

# Phosphate ore washing by Na<sub>2</sub>EDTA for cadmium removal: Optimization of the operating conditions

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This paper discusses the extraction of cadmium from phosphate ore by the washing method. Various parameters were investigated for the cadmium extraction from phosphate ore. The results from extraction tests showed that cadmium extraction depends on the nature and concentration of the extracting agent, the liquid/phosphate ore ratio, the temperature and the solution pH. The efficiency of the nine extracting agents for removing cadmium from phosphate ore was found to be in the order: Na<sub>2</sub>EDTA > citric acid > tartaric acid > ammonium citrate > calcium chloride > ammonium acetate > ammonium chloride > oxalic acid > ammonium hydroxide. In this study cadmium extraction kinetics was best described by the product layer diffusion control model.

**Keywords:** Phosphate ore washing; Cadmium; Environment; Extraction; Chemical processes; Optimization.

## INTRODUCTION

Each year, more than 30 million metric tons of phosphate nutrients are consumed worldwide; with more than 99% coming from phosphate rocks<sup>1</sup>. These products have helped farmers increase crop production and have made culture possible in nutrient-deficient lands. However, a possible negative effect of phosphate fertilizers is the contamination of cultivated lands by trace metals such as Cd, Cu, Mn, Ni, Pb and Zn naturally present in the phosphate rocks used to manufacture the fertilizers. Contamination by cadmium has been extensively studied given that cadmium is a non-essential element which accumulates potentially into plants tissues<sup>2,3</sup>. It can be present in relatively large amounts in chemical fertilizers (typically from traces to more than 150 mg kg<sup>-1</sup>)<sup>4,5</sup> depending on the phosphate rock origin. Phosphate ore industry usually tends to improve the quality of product by eliminating this toxic element. Extracting processes of cadmium in different types of soils have been the subject of many research works in recent years<sup>6-12</sup>. However, no study was found concerning the cadmium extraction from phosphate ore.

The aim of this study is to elaborate a simple and efficient method by which cadmium in phosphate ore would be decreased to lower levels. The influence of some parameters was taken into consideration, such as the reaction time, the nature and concentration of the extracting agent, the liquid/phosphate ore ratio (L/P), the pH and the temperature. The analysis of the results obtained was based on the extraction efficiency.

## MATERIALS AND METHODS

### Phosphate ore characterization

The phosphate samples used in this study originate from the phosphate mine of Djebel El Onk in north-east Algeria. After being air dried, the phosphate ores were passed through a 2 mm sieve. The mineralogy of the phosphate ore was determined using XRD (X-ray diffraction X'PERT MPD Philips) spectrometer and the elemental composition was determined using XRF (X-ray fluorescence X'PERT Philips) spectrometer.

To determine the phosphate ore pH; twenty five milliliters of bidistilled water were added to 10 g of phosphate ore. The mixture was stirred for 60 min and allowed to settle for 120 min. pH measurement was performed in the supernatant. pH was determined using a Hanna HI 9024 pH-meter.

For the determination of the organic matter in the phosphate, the sample was calcined at 450°C for 3 hours, and the observed mass loss was attributed to organic matter and thus represented the percentage by weight of organic matter (XP P 94-047)<sup>13</sup>.

To determine metal content, an acid digestion (HF/HClO<sub>4</sub>/HNO<sub>3</sub>) was performed on 1 g of phosphate ore, 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 by FAAS (flame atomic absorption spectrophotometer- Shimadzu AA 6200). To determine the cadmium fractionation in the phosphate, a five-step sequential extraction analysis was carried out. Knowing that partitioning of metal in different geochemical fractions could provide valuable information on metals reactivity and mobility<sup>14</sup>; speciation of cadmium before executing extraction was carried out. The sequential extraction method used for this purpose follows closely the scheme proposed by Tessier *et al.*<sup>15</sup> as described in Table 1, except for the digestion of the residual fraction. After each step, the extracts were centrifuged at 1000 rpm during 30 min to achieve a good separation. The supernatant was removed with a pipette and analyzed for cadmium content, whereas the residue was washed with 8 mL of H<sub>2</sub>O. After another 30 min of centrifugation, this wash solution was discarded before performing the next step.

