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RESEARCH ARTICLE

PURIFICATION OF EGYPTIAN INDUSTRIAL GRADE PHOSPHORIC ACID TO THE FOODGRADE QUALITY VIA SOLVENT EXTRACTION TECHNIQUE USING A NEW HYDROPHILIC AND HYDROPHOBIC EXTRACTANTS

***Laila A. Guirguis, Nagwa. I. Falila**
Nuclear Materials Authority (NMA), P.O Box 530, El-Maadi, Cairo, Egypt

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Corresponding Author

Laila A. Guirguis

Abstract

This paper describes the process of purification of Egyptian industrial grade phosphoric acid to the food grade quality through one step using methyl isobutyl ketone and ethyl alcohol as hydrophilic and hydrophobic extractants respectively. The optimum conditions achieved for one step extraction are phosphoric acid: ethanol: methyl isobutyl ketone ratio 1: 1: 7, room temperature, agitation time of 20 minutes and settling time of 5 minutes. Phosphoric acid (27% P_2O_5) at an O/A ratio of 1: 1 was used as a scrubbing agent in one stage, distilled water was used as a stripping agent, at room temperature, with O/A phase ratio 3: 1, settling time and agitation time of 5 minutes and 3 minutes respectively. The recovery of the extraction process achieved 99.7%

The starting P_2O_5 concentration was 39.5% whereas its uranium value was 73.5 ppm. The obtained purified phosphoric acid contains 39.5% P_2O_5 depleted from uranium, and the obtained phosphoric acid is concentrated under reduced pressure to 85% P_2O_5.The quality of the obtained acid agrees well with that of the international food grade quality phosphoric acid. Finally a technological flow sheet was elucidated.

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INTRODUCTION

The necessity of very pure phosphoric acid has been increased in recent years because of its valuable uses in certain non fertilizer applications such as in food stuffs, animal feed and detergents.

Wet process phosphoric acid was obtained by subjecting crude phosphate ores to wet processing with mineral acid, commonly sulphuric acid, to produce crude phosphoric acid, containing inorganic together with organic impurities (which originates from phosphate ores) and appear then in variable concentrations depending on crude phosphate origin and its pretreatment.

Many of these impurities particularly are removed from the acid using various techniques depending on the use for the acid grade intended. Calcium, magnesium, sulphate, iron, lead, cadmium, arsenic, uranium, chromium, REEs and organics are some impurities considered in the acid.

Many different techniques were applied for purification of wet process phosphoric acid to the food and technical grades however; solvent extraction is widely employed and forms the basis of the analytically and commercially operated purification units. Moreover, it is easy to recover any of the valuated elements from the rafinate as an added value to the solvent extraction process. Hydrophilic groups are usually polar, ionic and forming hydrogen bond such as COOH, OH, NH_2, SH, NOS, CHO and SO_3H [1].

It is well known that hydrated inorganic solvent tends to be more soluble in water than organic solvents, such as benzene and chloroform whereas organic substance tends to be more soluble in organic solvents than in water; unless they incorporate sufficient number of hydroxyl, sulphuric acid and hydrophilic groups. In solvent extraction, analysis for metals are concerned with method by which water solubility of inorganic cation may be

masked by interaction of appropriate organic reagents. This effect removes some or all of the water molecules associated with the metal ion to which solubility is due.

Ionic compounds are not extracted into organic solvents from the aqueous solution because of the large loss in electrostatic attraction energy which would occur. The most obvious way to make an ionic species extractable is to neutralize its charge, by the formation of neutral metal chelate complex or by ion association. The large and more hydrophobic molecules the better will be its extraction [2].

In Egypt, the first commercial plant of phosphoric acid by the dihydrate process (Norke- Hydro- fission process) using Sebayia ore has come into stream in late 1981 by Abu Zaabal Fertilizer and Chemical Company where the normal production of this plant was 600 ton P_2O_5 / year, Norke Hydro Fisson dehydrate process; the input ore should be ground that 65% passes into 100 mesh. The temperature of the reaction of sulphuric acid with the ore should be between70-85^{0}C. The produced dilute acid (30 % P_2O_5) could be concentrated to 45.5 % P_2O_5 by evaporating the free amount of sulphuric acid and should be between 43-50% whereby most of the impurities namely fluoride are precipitated [3]. There are many methods for the purification of industrial phosphoric acid from impurities such as solvent extraction, solvent precipitation, indirect purification, clarification and ion exchange. Complete reviews of these methods are given by El Rakaiby [3].

