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## Use of phytic acid for selective precipitation of undesirable metals (Al, Fe, Pb) contained in the leachates from hydrometallurgical processes

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### Abstract

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In hydrometallurgical processes, chemical precipitation is used either to recover dissolved valuable metals or to remove undesirable elements before electrolysis. Beside conventional reagents (Ca(OH)<sub>2</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>...) many authors tried to replace them by bio-sourced compounds, but unfortunately, without necessarily leading to an industrial use. This paper describes a study on the possibility to use phytic acid to remove Al<sup>3+</sup>, Fe<sup>3+</sup> and Pb<sup>2+</sup> from acidic leachates. This reagent, present in cereals and considered as an antinutrient, can be recovered from soaking waters of corn. In this work, five metal phytates were synthesized and characterized by TGA and ICP-OES leading to the following formulae: Al<sub>3</sub>C<sub>6</sub>H<sub>9</sub>P<sub>6</sub>O<sub>24</sub>·7H<sub>2</sub>O, Cu<sub>6</sub>C<sub>6</sub>P<sub>6</sub>O<sub>24</sub>·8H<sub>2</sub>O, Fe<sub>3.5</sub>C<sub>6</sub>H<sub>7.5</sub>P<sub>6</sub>O<sub>24</sub>·15H<sub>2</sub>O, Pb<sub>6</sub>C<sub>6</sub>P<sub>6</sub>O<sub>24</sub>·10H<sub>2</sub>O and Zn<sub>6</sub>C<sub>6</sub>P<sub>6</sub>O<sub>24</sub>·6H<sub>2</sub>O. Solubility of each metal phytate was measured in pure water at 20°C in order to determine their solubility product K<sub>s</sub> not available in literature. The conditional solubility as a function of the pH was then established to predict the possibility to perform selective precipitation. The results showed that phytic acid could be an interesting alternative precipitation reagent, able, from a thermodynamical point of view, to remove Al<sup>3+</sup>, Fe<sup>3+</sup> and Pb<sup>2+</sup> from copper or zinc leachates.

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**Keywords:** metal phytates, agro-resources, solubility measurement, precipitation

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### 1. Introduction

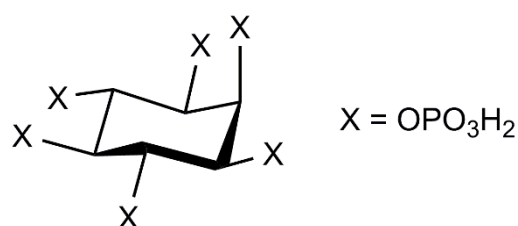
Chemical precipitation is the most common technology to remove or recover dissolved metals from different solutions such as wastewaters or industrial leachates from hydrometallurgical processes. In hydrometallurgy, precipitation is used either to purify leachates after Solid/Liquid separation or at the end of the process to recover metals under a valuable mineralogical form.

The most widely used reagents for the detoxication of liquid effluents are lime Ca(OH)<sub>2</sub>, mineral sulphides NaHS or Na<sub>2</sub>S and organic sulfides such as Tri-Mercapto-Triazine. In hydrometallurgical processes, metals are often precipitated with sodium hydroxide NaOH or sodium carbonate Na<sub>2</sub>CO<sub>3</sub>.

Beside these conventional reagents produced by chemical industry, various bio-sourced compounds, used to perform precipitation (selective or not) were found in the literature. These green reactants can be extracted or synthesized from agri-resources.

The most common “green reactant” identified in the literature is oxalic acid, which can be extracted from sorrel roots. Oxalic acid forms precipitates with a lot of cations like transition metals [1,2], rare earth elements [3,4], and uranides [5]. One of the most studied compounds are fatty acids, non-toxic compounds extracted from vegetable oil and animal fats. Many of them were considered as example: capric [6], lauric [7] acids. Dicarboxylic acids were also investigated as malonic [8] or succinic [9] acids. The use of other acids, derived from sugar molecules can be cited: gluconic [10] and lactobionic [11] acids. Among these “green reactant”, some of them are able to perform selective precipitation of metal cations such as sodium decanoate [12].

In this work, the possible use of phytic acid (or *myo*-inositol-1,2,3,4,5,6-hexakisphosphate) as precipitation reagent was investigated. This compound has a cyclohexane structure with six dihydrogenophosphate function carried by each carbon (Fig. 1). This acid represents 80 % of phosphorus contained in plants. Present at 6.39 wt.% in maize germ, 2.1-7.3 wt.% in wheat bran and 2.56-8.7 wt.% in rice bran [13], it is well known for its ability to form soluble complexes with many metal cations such as iron, zinc or calcium [14] decreasing the absorption of nutrients and their bioavailability in the organism by human body. Considered as an antinutrient, agri-food industry tries to reduce or eliminate this compound from cereals. Some works show that a large part of phytic acid can be simply removed by soaking cereals in water [15]. Soaking waters, containing between 0.5 and 2 wt.% of phytic acid, are considered as non-hazardous waste and are used in agricultural spreading for organic soil amendment [16]. In 1997, Tsao *et al* [17] estimated that it was possible to recover each year in United States about 50 Mt of phytic acid from corn steep liquor. Very few studies deal with the use of this compound. Seaman *et al* [18] demonstrated that phytic acid and phytates could be used for the in situ treatment of metals in contaminated soils and Tsao *et al* [17] used phytic acid in order to synthesize a chelating resin able to remove cations from liquid waste.



**Fig. 1.** Molecule of phytic acid [19]

Except works of Vasca *et al* [20] who determined the formula of 6 divalent metal (Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Sn<sup>2+</sup>) there is no other study found in the literature. In contrast, no solubility data of these compounds are available. By analogy with metal inorganic phosphates, it can be assumed that phytic acid will give insoluble precipitates with metal cations. In these conditions, this bio-sourced reactant will be use not for the recovery of valuable metals in leachate, but rather to remove undesirable cations from leachates in hydrometallurgy (mainly Al, Fe and Pb).

