

Purification of industrial phosphoric acid by minimizing iron and aluminium using natural raw clay

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Abstract— In order to purify the industrial phosphoric acid (45% P₂O₅) produced in the Tunisian Chemical Group of Gabes using SIAPE process by minimizing iron and aluminum content. We have used natural raw clay which is found suitable for removing these heavy metals from crude phosphoric acid. Several parameters such as the effect of the solid-liquid ratio of the clay and the effect of the initial concentration of phosphoric acid on the removal process by adsorption were investigated.

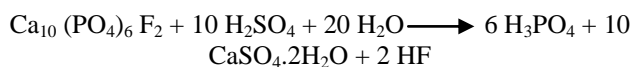
The experimental results obtained, showed that the natural raw clay supplied from Tunisian deposits “ELHICHA” has a moderately sorption capacity. The percentage of removal has reached its maximum 53 % for iron and 47 % for aluminum for an amount of clay of 16 g/l and for an initial concentration of 25% of P₂O₅.

Keywords—adsorption; clay; Heavy metals; purification; industrial area

I. INTRODUCTION

The phosphoric acid is the second mineral acid produced after the sulphuric acid. Its production in Tunisia represents approximately 1852 thousand tons (of P₂O₅) in 2003 [1]. It is used mainly as raw material for the production of fertilizers but also in the synthesis of pharmaceutical, alimentary products and formulation of the detergents, etc.

Industrially, it is produced from phosphate raw (Ca₁₀(PO₄)₆F₂) by its own process SIAPE [2]:



Indeed, approximately 10% of the impurities contained in the phosphate rock are found in the produced acid [3]. The presence of these impurities affects the quality and the quantity of the phosphoric acid [4, 5]: they influence the physico-chemical properties of the acid, cause problems during its concentration, its storage and its marketing. For this reason, about 95% of the acid produced by the wet process is directly used as fertilizers and excluded from the use in non fertilizer applications [6].

Among these impurities, iron aluminum and magnesium are the most dangerous metals presents in the industrial Tunisian phosphoric acid (45% P₂O₅) (table 1).

The majority of these heavy metals present such number of common properties, which make them dangerous for the three following principal reasons:

- Heavy metals are non-biodegradable in rapport of time.
- They are toxic with very weak concentrations.
- They tend to accumulate in the alive systems.

Iron for example is present in the majority of commercial phosphates at variable contents going from 0,1-0,4% in FeO₃ (Moroccan phosphate [7]) up to 3-4% (Egyptian phosphate [7-8]). While iron content, negatively affects the solubility of fertilizer P₂O₅ in water [9]. Many researches show also that aluminum (III) is implicated in a number of toxic process or Alzheimer's disease [10-12]; therefore high aluminum contents should be avoided.

The elimination of the metal impurities from the phosphoric acid produced worried the scientists especially since the last decade. Among the techniques used, we find the extraction by solvents, the flotation of ions, the liquid-liquid extraction, the process of exchange of ions, filtration on membrane, ultra filtration, nano filtration, opposite osmosis and the electrochemical techniques such as electrodialysis, chemical and electrochemical precipitation or the electrodeposition then adsorption [13-16].

These methods present some disadvantages at the industrial scale, among them:

- the use of expensive and sophisticated equipment
- difficult operation on industrial site and lack of applicability of certain processes to all the categories of phosphoric acid
- difficulty of separation of the phases

- opposite osmosis is a technique which requires a high consumption of energy due to the high necessary pressure (20 to 100 bar) [17, 18]
- nano and ultra filtration are expensive and cause problems of clogging of the membrane [19, 20]
- the processes of exchange of ions are not adapted to eliminate metal on an industrial scale from production [21]
- Flotation requires a series of optimization in order to improve the effectiveness of displacement of heavy metal [22, 23].

Several studies carried out have shown that the raw clay has a very important role as a powerful adsorbent for removing heavy metals contained in phosphoric acid, due to their high availability and relatively lower costs compared to industrial adsorbents. So we will be interested in this study by developing a simple method which consists on the removal of heavy metals presents in phosphoric acid using adsorption onto natural raw clay.

A study was conducted by MELLAH and al [6] on the adsorption of heavy metals from phosphoric acid by an Algerian activated bentonite. Some tests of zinc (II), cadmium (II) and chromium (III) adsorption contained in 5.5 M phosphoric acid pretreated (30% P_2O_5) were performed. The results showed a removal of 88% for zinc (II) and 89% for Cd (II) and chromium (III) of the initial concentrations.

In the same context, another study by Omri and al. [24] was interested by the purification of the industrial Tunisian phosphoric acid, using various types of clays in their natural state or modified for the adsorption of cadmium, fluorine, carbon and organic chlorides. The experimental results show good fixation of these impurities on these adsorbents. For cadmium is of about 50%, fluorine and chloride about 98%, and finally for organic carbon can close to 85%.

