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## TECHNOLOGICAL STUDIES ON THE SCRUBBING STAGE DURING PHOSPHORIC ACID PURIFICATION PROCESS FOR PRODUCTION OF PARTIALLY PURIFIED AND HIGHLY PURE GRADE PHOSPHORIC ACID

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### ABSTRACT

The production of highly pure grade phosphoric acid is very important due to its high economic value in the different industrial applications. One of the most important purification techniques is solvent extraction method which includes three main stages; extraction of  $P_2O_5$  followed by scrubbing process of the loaded organic solvent and finally stripping process of the  $P_2O_5$  using distilled water (DW). Scrubbing stage is considered as the most important stage of this technique that controls the purity degree of the phosphoric acid and also controls the economic cost of the purification process. In this paper, the effect of different added scrubber solutions on the scrubbing process of the tri-butyl phosphate (TBP) loaded organic solvent were studied. In this context, pure phosphoric acid, oxalic acid, sodium hydroxide and DW were studied, and the effects of the different factors on the  $P_2O_5$  amount loss from the loaded organic solvent such as the concentration of the added scrubber solution, stirring time and added scrubber solution to loaded organic solvent phase ratio were investigated. From the obtained data, DW was considered as the most preferable scrubber and iron was decreased from 40560 ppm to reach 10 ppm only, while Cu, Cd, Mn, Zn, U were not detected and F<sup>-</sup> was decreased to reach 8 ppm in the highly pure grade phosphoric acid.

### INTRODUCTION

The most important technological process for the purification of wet process phosphoric acid (WPPA) is the liquid/liquid extraction process. The solvents which are not soluble in water are the media which extract the phosphoric acid to a high degree of purity from the aqueous phase during an intensive mixing operation, the saturated solvent with phosphoric acid is separated from the aqueous phase which still contains some phosphoric acid and especially most of the impurities from the wet acid (Amin, 2010). The loaded organic solvent is then scrubbed (washed) to eliminate the con-

taminated impurities from the organic solvent and then the acid contained in the washed organic solvent is stripped with water, this procedure gives a pure diluted phosphoric acid which in a final step is concentrated (Amin, 2010). There are a lot of previous researches in the field of purifying phosphoric acid using organic solvents that shed light on phosphoric acid purification by applying three main steps (extraction, scrubbing then stripping process). The second step is the process of scrubbing (washing) the organic solvent loaded with phosphorus pentoxide and some undesirable impurities in order to remove the remain-

ing impurities involved during the extraction process, this step is one of the most important steps of the phosphoric acid purification which control the purity of phosphoric acid to be reached. In this concern, many researches have been carried out with the aim of purifying phosphoric acid using organic solvents, for example; Purification of WPPA by solvent extraction with methyl isobutyl ketone (MIBK) at 40 °C was investigated (Feki et al., 2002). Water immiscible organic acid phosphates used in conjunction with water immiscible organic sulfonic acids resulted in an improved process for the purification of phosphoric acid (James et al., 1977). The preferred group of the used sulfonic acids were the substituted sulfonic acids of formula I and II



Where in formula I, (R) is an alkyl group of from 5 to 25 carbon atoms or an alkanoyl group of 8 to 18 carbon atoms.  $[R]_m$  contains at least 8 carbon atoms when  $m$  is 2, while in formula II, (R) is an alkyl group of from 5 to 25 carbon atoms or an alkanoyl group of 5 to 18 carbon atoms.  $[R]_n$  contains at least 8 carbon atoms when  $n$  is 1 (James et al., 1977). Purification of WPPA with mixtures of MIBK and TBP was also investigated by Hannachi (Hannachi et al., 2007). Meab has described a process to purify WPPA using partially immiscible solvents such as alcohols, ketones, ethers and esters (MEAB, 1992). When ethers were selected as solvent, the effect of temperature was very important, while with alcohols and ketones it was less effective. The purification of commercial  $H_3PO_4$  from metallic impurities was studied using 2.55 M TBP in kerosene (Abu-Raia, 2006) and about 90%  $P_2O_5$  in 9.2 M  $H_3PO_4$  could be extracted in three stages at room temperature.

From the previous researches in the literature survey, there were many organic solvents that were used in the process of purifying

phosphoric acid, such as alcohols, ethers, ketones and tri-butyl phosphate (TBP). The main objective of the present study is not that how the extraction process of phosphorous pentoxide can be done, but the main aim focuses on the process of scrubbing (washing) of the organic solvent loaded with phosphorus pentoxide with some undesirable contaminated impurities. As the scrubbing step is considered the basis in the control of the purity of the purified acid, the higher is the scrubbing efficiency process, the higher is the obtained purity degree of phosphoric acid and vice versa. In this study, many of scrubber solutions (such as; pure phosphoric acid, oxalic acid, sodium hydroxide and distilled water) were studied in order to conduct a process for scrubbing (washing) the organic solvent with high efficiency and compare between these materials to choose the best and most suitable among them. The preferred scrubber solution can be selected according to the amount loss of the  $P_2O_5$  from the loaded organic solvent during the scrubbing process. In this purpose, the extraction process was studied using TBP as an organic solvent with the aim of loading and extracting phosphorus pentoxide by a suitable amount and then undergoing different applicable studies on the washing process of the loaded organic solvent (scrubbing process) using four different scrubber solutions. After the finishing of the scrubbing process, stripping of the phosphorous pentoxide can be achieved to produce highly pure grade phosphoric acid.

## EXPERIMENTAL

### Materials and Measurements

Tri-butyl phosphate (TBP) with 99% purity was provided from Merck Schuchardt, Germany, kerosene has been used as a diluent for preparation the organic solvent. Commercial WPPA with the following components ( $P_2O_5=44.0\%$ ,  $Fe=40.56$  g/l,  $Cu=0.0186$  g/l,  $Cd=0.015$ g/l,  $Mn= 1.86$ g/l,  $Zn= 0.68$ g/l,  $F=12.15$ g/l and  $U= 0.06$ g/l) was supplied from Abu-Zaabal Co., Cairo, Egypt. The used bentonite clay for achieving the removal pro-

cess of organic matter was supplied from Abu Tartur area. The fluoride content was determined by ion selective electrode, a Genway, model 3330 pH meter equipped with Orion model 94-09 BN fluoride electrode while P<sub>2</sub>O<sub>5</sub> was determined spectrophotometrically. Iron, cadmium, Copper, Manganese, and Zinc were determined by atomic absorption spectrometer of model (GBC 932-AAS).

**Calculations**

The concentration of the loaded (extracted) P<sub>2</sub>O<sub>5</sub> in the organic solvent was calculated from the difference between its concentration in the aqueous phase (phosphoric acid) before and after the extraction process, the yield was calculated from the equation:

$$\text{Yield (Y \%)} = \frac{[\text{P}_2\text{O}_5]_{\text{feed acid}} - [\text{P}_2\text{O}_5]_{\text{raffinate}}}{[\text{P}_2\text{O}_5]_{\text{feed acid}}} \times 100$$

or,

$$(E_{\text{Extn. \%}}) = \frac{100 D}{D + V_{\text{aq}} / V_{\text{org}}}$$

Where, V<sub>aq</sub> and V<sub>org</sub> are the volume of aqueous and organic phases respectively. The distribution ratio (D) was calculated from the total concentration of P<sub>2</sub>O<sub>5</sub> in the organic and aqueous phases.

The distribution ratio (D) was calculated from the equation:

$$D = \frac{\text{Total concentration of P}_2\text{O}_5 \text{ in organic phase}}{\text{Total concentration of P}_2\text{O}_5 \text{ in aqueous phase}} \times \frac{\text{volume of aq.}}{\text{volume of org.}}$$

**Analytical Procedure**

**Purification of wet process phosphoric acid**

The purification of (WPPA) to produce partially purified and highly pure grade phosphoric acid requires undergoing seven basic stages as follow; acid pre-treatment process,

removal of fluoride, decreasing iron content, extraction process of P<sub>2</sub>O<sub>5</sub>, scrubbing process of loaded solvent, stripping process and finally evaporation process.

**Acid pre-treatment with calcium bentonite clay**

The pre-treatment process for decreasing the content of organic matter from the crude wet process phosphoric acid has been previously studied by Amin (Amin, 2005). In this concern, 14g of bentonite clay was mixed with one liter of WPPA for 60 min. The absorption of the acid was measured before and after the process of the treatment by spectrophotometer at wavelength of 420 nm to determine the clarification of the acid.

