Distribution and extraction of chromium from phosphate ore
Assia Khelalfa, Rachid Delimi and Zahia Benredjem

ABSTRACT
Phosphate rocks are a vital and non-renewable resource which is crucial for agricultural uses. However, this raw material contains various contaminants such as Pb, Cr, Cu, Ni and Zn. Among these elements, chromium is considered as an essential micronutrient at low intake levels. Its occurrence in industrial products at higher concentration can cause a potential risk to plants, animals and human health. The objective of this work was to select a chemical reagent capable of efficiently extracting chromium from phosphate ore in order to reduce its content. The study of chromium speciation in phosphate ore allows us to evaluate its mobility and therefore its potential toxicity. To this end, the test and selection of the specific chemical reagent for efficient chromium extraction from phosphate ore were studied. The effects of some parameters were taken into consideration and optimized. The results show that the chromium content was reduced to approximately 30% in natural phosphate using citric acid as extracting solution. Sequential extractions proposed by the European Communities Bureau of Reference method were used to assess the distribution of chromium before and after chemical extraction. The results indicate that the distribution of chromium in the residual fraction is dominant.

Key words | availability, extraction, fertilizers, metals, speciation

INTRODUCTION
Phosphate rocks are a vital non-renewable resource mainly used in the manufacturing of phosphoric acid and fertilizers. Due to the massive use of these products in agriculture, mainly with the increase in world population, demand for phosphate rocks has increased. Fertilizers enhance the natural fertility of the soil or replace the chemical elements taken from the soil by harvesting, grazing, leaching or erosion (Tekin et al. 2001). Phosphorus fertilizers contain varying amounts of heavy metals and other rare earth elements released from the phosphate rocks during the fertilizer manufacturing process which, from a commercial point of view, results in a decrease in the quality of the final acid product and the need for various purification processes to remove these impurities (Mellah & Bauer 1995; Mellah & Benachour 2007). Chemical elements such as Zn, Co, Cr, and Cu are necessary or beneficial to plants and living organisms at certain levels, but they can be toxic when they are present at higher concentrations in the soils (Alloway & Ayres 1993). Among these metals, Cr can generate serious problems and diseases (nausea, skin ulcerations and lung cancer) when it accumulates at higher levels, and as the concentration reaches 0.1 mg/g body weight it can ultimately become lethal (Mertz 1974; Ajmal et al. 1984). The excessive application of fertilizers is the most probable source of heavy metals, contributing to their continuous accumulation in soils. These elements can be assimilated by plants, and thus contaminate the food chain and threaten human health.

In general, the content of chromium in phosphate ranges between 0.3 and 460 mg/Kg (Elvers et al. 1993). The total chromium content in Algerian phosphate rock is relatively higher than that in other countries except for Moroccan phosphate rock (Baysal et al. 2002). Chromium...
exists in the environment in two stable oxidation states Cr(III) and Cr(VI). Compared to Cr(VI), Cr(III) has low solubility and mobility in the environment, and is usually considered as a much less dangerous pollutant (Fandorf 1993). However, Cr(III) removal has attracted increasing interest in view of its oxidation to harmful Cr(VI) in the presence of oxidants in natural environments (Lazaridis & Charalambous 2005; Tadesse et al. 2006). One of the possibilities to avoid the increase of chromium concentration in soil consists of reducing its content in phosphate ore used for the production of fertilizer. Therefore more research is needed in order to investigate micronutrient and hazardous elements associated with phosphate rock use (Chien 2004).

Speciation of heavy metals, especially chromium, in phosphate rock has been the subject of much research in recent years (Pérez-lópez et al. 2013; Al-hwaiti et al. 2015). This work was focused on the extraction of chromium from a local phosphate rock (region of Djebel Onk, northeast of Algeria). The sequential extraction of chromium has been investigated in order to determine the speciation of chromium in the phosphate ore, which gives us information about the amount of mobile chromium in the raw material. The objective of this study was to develop a chemical extraction process which consists of chromium extraction by an extracting agent. The influence of different parameters on the chromium extraction, such as the nature of the extracting agent, its concentration, contact time, temperature, solid/liquid ratio and successive extractions, has been studied. Furthermore, the distribution of chromium in phosphate ore after chemical extraction has been examined in order to understand the effect of the extracting agent on the chromium removal from different phases.

**MATERIALS AND METHODS**

**Materials**

The phosphate rock used in the present study was from the Deposit of Djebel Onk in the north-east of Algeria. All the chemicals used have an analytical grade. Deionized water was used to prepare the solutions. Hydrochloric acid (Merck, 37%), citric acid (Sigma Aldrich, 99.5%) and Na₂EDTA (Merck, 99%) have been used as extracting reagents.

