

Successive Processes for Purification and Extraction of Phosphoric Acid Produced by Wet Process

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ABSTRACT

Different technologies were tested for purification of phosphoric acid produced by the wet process. Illiminite clay was found to be suitable for removal of humic acids and suspended materials from crude phosphoric acid. Minimizing of ferric ions from phosphoric acid was carried out using silica, while removal of fluoride was preceded by addition of carbonate salt. Isoamyl alcohol was used for extraction of P₂O₅ giving a value of 78.5%. Using McCabe-Thiele diagram, the number of stages for complete extraction of P₂O₅ was predicted to be two stages. Warm distilled water has a good efficiency for stripping of P₂O₅. Flow diagram for sequential treatment process and extraction is given.

Keywords: Crude phosphoric acid/ Purification/ Isoamyl alcohol/ Extraction/ Stripping.

INTRODUCTION

The process is called wet because concentrated sulfuric acid is used to digest the rock phosphate ores. By 1980, hemihydrate and improved dihydrate processes were developed and 30 - 50 % P₂O₅ wet process phosphoric acid plant, up to 1300 Mt/day, came up. The other dry process or electric furnace process of phosphoric acid manufacture is an efficient process which originally came up in 1935 but its use has declined except for the purpose of manufacture of elemental phosphorous or the acid as an intermediate for making phosphorous element. There are various phosphate ores types *e.g.*, fluoroapatite, Ca₁₀F₂(PO₄)₆, chlorapatite 3Ca₃(PO₄)₂CaCl₂ and phosphorite.^(1,2) Phosphoric acid is manufactured by the reaction of the ore (apatite), Ca₅(PO₄)₃(OH), with concentrated sulfuric acid in the temperature range of 70 - 80°C according to the following simplified reaction⁽³⁾:



The ore is invariably contaminated with fluoroapatite with the total fluoride content of the feedstock in the range of 3.5% - 4%. The strangely acidic reaction conditions favor the formation of HF, which dissolves silica and silica-like impurity minerals in the ore. Products of this reaction are various fluorosilicates, including the volatile silicon tetrafluoride (SiF₄), as well as hexafluorosilicic

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acid (H_2SiF_6) and/or its salts. Phosphoric acid reactor vessels are thus typically scrubbed to remove the volatile HF and SiF_4 . The other product of this reaction, calcium sulfate (gypsum) is typically pumped as slurry to tailing pond and process water is also stored for recycle in storage ponds. These ponds are typically fairly acidic ($\text{pH} < 2$) with very high dissolved content and with fluoride levels in the range of 0.35% - 1.35%.⁽⁴⁾, probably, fluoride ions are mostly in the form of HF and SiF_6^{2-} , however, the latter species may partially hydrolyze to SiF_4 from the ponds, which are of environmental concern.⁽⁵⁾

The wet process phosphoric acid has to be purified. Several physicochemical treatment techniques based on precipitation,^(6,7) adsorption,⁽⁸⁾ ion exchange,^(9,10) reverse osmosis,⁽¹¹⁾ and solvent extraction⁽¹²⁻¹⁵⁾ are available. None of these techniques is solely capable of carrying such task. The best practical results with respect to lowering the contents of impurities of the industrial phosphoric acid were obtained when combining chemical and solvent extraction methods.^(6,16)

Therefore, the objective of this work is to study the extraction of P_2O_5 from green phosphoric acid after removal of organic matter and removal of fluoride ions and heavy metals using isoamyl alcohol as extractant and further prediction of the number of stages required for complete extraction of the phosphoric acid in a pure form.

EXPERIMENTAL

2.1. Materials and measurements

Commercial wet process phosphoric acid (containing $\text{P}_2\text{O}_5 = 57.0\%$, $\text{Fe} = 2.6\%$, $\text{F} = 0.7\%$ and $\text{U(VI)} = 50$ ppm) was used. Illiminite was used as clay. All other chemicals and reagents were of A.R. grade and used without purification. The organic matter, iron and uranium content were determined using a Shimadzu UV-Visible 160A spectrophotometer.