### Experimental procedure

The leaching experiments were performed in a 250 mL glass reactor at atmospheric pressure. An automatic stirrer was used and a thermostat was employed to keep the reaction medium at constant temperature. In the extracting process, 50 mL of the extracting agent solution was put into the reactor, a specific amount of the sample (phosphate ore) was added to the solution and

**Table 1.** Sequential extraction procedure of cadmium in phosphate ore

Fraction	Designation	Method
1	Exchangeable	Extraction of 1 g of the sample with 8 mL (1 M MgCl <sub>2</sub> , pH= 7.0) for 1 h at room temperature with continuous agitation
2	Bound to carbonates	Leaching of the residue from fraction 1 at room temperature with 8 mL (1 M CH <sub>3</sub> COONa, pH= 5 adjusted with CH <sub>3</sub> COOH) for 1 h with continuous agitation
3	Bound to Fe–Mn oxides	Extraction of the residue from fraction 2 with 20 mL (0.04M NH <sub>2</sub> OH. HCl in 25% (v/v) CH <sub>3</sub> COOH) for 1 h at 96°C with occasional agitation
4	Bound to organic matter	Addition to the residue from fraction 3 of 3 ml (0.02M HNO <sub>3</sub> ) and 5 mL (H <sub>2</sub> O <sub>2</sub> 30%), pH adjusted to 2 with HNO <sub>3</sub> . Heating to 85 °C for 2 h with intermittent agitation.
5	Residual	Acid digestion of the residue from fraction 4.

the stirring started. After a certain period of time, the mixture was centrifuged, the supernatant was filtered through Whatman filter paper (45µm) and then analyzed.

#### Extraction tests

The influence of cadmium extraction parameters on phosphate ore was studied by adopting progressive steps to determine the optimum operating parameters.

These steps included (1) changing the nature of the extracting agent (CH<sub>3</sub>COONH<sub>4</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>EDTA, NH<sub>4</sub>Cl, NH<sub>4</sub>OH, CaCl<sub>2</sub>...) while fixing other conditions (Agitation rate = 400 rpm, L/P = 25, sampling time 24 h) and measuring the concentration of Cd(II) in the extracting solution; (2) changing the concentration of the extracting agent (0.01, 0.05, 0.125, 0.25 M) while fixing other conditions (extracting agent, agitation rate = 400 rpm, L/P = 25, sampling time 24 h) and measuring the concentration of Cd(II); (3) changing the phosphate/liquid ratio (200, 100, 50, 25, 10, 5, 2.5), selecting the optimum extracting agent and concentration from step (1) and (2) respectively and Agitation rate = 400 rpm, sampling time 2 h, temperature 25 °C, and measuring Cd(II) concentrations; (4) changing the temperature (25, 35, 45, 55 °C), choosing the optimum extracting agent, concentration, L/P from the above steps, and measuring Cd(II) concentrations; (5) changing the pH (4, 7, 9, 13), choosing the optimum extracting agent, concentration, L/P, temperature from above steps and measuring Cd(II) concentrations. In this way, the optimum conditions for Cd(II) extracting parameters could be determined. All the results were expressed as an average of three replicates with standard deviation.

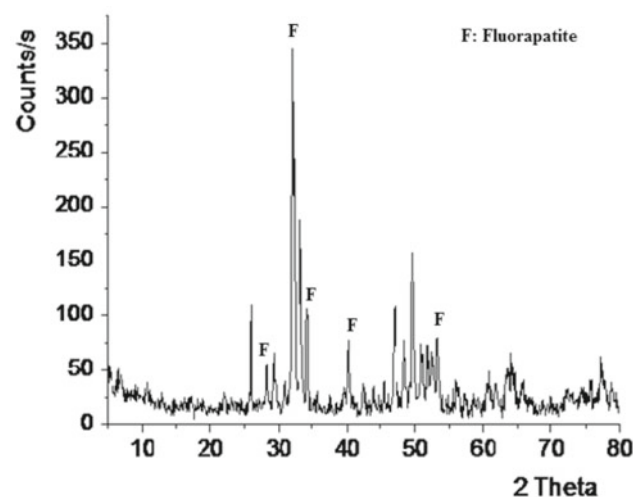
## RESULTS AND DISCUSSION

### Mineralogy and elemental composition

In this study the x-ray diffraction (XRD) analysis (Fig. 1) indicate that mainly fluorapatite existed in phosphate ore (2θ = 32.17; 33.28; 49.78; 64.17; 40.22; 34.33; 25.88).