**Removal of fluoride and iron**

Fluorine is undesirable in phosphoric acid (Amin, 2005) therefore, the process of removal of fluoride is very important before application of organic solvent extraction process. Also, one of the most important problems of Egyptian phosphoric acid is the containment of a very large concentration of iron (40.56 g/l) which prevents any process to purify the WPPA, therefore, the decreasing process of both fluoride and iron was necessary to be achieved after the acid pre-treatment step with clay and before applying the organic solvent process. In this respect (Amin, 2005), silicon dioxide (5.92 g/l) was slowly added with continuous stirring for 60 min at 70.0 °C this was followed by slow addition of (10.45 g/l) sodium carbonate and stirring for 60 min followed by addition of (26.67 g/l) potassium sulfate under continuous stirring for 60 min.

**Extraction process**

After achievement of the pre-treatment process and decreasing of fluoride and iron, the process of extracting the phosphorus pentoxide using TBP as organic solvent was carried out leaving most of the undesirable impurities in the raffinate acid. The different

parameters investigated were: organic solvent (TBP) concentration, phosphoric acid concentration and organic/aqueous phase ratio. Different volumes of organic and aqueous phases were equilibrated for 10 min under vigorous stirring in a thermostatted water bath. After phase separation, the concentration of  $P_2O_5$  in the aqueous phase before and after extraction was determined.

#### *Scrubbing process of the loaded solvent*

The purity degree of the phosphoric acid can be detected according to the scrubbing efficiency process. To achieve this target, the loaded organic solvent was washed (scrubbed) with four different aqueous materials, namely, pure phosphoric acid, oxalic acid, sodium hydroxide and distilled water. In this process, the different parameters studied were: the effect of stirring time, concentration of the scrubber solution and aqueous to organic loaded solution phase ratio. To achieve this purpose, different volumes of organic and scrubber solution were equilibrated for different stirring times into agitated stirring beaker.

#### *Stripping process*

In the stripping stage, the DW and the scrubbed loaded organic phases were mixed (stirred) for 5 min at room temperature and then allowed to settle for 20 min to separate in a funnel. This stage was done to strip (re-extract) the  $P_2O_5$  from the loaded organic solvent to produce diluted highly pure grade phosphoric acid.

#### *Evaporation process*

After achieving the purification process by applying suggested solvent extraction method, diluted stripped purified phosphoric acid (DSPPA) was produced. Evaporation process was necessary to raise the concentration of the produced phosphoric acid to meet the market requirements.

## RESULTS AND DISCUSSION

### **Purification of Phosphoric Acid**

The suggested method for the purification process of phosphoric acid can be done through the application of seven main stages through which the removal of organic matter and solid impurities and then reduction of the content of fluoride and iron were carried out in order to prepare the acid to enter the extraction process using TBP as an organic solvent. These three main steps (removal of organic matter, fluoride and iron) were very important to prepare the acid and hence directly impact on the purity degree of the final produced phosphoric acid and its color. So without undergoing these three steps, the produced purified phosphoric acid may still contain high concentration of iron and its color may be converted to greenish yellow by applying evaporation process to raise the concentration of the purified acid. The present study shows briefly the previously obtained optimum conditions of the first three steps (as previously studied by the same author Amin, 2005) and discusses in details the optimum conditions of the extraction process using TBP as organic solvent. The scrubbing process will be also studied and explained in details using four different scrubber solutions then finally shows the stripping process and production of both partially purified and highly pure grade phosphoric acid.

### **Acid pre-treatment process**

As previously studied (Amin, 2005), the pre-treatment of WPPA was undertaken using bentonite clay (A local clay existing at Abu Tartur, Egypt). In this step, 14.0g of bentonite was used for one liter of crude WPPA with constant stirring for 1hr at room temperature (Amin, 2005); in this process, 62.20% of the suspended solids and humic acids were removed. A flocculating agent as polyacrylamide type ionic flocculent at the concentration of 0.5 mg/l was added to enhance the settlement of the suspended materials (Amin, 2005). In the present study, the analysis of the

formed slurry (precipitate) during the application of this process was investigated; this analysis showed the determination of both the distribution size and the value of zeta potential of the formed precipitate; the obtained results

are shown graphically on Fig 1 for size distribution of the formed precipitate and in Fig 2 for zeta potential value. Figure 3 shows the flow chart of the pre-treatment process of the WPPA using calcium bentonite clay.

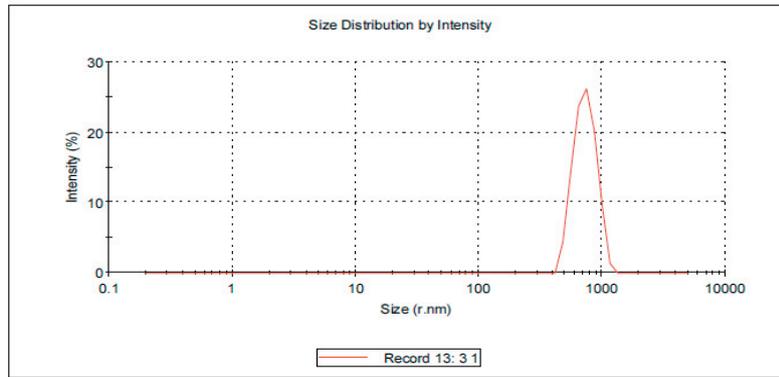


Fig. 1: Size distribution of the pre-treatment formed precipitate using calcium bentonite clay. Experiment conditions: amount of clay added 14 g/l,  $H_3PO_4$  concentration  $P_2O_5$  44%, stirring time 1 h and room temperature

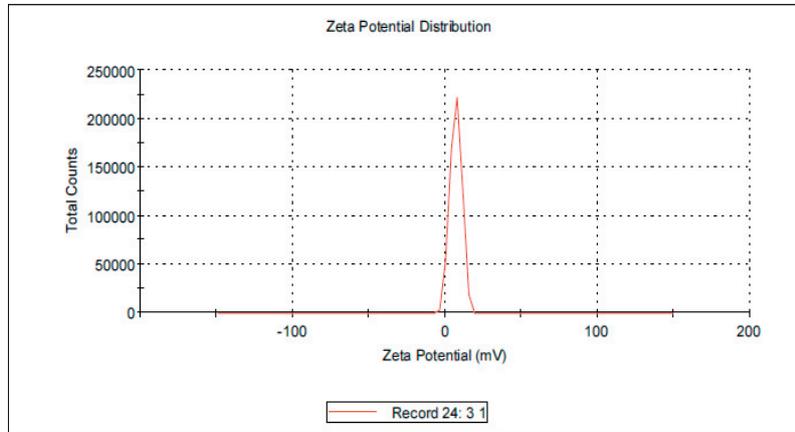


Fig. 2: Zeta potential value of the pre-treatment formed precipitate using calcium bentonite clay. Experiment conditions: amount of clay added 14 g/l,  $H_3PO_4$  concentration  $P_2O_5$  44%, stirring time 1 h and room temperature.

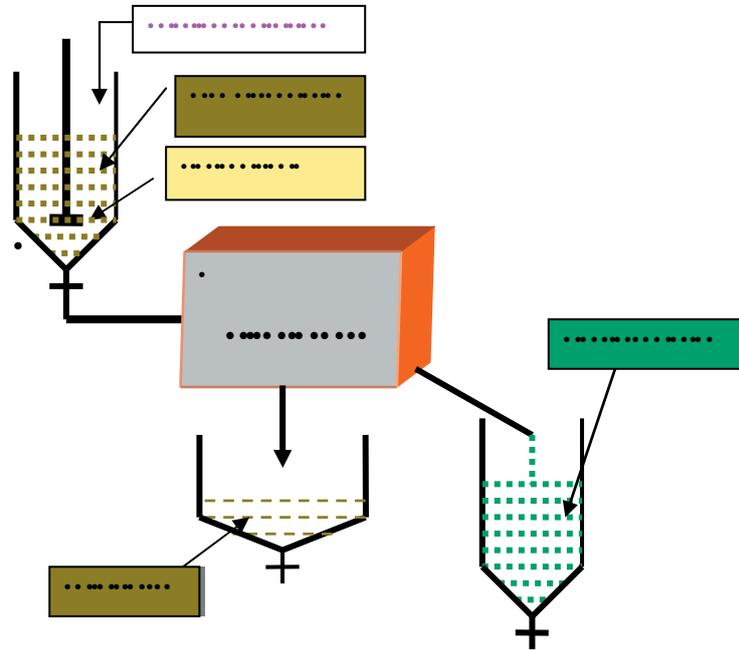
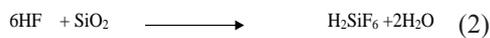


Fig. 3: Flow chart of the crude phosphoric acid pre-treatment process using bentonite clay. Experiment conditions (Amin, 2005): amount of clay added 14 g/l,  $\text{H}_3\text{PO}_4$  concentration  $\text{P}_2\text{O}_5$  44%, stirring time 1 h and room temperature.