2.2. Determination of P_2O_5 and fluorine

P_2O_5 was determined spectrophotometrically by a solution containing the yellow molybdo-vanadate phosphoric acid complex. The wavelength of 420 nm was chosen to provide adequate sensitivity and to minimize the effect of iron. On the other hand, the determination of fluorine in phosphoric acid was carried out using the Alizarine method after distillation.^(17,18) The concentration of fluorine was measured at wavelength equal to 625 nm. This spectrophotometric method has advantage over using ion selective electrode in the complete determination of fluoride (soluble and insoluble) while ion selective electrode is used for measuring the soluble fluoride ions only.

2.3. Extraction of silica from rice husk:

Raw rice husk (RH) was stirred with a solution of concentration 5% KOH at a weight ratio 1:12 (g/ml) of RH to solution, respectively and heated to boiling for 30 min. The mixture was then left overnight, filtered and washed twice with distilled water until the filtrate becomes neutral. To this filtrate, 10% HCl was added, until the pH of the solution reached 5 - 7 to precipitate the dissolved silica. The precipitate formed was filtered, dried and weighed.⁽¹⁹⁾

2.4. Procedure

All experimental runs were done after treating the crude H_3PO_4 (black acid) to eliminate the organic matters and convert the acid to green color. Hydrogen peroxide was used as oxidizing agent to ensure that all Fe(II) and U(IV) ions are oxidized to Fe(III) and U(VI).⁽²⁰⁾ Ozone and oxygen were

used before but it was found that, oxygen gas is inefficient while ozone gas reacts with uranium during the process. These disadvantages led us to use hydrogen peroxide as an oxidant. Other advantages of hydrogen peroxide are that it forms no precipitate with other reactants in the evaporated phosphoric acid strip solution as does the sodium compound oxidizers and with its use no noxious gas like chlorine is given off.

The clays of iliminite were used to remove humic acids and suspended materials from crude phosphoric acid. To 150 ml crude phosphoric acid, 2.0 g of iliminite clay were added, stirred for 50 min and the solution was left to allow all the suspended materials and humic acids to settle down. Purification of H_3PO_4 by minimizing its iron and fluoride ions content was conducted upon its primary treatment using iliminite clay. This study proceeds by adding the silica as adsorbing agent, in addition to the effect of temperature. 6.0 g of silica were added to primarily treated 150 ml crude H_3PO_4 , stirred for 30 min with addition of 1.25 g potassium carbonate. A flocculating agent (1.5 ml) was added and the mixture was left for 10 min for complete settling.

Extraction procedures were carried out by shaking 5 ml of the organic solvent with 5 ml of the crude acid in a separating funnel for 15 min at 25°C. The condition of the experiment was adjusted and the funnels were shaken using a thermostatic shaking water bath to achieve the equilibrium concentration. Each mixture was separated and the samples were analyzed spectrophotometrically for U and remaining concentration of iron. The difference between the initial concentration C_o and the equilibrium concentration C_e was calculated and used to determine the extraction percent E% as follows:

$$E \% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where, C_o the initial concentration of the solute in mg/L and C_e is the residual concentration of the solute in mg/L.

RESULTS AND DISCUSSION

3.1. Preliminary treatment

3.1.1. Removal of organic matter

Block and Valint⁽²¹⁾ indicated that there are many carboxylic acids in phosphoric acid produced by wet processes. These include citric acid, malic acid, lactic acid, succinic acid and fumaric acid. To study the effect of clays on purification of crude H_3PO_4 , a series of experiments was carried out on iliminite while the concentration of clay was 0.05–10.0 g/150 ml of crud phosphoric acid. The obtained solutions were measured at 420 nm which is considered as an indication for the presence of organic content. The obtained results, Table (1), clearly show that, iliminite gave good results for reduction of the organic matter content with activity of 85% at 2 g/150 ml of acid. In addition, the iron content was also affected by the addition of clay. Noticeable minimizing of iron concentration to 5800 ppm was observed, due to the clay addition from 25000 ppm (initial concentration). Also, it is shown that the % P_2O_5 is slightly affected and decreased up to 2.0%. In all cases, equilibrium uptake is reached, after about 15 minutes and 2 g is enough for removal of organic matter from 150 ml. This behavior can be interpreted as due to coating of the clay surface by the organic molecules present in the phosphoric acid and thereby rendering the hydrophobic part of the clay. It would be interesting to refer to Cotton and Wilkinson⁽²²⁾ who indicated that phosphoric acid and its crystalline hydrate form have tetrahedral phosphate groups connected by hydrogen bonds. The presence of water in more than 50% acid concentration would render the cationic forms of clay which are capable of adsorbing a

range of polar and non-polar molecules.^(23,24)