**Table 2.** Physicochemical characteristics of the phosphate ore sample

	Parameter	Content
Organic content (%)	OM	0.031
pH	pH <sub>H2O</sub>	11.51
Element oxide determinate by XRF (%)		
	P <sub>2</sub> O <sub>5</sub>	31.6–32.5
	SiO <sub>2</sub>	1.5–1.8
	CaO	52.0–53.5
	MgO	0.81–1.6
	Al <sub>2</sub> O <sub>3</sub>	0.41–0.47
	MnO	0.0012
	Fe <sub>2</sub> O <sub>3</sub>	1.79
Element determinate by FAAS (ppm)		
	Cd	16.5 ± 0.12
	Pb	37.0 ± 0.28
	Zn	170.0 ± 0.11
	Cu	09.0 ± 0.09
	Cr	146.0 ± 0.10

**Figure 1.** XRD spectra of phosphate ore

The results of elemental analysis (Table 2) show that the cadmium content in the phosphate ore is about 16.5 mg kg<sup>-1</sup>. The phosphate ore contains other heavy metals (Pb, Zn, Cu, Cr ...) at concentrations ranging from 09.0 to 170.0 mg kg<sup>-1</sup>.

### Cadmium speciation in the phosphate ore

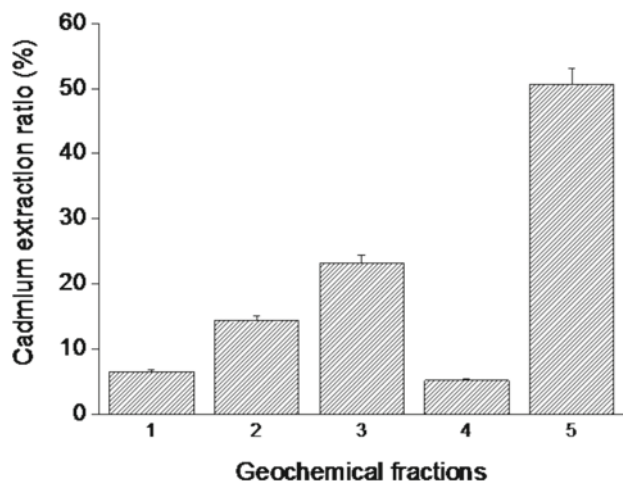
Only 6.55% of Cd content is readily exchangeable and approximately 14% is bounded to acido soluble fraction (Fig. 2). More than 23% of the total concentration is present in the metal bounded to Fe–Mn fraction. In addition, 50.55% of initial metal in this sample is present in the residual fraction, which might be difficult to remove.

### Choice of cadmium extracting agent

The aim of this study was to identify an efficient extracting agent that maximizes the amount of cadmium extracted. Nine different extracting agents, used as aqueous solution, were tested and compared. Fig. 3 shows that, among the extracting agents studied, Na<sub>2</sub>EDTA is the most effective in extracting cadmium from phosphate ore. The extraction efficiency results are represented by following sequence:

Na<sub>2</sub>EDTA > citric acid > tartaric acid > ammonium citrate > calcium chloride > ammonium acetate > ammonium chloride > oxalic acid > ammonium hydroxide.

According to the literature<sup>16–20</sup>, the cadmium extraction



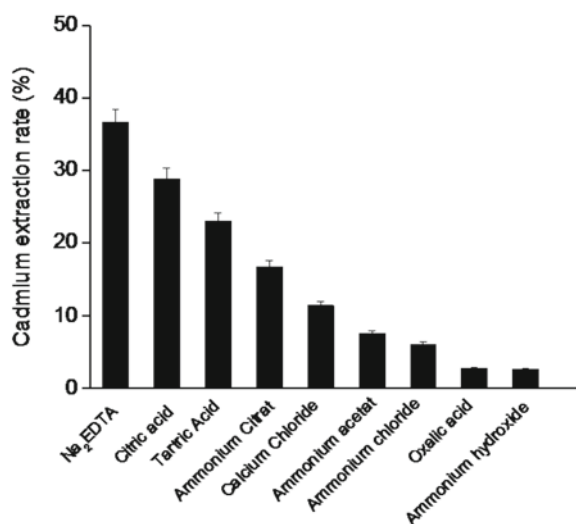
**Figure 2.** Speciation of cadmium in the different geochemical fractions of phosphate ore (1: exchangeable. 2: bound to carbonates. 3: bound to Fe–Mn oxides. 4: bound to organic matter. 5: residual)