### Decreasing of fluoride content

The second step after the removal of organic and suspended solids was the removal of fluoride from pre-treated phosphoric acid (Amin, 2005). Fluoride was found in phosphoric acid in two main forms; silicon tetrafluoride ( $\text{SiF}_4$ ) and hydrogen fluoride (HF), it is well known that, silicon tetrafluoride is more volatile than hydrogen fluoride (Amin, 2005).

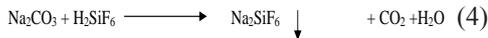


The primary chemical reactions applicable in down stream scrubbing equipment and con-

densers during defluorination (Amin, 2005) are the hydrolysis of silicon tetrafluoride to fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), equation 1 and the reaction of silica with hydrogen fluoride, equation 2. As long as the molar ratio of hydrogen fluoride to silicon tetrafluoride is at least 2, no reactively produced silica will be present to deposit onto the system components. By summation of the two equations (1) and (2):



From the equation 3, 18 moles of fluoride are needed with 3 moles of silicon to form 3 moles of fluosilicic acid. Sodium carbonate must be then added to convert the soluble fluosilicic acid to insoluble sodium hexafluoro silicate which is easily separated (Amin, 2005).



As studied in previous work (Amin, 2005), 5.9 g silicon dioxide was added to one liter of the pre-treated acid with continuous stirring for one hour under 70 °C, this step was followed by addition of 10.5 g sodium carbonate slowly with stirring for one hour under the same temperature; this treatment gave fluoride removal efficiency 92% (Amin, 2005).

**Decreasing the iron content**

The amount of potassium sulfate added was determined stoichiometrically according to the following equation (Amin, 2005):



The iron was precipitated in a complex known as Lehr's salt ( $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$ ) (Amin, 2005), by addition of 26.7 g of potassium sulfate on one

liter of the phosphoric acid with continuous stirring for one hour under heating at 70°C; by applying this step the iron can be decreased successfully to 60% (Amin, 2005). While in the present study, the size distribution and zeta potential were determined, Fig. 4 shows the size distribution of the formed precipitate during the removal process of both fluoride and iron which occurred in the same agitated beaker and hence appeared as one obtained precipitate, while Fig 5 shows the value of zeta potential of the same formed precipitate. The flow chart of the process is represented in Fig. 6. By applying this stage, iron can be decreased to 60% removal efficiency and about 16.22 g/l iron still remained in the pre-treated phosphoric acid.

**Extraction Process**

After achieving the pre-treatment of the acid and reducing the content of fluoride and iron, the extraction process of the acid using

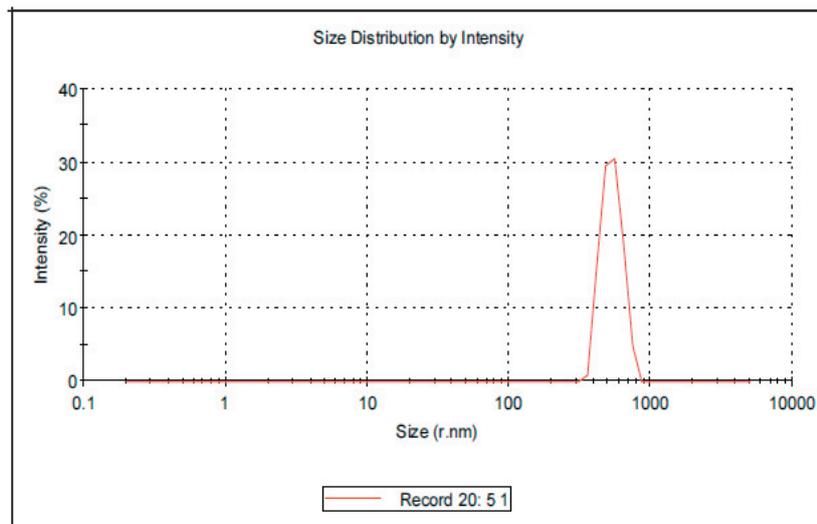


Fig. 4: The size distribution of the formed precipitates of both fluoride and iron. Experiment conditions: 5.9 g/l SiO<sub>2</sub> followed by addition of 10.5 g/l of Na<sub>2</sub>CO<sub>3</sub> and finally addition of 26.7 g/l of K<sub>2</sub>SO<sub>4</sub> for stirring 1 h for each addition under heating at 70 °C

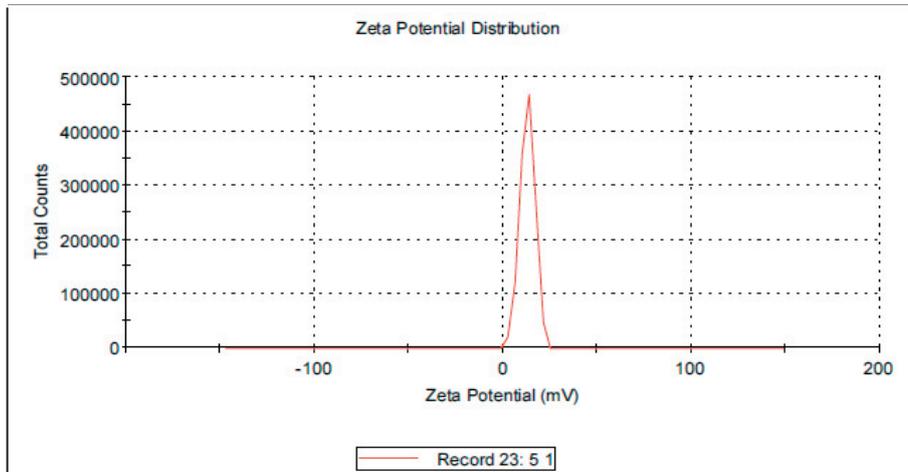


Fig. 5: Zeta potential of the formed fluoride and iron precipitates. Experiment conditions: 5.9 g/l  $\text{SiO}_2$  followed by addition of 10.5 g/l of  $\text{Na}_2\text{CO}_3$  and finally addition of 26.7 g/l of  $\text{K}_2\text{SO}_4$  for stirring 1 h for each addition under heating at 70 °C

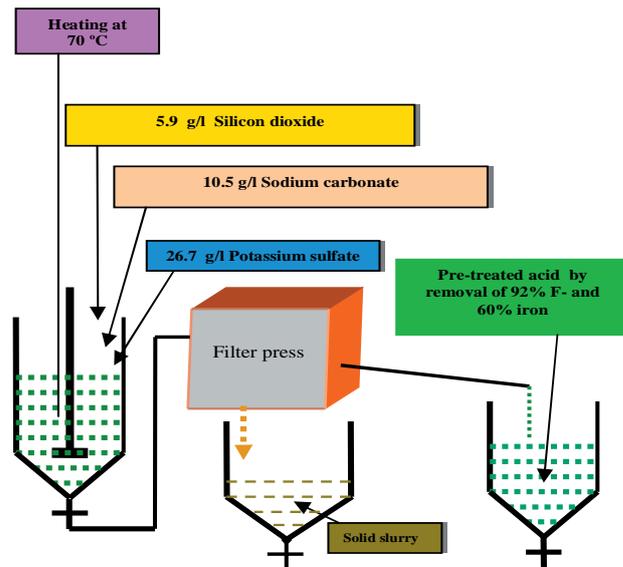


Fig. 6: Flow chart of the removal process of both fluoride and iron from pre-treated phosphoric acid. Experiment conditions (Amin, 2005): 5.9 g/l  $\text{SiO}_2$  followed by addition of 10.5 g/l of  $\text{Na}_2\text{CO}_3$  and finally addition of 26.7 g/l of  $\text{K}_2\text{SO}_4$  for stirring 1 h for each addition under heating at 70 °C.

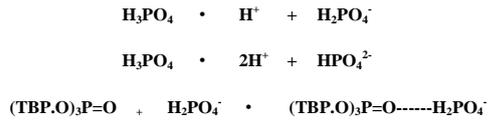
TBP in kerosene as an organic solvent was done to extract the phosphorous pentoxide and load it on the organic phase leaving most of undesirable impurities in the raffinate acid. In this concern, many of important factors were studied to determine the preferable optimum conditions for application of the extraction process.

**Effect of TBP concentration**

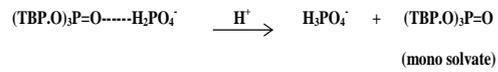
The extraction of P<sub>2</sub>O<sub>5</sub> from pre-treated phosphoric acid (9.20 M) was studied at room temperature using TBP as organic solvent. In this respect, The TBP concentration was varied from 1.5 to 3.0M (kerosene has been used as a diluent) for a stirring time of 10 min and org./aq. phase ratio equal to 3:1. The results are presented graphically on Fig. 7 as a relation between the TBP concentration and P<sub>2</sub>O<sub>5</sub> extraction efficiency percent.