**Preparation of phosphate ore sample**

The phosphate ore samples were air-dried, crushed and sieved to <2 mm before analysis. The pH was measured (pH meter HANNA HI 9024) in deionized water, respecting a solid: solution ratio equal to 1: 2.5. Organic matter percentage was determined by heating the dried samples at 450 °C for 3 h (XP P 94-047 1998). Total metal concentrations in the sample were determined by FAAS (flame atomic absorption spectrophotometer; Shimadzu AA6200) after acid digestion (HNO₃/HF/HClO₄) according to AFNOR norm (AFNOR 1996). An ultraviolet-visible spectrometer (Jenway) was used to determine the amount of P₂O₅ in the filtered solution by means of the vanadomolybdophosphoric acid colorimetric method. The mineralogical characterization of the raw ore was determined by X-ray diffraction (XRD) using an XRD XPERT MPD Philips spectrometer, and the elemental chemical composition was determined by X-ray fluorescence (XRF) using an XRF XPERT Philips spectrometer. The physical and chemical properties of the phosphate ore sample studied are summarized in Table 1.

**Table 1** | Physical and chemical properties of the phosphate ore sample

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (H₂O)</td>
<td>11.46 ± 0.60</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Main oxides (%)</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>32</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.65</td>
</tr>
<tr>
<td>CaO</td>
<td>52.75</td>
</tr>
<tr>
<td>MgO</td>
<td>1.20</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.44</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.79</td>
</tr>
<tr>
<td>Trace metals (mg/Kg)</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>Cu</td>
<td>17 ± 0.33</td>
</tr>
<tr>
<td>Ni</td>
<td>25.38 ± 0.38</td>
</tr>
<tr>
<td>Zn</td>
<td>146 ± 2.05</td>
</tr>
<tr>
<td>Cr</td>
<td>195 ± 11</td>
</tr>
</tbody>
</table>

*aAverage of three replicates of the ore sample; SD, standard deviation.*
Sequential extraction

A sequential extraction proposed by the European Communities Bureau of Reference (BCR) ([Ure et al. 1993]) was applied to determine the Cr speciation in the phosphate rock. The sequential extraction was performed on 1 g of ore sample by using the appropriate reagents to give the following fractions: F1: exchangeable and acid-soluble fraction; F2: bound to Mn, Al and Fe oxides; F3: bound to organic matter and sulfur; F4: residual metal fraction (dissolved by acid attack with HNO3, HF and HClO4). All the extractions were carried out in triplicate. The sequential extraction procedure is summarized in Table 2. Following each extraction step, the supernatant was separated from the solid residue by centrifugation, and kept at 4°C until analysis. All residues were washed after every extraction, and the washing solutions were discarded. The concentration of Cr in the extracts was determined by FAAS.

Chemical extraction procedure

The extraction experiments were investigated using three different extracting agents: hydrochloric acid, citric acid and Na2EDTA; 5 g of phosphate ore with 50 mL of extracting solution were placed in a 100 mL beaker. The samples were then stirred for 24 h. All tests were performed in triplicate and the results were presented as an average of the triplicate extracts, with an error of no more than 10%. The remaining samples were extracted by a sequential extraction. The kinetic extraction experiment was performed with extracting reagent solution at a well-determined concentration and solid/liquid ratio. The extraction times range from 15 min to 24 h. The effects of the variable extracting parameters, such as the nature and concentration of the extracting agents, contact time, temperature, solid/liquid ratio and successive extractions, on the chromium extraction rate were assessed. All extraction experiments were carried out at room temperature, while stirring at 180 rpm. The supernatant was removed, filtered through 0.45 μm filters and analyzed. The percentage of Cr extracted was calculated from the following equation ([Reddy & Chinthamreddy 2000; Goh & Lim 2005]):

\[
E(\%) = \frac{C_f \times V}{C_T \times M} \times 100\% \tag{1}
\]

where \(E\): percentage of Cr extracted (%); \(C_T\): total Cr content in soil (mg/Kg soil); \(C_f\): concentration of Cr in filtrate (mg/L); \(V\): volume of the added solution (L); and \(M\): soil mass (Kg).