3.1.2. Minimizing iron using Silica

In order to achieve a procedure giving high removal of iron and fluoride, silica extracted from rice husk was tested. A series of experiments was carried out on green phosphoric acid treated with iliminite clay as a preceding step under the following conditions: 5 g silica/150 ml acid, stirring time: 60 min, and temperature, 25°C. It is worthy to mention that the addition of silica gave 80% minimizing efficiency for iron, P₂O₅ loss is 1%. Also, it was found that fluoride reacted with silica to form SiF₄.

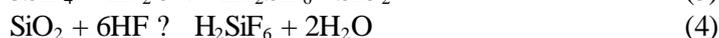
Table (1): Removal of organic matter and iron content by iliminite clay

Iliminite (g/150 ml)	Removal efficiency of Organic matter (%)	Loss of P ₂ O ₅ (%)
0.05	25	0.1
0.1	37	0.7
0.5	45	1.2
1.5	67	2.0
2.0	85	2.0
3.0	86	2.4
5.0	90	2.5
10.0	92	2.6

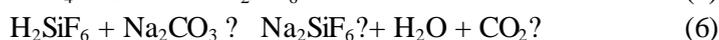
3.1.3. Minimizing fluoride by adding sodium carbonate

The free fluorine in the phosphoric acid, or that which is not tied up with metallic impurities, is present as either HF or SiF₄.⁽²⁵⁾ The silicon tetrafluoride tends to have a higher vapor pressure and is, therefore, relatively easy to volatilize from the acid. The addition of reactive source of silicon is necessary to defluorinate the acid to an acceptable level.⁽²⁶⁾ The additives used for minimizing iron are also taken for reduction of fluoride content which is presented by 0.8% in acid. Sodium carbonate was added to form suspended potassium fluosilicate while a flocculent was added to enhance precipitation and the fluoride ion was analyzed in phosphoric acid. By this step, wet process phosphoric acid was defluorinated to reach 0.15%. This level is considered as acceptable limit for production of dicalcium phosphate (animal feed supplement). The factors studied include the amount of sodium carbonate (0.5, 1.0, 3.0, 5.0, 8.0 and 10.0 g), shaking time (30, 60, 120 and 240 min) and temperature (25, 35, 50, 70-°C). The process carried out on ??? ml phosphoric acid (P₂O₅ % = 57%; F = 0.7 %). It was found that 5.0 g of sodium carbonate was enough to reduce the concentration of fluoride from 0.8% to less than 0.044% at 50°C and 60 min as shaking time.

From the optimum conditions obtained, the fluoride decreased to 0.044% with removal efficiency of 95% at 50°C with loss of not more than 2% P₂O₅. This may be explained on the basis of the following reactions:



The net reaction could be represented as follows



3.2. Extraction Investigations

3.2.1. Extraction of Uranium

The phosphoric acid produced from phosphate rocks usually contains U in the range of 50–300 mg/L.⁽²⁷⁾ The average assay of uranium (U) in Egyptian phosphate ores is about 60 ppm.⁽²⁸⁾

3.2.1.1 Influence of extractant concentration

The extraction of uranium and iron was carried out with varying concentrations of HDEHP in the range 0.005-0.1 M. The percentage of extraction of both metal ions increased with increasing extractant concentration (Fig.1). It varied in the range 10-96 % for uranium and 0.5-99 % for iron. Extraction of both metal ions was linear up to 0.05 M concentration and reached a maximum when the extractant concentration reached 0.08 M or more. The plot of log distribution ratio (D) vs log [HDEHP] for both metal ions (Fig. 2) shows the slopes of 2.04 for uranium and 2.8 for iron in the extractant concentration range 0.005-0.08 M, indicating the requirement of 2 moles of extractant per mole of uranium ion and 3 moles for iron.

