0.125 M and increasing the L/P ratio. The results, illustrated in Fig. 4, show that the L/P increase has a positive effect on the extraction of cadmium. For economic reasons, it would be better to treat the largest quantity of phosphate ore using a given volume and concentration of Na_2EDTA. The European commission directive of 5 December 2005 limited the cadmium content in phosphate at (European Commission, 2005). Therefore, an L/P ratio of 25 can be taken to give 10 mg/kg of cadmium content in phosphate ore.

3.3. Cadmium extraction by microwave-assisted extraction

The mixture of phosphate ore and extracting agent was also treated by microwave irradiation. The effects of microwave power and microwave irradiation time on cadmium extraction were investigated.

3.3.1. Effect of microwave power on cadmium extraction

To assess the effects of microwave power on cadmium extraction, the tests were performed under the following typical conditions: the range of microwave power was 100–400 W, microwave irradiation time was 5 min and the mass ratio of Na_2EDTA solution to phosphate ore was 1/25. The effect of microwave power on the extraction rate of cadmium is shown in Fig. 5. Obviously, the increasing of microwave power leads

Table 2 Evolution of cadmium concentration with time.

Time (h)	Kinetic of extraction (C_i/C_e)	Cadmium extraction efficiency (%)
1	0.88	32
2	0.96	36
30	Equilibrium	48

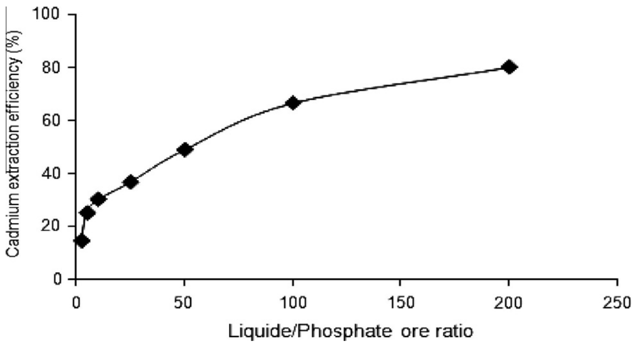

Figure 4 Effect of liquid/phosphate ore ratio on extraction efficiency of cadmium (0.125 M Na_2EDTA, 400 rpm, 25 °C, 2 h).

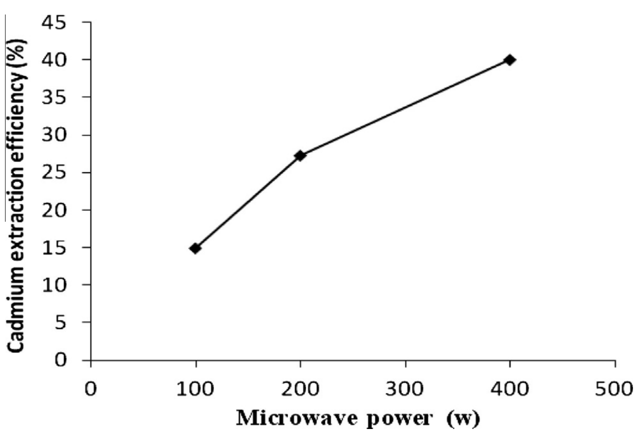

Figure 5 Effect of microwave power on cadmium extraction (0.25 M Na_2EDTA, L/P = 25, 5 min).

to a higher extraction rate of cadmium. In microwave field, the migration of ionic species and/or rotation of dipolar species promote the liquid–solid reaction process due to the increased contact area of reactants and the extraction reaction rate constant. The cadmium efficiency reaches 40.1% when the microwave power is set at 400 W. According to the results, when the microwave power increases progressively, some unfavorable phenomena occur, such as slurry sputtering. Therefore, the optimum microwave power should be set at 400 W.

3.3.2. Effect of microwave irradiation time on cadmium extraction

Tests with various microwave irradiation time were conducted under the typical conditions mentioned above. The results of the different tests, illustrated on Fig. 6, show that the extraction efficiency increases with time of exposure to radiation. The extraction efficiency of cadmium-assisted microwave (40%) obtained for a treatment of 5 min is similar to that obtained by a simple extraction for 2 h (38%). The results suggest that extending the time exposure to radiation in the mixture over 5 min increases the extraction efficiency of cadmium. However, to preserve the properties of the ore the time exposure is limited to 5 min. In effect for a period of an assisted extraction microwave than 5 min, due to the high heat in the reactor, it seemed that the ore deteriorates and takes a different aspect of his initial appearance.