Experimental

Materials

- The starting materials for the present work is a commercial wet process phosphoric acid (39.5% P_2O_5) which is kindly supplied by Polyserve for Fertilizer Company, Cairo, Egypt (from the evaporator unit after filtration).
- Methyl isobutyl ketone from Merck chemical company.
- Ethyl alcohol from BDH.
- Activated carbon locally produced.
- The reagents used in this work were of analytical grade quality. Double distilled water was used in all preparations.

Instrumentations

- A Shimadzu 160 A double beam UV spectrophotometer having a wave length range of 200-1100 nm was used for spectrophotometric determination of sulphate, phosphate, total rare earth elements and uranium.
- An atomic absorption spectrophotometer Unicam 969 supplied with acetylene and nitrous oxide burner heads, regulators and integrated reading in absorbance, was used for the determination of most of the impurities.
- Sherwood 410 flame photometer was used for the determination of sodium and potassium.
- A centrifuge Nf 815 was used to separate aqueous and organic phases during the solvent extraction work.
- A Jenway pH meter is applied satisfactorily in the present work and calibrated daily using two successive buffer solutions (pH 4 and 7 or 7 and 10).

Procedure for chemical analysis

A number of chemical and instrumental methods of analysis were used for the quantitative determination of major, minor and trace elements of the present phosphoric acid [4]. Anion exchange method is used in the present study for the analysis of phosphoric acid. This method was applied [5] and has the advantage over the direct method in that it separates the phosphate radical completely from the metal cations using the strongly cationic resin Dowex 50x8, 50-100 mesh in hydrogen form in a glass column of 21 cm length and 3.8 cm cross section. The metal cations are retained in the column while the phosphoric acid is passed quantitatively in to the effluent. The cations are eluted afterwards from the resin using 4N HCl. Thus, one gram of crude phosphoric acid is diluted with water to 100 ml and passed through the ion exchange column at a rate of 2 ml/ minute. The column is washed by 0.0175N HCl and separated anions are collected in 500 ml measuring flask. The retained cations are then eluted with 4N HCl until the column is free from them (iron test) and diluted to 100 in a volumetric flask.

Procedure for Extraction

Extraction was carried out in a beaker with a magnetic stirrer placed in a thermostat to control the temperature. Few grams of each of the aqueous and organic phases were mixed for 25 minutes and allowed to separate for 20 minutes in a separating funnel. The concentration of P_2O_5 in the aqueous phase was determined by the citroammonium molybdate method, whereas the concentration of P_2O_5 in the solvent was calculated from the material balance.

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

$$D = [P_2O_5]_{organic} / [P_2O_5]_{aqueous} \quad [1]$$

Where $[P_2O_5]$ = weight percent of P_2O_5

The P_2O_5 extraction percentage (%E) was calculated from the following equation:

$$\% E = 100 D (P) / 1 + (P) D \quad [2]$$, Where

P (phase ratio) = value of organic / value of aqueous

D is the distribution ratio

The degree of phase separation was determined by measuring the change of height of the interface from the bottom of the column with time.

Result and Discussions

Chemical analysis

The obtained complete chemical analysis of our locally industrially produced phosphoric acid is shown in Table 1.

Table 1: Complete chemical analysis of industrial grade phosphoric acid (In put acid)

Major and Minor elements		Trace elements (ppm)	
Component	**Assay (%)**	**Component**	**Assay (ppm)**
P_2O_5	39.5	U	73.5
Fe_2O_3	1.5	Cr	125
TiO_2	0.015	V	90
Al_2O_3	1.03	Ni	55
CaO	3.9	Cu	9
MgO	1.2	Zn	240
SiO_2	0.02	Mo	340
MnO	0.106	Cd	U.D.L
SO_4^{--}	6.1	Pb	U.D.L
Cl^-	0.00045	Co	U.D.L
K_2O	0.25	REE	407
Na_2O	0.34		
Combined water	48.09		
Total	102.05		

U.D.L = under detection limit

Effect of aliphatic solvent on the extraction of phosphoric acid

The effect of number of carbon atoms on the extraction of impure phosphoric acid was investigated, meanwhile the time of phase separation was measured under the same experimental conditions and the results are plotted in Figure (1).