RESULTS AND DISCUSSION

Mineralogical and chemical properties

The chemical and mineralogical analyses were performed using XRD spectra and XRF, and their results are given in Figure 1 and Table 1, respectively. It can be seen from Figure 1 that the main mineralogical phases of the raw ore are apatite (fluorapatite) with other secondary minerals such as dolomite, calcite, quartz and iron oxide minerals (hematite, magnetite and goethite). In addition to the major elements (P, Ca, Al, Fe, Mg, etc.), the phosphate rock contains heavy metals in trace amounts, such as Pb, Cu, Ni, Zn and Cr (Table 1). The high concentration of CaO (52.7%) explains the high basicity (pH = 11.4 ± 0.60) of the ore. It is noticed that the chromium content is higher than the maximum level tolerated in the soil, which is fixed to 150 mg/kg ([Henin 1983]). While for Pb, the recorded content is less than the maximum level tolerated in phosphates ([European Commission 2005]).

Speciation of chromium in phosphate ore

The results of the sequential extraction of Cr in phosphate ore are shown in Figure 2. The extracted percentage
values of Cr are in respect to the sum of the four fractions. The values represent the average extraction performed on triplicate samples. The errors related to the sequential extraction process were about 15%, which is acceptable as they are in the range of 10 to 20% (Quevauviller et al. 1994). As the results show, the amount of Cr extracted in the first, more soluble, fraction (i.e. exchangeable and acid-extractable fraction) was less than 6% of the total content. The metals of this fraction are considered the most dangerous portion due to their easy liberation into the environment, whereas a minor amount (3%) of Cr was found in a reducible form compared with the other three fractions, which indicates that it did not form bound to Mn, Al or Fe oxides. The percentage of Cr released of the oxidizable fraction was relatively low (about 16% of total Cr content). This result can be explained by the low organic matter content in the ore sample as shown in Table 1. Chromium is well known for forming specific complexes with soil organic matter (McGrath 1993). Several researchers have revealed that the low organic carbon content leads to a decrease in the Cr complexation, and hence its concentration decreases in this fraction (Mandal et al. 2011). The majority of Cr was found in the residual fraction (>75%) of total Cr content. The presence of chromium in the residual fraction may reflect its natural occurrence in the parent rock. Similar results were found by Nolting et al. (1996) and Algan et al. (2004), who stated that Cr is mainly in detrital form in soils and sediments. Pérez-lópez et al. (2010) found that Cr was entirely associated with the residual fraction in Moroccan phosphate ore. Badri (1984) reported that metals in this fraction are not available to plants and are strongly bound to secondary minerals in the soil besides sulfur and phosphate. In addition, the total concentration in the mobile fraction (based on the sum of the first three fractions: exchangeable and acid-soluble (F1), reducible (F2) and oxidizable (F3)) did not exceed 25% of the total Cr content. Hence, this Cr percentage is available to soil organisms and plants under changing environmental conditions (Mandal et al. 2011).
Optimization of extraction conditions

Effect of extracting agent

The effect of the nature of the extracting agent was tested using different extracting agents such as dilute hydrochloric acid, citric acid and Na₂EDTA. The extractions were performed at pH 2. It is known that at this pH value, the Cr(III) ions are the predominant species and the formation of phosphate complexes is negligible (Schrödter et al. 1998). The experiments were carried out at an extracting agent concentration of 0.25 mol/L with a solid/liquid ratio of 1:10 under stirring for 24 h. The results in Figure 3 show that the extraction rate of chromium varies considerably with the nature of extracting agents in the following order: citric acid (30%) > Ethylenediaminetetraacetic acid (EDTA) (23.60%) > HCl (6.32%), where citric acid and EDTA ensure the greatest removal of chromium. Furthermore, the dissolved chromium concentration was more effective with citric acid than with EDTA, even if the formation constant of the EDTA-Cr complex (log K = 23.4) is greater than the formation constant of the citric acid-Cr complex (log K = 8.7) at 0.1 mol/L ionic strength (Pettit & Powell 2001; Schecher & McAvoy 2001). Other investigators also observed similar discrepancies between stability constant values and metal extractability from contaminated soils (Kirpichtchikova et al. 2006; Jean et al. 2007; Wuana et al. 2010). Previous studies have shown the efficiency of carboxylic acids washing for extracting chromium compared with DTPA (diethylenetriamine pentaacetic acid) and EDTA (Pichtel & Pichtel 1997; Sun et al. 2001; Hong et al. 2002; Mühlbachová 2011). However, the level of Cr extracted by HCl was low compared with citric acid and EDTA.

Chromium extraction from the phosphate ore using extracting solution also results in the dissolution of other elements, leading to their loss. The market value of phosphate ore is mainly determined by the phosphorus content expressed as P₂O₅. In our case, the losses of P₂O₅ caused by extraction with citric acid, EDTA and HCl are 0.83%, 1.22% and 1.17%, respectively. Therefore, citric acid was selected for study in subsequent experiments.