efficiency with  $\text{Na}_2\text{EDTA}$  highly depends on soil characteristics, cadmium fractionation and the concentration of competitive cations in the washing solution, such as Fe (III) and Ca (II). In fact, the concentration of Fe (III) in the washing solution was a crucial parameter for the stability of metal- $\text{Na}_2\text{EDTA}$  complexes because Fe (III) may form more stable complexes with  $\text{Na}_2\text{EDTA}$  ( $\log k = 26.5$ ) compared to most heavy metals such as Cu(II) ( $\log k = 19.7$ ), Pb(II) ( $\log k = 19.5$ ), Zn(II) ( $\log k = 17.5$ ), Cd(II) ( $\log k = 17.4$ ), Ca(II) ( $\log k = 10.65$ )<sup>21</sup>. Metal concentrations (Fe, Zn, Pb, Mg, Cr, Ca) in the leaching solution were 31.32, 0.99, 1.11, 0.61, 0.54, 10.00  $\text{mg L}^{-1}$ , respectively, were relatively higher than cadmium (0.24  $\text{mg L}^{-1}$ ). This result explains why the rate of extraction of cadmium by  $\text{Na}_2\text{EDTA}$  is not very high. In order to optimize other parameters,  $\text{Na}_2\text{EDTA}$  will be used as the extracting agent.

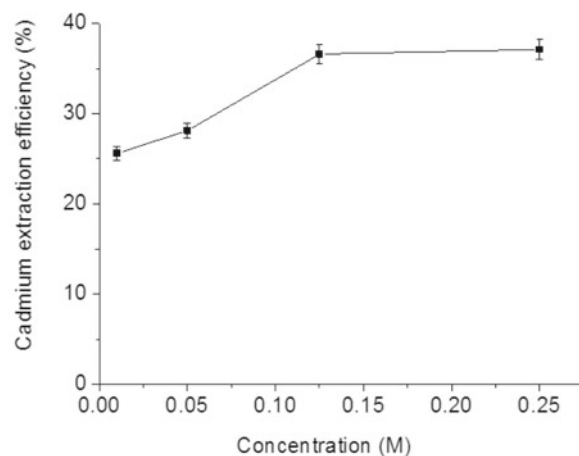
### Influence of physical and chemical parameters on the cadmium extraction

#### Influence of $\text{Na}_2\text{EDTA}$ concentration

The study of the effect of  $\text{Na}_2\text{EDTA}$  concentration on the cadmium extraction efficiency was carried out for



**Figure 3.** Cadmium extraction efficiency of different extracting agents. (0.5 M. L/P = 25. 400 rpm. 25°C. 24 h)

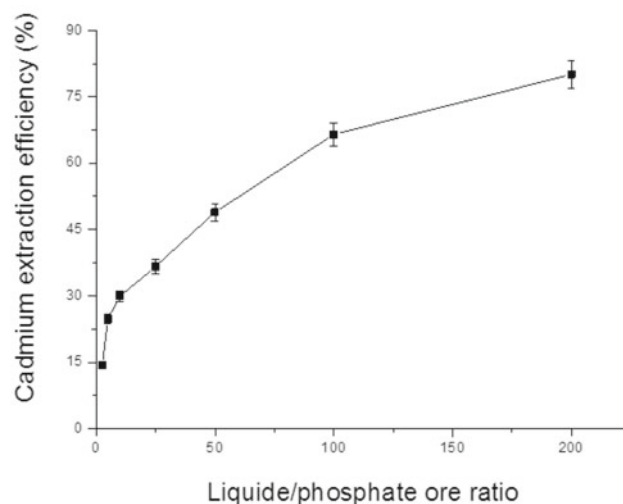


**Figure 4.** Effect of concentration on extraction efficiency of cadmium by  $\text{Na}_2\text{EDTA}$  (L/P = 25. 400 rpm. 25°C. 2 h)