In this study, five cations were investigated: Cu<sup>2+</sup> and Zn<sup>2+</sup> as valuable metals and Al<sup>3+</sup>, Fe<sup>3+</sup> and Pb<sup>2+</sup> as undesirable species. The first part of this work is devoted to the determination of the formula of each metal phytate. Then, their solubility was measured in order determine solubility product  $K_s$  and to establish the solubility domain of each metal by superimposing solubility curves of phytate and hydroxide.

## 2. Materials and Methods

### 2.1. Materials

All salts were purchased from different suppliers: iron chloride (FeCl<sub>3</sub>) (Sigma-Aldrich, 97 %), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) (Sigma-Aldrich, > 99%), aluminum chloride (AlCl<sub>3</sub>.6H<sub>2</sub>O) (Fluka, 99 %), zinc sulfate (Zn(SO<sub>4</sub>).7H<sub>2</sub>O) (VWR, 99.5 %), copper chloride dihydrate (CuCl<sub>2</sub>.2H<sub>2</sub>O) (VWR, > 96 %), hydrochloric acid (HCl) (Sigma-aldrich, 37 %), sodium hydroxide (NaOH) (VWR, 97 %) and phytic acid (Acros Organics, 50 %). Solutions of metal cations with concentrations close to 1.1 mol.L<sup>-1</sup> were prepared for the synthesis of the precipitates corresponding to the concentration of commercial phytic acid. All solutions were prepared with deionized water (< 0.2 μS.cm<sup>-1</sup>).

### 2.2. Precipitation of metal phytates

Metal phytates were prepared by adding phytic acid to metal cations solutions at controlled pH: pH=1 for iron, pH=1.2 for lead, pH=2.1 for aluminium, pH=3.0 for zinc and pH=3.2 for copper. These values were chosen to precipitate the maximum amount of metal phytate without co-precipitating

metal hydroxide. pH measurement and adjustment were performed with a Metrohm Tiamo Titrand 809 titrator. The solutions were stirred for 30 minutes at 400 rpm. Then, pulps were filtered through a 0.22  $\mu\text{m}$  pore size filter, washed thoroughly with deionized water and finally dried at 105  $^{\circ}\text{C}$  for 24 h.

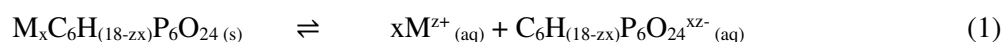
### 2.3. Chemical analysis

Precipitates were first analyzed by X-Ray Fluorescence using a Bruker AXS GmbH -S4 Explorer WDXRF spectrometer in order to check the presence or absence of chloride in the compounds and by X-Ray Diffraction with a Bruker D8 Advance diffractometer ( $K_{\alpha 1}=1,5406 \text{ \AA}$ ). For this, a semi-quantitative analysis was performed on pelletized samples. Then, precipitates were digested with hydrochloric acid  $\text{HCl } 6 \text{ mol.L}^{-1}$ , except lead phytate for which nitric acid  $\text{HNO}_3 \text{ } 7 \text{ mol.L}^{-1}$  was used. Metals and phosphorus were measured by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) using a Perkin Elmer Avio 200-OES. Crystallization water of solids was determined with a ThermoGravimetric Analyzer coupled with Mass spectrometry (TGA-MS) (Setsys Ev 1750 Tga - Setaram / Ms Omnistar Gsd 301c - Pfeiffer Vacuum).

### 2.4. Solubility study

#### 2.4.1. Theoretical metal speciation

Cations interact with the phosphoric acid functions of phytic acid, and, from a theoretical point of view, a total of 12 protons could be replaced. The reaction corresponding to the solubility equilibrium of a metal phytate ( $\phi$ ) in pure water is (Eq. (1)):



where  $x$  corresponds to the stoichiometry of the metal precipitate and  $z$  the charge of the cation. For this equation, it can be assumed that one single molecule of phytic acid can interact with several metallic cations. In this case, solubility product  $K_s$  is given by (Eq. (2)):

$$K_s = (a_{\text{M}^{z+}})^x (a_{\phi^{xz-}}) \quad (2)$$

$a_{\text{M}^{z+}}$  and  $a_{\phi^{xz-}}$  are respectively the activities of metallic cation and phytic acid, which can be calculated according to (Eq. (3)):

$$a_i = \gamma_i C_i \quad (3)$$

where  $C_i$  and  $\gamma_i$  are respectively the concentration and the activity coefficient of element  $i$ . For an ionic strength lower than  $10^{-2} \text{ mol.L}^{-1}$ , activity coefficients are calculated with the following Debye-Hückel equation (Eq. (4)):

$$\log \gamma_i = -0.5 z_i^2 \sqrt{I} \quad (4)$$

with  $I$ , the ionic strength. In pure water, by substituting Eq. (3) into Eq. (2), the solubility product can be written as (Eq. (5)):

$$K_s = (\gamma_{\text{M}^{z+}})^x (\gamma_{\phi^{xz-}}) [\text{M}^{z+}]^x [\phi^{xz-}] \quad (5)$$

For a given pH, phytic acid and metallic cations can be found in different acido-basic forms. Table 1 shows the 12 acidity constants of phytic acid determined by Marolt *et al* [21]. Acidity constants of the five metal cations studied [22] are given in Table 2.