Effect of citric acid concentration

The effect of citric acid concentration as an agent for chromium extraction from natural phosphate was studied in the range of 0.001 to 0.25 mol/L with a solid/liquid ratio of 1:10 for 24 h. From the extraction results shown in Figure 4, the effectiveness of chromium extraction increases proportionally with the increase in citric acid concentration up to 0.1 mol/L. After this value, the citric acid concentration does not significantly affect the chromium extraction rate. The increase in chromium extraction with the citric acid concentration may be due to the increase in proton activity. This acidity also promotes the solubility of the inorganic phosphorus, resulting in a loss of P₂O₅ (Table 3). However, it is important to note that the acid concentration should not be increased to more than the required level in order to avoid acid attack on the phosphate minerals. Several authors

![Figure 3](https://iwaponline.com/jwrd/article-pdf/6/4/524/376356/jwrd0060524.pdf)

**Table 3** | Evolution of P₂O₅ loss with the concentration of citric acid

<table>
<thead>
<tr>
<th>Concentration (mol/L)</th>
<th>0.001</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.10</td>
<td>2.46</td>
<td>2.10</td>
<td>1.90</td>
<td>1.35</td>
</tr>
<tr>
<td>P₂O₅ loss (%)</td>
<td>–</td>
<td>0.05</td>
<td>0.10</td>
<td>0.48</td>
<td>0.83</td>
</tr>
</tbody>
</table>
have demonstrated that the solubilization of phosphates enhances with the decrease in pH (Hedley et al. 1990; Hinsinger 2001). The concentration of 0.1 mol/L was chosen to investigate the effect of the other parameters.

**Effect of contact time**

The extraction kinetics was followed for a period of 24 hours for a citric acid concentration of 0.1 mol/L and a solid/liquid ratio of 1:10. Figure 5 indicates two steps, one is fast and the other one is slow. The fast step corresponds to the metals found in mobile form (i.e. exchangeable and non-specifically adsorbed species) which were extracted in a short period (<2 h). However, in the slower step, the metals were released from a less mobile form (i.e. retained in organic matter and oxides) over a longer period (Lebourg et al. 1999). The chromium extraction rate obtained for reaction times of 2 and 24 hours are equal to 24.74% and 28.71%, respectively. Thus the longer extraction period leads to a small increase in extraction rate. For further study, a contact period of 2 h was selected.

**Effect of temperature**

The temperature effect on chromium extraction has been investigated in the temperature range 25–85 °C with 0.1 mol/L of citric acid and a reaction time of 2 h. The results obtained (Table 4) show a relatively small effect of temperature on chromium extraction. In fact, one can see from Table 4 that when the temperature increases from 25 °C to 60 °C, the chromium extraction rate increases only from 24.47% to 29.09%, respectively. The further elevation of the temperature up to 85 °C leads to a chromium extraction rate equal to 37.65%. However, a high temperature is not suitable with organic chelant agents because of their low boiling points and decomposition (Demir et al. 2005; Oral et al. 2005). The extraction efficiency of Cr was found to be optimum at room temperature.

**Effect of solid/liquid ratio**

The study of the solid/liquid ratio effect is an important parameter for solid material leaching (Kosson et al. 2002; van der Sloat et al. 2003). The solid/liquid ratio effect on Cr extraction was studied by changing the ore mass from 0.25 to 10 g while the extracting agent volume was kept constant and equal to 50 mL in separate experiments (Bordas & Bourg 2001; Aydogan et al. 2005; Erdem & ÖZverdi 2008; Grabarczyk 2008). As shown in Figure 6, the residual chromium content in phosphate ore increases with the increase in solid/liquid ratio. The choice of the solid/liquid ratio must take into account two aspects: (i) the economic aspect of treating the maximum potential amount of the material; and (ii) the environmental aspect of respecting the maximum tolerated level of chromium in the soil of 150 mg/kg (Henin 1983). Otherwise, the application of solid/liquid ratios of 1:10 and 1:5 leads to values of the remaining chromium in the ore equal to 147.27 mg/kg and 165.68 mg/kg, respectively. The ratio that meets the economic and environmental requirements is 1:10.