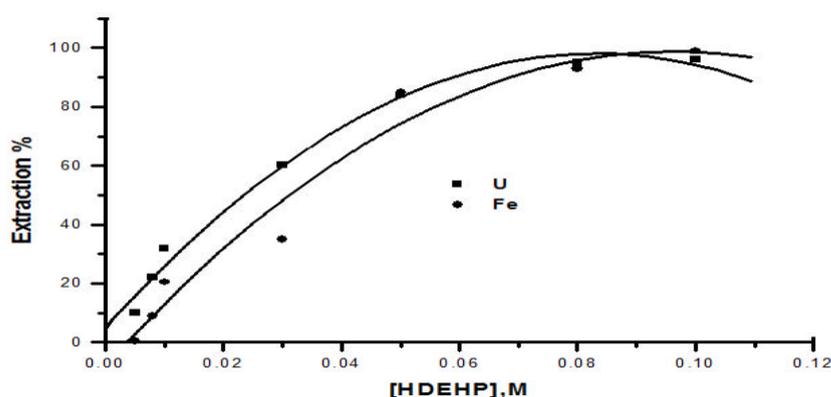


Fig.1. Extraction of uranium and iron by HDEHP from phosphoric acid medium

3.2.2. Extraction of P₂O₅ by different alcohols

After removal of organic matter, iron, fluoride and uranium, the extraction of P₂O₅ from the other impurities easily proceeds' use isoamyl alcohol. This alcohol is mainly used for extraction because of its stability, low solubility and selectivity for H₃PO₄. In addition, the extraction of the impurities such as uranium, heavy metals, iron and fluoride from wet phosphoric acid by alcohol is not significant. Different alcohols were used such as pentanol, hexanol, heptanol, octanol and isoamyl alcohol and kerosene was used as diluent. From the data obtained it was found that extraction of P₂O₅ follows the order isoamyl alcohol > pentanol > hexanol > heptanol > octanol as shown Fig.3. As the complexity of alcohols (site chain of carbon) increases, the London dispersion force increases and that leads to decrease in percent removal. Therefore, the isoamyl alcohol was used for the detailed study of extraction of phosphoric acid.

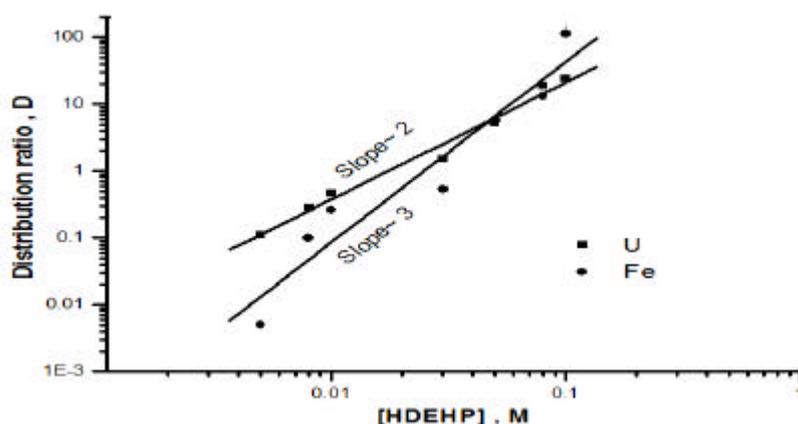


Fig. 2. Effect of HDEHP concentration on the extraction of uranium and iron from phosphoric acid medium.