**Table 1**

Acidity constants of the phytic acid in water at 25 °C

LH <sub>12</sub> /LH <sub>11</sub>	LH <sub>11</sub> /LH <sub>10</sub>	LH <sub>10</sub> /LH <sub>9</sub>	LH <sub>9</sub> /LH <sub>8</sub>	LH <sub>8</sub> /LH <sub>7</sub>	LH <sub>7</sub> /LH <sub>6</sub>
< 10 <sup>-1.5</sup>	< 10 <sup>-1.5</sup>	< 10 <sup>-1.5</sup>	< 10 <sup>-1.5</sup>	10 <sup>-1.92</sup>	10 <sup>-2.73</sup>
LH <sub>6</sub> /LH <sub>5</sub>	LH <sub>5</sub> /LH <sub>4</sub>	LH <sub>4</sub> /LH <sub>3</sub>	LH <sub>3</sub> /LH <sub>2</sub>	LH <sub>2</sub> /LH	LH/L
10 <sup>-4.96</sup>	10 <sup>-6.23</sup>	10 <sup>-7.95</sup>	10 <sup>-9.4</sup>	10 <sup>-9.3</sup>	10 <sup>-9.6</sup>

**Table 2**

Acidity constants of different metal cations in water at 20 °C

	M <sup>z+</sup> /MOH <sup>z-1+</sup>	MOH <sup>z-1+</sup> /M(OH) <sub>2</sub> <sup>z-2+</sup>	M(OH) <sub>2</sub> <sup>z-2+</sup> /M(OH) <sub>3</sub> <sup>z-3+</sup>	M(OH) <sub>3</sub> <sup>z-3+</sup> /M(OH) <sub>4</sub> <sup>z-4+</sup>
Zn <sup>2+</sup>	10 <sup>-8.997</sup>	10 <sup>-8.797</sup>	10 <sup>-10.297</sup>	10 <sup>-12.397</sup>
Cu <sup>2+</sup>	10 <sup>-7.497</sup>	10 <sup>-8.697</sup>	10 <sup>-10.685</sup>	10 <sup>-13.101</sup>
Pb <sup>2+</sup>	10 <sup>-7.597</sup>	10 <sup>-9.497</sup>	10 <sup>-10.997</sup>	10 <sup>-11.608</sup>
Al <sup>3+</sup>	10 <sup>-4.997</sup>	10 <sup>-5.097</sup>	10 <sup>-6.697</sup>	10 <sup>-5.897</sup>
Fe <sup>3+</sup>	10 <sup>-2.187</sup>	10 <sup>-2.407</sup>	10 <sup>-7.966</sup>	10 <sup>-9.028</sup>

In addition, the different acido-basic forms of phytates are able to form complexes with these five cations [14,24]. The stability constants of these complexes are gathered in Table 3.

**Table 3**

Formation constants of complexes between metal cations and deprotonated forms of phytic acid in water at 20 °C

	[M(H <sub>2</sub> φ)] <sup>12-z-2-</sup>	[M(H <sub>3</sub> φ)] <sup>12-z-3-</sup>	[M(H <sub>4</sub> φ)] <sup>12-z-4-</sup>	[M(H <sub>5</sub> φ)] <sup>12-z-5-</sup>	[M(H <sub>6</sub> φ)] <sup>12-z-6-</sup>
Zn <sup>2+</sup>		10 <sup>11.3</sup>	10 <sup>10.3</sup>	10 <sup>8.54</sup>	10 <sup>6.94</sup>
Cu <sup>2+</sup>		10 <sup>13.5</sup>	10 <sup>12.15</sup>	10 <sup>9.07</sup>	10 <sup>5.73</sup>
Pb <sup>2+</sup>	10 <sup>9.0</sup>	10 <sup>7.4</sup>	10 <sup>6.0</sup>	10 <sup>4.5</sup>	10 <sup>3.2</sup>
Al <sup>3+</sup>	10 <sup>23.7</sup>	10 <sup>20.1</sup>	10 <sup>16.4</sup>	10 <sup>12.2</sup>	10 <sup>8.48</sup>
Fe <sup>3+</sup>	10 <sup>19.2</sup>	10 <sup>18.2</sup>	10 <sup>12.7</sup>	10 <sup>8.99</sup>	

Taking into account acido-basic properties of cations and phytic acid, K<sub>s</sub> is replaced by the conditional solubility product, noted K<sub>s</sub><sup>cond</sup>, which can be written as (Eq. (6)):

$$K_s^{\text{cond}} = (\gamma_M)^x (\gamma_\phi) [M]^x [\phi] \quad (6)$$

[M] is the sum of the concentrations of all acido-basic and complex forms of the metallic cation in solution. [φ] corresponds to the conservation of matter for phytic acid including all acido-basic forms and all metal phytates complexes.

According to Ringbom [25] the conditional solubility product can be written (Eq. (7)):

$$K_s^{\text{cond}} = K_s \alpha_M^x \alpha_\phi \quad (7)$$

where α<sub>M</sub> and α<sub>φ</sub> correspond to the reaction coefficients of metal cation and phytate.

For the different cations, the stability constants of metal/phytate complexes must be included in the calculation. α<sub>M</sub> and α<sub>φ</sub> can be determined by (Eq. (8-9)):

$$\alpha_M = \frac{[M]}{[M^{z+}]} = 1 + \frac{[\text{MOH}^{z-1+}]}{[M^{z+}]} + \frac{[\text{M(OH)}_2^{z-2+}]}{[M^{z+}]} + \dots + \frac{[\text{M(OH)}_n^{z-n+}]}{[M^{z+}]} + \frac{[\text{M(H}_2\phi)^{12-z-2-}]}{[M^{z+}]} + \dots + \frac{[\text{M(H}_6\phi)^{12-z-6-}]}{[M^{z+}]} \quad (8)$$

$$\alpha_\phi = \frac{[\phi]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} = 1 + \frac{[\text{C}_6\text{H}_{17}\text{P}_6\text{O}_{24}^-]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} + \frac{[\text{C}_6\text{H}_{16}\text{P}_6\text{O}_{24}^{2-}]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} + \dots + \frac{[\text{C}_6\text{H}_6\text{P}_6\text{O}_{24}^{12-}]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} + \frac{[\text{M(H}_2\phi)^{12-z-2-}]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} + \dots + \frac{[\text{M(H}_6\phi)^{12-z-6-}]}{[\text{C}_6\text{H}_{18}\text{P}_6\text{O}_{24}]} \quad (9)$$

For all phytates precipitates, the relationship between the solubility and the solubility product is (Eq. (10)):

$$S = \sqrt[x+1]{\frac{K_s}{x^x}} \quad (10)$$

This relationship is the same for conditional solubility and corresponding solubility product (Eq. (11)):

$$S^{\text{cond}} = \sqrt[x+1]{\frac{K_s^{\text{cond}}}{x^x}} \quad (11)$$

By replacing the conditional solubility product by equation (Eq. (7)), the conditional solubility can be written as (Eq. (12)):

$$S^{\text{cond}} = \sqrt[x+1]{\frac{K_s \alpha_M^x \alpha_\phi}{x^x}} \quad (12)$$