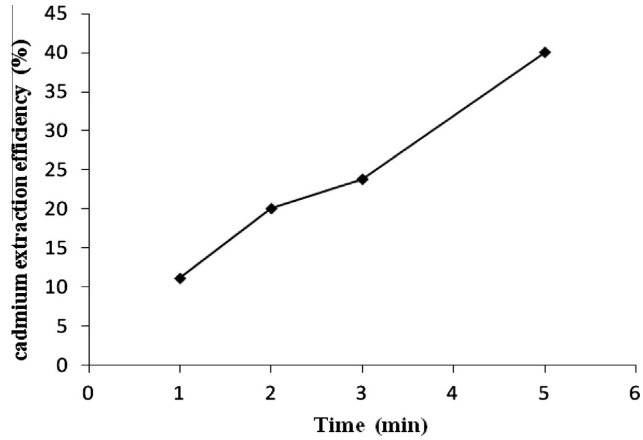

Figure 6 Effect of microwave irradiation time on cadmium extraction (0.25 M Na_2EDTA, L/P = 25, 400 W).

4. Conclusion

This study shows that cadmium extraction by Na_2EDTA induced a two-step extraction process: a rapid extraction within the first hour and a subsequent gradual release that occurred over the following hours.

The cadmium extraction efficiency increases progressively with increasing Na_2EDTA concentration, number of consecutive extraction and liquid/phosphate ratio in the 5–200 range. The application of optimum operating conditions (0.125 M Na_2EDTA, L/P = 25, 2 h) will produce a treated phosphate meet European requirement on cadmium content in phosphates of Djebel El Onk (Algeria).

The power increase of microwave causes an increase in cadmium extraction efficiency. Microwave can accelerate the extraction process and significantly reduces the duration of treatment.

References

Elliott, H.A., Brown, G.A., 1989. Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils. Water, Air, and Soil Pollution 45 (3–4), 361–369.

European Commission, 2005. Directive n 2005/87/Ce of Commission of December. Official journal of European Union, l318/19–l318/24.

Hong, J.J., Yang, S.M., Choi, Y.K., Lee, C.H., 1995. Precipitation of tricarboxylic acid biosurfactant derived from spiculisporic acid with metal ions in aqueous solution. Journal of Colloid and Interface Science 173 (1), 92–103.

Keith Syers, J., 2001a. Progress in the development of decadmiation of phosphorus fertilizers. In: Conference Fertilizer in Focus. Fertilizer Industry Federation of Australia, Inc., pp. 28–29.

Keith Syers, J., 2001b. The scope environmental cadmium project: implications for the fertilizer industry. In: 69th IFA Annual Conference, Sydney, Australia, pp. 21–24.

Kim, C., Ong, S.K., 1998. The selective reaction of lead and amorphous iron with EDTA in lead sulfate-contaminated soil system. Korean Journal of Environmental Engineering Research 3 (3), 167–174.

Lee, C.C., Marshall, W.D., 2002. Recycling of complexometric extractants to remediate a soil contaminated with heavy metals. Journal of Environmental Monitoring 4, 325–329.

Norvell, W.A., 1984. Comparison of chelating agents as extractants for metals in diverse soil materials. Soil Science Society of America Journal 48 (6), 1285–1292.

Olsen, S.R., Sommers, L.E., 1982. Phosphorus, Methods of Soil Analysis. Agronomy Series N 9, Part 2, second ed. Soil Society of America, Inc., Madison, WI

Polettini, A., Pomi, R., Rolle, E., 2007. The effect of operating variables on chelant assisted remediation of contaminated dredged sediment. Chemosphere 66, 866–877.

Reddy, K.R., Chinthamreddy, S., 2000. Comparison of extractants for removing heavy metals from contaminated clayey soils. Soil and Sediment Contamination 9, 449–462.

Reed, B.E., Carriere, P.C., Moore, R., 1996. Flushing of a Pb(II) contaminated soil using HCl, EDTA and $CaCl_2$. Journal of Environmental Engineering 122, 48–50.

Schramel, O., Michalke, B., Kettrup, A., 2000. Study of the copper distribution in contaminated soils of hop fields by single and sequential extraction procedures. The Science of the Total Environment 263, 11–22.

Strawn, D.G., Sparks, D.L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Science Society of America Journal 64, 144–156.

Sun, B., Zhao, F.J., Lombi, E., McGrath, S.P., 2001. Leaching of heavy metals from contaminated soils using EDTA. Environmental Pollution 113, 111–120.