The obtained results show clearly that the extraction percent increased with the increase in the TBP concentration reaching 50.6% using 2.5 M TBP. Evidently, a satisfactory obtained straight line shows the increase of extraction percent of P<sub>2</sub>O<sub>5</sub> with the concentration

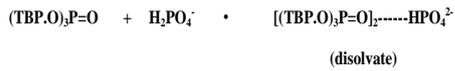
of TBP. Eid, (Eid et al., 1999) showed that the extraction of H<sub>3</sub>PO<sub>4</sub> by TBP involves the formation of hydrate di- and mono solvate. At low H<sub>3</sub>PO<sub>4</sub> concentration, H<sub>3</sub>PO<sub>4</sub>-TBP is the main extracted species and the H<sub>3</sub>PO<sub>4</sub>-TBP fraction increases as H<sub>3</sub>PO<sub>4</sub> concentration increases (Eid et al., 1999). In general, the extraction of H<sub>3</sub>PO<sub>4</sub> by TBP as organic solvent occurs through an aggregate formation between the acid and the solvent as follows:



At high concentration:



At low concentration, where the ionization of the acid is relatively high:



This interpretation has been previously in-

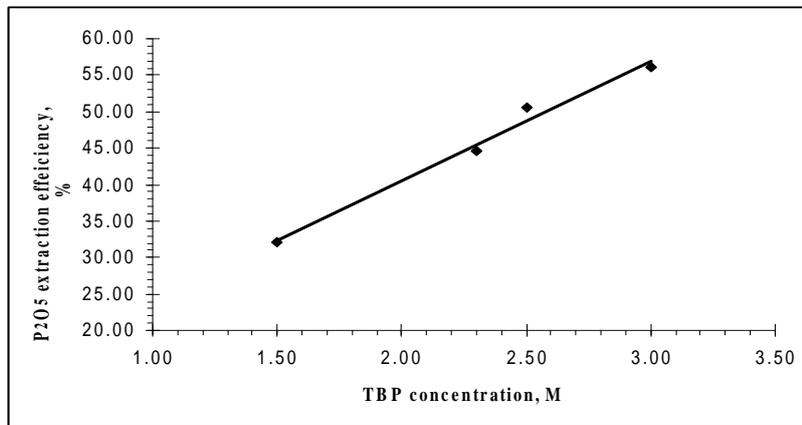


Fig. 7: The relation between the P<sub>2</sub>O<sub>5</sub> extraction efficiency percent and the TBP concentration. Experiment conditions: Phosphoric acid concentration 9.2 M, organic to phosphoric acid phase ratio 3:1, stirring time 10 min and room temperature

roduced by both (Eid et al., 1999 and Amin, 2010).

#### The effect of phosphoric acid concentration

The extraction of  $P_2O_5$  from pre-treated phosphoric acid in the range of 2.16 to 9.20 M, using 2.5 M TBP as organic solvent at room temperature, stirring time of 10 min and org./ aq. phase ratio equal to 3:1 was investigated. The results presented on Fig. 8 show that the extraction percent increased with the increase of the acid concentration to reach an extraction percent of 50.6% at phosphoric acid concentration of 9.20M. In the extracted species, the protons of the acid may form a hydrogen bond with an oxygen atom and thus its extraction is quite reasonable (Amin, 2010). The oxygen atom of the used solvent molecule should combine with the hydrogen atoms of the hydrate water molecule which combine with the proton of the strong acid through its oxygen. In the aqueous phase the phosphoryl oxygen and the three protons of the phosphoric acid

should be hydrogen bonded with water molecules and thereafter these water molecules are removed by the solvation with the solvent (Amin 2010). The hydration on the phosphoryl oxygen may continue to improve the extraction of the phosphoric acid. In the aqueous phase, a proton dissociated from a strong acid should combine with oxygen atom of water molecules. However, the proton should also be able to combine with the phosphoryl oxygen atom of phosphoric acid solvated with the used TBP organic solvent in the organic phase by forming a hydrogen bond (Amin, 2010).

The same trend of the obtained results was revealed by both Amin (Amin, 2010) and Abu-Raia (Abu-Raia, 2006).

#### Effect of TBP to phosphoric acid phase ratio

The effect of the org. / aq. phase ratio on  $P_2O_5$  extraction from concentrated phosphoric acid (9.20 M) was investigated at org. / aq. phase ratio varying from 1.0 to 5.0. All the ex-

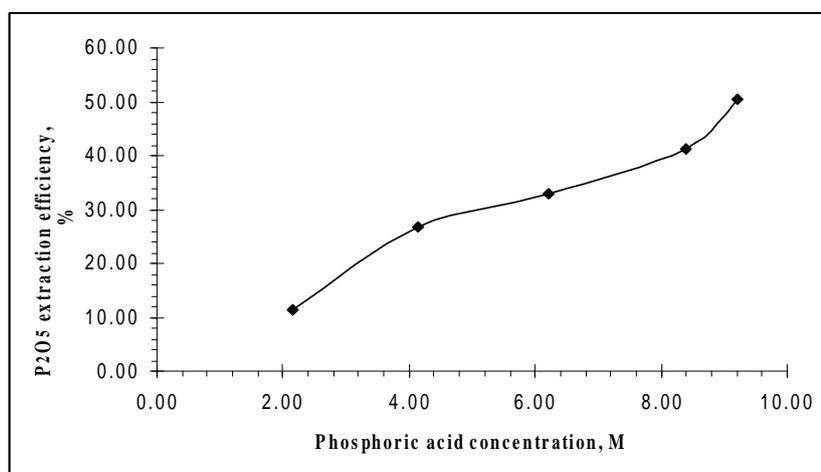


Fig. 8: The relation between the  $P_2O_5$  extraction efficiency percent and phosphoric acid concentration. Experiment conditions: TBP concentration 2.5, organic to phosphoric acid phase ratio 3:1, stirring time 10 min and room temperature.

periments were performed using TBP 2.5 M for stirring time 10 min at room temperature. Figure 9 depicts clearly that the extraction continuously increased with the increase of org./aq. phase ratio to reach 60.7 % for org./aq. 5:1. The organic to aqueous phase ratio 3:1 is a preferable choice that gave  $P_2O_5$  extraction efficiency percent of 50.6%.

It is clear that from all the obtained data in this study, by applying the obtained optimum conditions for the extraction process (TBP concentration 2.5M, phosphoric acid concentration 9.2M, organic to aqueous phase ratio 3:1 and stirring for 10 min under room temperature), 50.6% of the  $P_2O_5$  was successfully extracted and loaded on the organic phase leaving most of the impurities in the raffinate acid. In this stage, about 81.5% of iron was successfully removed by the extraction process and transferred into the raffinate acid while the remaining 3.0 g/l iron still contaminated the  $P_2O_5$  on the loaded TBP solvent. Therefore, that it was very important to undergo a scrubbing process (washing) of the loaded organic

solvent to remove the remained iron from it.

#### Scrubbing Process of the Loaded Solvent

This process is one of the most important steps in the phosphoric acid purification procedures, where this step controls the purity degree of the purified acid and the economics of the phosphoric acid purification process. Many, if not most of the previous research papers and reports in the literature survey are based on the use of pure phosphoric acid in the process of washing (scrubbing) process of the loaded organic solvent, but although the use of pure phosphoric acid in the scrubbing process can give acceptable results, but it is not economic in cost because of the consumption of large amounts of pure acid to conduct the process. The application of this method on the purification of the Egyptian phosphoric acid is very difficult because the Egyptian acid contains high concentration of iron and undesirable impurities contaminated with the phosphorus pentoxide in the organic phase during the extraction process. The present

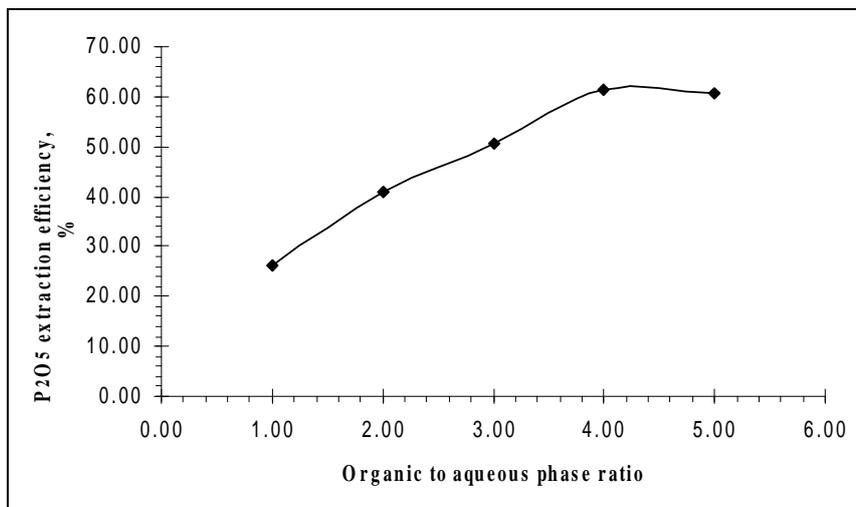


Fig. 9: The relation between the  $P_2O_5$  extraction efficiency percent and TBP organic solvent to phosphoric acid phase ratio. Experiment conditions: TBP concentration 2.5, Phosphoric acid concentration 9.2 M, stirring time 10 min and room temperature.

study shows the important trials done in order to find alternative methods that give acceptable scrubbing results and are of less economical costs. These trials included the use of pure phosphoric acid, oxalic acid, sodium hydroxide and distilled water (DW).