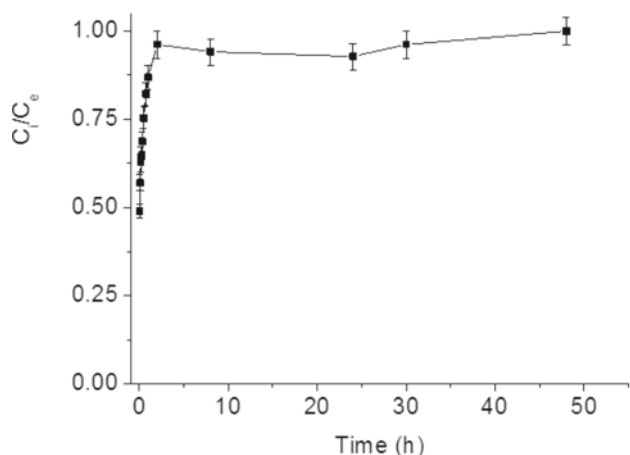
concentrations ranging from 0.01 to 0.25 M. The extraction of cadmium increased with increasing  $\text{Na}_2\text{EDTA}$  concentration and reached 36.60% (Fig. 4). As can be seen from the same curve when the concentration of  $\text{Na}_2\text{EDTA}$  varies from 0.01 to 0.125 M, the concentration of cadmium extracted increases accordingly and becomes constant after 0.125 M. It can be considered that the optimal  $\text{Na}_2\text{EDTA}$  concentration is equal to 0.125 M.

#### Influence of liquid/phosphate ore ratio

In order to investigate the effect of L/P on cadmium extraction, a series of extractions were conducted while maintaining the  $\text{Na}_2\text{EDTA}$  concentration at 0.125 M and increasing the L/P ratio. The results are illustrated in Fig. 5. These show that increasing the L/P ratio had a positive effect on the final extraction of cadmium. It was observed that as the phosphate ore to liquid ratio decreases, the extracting rate increases. This might be attributed to the fact that the amount of reagent compensation to every particle decreases with increasing the solid amount in the suspension. For economic reasons it would be desirable to treat the largest quantity of phosphate ore using a given volume and concentration of  $\text{Na}_2\text{EDTA}$ , but the European commission directive



**Figure 5.** Effect of liquid/phosphate ore ratio on the extraction efficiency of cadmium (0.125 M  $\text{Na}_2\text{EDTA}$ . 400 rpm. 25°C. 2 h)

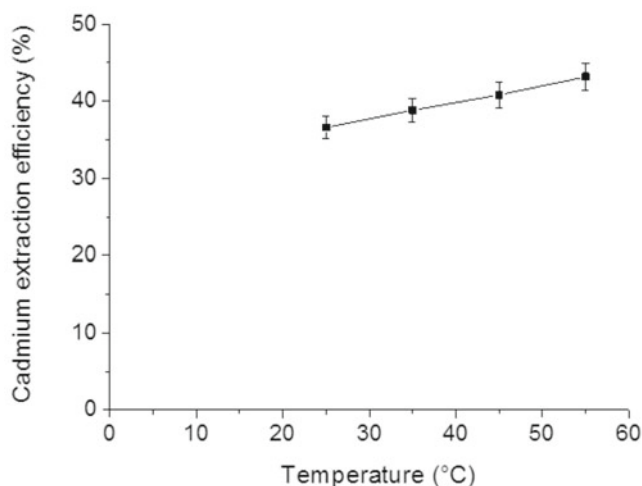


**Figure 6.** Kinetics of cadmium extraction with 0.125 M  $\text{Na}_2\text{EDTA}$ .  $C_t$ : cadmium concentration in washing solution at time  $t$ .  $C_e$ : cadmium concentration in extraction solution at equilibrium. ( $L/P = 25$ . 400 rpm.  $25^\circ\text{C}$ . 48h)

of 5 December 2005 limited the cadmium content in phosphate at  $10 \text{ mg kg}^{-1}$  of phosphate<sup>22</sup>. Therefore, the  $L/P = 25$  which gives a final content of cadmium in phosphate ore equal  $10.3 \text{ mg kg}^{-1}$  was retained.