So the logarithm of the conditional solubility can be calculated by equation (Eq. (13)):

$$\text{Log}(S^{\text{cond}}) = \log\left(\sqrt[x+1]{\frac{K_s \alpha_M^x \alpha_\phi}{x^x}}\right) \quad (13)$$

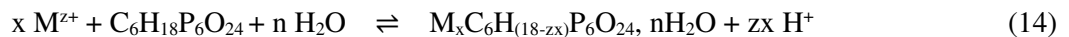
#### 2.4.2. Solubility measurement

Solubility of metal phytates was measured according to the analytical method [26] described in the literature: five pulps of the same precipitate were prepared by adding 0.3 g of precipitate to 50 mL of pure water. Pulps were maintained at 20 °C by using a double wall glass cell connected to a circulation cryostat (Bioblock Scientific 911 BB). Solutions were mixed with a magnetic stirrer at 400 rpm for an equilibrium time previously determined by following the conductance. The glass cell was covered to prevent absorption of CO<sub>2</sub> from atmosphere. Then, pulps were filtered through a 0.22 μm pore size filter. pH and concentrations of each metal cation were measured.

### 3. Results and Discussions

#### 3.1. Characterization of precipitates

The formation of a precipitate between phytic acid and metal cations can be written as follows, by considering that the precipitate can eventually contain water of crystallization (Eq. (14)):



where n corresponds to the molecule number of crystallization water.

Elemental analysis was performed on each precipitate in order to determine the value of x and TGA-MS was achieved to determine the value of n.

##### 3.1.1. Elemental analysis

Table 4 gives metals and phosphorus contents calculated from ICP-OES measurements. Each metal phytate was synthesized and characterized three times demonstrating a good reproducibility of the results. No chloride was found in precipitates by X-Ray Fluorescence.

**Table 4**  
Elemental analysis of metal/phytate precipitates

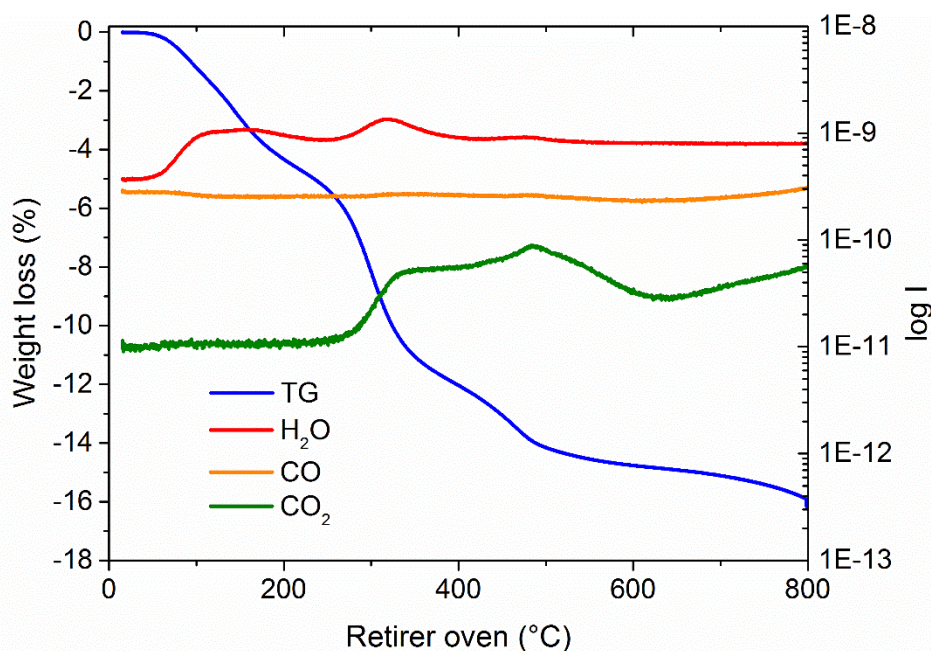
	Pb <sup>II</sup>	Zn <sup>II</sup>	Cu <sup>II</sup>	Fe <sup>III</sup>	Al <sup>III</sup>
Metal mass content (wt.%)	58.3 ± 0.1	34.6 ± 0.6	36.2 ± 0.2	17.4 ± 0.3	9.5 ± 0.3
Phosphorus mass content (wt.%)	8.9 ± 0.1	15.8 ± 0.5	15.9 ± 0.2	16.5 ± 0.2	15.9 ± 0.2

### 3.1.2. Thermogravimetric analysis

Fig. 2. presents the TGA curve obtained for zinc phytate. The blue line, which decreases with temperature, corresponds to the loss of mass. The three other curves correspond to the logarithm of the signal intensity obtained in mass spectrometry for water (red), carbon monoxide (orange) and carbon dioxide (green).

Up to 200 °C, only the signal of water varies. Between 200 °C and 400 °C water and CO<sub>2</sub> were released due to the degradation of the phytic acid molecule. The ratio of the H<sub>2</sub>O and CO<sub>2</sub> signals allow to calculate the percentage of water and carbon dioxide released. This ratio is equal to 95 %, which corresponds to the loss of mass due to the liberation of water. At higher temperatures, the water signal does not vary. Only CO<sub>2</sub> was released.

The loss of mass at 400 °C is used to calculate the value of n, the number of water molecules in the formula of precipitate. For zinc phytate, n is equal to 6.