### Scrubbing using pure phosphoric acid

#### *Effect of scrubber phosphoric acid concentration*

The effect of the concentration of phosphoric acid used for scrubbing was studied using pure phosphoric acid of concentration in the range of 1.0 to 5.8M. The washing acid to organic extract phase ratio was 1.0 and stirring time was 5.0 min at room temperature. The results obtained are represented graphically on Fig. 10. The results reveal that by increasing the scrubber acid concentration, the  $P_2O_5$  transferring (loss) from organic phase to scrubber acid decreased reaching a zero value at 5.8 M scrubber acid concentration while the  $P_2O_5$  loss from the loaded organic solvent

increased by decreasing the concentration of pure phosphoric acid scrubber solution and reached about 5.0%  $P_2O_5$  loss by using 1M scrubber acid.

#### *Effect of loaded organic solvent to scrubber phosphoric acid phase ratio*

A series of experiments was performed with different loaded organic solutions to scrubber acid ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The experiments were conducted using 5.8M scrubber acid concentration and stirring time 5.0 min. The results were represented on Fig. 11 reveal that by increasing the scrubber acid to the loaded organic solution ratio, the  $P_2O_5$  transferring (loss) from the loaded organic solution to washing acid phase increased. At loaded organic solution to acid washing phase ratio equal to 1:1 there was no transfer of  $P_2O_5$  between the two phases.

#### *Effect of stirring time on the scrubbing process*

The effect of stirring time was studied in

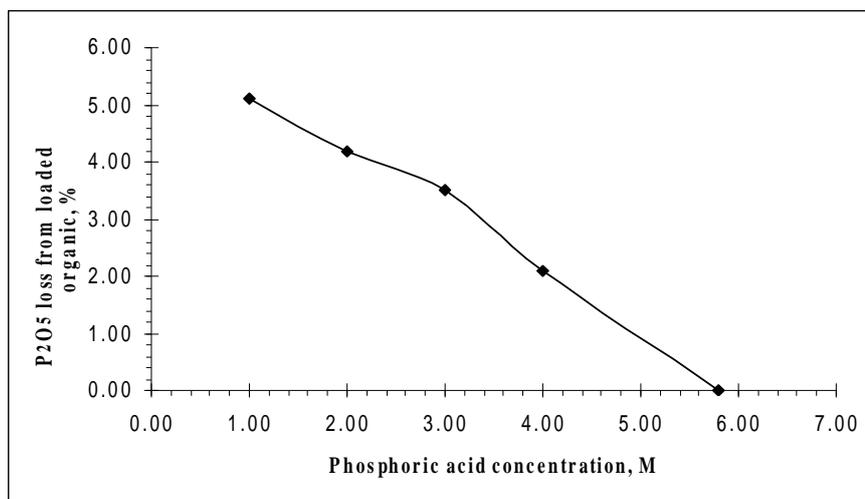


Fig. 10: The effect of pure phosphoric acid concentration on the scrubbing process. Experiment conditions: loaded organic solvent to pure phosphoric acid phase ratio 1:1, stirring time 5 min and room temperature

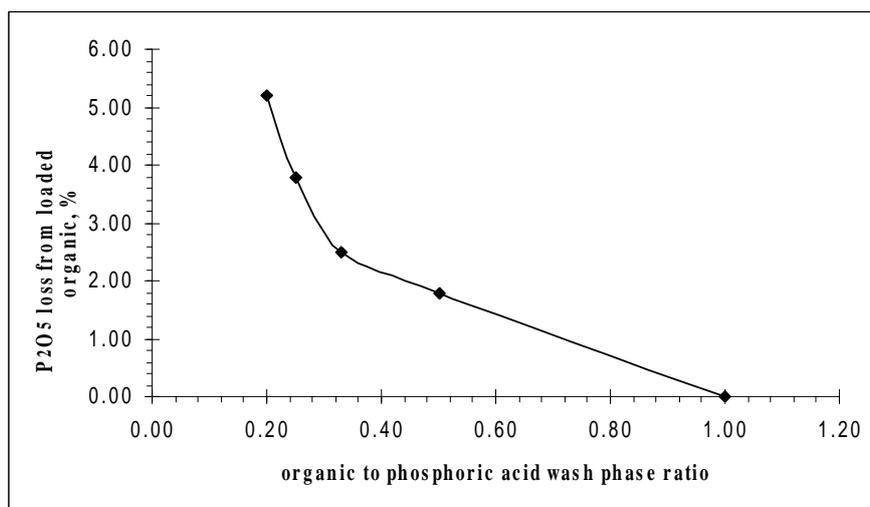


Fig. 11: The effect of organic to washing phosphoric acid phase ratio on the  $P_2O_5$  loss % from the loaded solvent. Experiment conditions: Pure phosphoric acid concentration 5.8 M, stirring time 5 min and room temperature.

the range of 1.0 to 20.00 min. The loaded organic solution to scrubber acid phase ratio was 1:1 and the scrubber acid concentration was 1.0 M. The results represented on Fig. 12, indicate that the process was fast and increased with time till 5 min. then remained nearly constant with further increase in the stirring time from 5 to 20 min. where time had a negligible effect on the  $P_2O_5$  loss from the loaded organic solvent.

From the obtained data, pure phosphoric acid can be used in the scrubbing process of the loaded organic solvent using phosphoric acid concentration of 5.8 molar with stirring time for 5 minutes and organic solvent to washing phosphoric acid phase ratio equal to 1: 1. By applying these optimum conditions, phosphorus pentoxide was not lost and there was no  $P_2O_5$  amount transferred from the loaded organic solvent to the washing phosphoric acid (scrubber acid) but the amount of consumed pure phosphoric acid by applying this method is very large, which prevented the application

of this scrubbing method from the economic point of view. By using pure phosphoric acid (concentration of 1 M), the loss amount of  $P_2O_5$  from the loaded organic solvent reached about 5%. Therefore, pure phosphoric acid cannot be used for up scaling the process of the suggested method of phosphoric acid purification from the economic point of view.

#### **Scrubbing using oxalic acid**

**Effect of oxalic acid concentration :** Oxalic acid has been used in many previous studies to remove iron from organic solvents loaded with uranium (Amin, 2018; Singh et al., 2006). The effect of oxalic acid concentration on the  $P_2O_5$  transferred from loaded organic solution was studied in the concentration range 1.0 – 15.0% (wt/v). The loaded organic solution to scrubber oxalic acid ratio was 20:1 and the stirring time was 5.0 min. The results on Fig. 13 reveal that, by increasing the scrubber oxalic acid concentration, the  $P_2O_5$  transferring (loss) from organic extract phase to scrubber acid

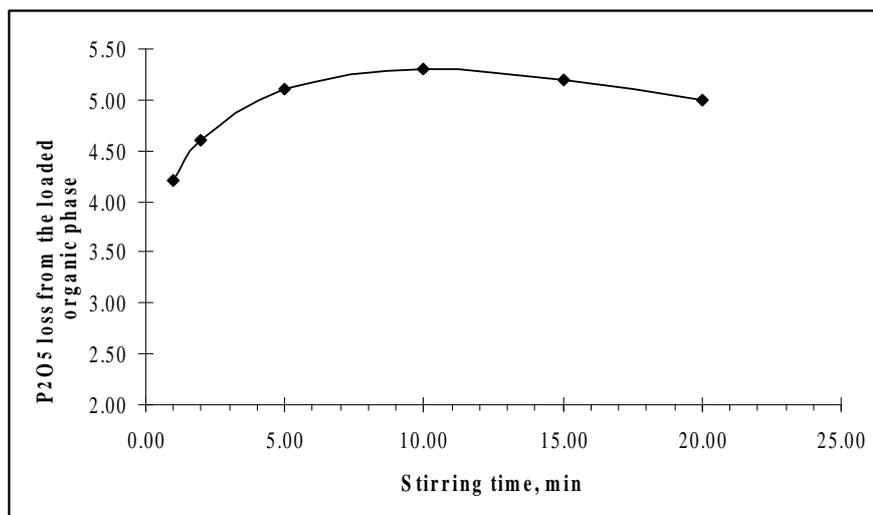


Fig. 12: The effect of the stirring time on the P<sub>2</sub>O<sub>5</sub> loss % from the loaded organic solvent. Experiment conditions: loaded organic solvent to pure phosphoric acid phase ratio 1:1, pure phosphoric acid concentration 1.0 M and room temperature.