#### Kinetics 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  $\text{Na}_2\text{EDTA}$ . The kinetic experiment (Fig. 6) indicates that  $\text{Na}_2\text{EDTA}$  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 (86.90%) of Cd (II) was extracted within the first hour. With further mixing, the removal approached a plateau after 30 h and remained almost constant. Cadmium concentration obtained after 2 h represents 96% of its equilibrium concentration. Therefore, an extraction time of 2 h was chosen for the study of the influence of other parameters.



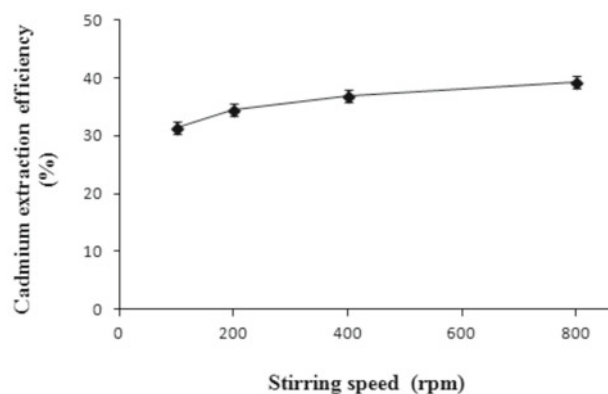
**Figure 7.** Effect of temperature on the extraction efficiency of cadmium (0.125 M  $\text{Na}_2\text{EDTA}$ .  $L/P = 25$ . 400 rpm. 2 h)

#### Influence of temperature on cadmium extraction

The temperature effect was studied in the range:  $25\text{--}55^\circ\text{C}$ . The extracted cadmium concentration was measured after 120 min of contact of the phosphate ore with  $\text{Na}_2\text{EDTA}$ . Fig.7 shows that an increase in the temperature leads to a small increase in the amount of cadmium extracted. It can be concluded that the influence of temperature on the cadmium extraction is slight. Therefore, the temperature of  $25^\circ\text{C}$  was chosen for the subsequent experiments.

#### Influence of stirring speed

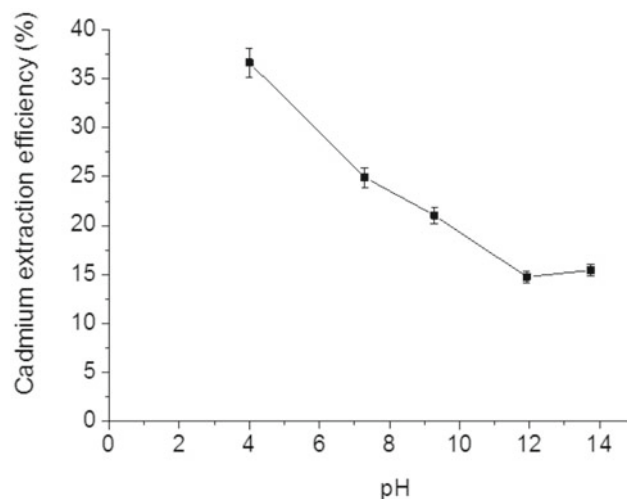
The stirring speed effect on the extracting rate was investigated in the frequency range of 100–800 rpm. The results show that after 120 min extracting time 34.23% of cadmium in the low stirring speed and 39.10% of cadmium in the high stirring speed was extracted. It is observed from Fig. 8 that the leaching rate increases with increasing stirring speed.



**Figure 8.** Effect of stirring speed on the extraction efficiency of cadmium (0.125 M  $\text{Na}_2\text{EDTA}$ .  $L/P = 25$ .  $25^\circ\text{C}$ . 2 h)

#### Influence of pH on cadmium extraction

Solution pH is another important factor determining the extraction efficiency, because it can influence the soil's retention of metals by adsorption<sup>23</sup> and affect the capability of chelating agents to extract the metals from soil. In general a lower solution pH gives higher extraction efficiency. Fig. 9 shows the highest extraction efficiency of cadmium from phosphate ore was obtained