**Fig. 2.** Zinc phytate thermogravimetric analysis

The TG analysis, applied to all metal phytates, gave us the following formulae: Al<sub>x</sub>C<sub>6</sub>H<sub>(18-zx)</sub>P<sub>6</sub>O<sub>24</sub>·7H<sub>2</sub>O - Cu<sub>x</sub>C<sub>6</sub>H<sub>(18-zx)</sub>P<sub>6</sub>O<sub>24</sub>·8H<sub>2</sub>O - Fe<sub>x</sub>C<sub>6</sub>H<sub>(18-zx)</sub>P<sub>6</sub>O<sub>24</sub>·15H<sub>2</sub>O - Pb<sub>x</sub>C<sub>6</sub>H<sub>(18-zx)</sub>P<sub>6</sub>O<sub>24</sub>·10H<sub>2</sub>O - Zn<sub>x</sub>C<sub>6</sub>H<sub>(18-zx)</sub>P<sub>6</sub>O<sub>24</sub>·6H<sub>2</sub>O. Thanks to n values and with the help of the data of Table 4, the x value for each compound can be determined and a formula is proposed (Table 5).

**Table 5**  
Formulae of metal phytate precipitates

Pb <sup>II</sup>	Zn <sup>II</sup>	Cu <sup>II</sup>	Fe <sup>III</sup>	Al <sup>III</sup>
Pb <sub>6</sub> C <sub>6</sub> P <sub>6</sub> O <sub>24</sub> ·10H <sub>2</sub> O	Zn <sub>6</sub> C <sub>6</sub> P <sub>6</sub> O <sub>24</sub> ·6H <sub>2</sub> O	Cu <sub>6</sub> C <sub>6</sub> P <sub>6</sub> O <sub>24</sub> ·8H <sub>2</sub> O	Fe <sub>3.5</sub> C <sub>6</sub> H <sub>1.5</sub> P <sub>6</sub> O <sub>24</sub> ·15H <sub>2</sub> O	Al <sub>3</sub> C <sub>6</sub> H <sub>3</sub> P <sub>6</sub> O <sub>24</sub> ·7H <sub>2</sub> O

Thereafter, the completely deprotonated form of phytic acid will be noted φ.

**Note:** XRD analysis showed the amorphous nature of all synthesized compounds.

## 3.2. Solubility determination

### 3.2.1. Solubility

Solubility measurements were repeated five times. The results with their standard deviation are gathered in Table 6. Zinc phytate has the highest solubility ( $2 \times 10^{-5} \text{ mol.L}^{-1}$ ). The solubility of the other metal phytates are lower, with values ranged between  $2 \times 10^{-6} \text{ mol.L}^{-1}$  and  $3 \times 10^{-6} \text{ mol.L}^{-1}$ .

**Table 6**

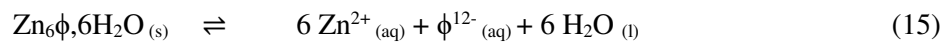
Experimental determination of the solubility for each metal phytate at equilibrium pH

	pH	Solubility ( $\text{mol.L}^{-1}$ )	Solubility ( $\text{g.L}^{-1}$ )
$\text{Pb}_6\phi, 10\text{H}_2\text{O}$	$4.25 \pm 0.04$	$2.59 \pm 0.15 \times 10^{-6}$	$5.36 \pm 0.30 \times 10^{-3}$
$\text{Zn}_6\phi, 6\text{H}_2\text{O}$	$6.80 \pm 0.03$	$2.14 \pm 0.04 \times 10^{-5}$	$2.42 \pm 0.04 \times 10^{-2}$
$\text{Cu}_6\phi, 8\text{H}_2\text{O}$	$6.53 \pm 0.02$	$2.31 \pm 0.03 \times 10^{-6}$	$2.71 \pm 0.04 \times 10^{-3}$
$\text{Fe}_{3.5}\text{H}_{1.5}\phi, 15\text{H}_2\text{O}$	$3.92 \pm 0.02$	$2.46 \pm 0.12 \times 10^{-6}$	$2.74 \pm 0.14 \times 10^{-3}$
$\text{Al}_3\text{H}_3\phi, 7\text{H}_2\text{O}$	$3.52 \pm 0.01$	$2.97 \pm 0.25 \times 10^{-6}$	$2.55 \pm 0.21 \times 10^{-3}$

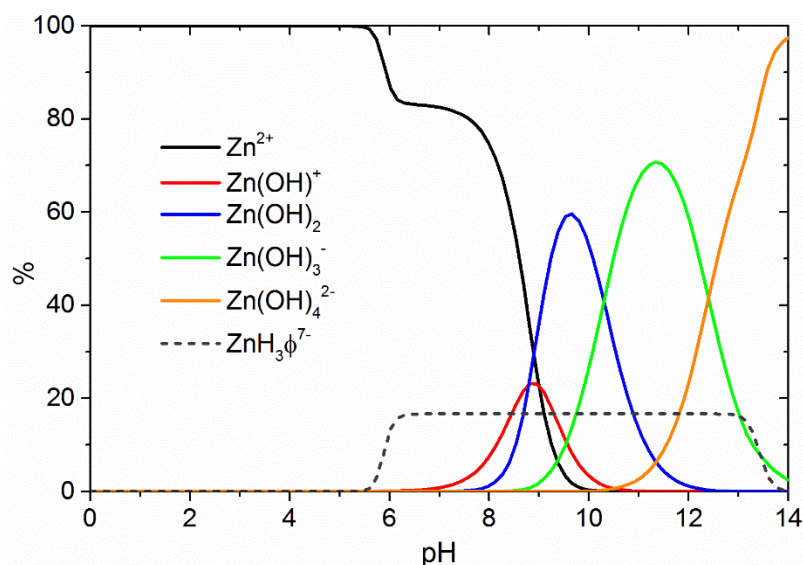
### 3.2.2. $K_s$ calculation

- *Example of zinc phytate*

In order to explain the method used for  $K_s$  determination, the zinc phytate case was chosen. The solubility equilibrium of zinc phytate in water is (Eq. (15)):