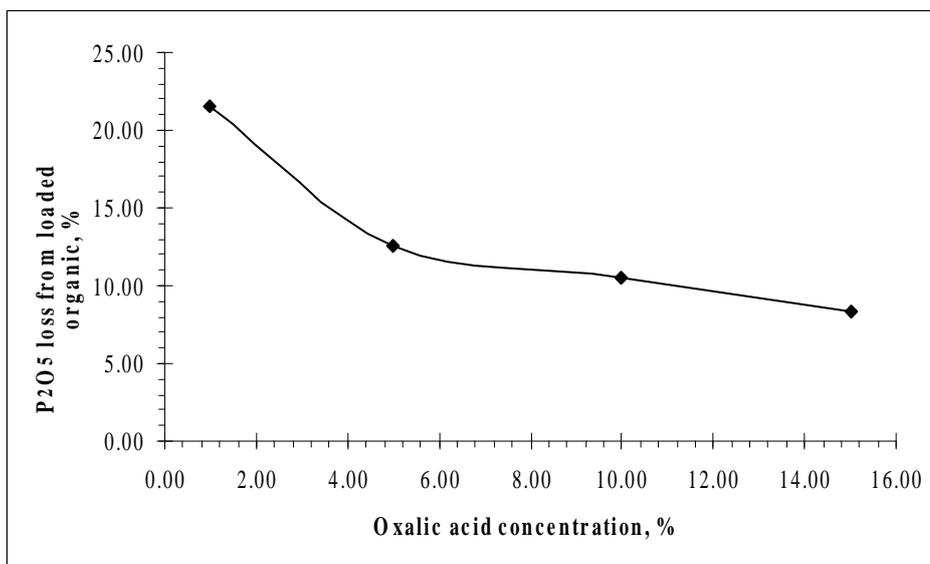


Fig. 13: Effect of oxalic acid concentration on the P<sub>2</sub>O<sub>5</sub> loss % from the loaded organic solvent. Experiment conditions: Loaded organic solvent to oxalic acid phase ratio 20:1, stirring time 5 min and room temperature.

phase was decreased reaching 8.3% loss at the maximum concentration of the used oxalic acid (15%), for this reason (high loss of  $P_2O_5$ ) oxalic acid is unsuitable for using as scrubber solution of the loaded organic solvent.

**Effect of loaded organic solvent to oxalic acid phase ratio :** A series of experiments was performed with different loaded organic solution to scrubber oxalic acid ratios ranging as 1:1, 5:1, 10:1 and 20:1. The experiments were conducted using 15% scrubber oxalic acid concentration and stirring time 5.0 min. From the results represented on Fig 14, the  $P_2O_5$  transferring (loss) from organic extract phase increased by increasing the organic extract to scrubber oxalic acid ratio. But, by increasing the scrubber acid to loaded organic solution phase ratio, the  $P_2O_5$  transferred from organic extract to washing (scrubber) acid phase decreased.

**Effect of stirring time on the  $P_2O_5$  loss percent from loaded solvent :** The effect of stirring time was studied in the range of 1.0 to

20.0 min. The loaded organic solution to washing (scrubber) oxalic acid phase ratio was 20:1 and scrubber oxalic acid concentration was 15%. Figure 15 shows clearly that after 15 min. there was nearly no effect of stirring time on the content of the  $P_2O_5$  in the organic phase. Unfortunately, the use of oxalic acid in the scrubbing process did not give satisfactory results due to the loss of a large amount of phosphorus pentoxide (8.3%) from the loaded organic solvent.

#### Scrubbing using sodium hydroxide

##### **Effect of sodium hydroxide concentration :**

The effect of the concentration of sodium hydroxide used for scrubbing was studied in the range of 1.0 to 30.0 %. The washing (scrubber) sodium hydroxide to the loaded organic solution ratio was 1:20 and stirring time was 5.0 min at room temperature. The results obtained are represented graphically on Fig. 16. The results reveal that by increasing the sodium hydroxide wash (scrubber) concentration, the  $P_2O_5$  transferring (loss) from organic phase to wash sodium hydroxide increased reaching

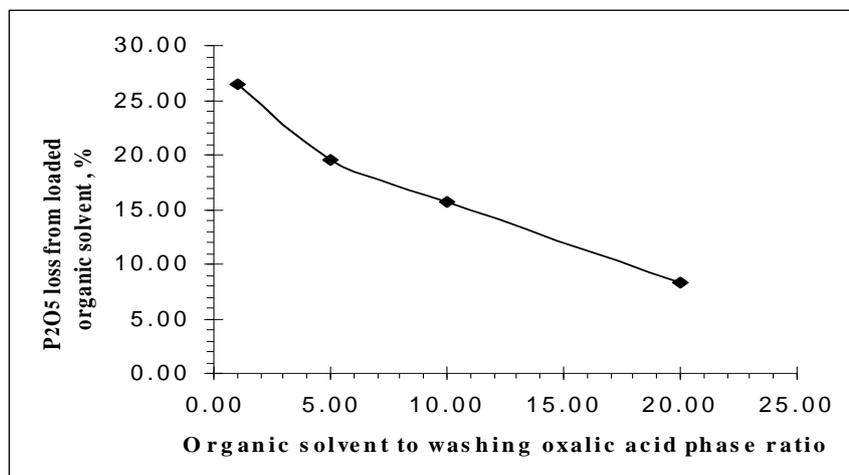


Fig. 14: Effect of loaded organic solvent to washing oxalic acid phase ratio on the  $P_2O_5$  loss % from the loaded organic solvent. Experiment conditions: oxalic acid concentration 15% (wt/v), stirring time 5 min and room temperature.

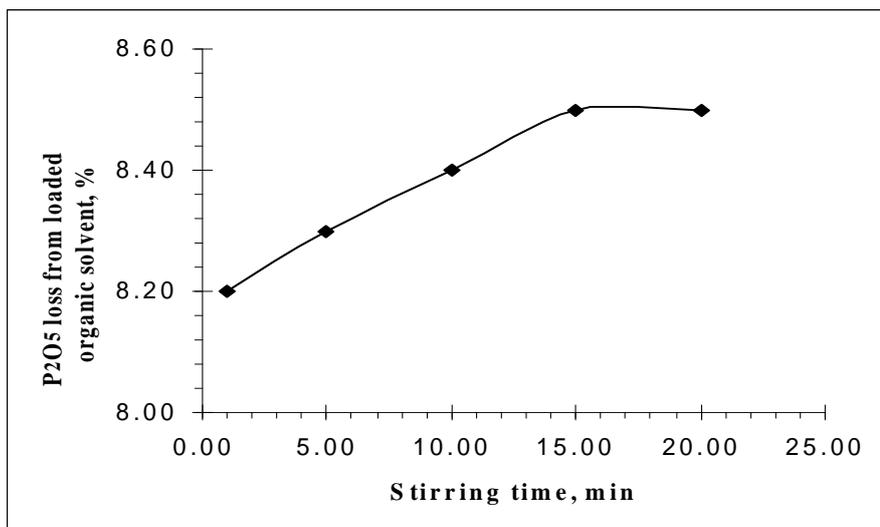


Fig. 15: Effect of stirring time on the P<sub>2</sub>O<sub>5</sub> loss % from the loaded organic solvent using oxalic acid solution. Experiment conditions: loaded organic solvent to oxalic acid phase ratio 20:1, stirring time 5 min, oxalic acid concentration 15% (wt/v) and room temperature.