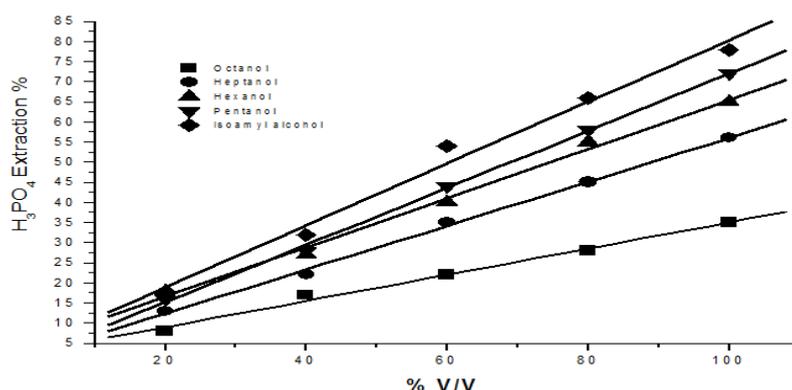


Fig. 3. Effect of different alcohols on the extraction of H_3PO_4

3.2.2.1. Effect of shaking time on extraction

The effect of shaking time on the extraction of P_2O_5 by isoamyl alcohol was investigated by using 60% isoamyl alcohol. The extraction was carried out under the same previous conditions: $P_2O_5 = 57$ wt%, O/A = 1/1 and $T = 25^\circ C$. The time of mixing was varied from 1 to 30 min. The results show that the removal of P_2O_5 increases vastly to 75% within the first 5 min and then slightly increases (78%) till 15 min. This indicates that the reaction is rapid and the diffusion which is influenced by stirring has very little influence on the extraction. Thus, the mixing time was fixed at 5 minutes for other experiments.

3.2.2.2. Effect of temperature on extraction

The effect of temperature on the extraction of P_2O_5 by isoamyl alcohol was investigated using a phase ratio O/A = 1/1 with shaking time at 5 min. The temperature covered the range from 25 to $55^\circ C$. The results plotted in Fig. 4 as a relation between the extraction percent of P_2O_5 versus temperature show that the extractions yield decreases when temperature increases, i.e. the reaction is endothermic in nature.

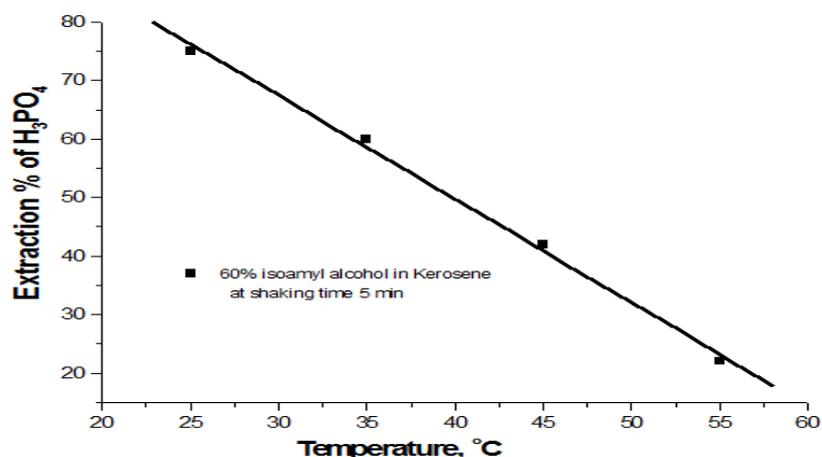


Fig. 4. Effect of Temperature on the extraction of H₃PO₄ by isoamyl alcohol

3.2.2.3. Effect of aqueous/organic (A/O) phase ratio

The effect of A/O phase ratio is shown in Table (2). The data represented in this table indicate that, the extraction efficiency decreases as the aqueous phase volume increases due to the increase in the viscosity of the aqueous phase which therefore decreases the coefficient of mass transfer.

Table (2): Effect of phase ratio A/O on the extraction efficiency of H₃PO₄ by 60% isoamyl alcohol

Phase ratio A/O	Extraction efficiency %
	Isoamyl alcohol
1:1	78
2:1	65
3:1	42
4:1	33

Shaking Time= 5min

Temp.: 25°C

3.2.2.4. Effect of sulfate ions on Extraction

Since sulfuric acid is usually used for leaching phosphate rock for production of phosphoric acid, an appreciable amount of sulfate ions is always present in the phosphoric acid after separation of phosphogypsum. This anion can form neutral or anionic species with some metal ions. Some of these species are unextractable, especially anionic species with most of organic extractants. The influence of sulfate anions was investigated by spiking different concentrations of sodium sulfate (50 to 600 ppm). The data obtained reveal that, sulfate ions have a slight influence on the extraction efficiency of P₂O₅ after removal of iron and uranium. The insignificant influence of the sulfate ions on the extraction efficiency of phosphoric acid can be explained in terms of a competition of sulfate ions with anionic species which are still present in low concentrations through the extraction by isoamyl alcohol.