**Figure 9.** Effect of pH of extraction solution on the extraction efficiency of cadmium (0.125 M  $\text{Na}_2\text{EDTA}$ .  $L/P = 25$ . 400 rpm.  $25^\circ\text{C}$ . 2 h)

at pH = 4. In the pH range of 4.0–13.0, the extraction efficiency of cadmium decreased when the pH increased. Metals bound to soil hydrous oxides can often be retrieved simply by lowering the pH because protons can promote oxide dissolution. Besides, hydrogen ions are rather weak competitive cations which can replace the adsorbed heavy metals via a cation exchange mechanism. As the H<sup>+</sup> ion concentration increases the particle surface generally becomes increasingly protonated and acquires a positive charge, thus promoting extraction of metals<sup>23,24</sup>. This can explain why the removal in the low pH range is higher than the removal in the high pH range. In addition, as the pH becomes more alkaline, the ability of Na<sub>2</sub>EDTA to enhance metals solubility decreases because hydrolysis is favored over complexation by Na<sub>2</sub>EDTA<sup>14,23</sup>.

### Kinetic analysis

The rate of reaction between a solid and solution can be expressed in terms of the heterogeneous reaction models. The rate may be controlled by<sup>25</sup>:

- film diffusion control model;
- chemical reaction control model or
- product layer diffusion control model.

By applying the above models to the experimental data obtained in this study one find the kinetic mechanism in the leaching process. Reaction time  $t$ , is given as a function of the fractional leaching for surface chemical reaction control model, diffusion through the solution control model, and diffusion product layer control model cases.

#### Film diffusion control model

The kinetics of solution diffusion control model ( $A_1$ ) is given by the following equation<sup>25</sup>

$$k_1 t = [x] \quad (1)$$

Where  $k_1$  is the reaction rate constant (min<sup>-1</sup>),  $t$  the time (min),  $x$  is the fraction extracted. The leaching rates were calculated at various temperatures. The results are shown in Table 3. The results were also analyzed by us-

ing the film diffusion control model given in Eq. (1) and  $x$  values were determined. The plot of  $[x]$  versus time  $t$  at 25 °C is shown in Fig. 10. The solution diffusion control model plot of  $[x]$  versus time  $t$  does not produce a straight line. Therefore, this kinetic analysis showed that the process does not fit the solution diffusion control model. The results were further analyzed by the surface chemical reactions control model.

#### Surface chemical reactions control model

The kinetics of the chemical reaction control model ( $A_2$ ) is given by the following equation<sup>25</sup>:

$$k_2 t = [1-(1-x)^{1/3}] \quad (2)$$

where  $k_2$  is the reaction rate constant (min<sup>-1</sup>),  $t$  the time (min),  $x$  is the fraction extracted. The results were analyzed by using the surface chemical reactions control model given in Eq. (2) and  $[1-(1-x)^{1/3}]$  values were calculated. The plot of  $[1-(1-x)^{1/3}]$  versus time  $t$  at 25 °C is shown in Fig.10. The surface chemical reactions control model plots of  $[1-(1-x)^{1/3}]$  versus time  $t$  did not produce a straight line. Therefore, this kinetic analysis shows that the process does not fit the surface chemical reactions control model. The results were further analyzed by the product layer diffusion control model.

#### Product layer diffusion control model

The kinetics of product layer diffusion control model ( $A_3$ ) is given by the following equation<sup>25</sup>:

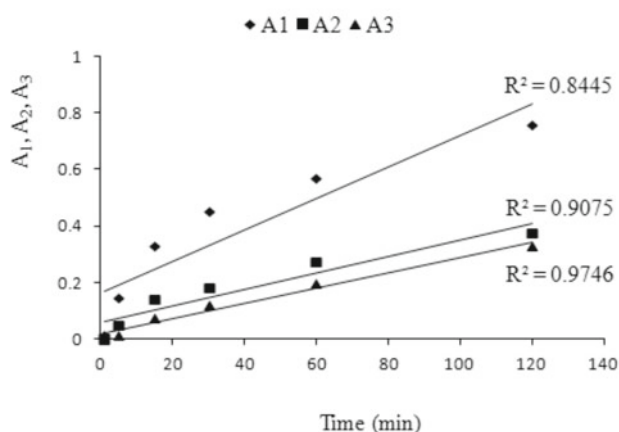
$$k_3 t = [1-3(1-x)^{2/3} + 2(1-x)] \quad (3)$$

Where  $k_3$  is the reaction rate constant (min<sup>-1</sup>),  $t$  the time (min),  $x$  is the fraction extracted.