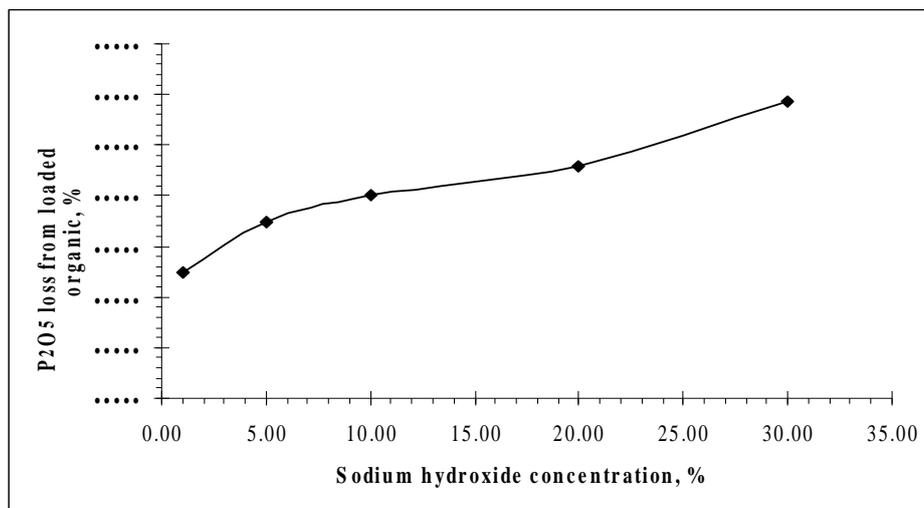


Fig. 16: Effect of sodium hydroxide concentration on the P<sub>2</sub>O<sub>5</sub> loss % from the loaded organic solvent. Experiment conditions: loaded organic solvent to sodium hydroxide phase ratio 20:1, stirring time 5 min and room temperature

36.7% by washing with 30% (wt/v) sodium hydroxide solution.

Unfortunately, by studying the effect of sodium hydroxide concentration on the scrubbing process, it was clear that a very large loss occurred in the content of phosphorus pentoxide from the loaded organic solvent (about 30 to 36.7%), therefore the organic solvent washing process using a solution of sodium hydroxide was not entirely satisfactory.

**Scrubbing using distilled water** : The use of distilled water in the process of washing organic solvent (scrubbing process) was one of the most important economic methods which was proposed by the present study to remove the remaining undesirable impurities contaminating the organic solvent during the extraction of phosphorus pentoxide to produce highly pure grade phosphoric acid that can be used in the food industries.

**Effect of loaded organic solvent to distilled water phase ratio:**The effect of the loaded organic solvent to distilled water (DW) phase

ratio was investigated in the range 20:1, 30:1, 40:1, 50:1 and 60:1. The obtained results are represented graphically on Fig. 17. The results reveal clearly that the  $P_2O_5$  loss from the loaded organic solvent reached 44.6% by using organic to DW phase ratio equal to 20:1, while the  $P_2O_5$  loss percent decreased to reach 1.6% only in case of washing the loaded organic solvent with DW when the ratio of the loaded organic solution to DW equals 60:1. This means that the more is the increase in the organic to DW phase ratio, the more is the decrease in the  $P_2O_5$  loss from the loaded organic solvent. The partially purified phosphoric acid was produced during applying the scrubbing stage, the iron and other impurities were transferred during this stage from the loaded organic solvent to the scrubber DW. The produced scrubber DW from this stage can be used as partially purified phosphoric acid of phosphorus pentoxide concentration of about 30%. After achieving the scrubbing process and production of the partially purified phosphoric acid; stripping process of phosphorus pentoxide from the washed loaded organic solvent was done

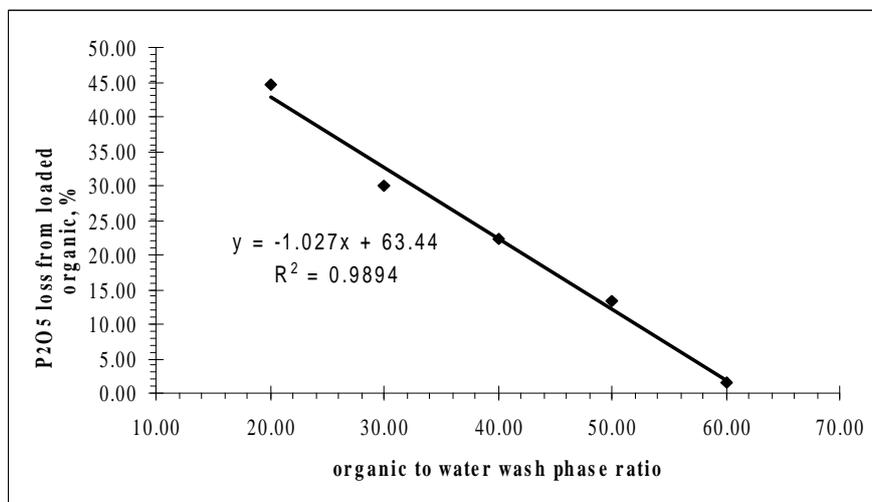


Fig. 17: Effect of loaded organic solvent to distilled water phase ratio on the  $P_2O_5$  loss % from the loaded organic solvent during the scrubbing process. Experiment conditions: stirring time 5 min under room temperature.

to produce highly pure grade diluted phosphoric acid.

Finally, from the obtained results of the scrubbing process, it was clearly deduced that DW was the most preferable scrubber for the loaded organic solvent because DW is very cheap and available in comparison with other studied scrubber solutions and also DW gave a very small loss of the  $P_2O_5$  from the loaded organic solvent in the case of applying the suggested optimum conditions.

### Stripping Process

After achieving the scrubbing of the loaded organic phase, stripping of the phosphorus pentoxide was done to re-extract the  $P_2O_5$  from the loaded organic solvent (TBP) using DW. To achieve this purpose, pure loaded organic solvent was stirred for 5.0 min with DW by phase ratio 1:1 under room temperature. By applying this stage, highly pure grade diluted phosphoric acid could be successfully obtained.

### Evaporation process

After achieving the purification process by applying the suggested seven stages, diluted stripped purified phosphoric acid (DSPPA) was produced. Evaporation process was necessary to raise the concentration of the produced phosphoric acid to meet the market requirements. Table 1 shows the chemical specifications of crude phosphoric acid, pre-treated phosphoric acid, partially purified phosphoric acid (faint acid produced as bi-product during the scrubbing stage), highly pure grade phosphoric acid and Egyptian standard phosphoric acid specification number 4575/2006. Figure 18 shows the comparison between the crude, partially purified and food grade phosphoric acid using the suggested method. Figure 19 shows the flow chart of the suggested process in this study to purify the Egyptian wet process phosphoric acid for production of both partially and highly pure grade phosphoric acids.

Table 1 : Chemical specification of different types of phosphoric acid, crude, pre-treated, partially purified, highly pure grade phosphoric acid and Egyptian standard specification No. 5475/2006

Constituent	Crude $H_3PO_4$	Pre-treated $H_3PO_4$	Partially purified $H_3PO_4$	Highly pure grade $H_3PO_4$	Egyptian standard $H_3PO_4$ specification No. 5475/2006
$P_2O_5$	44.0 %	44.0%	30.0%	60.0%	61.6%
g/l					
Fe	40.56	16.22	3.0	0.01	0.02
Cu	0.0186	0.018	0.005	N.D	-
Cd	0.015	0.0146	0.0002	N.D	-
F <sup>-</sup>	12.15	0.972	-	0.008	0.01
Mn	1.86	1.85	0.0008	N.D	-
Zn	0.68	0.645	0.0002	N.D	0.003
U	0.06	0.06	N.D	N.D	-

N.D: Not Detected



Fig. 18: Comparison between Brown crude phosphoric acid, faint green partially purified phosphoric acid and colorless highly pure grade phosphoric acid

### CONCLUSION

This paper deals with some technological studies on the scrubbing stage carried out during the purification process of wet process phosphoric acid. In this context, this paper studied the effect of four different scrubbing solutions to choose the best scrubber which could efficiently scrub the phosphoric acid from the loaded TBP organic solution with the minimal loss of  $P_2O_5$ . The obtained results indicate that DW is the most efficient and cost effective scrubber of phosphoric acid from the loaded TBP organic solution. The suggested method through this study was summarized by the application of main seven stages which must be achieved in the same proposed order to purify the Egyptian wet process phosphoric acid for production two types of phosphoric acid: first was partially purified phosphoric acid that can be used in different phosphate

salts industry while the second type was highly pure grade phosphoric acid that can be used in food industry. The suggested method (seven stages are summarized as follow;

- 1- Removal of organic matter and this step occurred by treatment of the crude phosphoric acid using 14 g calcium bentonite clay per one liter acid.
- 2- Decrease of the fluoride content by treatment of the acid with silicon dioxide followed by addition of sodium carbonate.
- 3- Decrease of Iron in the same previous step by addition of potassium sulfate.
- 4- Solvent extraction process using TBP as organic solvent which was achieved after preparation of pre-treated phosphoric acid produced from the application of the previous three steps; in this concern 2.5 M of TBP dilut-