According to data in a study developed by El-Bayaa and al. [25] for the elimination of iron (III) ions and uranium (VI) ions from 5 M phosphoric acid (52% P_2O_5) through silica sand. The maximum removal of iron (III) ion was 84% with a dose of 60 g of adsorbent/l and for uranium (VI) ions was 75% with a dose of 200 g of adsorbent/l.

El-Sofany and al. [26] studied the cadmium, copper, zinc and lead removals from phosphoric acid by the use of impregnated charcoal. The removal rate was 43.7% for the (Cd), 36.74% for the (Zn), 27.45% for the (Cu) and 9.12% for (Pb).

The aim of this study is to maximize the removal capacity of aluminum and iron ions presents in industrial phosphoric acid obtained from TCG of Gabes-Tunisia by adsorption onto natural raw clay as an adsorbent.

II. EXPERIMENTAL

A. Phosphoric acid

All experimental runs were done using an industrial phosphoric acid (45% P_2O_5) with a density of 1.5 obtained from the Tunisian Chemical Group of Gabes, Tunisia.

The composition of this acid and its content of heavy metals are mentioned in table 1.

TABLE 1: CHEMICALS ANALYSIS OF INDUSTRIAL PHOSPHORIC ACID (P_2O_5 45%)

Metal	Composition (ppm)
P_2O_5	44.82 %
Al	3741
Fe	2425
Mg	5564
Cd	28
Cr	246
Mn	28
V	59
Zn	233

The crude acid was initially purified from organic matter in its manufacture. We can clearly note as shown in table 1 that the most dangerous metals with high contents are respectively the aluminum, iron and the magnesium. For this reason, we are interested in this study to minimize the amount of aluminum and iron in presence of others heavy metals.

B. Natural raw clay

The natural raw clay was supplied from the south Tunisian deposits (Hicha, El Hamma). It is a calcium, grey smectite and in a powder form. Its specific surface is around 86 m^2/g .

The composition of this clay is highly variable, depending on the local rock sources and conditions. Natural row clay was subjected to Chemical analysis before starting the experiments. Chemical analysis showed that the presence of large amount of silica as shown in Table 2.

TABLE 2: PHYSICO-CHEMICAL CHARACTERISTICS OF THE NATURAL RAW CLAY (%)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	MgO	Na ₂ O	TiO ₂
2.63	47.01	19.47	11.78	0.52	1.07	2.1	0.93	0.03

C. Apparatus

The concentration of the elemental composition of the industrial phosphoric acid was analyzed by atomic-absorption spectrophotometer using an inductively coupled mass spectrometry (ICP-MS) in the Tunisian Chemical Group laboratory's of Gabes.

D. Adsorption studies

Batch mode adsorption studies for aluminum and iron removal in presence of others metals were carried out to investigate the effect of adsorbent dose and volume to weight ratio at 25°C. The crude acid solutions were introduced with its appropriate amounts of clay ranging from 0.1 to 0.8 g per 50 ml of industrial acid. Tests were shaken at a speed of 450

rpm and maintained at a temperature of 25 °C for two hours. When equilibrium is reached, samples will be centrifuged, filtered and analyzed.

E. Data analysis

The percentage of removal R (%) was calculated as:

$$R (\%) = \frac{(C_o - C_e) * 100}{C_o}$$

Where C_o is the initial of metal concentration in acid solution (ppm), C_e is the equilibrium metal concentration in acid solution (ppm).

TABLE 3: CHEMICAL ANALYSIS OF INDUSTRIAL PHOSPHORIC ACID (45% P_2O_5) BEFORE AND AFTER ADSORPTION WITH (16 G/L) OF NATURAL RAW CLAY

Constituent	Content before adsorption (ppm)	Content after adsorption (ppm)	Removal (%)
Al	3741	3392	9,33
Fe	2425	2272	6,31
Mg	5564	5094	8,48
Cd	28	27	3,57
Cr	246	219	10,96
Mn	28	24	14,29
V	59	49	16,95
Zn	233	205	12,02

III. RESULTS AND DISCUSSION

A preliminary test of adsorption was carried out for the industrial phosphoric acid (45% P_2O_5) with density of 1.5, which contains 3741 ppm of aluminum and 2425 ppm of iron in presence of others metal. Three doses of natural raw clay are used respectively 2, 8 and 16 g/l to evaluate the capacity of purification in a concentrate acidic media.

Fig.1 show that the maximum of removal obtained for the two metals in concentrate phosphoric acid solutions is less than 10 % whatever the dose of the clay used.

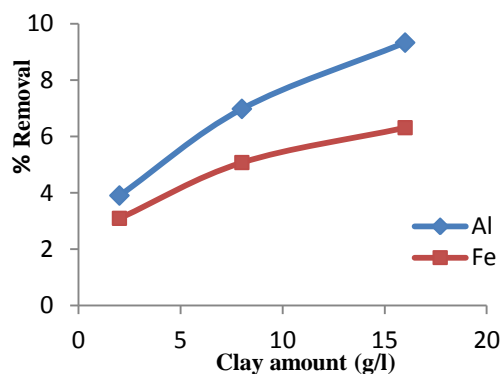


Fig1. Capacity of removal of metals in concentrate industrial phosphoric acid

An optimization of the parameters of the process is obligatory to have an effective interpretation.