3.2.2.5. Extraction isotherm of P₂O₅

The number of stages for extraction of H₃PO₄ with 60% isoamyl alcohol from phosphoric acid was calculated by McCabe-Thiele method which shows that two stages are enough to reduce the P₂O₅ content in wet phosphoric acid to less than 5%, as shown in Fig. 5.

3.2.2.6. Stripping of P₂O₅ from loaded isoamyl alcohol

The stripping of H₃PO₄ from loaded isoamyl alcohol by distilled water, 0.1 M HNO₃ and 0.1 M NaOH was studied. The stripping was carried out at different temperature (20-50°C) for P₂O₅ = 75 %. The results given in Table (3) show that the stripping of P₂O₅% increases with temperature. For economic reasons, Distilled water was used for complete study of stripping of H₃PO₄ at 40° C as shown in Fig. 6.

3.2.2.6.1. Effect of aqueous/organic (A/O) phase ratio on the stripping efficiency

The effect of A/O phase ratio is shown in Table 3. The data represented in this table indicate that, the stripping efficiency slightly decreases as the aqueous phase volume increases till A/O 3:1 and dramatically decrease to its half value at phase ratio 5:1.

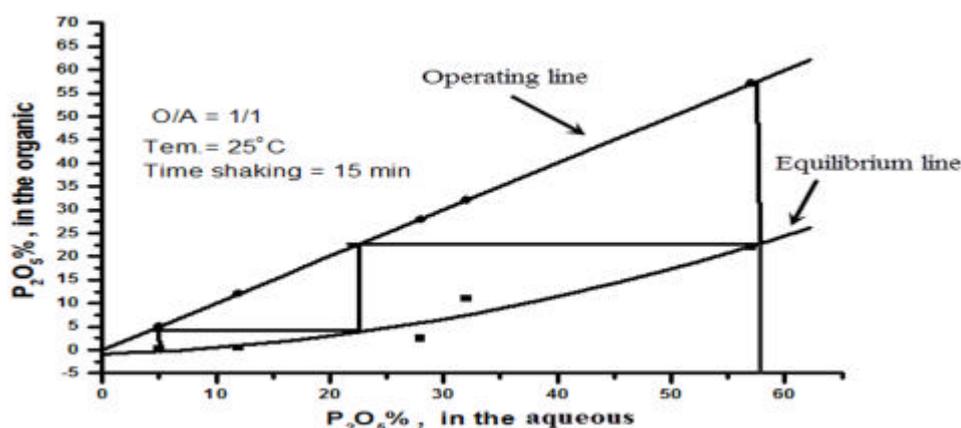


Fig. 5. McCabe -Thiele diagram for the extraction of H₃PO₄ by isoamyl alcohol

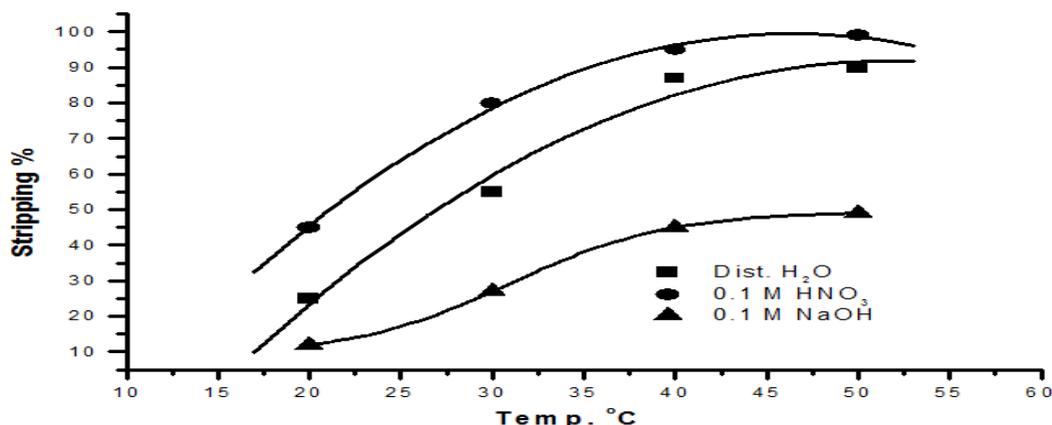


Fig. 6. Effect of Temperature on the stripping of loaded isoamyl alcohol by different stripping agents.