**Table 4 | Effect of temperature on chromium extraction (0.1 mol/L citric acid, solid/liquid ratio: 1/10, contact time: 2 h)***

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>25</th>
<th>35</th>
<th>55</th>
<th>65</th>
<th>85</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (%)</td>
<td>24.47</td>
<td>25.17</td>
<td>27.38</td>
<td>29.09</td>
<td>37.65</td>
</tr>
</tbody>
</table>

*Figure 5 | Effects of contact time on chromium extraction (0.1 mol/L citric acid, solid/liquid ratio: 1/10, 25 °C); Ct, Ce: chromium concentrations in the extract at time t and at equilibrium, respectively.*

*Figure 6 | Effect of solid/liquid ratio on chromium extraction (0.1 mol/L citric acid, contact time: 2 h, 25 °C).*
Effect of successive extractions

Renewing the extracting solution for metal extraction from solids limits re-adsorption of the extracted elements, and increases the extraction rate of any metal-containing particles by maintaining under-saturated conditions as in stirred-flow extractions (Strawn & Sparks 2000). In order to investigate the renewal effect of the extracting solution on Cr extraction efficiency, successive extractions for 2 h with 0.1 mol/L of citric acid solution and a solid/liquid ratio of 1:10 were carried out on the same phosphate ore sample and the results are illustrated in Table 5. The first extraction cycle gives the highest chromium extraction rate (24.47%). The second extraction cycle permitted the extraction of 9.32% of Cr with a global loss between the first two extractions in P2O5 of 1.14%. However, the third and the fourth extraction cycles generated lower chromium extraction rates with important losses in P2O5 (2.36, 3.45%). We consider that two successive extractions lead to an acceptable extraction rate of chromium and phosphorus content loss.

Distribution of chromium in phosphate ore after citric acid extraction

In order to determine the extraction capacity of the extracting agent compared with the nature of each Cr fraction, a sequential extraction was applied before and after chemical extraction. Chemical extraction was performed with both extractants, citric acid and EDTA, at a concentration of 0.1 mol/L. The results of the remaining chromium distribution in the ore after chemical extraction are illustrated in Table 6. From the results obtained, the Cr of the first two fractions (exchangeable and reducible fractions) was completely removed by the citric acid. As with the citric acid, EDTA extracted all of the chromium content in the fraction F1 (exchangeable fraction). However, EDTA extracted only a small part of the chromium in the fraction F2 (reducible fraction). The chromium content bound to the organic matter and the sulfur compounds (fraction 3) was significantly decreased after chemical extraction with citric acid or EDTA. Indeed, extraction with citric acid and EDTA reduced the chromium content of 30.72 ± 2.66 mg/kg to 5.91 ± 0.01 mg/kg and 10.30 ± 1.18 mg/kg, respectively. However, the extraction efficiency of the two extracting agents (citric acid and EDTA) for the chromium in the residual phase (F4) was very low. Several authors (Zemberyov et al. 2006; Sakan et al. 2009; Ben Achiba et al. 2010) have indicated that chromium found in F4 is bound to the crystal lattice mineral. This study shows that citric acid is effective for chromium extraction in the mobile fractions (F1, F2 and F3) and is much less effective for chromium extraction in the quasi-immobile form (F4).

CONCLUSION

In the present work, we have studied the determination of chromium behavior and its distribution in a local natural phosphate ore. The results show that, between some extracting reagents tested, citric acid was the most efficient for removing chromium from phosphate ore. The study of the

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Successive extraction results (solid/liquid ratio: 1/10, contact time: 2 h, 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st cycle</td>
</tr>
<tr>
<td>Cr extracted (%)</td>
<td>24.47</td>
</tr>
<tr>
<td>P2O5 loss (%)</td>
<td>0.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Chromium distribution in different phases of phosphate ore before and after chemical extraction (F1: exchangeable and acid-soluble fraction, F2: reducible fraction, F3: oxidizable fraction, F4: residual fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractions</td>
<td>F1</td>
</tr>
<tr>
<td>Ore sample</td>
<td>11.66 ± 0.44</td>
</tr>
<tr>
<td>Citric acid</td>
<td>–</td>
</tr>
<tr>
<td>Na2EDTA</td>
<td>–</td>
</tr>
</tbody>
</table>

*aAverage values (mg/Kg) ± standard deviation.*
The effect of some parameters shows that the optimum conditions for efficient removal of chromium from the raw material are: contact time: 2 h, citric acid concentration: 0.1 mol/L, and a desired solid/liquid ratio of 1:10 at room temperature. Two successive extractions with 0.1 mol/L of citric acid are recommended in chromium extraction for preservation of the phosphate minerals. Furthermore, the sequential extractions study before and after chemical extraction of chromium shows that citric acid and EDTA are effective in extracting the chromium from the mobile fraction. Phosphate ore treated with one of these two extracting agents presents a lower risk of assimilation of chromium by plants. Thus, to determine the bioavailability of chromium content in the different fractions, it is necessary to perform additional experiments, including biological tests on plants, in order to correlate the results of chemical extractions with the amounts absorbed by plants.

ACKNOWLEDGEMENTS

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