A. Effect of the initial concentration of the phosphoric acid

Four samples were put at fixed temperature 25 °C, stirring velocity of 450 rpm, a time of 2 hours of agitation and a dose of natural raw clay of 16 g/l. Four initial density of industrial phosphoric acid were respectively studied 1.5, 1.4, 1.3 and 1.2 which refer to the following concentration of P_2O_5 44.82 %, 39.5 %, 31.59 % and 24.42 % obtained by dilution of the concentrate one by bi-distillate water.

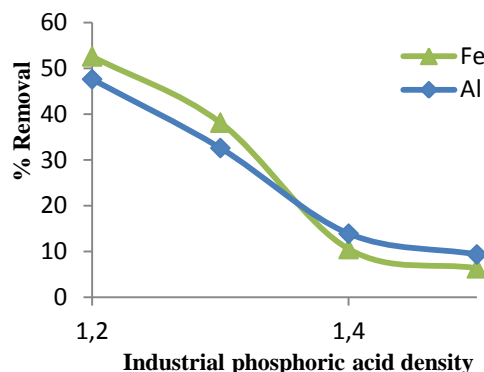


Fig.2. Effect of the initial concentration of the acid for iron and aluminum removal for a dose of natural clay of 16 g/l.

Fig.2 shows well that the concentrated industrial acid media disadvantages the adsorption of aluminum and iron. It is noticed that with initial concentration of acid 5 M (approximately 25% in P_2O_5) we have obtained the maximum percentage of removal of metals approximately 50%.

For both metals, the effect of the initial concentration in acid influences much its elimination. For the iron, its removal percentage passes from 53 to 10% by increasing the initial density of acid from 1.2 to 1.5.

B. Effect of the solid-liquid ratio of the raw clay on the process

By fixing the temperature at 25 °C, the stirring velocity to approximately 450 rpm and a time of 2 hours of agitation: we have varied the amount of the clay respectively from 2 to 16 g/l to evaluate the effect of the clay on the adsorption of the metals for different initial concentration of phosphoric acid.

The analyses by ICP showed that the capacity of elimination of iron reached its maximum 53% and also 47 % of aluminum for an amount of clay of 16 g/l and for an initial concentration of 25% of P_2O_5 . The removal percentage increases on increasing the dose of clay.

The two figures 3 and 4 show also that the percentage of removal increases on decreasing the initial concentration of acid although using a less amount of clay 2 g/l, it passes from 3% to 41% for aluminum and from 3 to 34% for iron.

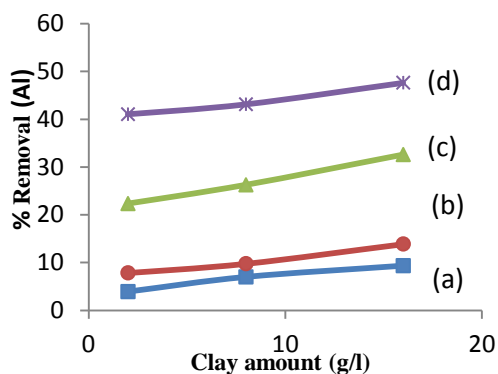


Fig.3: Effect of the amount of the clay on the elimination of aluminum for different initial concentration of industrial phosphoric acid: (a) d=1.5, (b) d=1.4, (c) d=1.3, (d) d=1.2

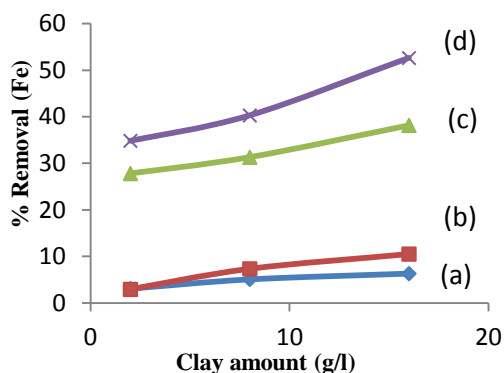


Fig.4: Effect of the amount of the clay on the elimination of iron for different initial concentration of industrial phosphoric acid: (a) d=1.5, (b) d=1.4, (c) d=1.3, (d) d=1.2

IV. CONCLUSION

This work concerned the purification of industrial phosphoric acid containing high percentages of aluminum and iron using adsorption onto natural raw clay. The method has exploiting moderating degree of purification for very concentrate solutions (45% P_2O_5).

We obtained more than 50% for iron removal and more than 45% for aluminum one for an amount of clay of 16 g/l and for an initial concentration of 25% of P_2O_5 .

These results encourage us to extend the protocol to remove others ions present in the concentrate acid, such as cadmium, magnesium and or with other types of adsorbents.

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