It is clear that ethanol is the best hydrophilic solvent on the extraction process.

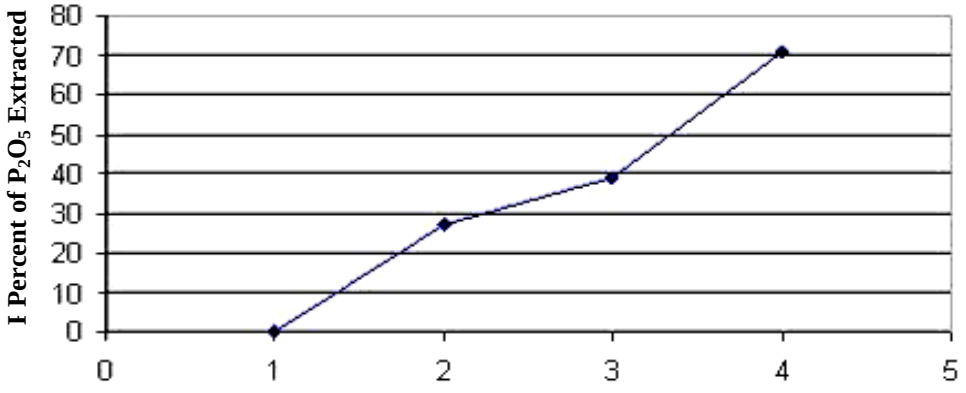

Figure (1): Effect of number of carbon atoms of aliphatic solvent on extraction

Process

Effect of ethanol phase ratio on the extraction process

Different amounts of ethanol namely 0.5, 1, 1.5 and 2 part per volume of ethanol are mixed separately to constant volume of impure phosphoric acid (1 part) and MIBK (4 parts) where other separation conditions are kept constant. The obtained results are shown in Figure (2).

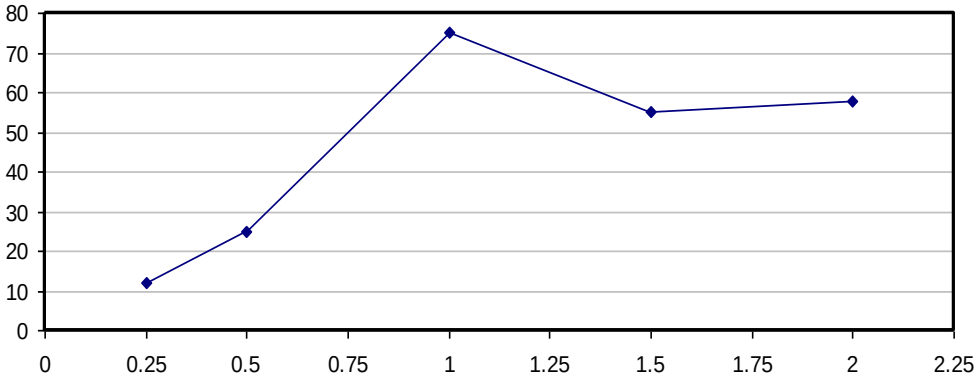

Figure (2): Effect of Ratio of hydrophilic solvent (ethanol) tion process

It's clear from Figure (2) that the best mixing phase ratio of ethanol is 1 part.

Effect of MIBK phase ratio on the extraction process

The effect of MIBK phase ratio was studied in the range from 1 to 9 parts by volume per one part of phosphoric acid and one part ethanol. From the results illustrated in Figure (3), it is obvious that the best mixing phase ratio is 7 parts of MIBK.