Table (3): Effect of phase ratio A/O on the stripping efficiency of H₃PO₄

Phase ratio A/O	Stripping efficiency %
	Distilled water
1:1	90
2:1	87
3:1	82
4:1	63
5:1	50

[Isoamyl alcohol]= 60% , Time: 5 min, Temp.: 25°C

3.3. Sequential treatment process

Fig. 7 shows the process used to eliminate the organic matter, Fe, F and U and their sequential order for extraction and stripping of P₂O₅ by isoamyl alcohol and warm distilled water, respectively. High extraction of P₂O₅ by isoamyl alcohol is reached mainly due to the removal of iron, organic matter, F and U firstly from crude acid. Finally, pure and colorless 50% P₂O₅ was obtained.

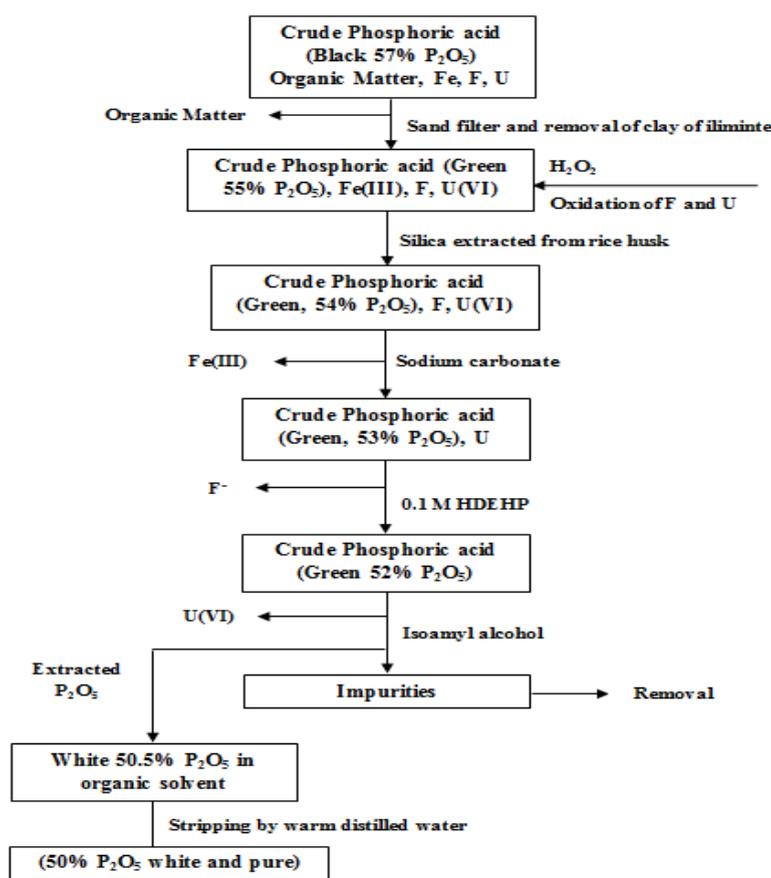


Fig. 7. Flow diagram for sequential treatment processes and extraction of P₂O₅ from crude phosphoric acid.

CONCLUSION

1. Isoamyl alcohol as selective organic solvent plays an important role when used as extractant for extraction of P_2O_5 .
2. The shaking time has a significant effect on extraction process while temperature has a negative effect on the extraction of P_2O_5 but it has a positive effect on stripping process.
3. According to McCabe-Thiele diagram, the extraction process needs only two stages.
4. Sulfate anion has an insignificant effect on the extraction of P_2O_5 .
5. After extraction of uranium and removal of iron, fluoride and organic matter, almost pure phosphoric acid solution can be obtained after extraction using isoamyl alcohol.

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