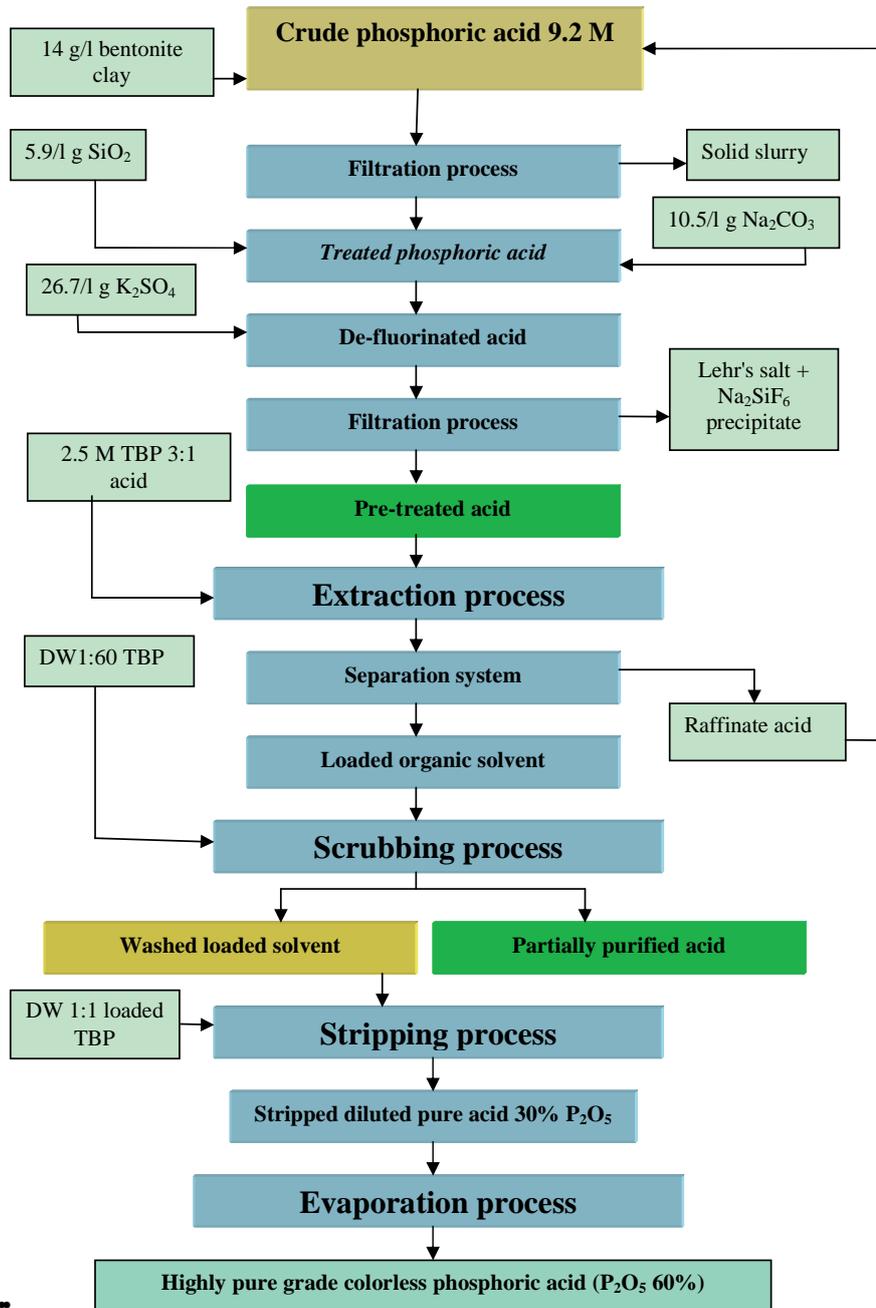


Fig. 19: Flow chart of the seven stages of the suggested wet process phosphoric acid purification technique

ed with kerosene was mixed with pre-treated phosphoric acid with organic to phosphoric acid phase ratio equal to 3:1 under room temperature.

5- After the extraction process, application of scrubbing process was necessary to eliminate the remaining undesirable impurities contaminating the loaded organic solvent. In this context, four different types of scrubber agent were studied and it was found that distilled water (DW) was considered as preferable scrubber solution for elimination of all the contaminating impurities from the loaded organic solvent.

6- Stripping stage was applied to re-extract the phosphorus pentoxide from pure loaded organic solvent by mixing it with distilled water with phase ratio of 1:1.

7- Finally evaporation process occurred to raise the concentration of stripped diluted pure phosphoric acid to meet the requirement market specifications. By applying the suggested method for purification of the phosphoric acid, iron was decreased to reach 10 ppm in the highly pure grade phosphoric acid, also Cu, Cd, Zn, Mn and U were not detected, while F was decreased to 8 ppm in the highly pure grade phosphoric acid.

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## دراسات تكنولوجية على مرحلة الغسيل اثناء تنقية حمض الفوسفوريك لانتاج حمض فوسفوريك منقى جزئيا وحمض فوسفوريك نقي بدرجة عالية

مصطفى ابراهيم امين

يتناول هذا البحث موضوع هام جدا وهو تنقية حمض الفوسفوريك المصرى بطريقة تطبيقية اقتصادية يمكن من خلالها تطبيق الطريقة المقترحة على وحده نصف صناعيه حيث تم التركيز فى هذه الدراسه على ايجاد واقتراح طريقه اقتصاديه لعملية غسيل المذيب العضوى ثلاثى بيوتيل الفوسفات المحمل بخامس اكسيد الفوسفور وذلك اثناء تطبيق عملية تنقية حمض الفوسفوريك باستخدام تقنية الإستخلاص بالمذيبات العضويه وللحصول على حمض فوسفوريك منقى جزئيا يمكن استخدامه فى العديد من الصناعات التطبيقية وايضا للحصول على حمض فوسفوريك عالى فى درجة النقاء تم اقتراح طريقه تطبيقية من خلال هذه الدراسه وتشمل دراسة وتطبيق عملية تنقيه مكونه من سبعة مراحل اساسيه وهى بالترتيب: المعالجه الاولييه لحمض الفوسفوريك، ازالة الفلورايد، تقليل محتوى الحديد (تعتبر الثلاث مراحل الاولى هى مراحل اساسيه لتجهيز حمض الفوسفوريك قبل تطبيق عملية التنقيه بالمذيبات العضويه وقد تم دراستهم من قبل بمعرفة نفس المؤلف)، استخلاص خامس اكسيد الفوسفور باستخدام ثلاثى بيوتيل الفوسفات، عملية غسيل المذيب العضوى المحمل بخامس اكسيد الفوسفور وذلك بدراسة اربعة انواع مختلفه من المحاليل (حمض الفوسفوريك النقى، حمض الاوكساليك، هيدروكسيد الصوديوم والماء المقطر)، اجراء عملية الاسترجاع لخامس اكسيد الفوسفور واخيرا اجراء عملية تبخير لزيادة تركيز حمض الفوسفوريك النقى وقد اكدت النتائج ضرورة عمل غسيل للمذيب العضوى المحمل بخامس اكسيد الفوسفور وذلك باستخدام الماء المقطر والذي يعتبر الافضل اقتصاديا وتطبيقيا من بين المحاليل التى تمت دراستها من خلال هذا البحث لازالة الحديد المتداخل مع خامس اكسيد الفوسفور اثناء تطبيق عملية الاستخلاص وقد اظهرت النتائج المعملية ان استخدام الماء فى عملية الغسيل هو الافضل والانسب من وجهة النظر الاقتصادية وانه بتطبيق الظروف المعملية المتلى لعملية الغسيل باستخدام الماء المقطر يتم فقد ١,٦ ٪ فقط من محتوى خامس اكسيد الفوسفور المحمل وازالة كل الحديد المتداخل حيث يتم انتاج حمض الفوسفوريك المنقى جزئيا اثناء تطبيق هذه المرحله.

ويتطبيق عملية الاسترجاع لخامس اكسيد الفوسفور بعد اتمام عملية الغسيل بشكل كامل يتم استرجاع خامس اكسيد الفوسفور وانتاج حمض فوسفوريك مخفف عالى النقاوه يمكن استخدامه فى الصناعات الغذائيه وذلك بعد تبخيره وتركيزه حيث لا يتعدى تركيز الحديد به على ١٠ جزء فى المليون والفلورايد حوالى ٨ جزء فى المليون وباقى الشوائب النحاس والكادميوم والمنجنيز والزنك واليورانيوم دون مستوى القياس.