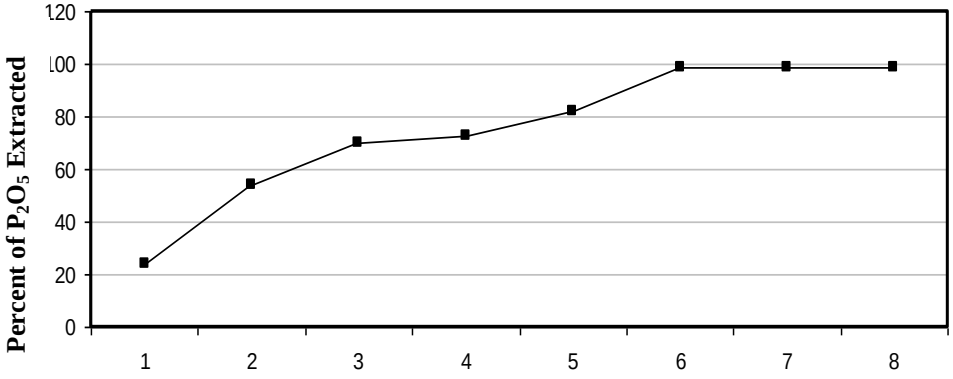

Figure (3) the extraction process

Ratio of hydrophobic solvent (MIBK)

Effect of mixing time on the extraction process

The effect of mixing time (contact time) on the extraction process was investigated. The extraction was carried out at optimum previously determined values and at room temperature. The mixing time was varied from 10 to 30 minutes. The results are gathered and represented in Figure (4). Since the plateau region starts at a mixing time of 25 minutes, hence this mixing time was adopted for further experiments.

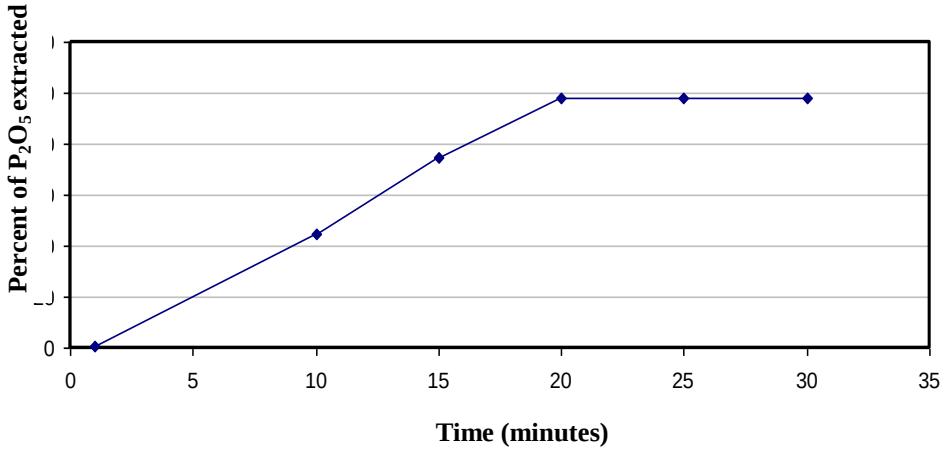

Figure (4): Effect of mixing time on the extraction process

Effect of temperature on the extraction process

This effect was studied at different temperatures (10 ºC to 60 ºC) at the previously determined optimum extraction conditions. An extraction of 99.7%was achieved at room temperature; therefore, it is a usual practice to carry out the extraction process at this temperature. The results are shown in Figure (5).

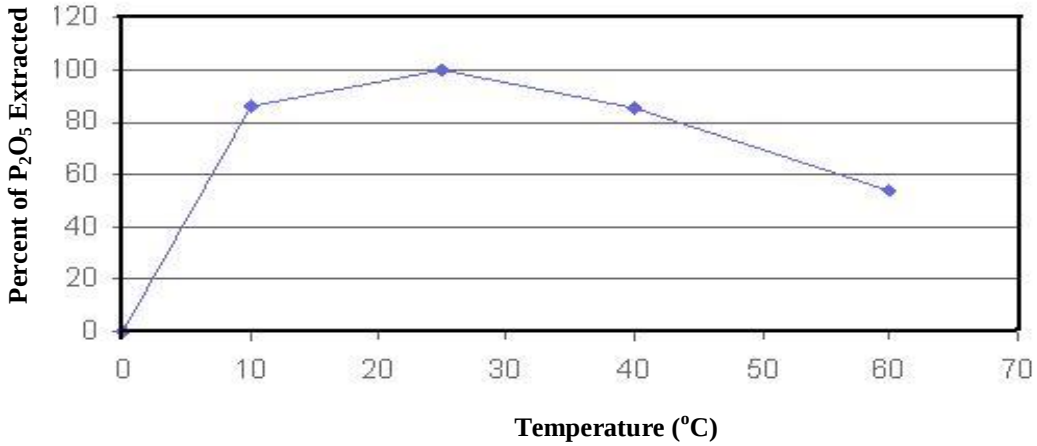

Figure (5): Effect of temperature on the extraction process

The relation between the equilibrium constant K and the temperature is given by Van Hoff's equation:

$$D \ln K / dT = \Delta H / R \cdot T^2$$

By integration

$$\text{Ln } K = (-\Delta H / R) (1 / T) + a$$

And since the distribution ratio D is related by definition to the equilibrium constant K the previous equation could be written as follows:

$$\text{Ln } D = (-\Delta H / R) (1 / T) + á$$

Extraction Isotherm and Construction of McCabe-Thiele Diagram for the Extraction Process

An extraction isotherm is a plot of the equilibrium concentration of the extracted species in the extracted phase against its concentration in the rafinate layer at a given temperature. Data for the extraction isotherm could be easily obtained from either single contacts of a fixed volume of aqueous feed (phosphoric acid) with different volumes of organic feed (MIBK) (i.e. the phase ratio variation method) or else by repeated contact of one and the same aliquot of the aqueous feed with several aliquots of the fresh organic feed of equal volume.

In this study we use the phase ratio variation method for construction of the extraction isotherm of P_2O_5 with organic mixture of MIBK and ethanol from the phosphoric acid (39.5 % P_2O_5), the phase ratios are in the range of 1:1:7 (phosphoric acid: ethanol: MIBK), the extraction was carried out at the same previous conditions. The results are represented in Figure (6) where P_2O_5 concentration in the solvent is plotted versus P_2O_5 concentration in the rafinate.

The obtained data were used to construct the McCabe-Thiele diagram which is a composite plot of the extraction isotherm and the operating line. The latter could be established by only one point, which corresponds to the final rafinate composition and the ratios of the aqueous to organic phases that determines the slope of the line as it is a straight line. The ideal stages are stripped off by extending a horizontal line from the vertical extremely of the operating line to intersect the isotherm, then a vertical intercept to the operating line to intersect the isotherm, and so on until the other extremely of the operating line is intersected.

The separation curve (equilibrium line) is then constructed as in Figure (6), the next step in construction of McCabe-Thiele diagram was to try a number of operating lines. The slope is equal to the ratio of aqueous/organic volumes. The theoretical number of stages could be stepped of upon the diagram in Figure (6). It is clear that one theoretical stage is quite adequate for P_2O_5 recovery, if the operating line is at an O/A phase ratio equal to 7/1.

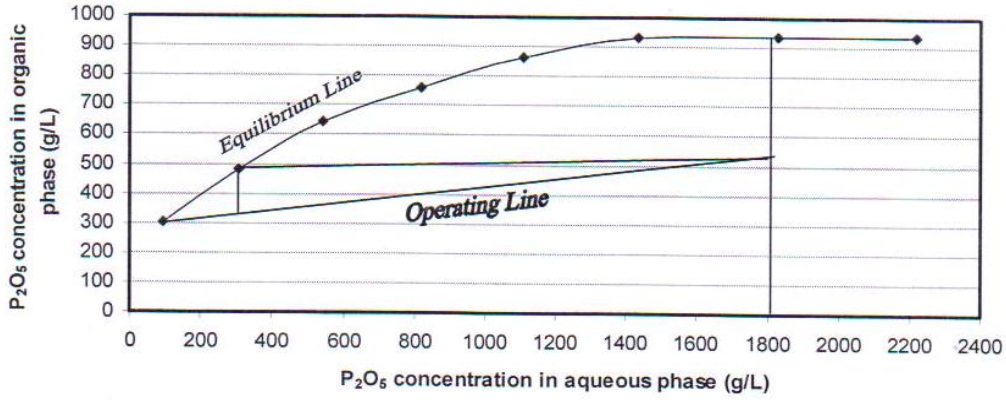

Figure (6): Mc Cabe Thiele diagram for the extraction process

Stripping

Having determined the optimum conditions for the extraction process a stock solution of about five liters was prepared for the stripping process.

Effect of different stripping reagents

Distilled water, 3% and 6 % phosphoric acid were tried to find out the most suitable reagent for the stripping process at an aqueous to organic phase ratio 1: 3, room temperature, 5 minutes mixing time and 3 minutes settling time. It is clear from the obtained results shown in Table 2 that distilled water can be used as a stripping agent.