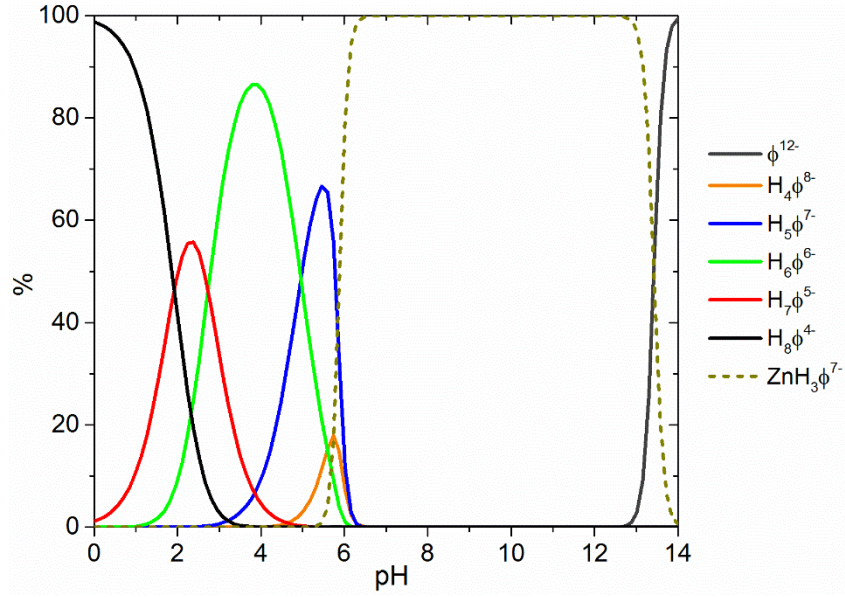


In this case, six metallic cations are solubilized for one single molecule of phytate. According to the formula of  $\text{Zn}^{2+}$ /phytates complexes (Table 3), one zinc cation could be engaged with one molecule of phytate. The remaining  $\text{Zn}^{2+}$  cations are under their acido-basic forms. In order to calculate  $\alpha_{\text{Zn}}$  and  $\alpha_{\phi}$  at the equilibrium pH, it is necessary to establish the species distribution diagrams, presented in Fig. 3. and in Fig. 4. These diagrams were drawn with the help of Hyperquad Simulation and Simulation (Hyss) software [27].



**Fig. 3.** Species distribution diagram of zinc vs pH





**Fig. 4.** Species distribution diagram of  $Zn^{2+}$ /phytates vs pH

At pH = 6.8, equilibrium pH measured during solubility experiments for zinc phytate, divalent zinc is distributed as follows: 16.7% under  $ZnH_3\phi^{7-}$  complex form, 82.7 % under  $Zn^{2+}$  form and 0.6 % under  $Zn(OH)^+$  form. During solubility experiments, ionic strength was not fixed. Therefore, its value has to be calculated with concentrations determined by ICP according to: (Eq. (16))

$$\begin{aligned}
 I &= \frac{1}{2} (2^2 \times [Zn^{2+}] + 1^2 [Zn(OH)^+] + 7^2 \times [Zn(H_3\phi)]^{7-} + 7^2 \times [Zn(H_3\phi)]^{7-}) \\
 &= \frac{1}{2} ((2^2 \times \frac{82,7}{100} + 1^2 \times \frac{0,6}{100} + 7^2 \times \frac{16,7}{100}) \times [Zn^{II}] + 7^2 \times [\phi]) = 1.26 \times 10^{-3} \text{ mol.L}^{-1}
 \end{aligned} \tag{16}$$

Where  $[Zn^{II}]$  corresponds to the free zinc concentration (not complexed with phytates). Thanks to I value, activity coefficients  $\gamma_{Zn}$  and  $\gamma_{\phi}$  were calculated using equation the Eq. (4) and therefore to access to the conditional solubility product of  $Zn_6\phi_6 \cdot 6H_2O$  (Eq. (17)).

$$K_s^{\text{cond}} = (\gamma_{Zn})^6 * (\gamma_{\phi}) * [Zn^{II}]^6 \times [\phi] = 7.57 \times 10^{-31} \tag{17}$$

In zinc precipitate, phytate is under the fully deprotonated form. The reaction coefficient  $\alpha_{\phi}$  of this specie was calculated as follow (Eq. (18)):

$$\alpha_{\phi} = \frac{[\phi]}{[C_6H_6P_6O_{24}^{12-}]} = 1 + \frac{0.10}{6.37 * 10^{-15}} = 1.57 \times 10^{13} \tag{18}$$

For zinc, the reaction coefficient  $\alpha_{Zn}$  was calculated from Eq. (19).

$$\alpha_{Zn} = \frac{[Zn^{II}]}{[Zn^{2+}]} = 1 + \frac{0.006}{0.50} + \frac{0.10}{0.50} = 1.21 \tag{19}$$

The solubility product was finally calculated according to (Eq. (20)):

$$K_s = \frac{K_s^{\text{cond}}}{\alpha_{Zn}^6 * \alpha_{\phi}} = \frac{7.57 * 10^{-31}}{1,21^6 * 1,57 * 10^{13}} = 1.54 \times 10^{-44} \tag{20}$$

- *Other metal phytates*

The same calculation method was used for the determination of the solubility product of each metal phytate. The species distribution diagrams of each metal and for all  $M^{z+}$ /phytates systems were established using Hyss. Species distribution of phytic acid and metals at the experimental equilibrium pH are given in Table 7.

**Table 7**

Species distribution of phytic acid and metals at the experimental equilibrium pH

pH	Phytic acid distribution (%)					Metals distribution (%)				
	$H_8\phi^{4-}$	$H_7\phi^{5-}$	$H_6\phi^{6-}$	$H_5\phi^{7-}$	$[M(H_3\phi)]_{12-z-3-}$	$M^{z+}$	$M(OH)_{(z-1)+}$	$M(OH)_2_{(z-2)+}$	$[M(H_3\phi)]_{12-z-3-}$	
Pb <sup>II</sup>	4.3	0	2.4	80.9	16.5	0	100	0	0	0
Zn <sup>II</sup>	6.8	0	0	0	0	100	82.7	0.6	0	16.7
Cu <sup>II</sup>	6.5	0	0	0	0	100	74.3	9	0	16.7
Fe <sup>III</sup>	3.9	1.8	37.8	59.9	0.5	0	0.1	3	97	0
Al <sup>III</sup>	3.5	7.0	56.9	35.9	0.1	0	96.7	3.2	0.1	0

From data of Table 7, ionic strength, activities coefficients and  $K_s^{\text{cond}}$  values were calculated.  $K_s$  were then determined after calculation of metals and phytates reaction coefficients  $\alpha_M$  and  $\alpha_\phi$ . Table 8 presents the results obtained at each step of the calculation.