The results were also analysed by using the product layer diffusion control model given in Eq.(3) and  $[1-3(1-x)^{2/3} + 2(1-x)]$  values were calculated. The plot of  $[1-3(1-x)^{2/3} + 2(1-x)]$  versus time  $t$  at 25 °C is shown in Fig. 10. The product layer diffusion control model plots of  $k_3 t = [1-3(1-x)^{2/3} + 2(1-x)]$  versus time  $t$  resulted in a straight line.

Furthermore, regression coefficients ( $R^2$ ) were calculated for the three models.  $R^2$  values were 0.8440 for the solution diffusion control model, 0.9070 for the surface chemical reactions control model, and 0.9740 for the product layer diffusion control model. The highest regression coefficient was observed in the product layer diffusion control model. Therefore, the product layer diffusion control mathematical model was chosen as the control model in this extraction process. The kinetics of the product layer diffusion control model is shown in Fig.11.

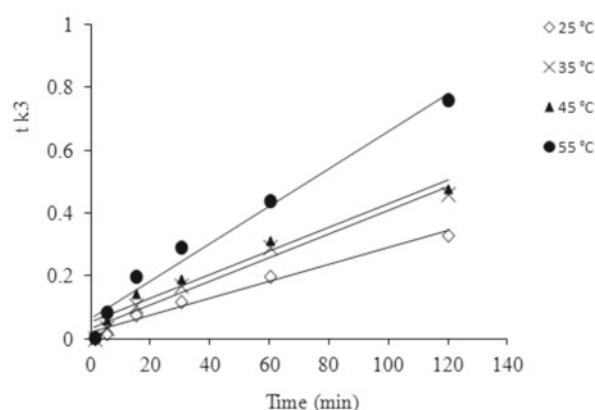
The rate constant values  $k_1$ ,  $k_2$  and  $k_3$  and correlation coefficients ( $R^2$ ) for the three models were calculated at various temperatures from Eqs. (1)–(3). The results are given in Table 3. These results show that rate constants increases with increasing the temperature for cadmium extraction.



**Figure 10.** The variation in  $A_1$ ,  $A_2$  and  $A_3$  with time at temperature of 25°C ( $A_1 = x$ ,  $A_2 = 1-(1-x)^{1/3}$ ,  $A_3 = 1-3(1-x)^{2/3} + 2(1-x)$ )

**Table 3.** Values  $k_1$ ,  $k_2$ ,  $k_3$  and  $R^2$  of  $A_1$ ,  $A_2$  and  $A_3$  models at different temperatures

Temperature (K)	$A_1$		$A_2$		$A_3$	
	$k_1$ (min <sup>-1</sup> )	$R^2$	$k_2$ (min <sup>-1</sup> )	$R^2$	$k_3$ (min <sup>-1</sup> )	$R^2$
298	0.005	0.844	0.002	0.868	0.002	0.974
308	0.005	0.637	0.003	0.784	0.003	0.955
313	0.004	0.628	0.003	0.788	0.004	0.972
323	0.004	0.456	0.003	0.610	0.006	0.975



**Figure 11.** The variation in  $[1-3(1-x)^{2/3} + 2(1-x)]$  with time at various temperatures

## CONCLUSION

The study focused on the elimination of cadmium from phosphate ore by chemical extraction. The results obtained show that among the agents studied,  $\text{Na}_2\text{EDTA}$  is the best extraction agent for cadmium. The kinetics of cadmium extraction is relatively rapid. The extraction pseudo-equilibrium is reached after almost two hours of the contact.  $\text{Na}_2\text{EDTA}$  induced a two-step extraction process, in which a rapid extraction within the first hours followed by a gradual release that occurred over the following hours. The concentration of  $\text{Na}_2\text{EDTA}$  and the L/P ratio are optimized to 0.125 M and 25 respectively. The influence of temperature on the extraction of cadmium is slight. Nevertheless there is a negligible increase in the extraction rate with increasing temperature. On the other hand, the influence of pH on the extraction of cadmium is important. The extraction efficiency of cadmium decreases with the increase of pH in the 4.0–13 range. In this study cadmium extraction kinetics is best described by the product layer diffusion control model.

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