**Table 8**

Solubility product determination for each metal phytate from experimental solubility by considering the ionic strength

	I (mol.L <sup>-1</sup> )	$\gamma_M$	$\gamma_\phi$	$K_s^{\text{cond}}$	$\alpha_M$	$\alpha_\phi$	$K_s$	pK <sub>s</sub>
Pb <sub>6</sub> φ,10H <sub>2</sub> O	8.02x10 <sup>-5</sup>	0.960	0.676	1.93x10 <sup>-35</sup>	1.00	8.20x10 <sup>21</sup>	2.36x10 <sup>-57</sup>	56.6
Zn <sub>6</sub> φ,6H <sub>2</sub> O	1.26x10 <sup>-3</sup>	0.625	0.135	7.53x10 <sup>-31</sup>	1.21	1.57x10 <sup>13</sup>	1.54x10 <sup>-44</sup>	43.8
Cu <sub>6</sub> φ,8H <sub>2</sub> O	1.34x10 <sup>-4</sup>	0.860	0.520	3.36x10 <sup>-36</sup>	1.34	1.4x10 <sup>13</sup>	4.11x10 <sup>-50</sup>	49.4
Fe <sub>3.5</sub> H <sub>1.5</sub> φ,15H <sub>2</sub> O	8.30x10 <sup>-5</sup>	0.991	0.751	3.33x10 <sup>-24</sup>	2.54x10 <sup>3</sup>	8.40x10 <sup>12</sup>	4.80x10 <sup>-49</sup>	48.3
Al <sub>3</sub> H <sub>3</sub> φ,7H <sub>2</sub> O	7.38x10 <sup>-5</sup>	0.912	0.745	1.18x10 <sup>-21</sup>	1.546	4.18x10 <sup>14</sup>	7.64x10 <sup>-37</sup>	36.1

### 3.2.3. Conditional solubility as a function of the pH

Thanks to the  $K_s$  values determined and with the help of equation (13), it is possible to draw the solubility curve of each metal phytate taking into account the possible formation of metal hydroxides, Pb(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>, Cu(OH)<sub>2</sub>, Al(OH)<sub>3</sub> and goethite FeOOH. For this, Hyss software was used to calculate  $\alpha$  values. These  $\alpha$  values were then introduced in Origin 9.0[28] software to plot solubility curves. All curves are gathered in Figure 5 to obtain a solubility domain, which is the superposition of metal phytates and metal hydroxides. The predominating solubility domain for each solid is delimited on the diagram by a vertical dot line. To the left of this line, metal phytate is the predominant solid phase, whereas at higher pH, the predominant solid phase is metal hydroxide.

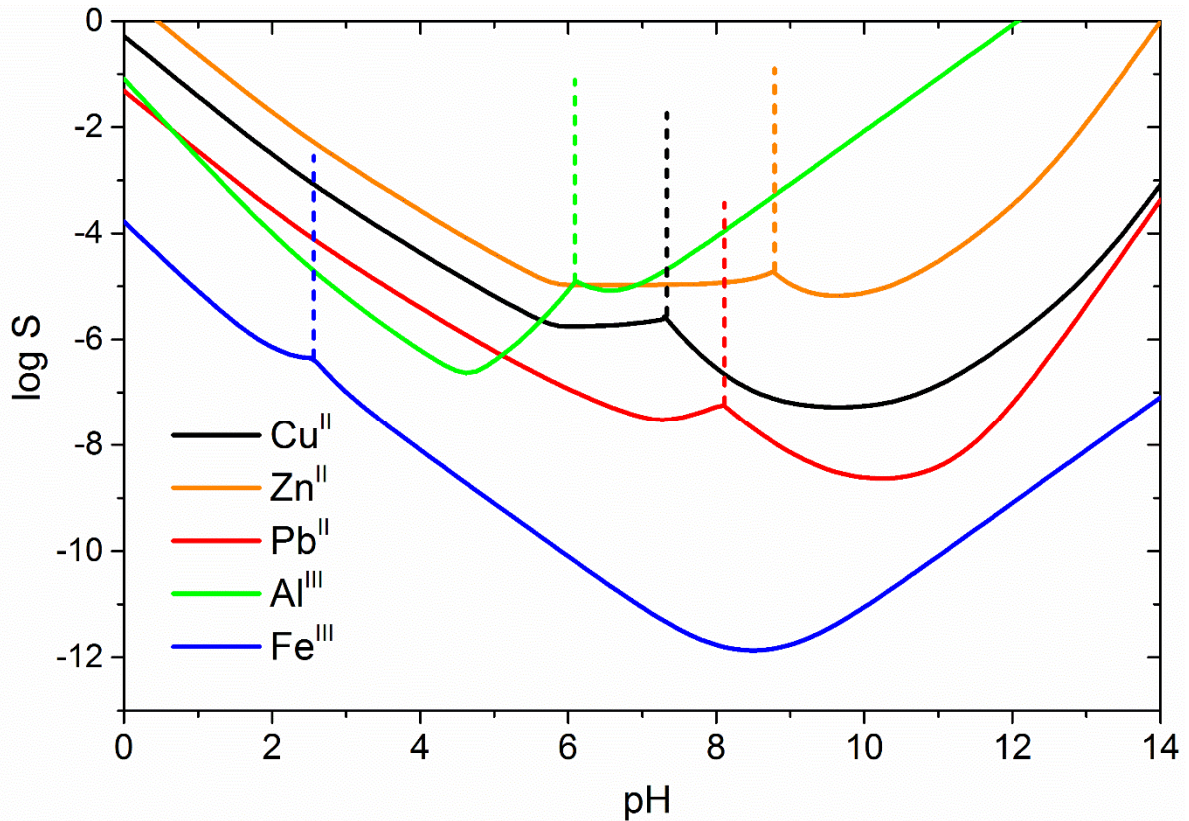


Fig. 5. Solubility of metal phytates as a function of pH.

Whatever the cation, metal phytates have a lower solubility than the corresponding hydroxides. These compounds are preferentially precipitated at low pH.

From a theoretical point of view, Figure 5 can be a tool to predict the feasibility of a separation. If we consider a binary mixture  $M_1$ - $M_2$  where  $M_1$  is an undesirable cation ( $Al^{3+}$ ,  $Fe^{3+}$  and  $Pb^{2+}$ ) and  $M_2$  a valuable metal ( $Cu^{2+}$ ,  $Zn^{2+}$ ), to find the best conditions for selective removal, we have to search from both solubility curves the greatest difference between  $\log[M_2]$  and  $\log[M_1]$ .  $\log S_{M_2} - \log S_{M_1}$  is calculated for pH values ranging between the minimal value required to reach the lowest solubility of  $M_1$  phytate and the maximal value which is the boundary between phytate and hydroxide of the same metal. Results are given in Table 9.

Table 9

Theoretical feasibility of selective precipitation for cation mixture  $M_1 - M_2$  determined from solubility curves of Fig. 5.

$M_1 - M_2$ mixtures	Maximal values of $\log S_{M_2} - \log S_{M_1}$	pH range
$Al^{3+} + Cu^{2+}$	1.84	$4 < \text{pH} < 6$
$Fe^{3+} + Cu^{2+}$	3.71	$1.4 < \text{pH} < 2.5$
$Pb^{2+} + Cu^{2+}$	1.91	$< 7.3$
$Al^{3+} + Zn^{2+}$	2.64	$4 < \text{pH} < 6$
$Fe^{3+} + Zn^{2+}$	4.50	$1.4 < \text{pH} < 2.5$
$Pb^{2+} + Zn^{2+}$	2.56	$7.3 < \text{pH} < 8.1$
$Zn^{2+} + Cu^{2+}$	0.80	$0 < \text{pH} < 7.3$

From a theoretical point of view, these mixtures can be classified in three groups:

- If  $\log S_{M_2} - \log S_{M_1} > 2$ , more than 99% of the cation  $M_1$  can be precipitated without embedding more than one percent of the cation  $M_2$ . This condition is verified for  $Fe^{3+}/Cu^{2+}$ ,  $Pb^{2+}/Cu^{2+}$ ,  $Al^{3+}/Zn^{2+}$ ,  $Fe^{3+}/Zn^{2+}$  and  $Pb^{2+}/Zn^{2+}$  mixtures. Phytic acid appears as an interesting reagent for the removal of iron as example from hot acidic leachate in zinc hydrometallurgy [29].

- If  $1 < \log S_{M2} - \log S_{M1} < 2$ , the separation seems to be feasible and can be experimentally studied. This is the case of  $Al^{3+}/Cu^{2+}$  and  $Pb^{2+}/Cu^{2+}$  mixtures.
- If  $\log S_{M2} - \log S_{M1} < 1$ , the selective precipitation will be difficult or impossible. More than 10 % of the second cation will precipitate. According to a value of 0.90, it seems to be impossible to use phytic acid for the selective precipitation of zinc in spent chloride brass pickle liquors.

## 4. Conclusion

The aim of this study was to evaluate the feasibility of using phytic acid to remove undesirable metals in the leachates from hydrometallurgical processes. This compound is an abundant agri-resource easily extractable from cereals by a simple soaking in hot water. Five metal cations were investigated: aluminium, copper, iron, lead and zinc. With the help of elemental analysis and TGA-MS, formulae of metal phytates were determined and are the following:  $Al_3C_6H_9P_6O_{24} \cdot 7H_2O$ ,  $Cu_6C_6P_6O_{24} \cdot 8H_2O$ ,  $Fe_{3.5}C_6H_{7.5}P_6O_{24} \cdot 15H_2O$ ,  $Pb_6C_6P_6O_{24} \cdot 10H_2O$  and  $Zn_6C_6P_6O_{24} \cdot 6H_2O$ .

Then the solubility in water at 20°C of each metal phytate was measured using analytical method. These solubilities are ranged between  $2.1 \times 10^{-5}$  and  $2.3 \cdot 10^{-6} \text{ mol.L}^{-1}$ . Finally, experimental results were used to plot solubility of metal phytates as a function of pH. Superimposing the five solubility curves gives a tool to predict the feasibility of separation from a theoretical point of view. This study shows that phytic acid appears as an interesting reagent for the removal of  $Al^{3+}$ ,  $Fe^{3+}$  and  $Pb^{2+}$  contained in the leachates from hydrometallurgical processes.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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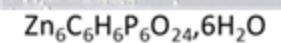
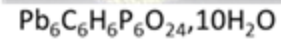
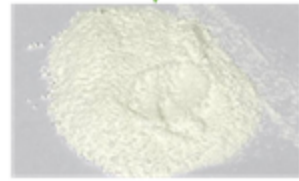
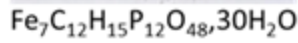
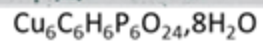
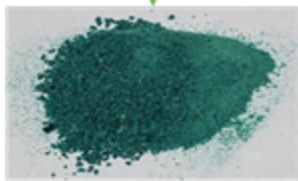
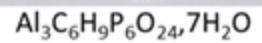
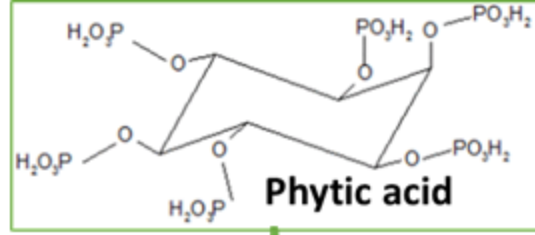
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Soaking of corn  
in water



**Conditional solubility of metal phytates**