Table 2: Effect of Different reagents on the stripping process

Reagent	Percentage stripping P_2O_5
Distilled water	99.7
3% diluted phosphoric Acid	96.1
6% diluted phosphoric Acid	92.3

Effect of organic / aqueous phase ratio on the stripping process

Different organic to aqueous phase ratio namely 1/2, 1/1, 2/1, 3/1 and 4/1 were used to get the optimum phase ratio for stripping P_2O_5 from the organic phase while the other stripping factors are kept as before. From the results illustrated in Figure (7) the best organic to aqueous phase ratio could be taken as 3/1.

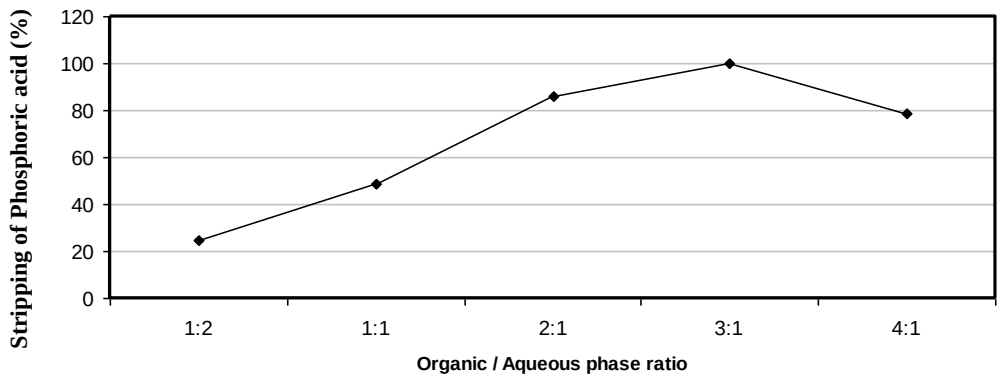

Figure (7): Effect of organic / aqueous phase ratio on the stripping process

Effect of contact time on the stripping process

The effect of contact time on the attainment of equilibrium state has been studied at time intervals from 5 to 20 minutes. The obtained results illustrated in Figure (8) shows that 5 minutes mixing is the optimum; whereas the settling time is about 3 minutes.

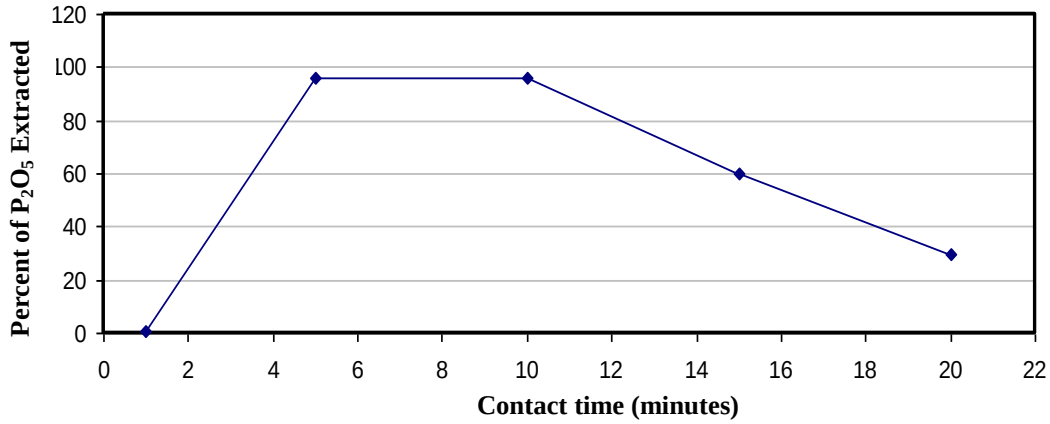

Figure (8): Effect of contact time on the stripping process

Effect of temperature on the stripping process

This effect was studied at different temperatures (10 ºC to 60 ºC) at the previously determined optimum extraction conditions. The percent P_2O_5 extracted was 99.7% at room temperature therefore; it is a usual practice to carry out the stripping process at this temperature. The results are shown in Figure (9).

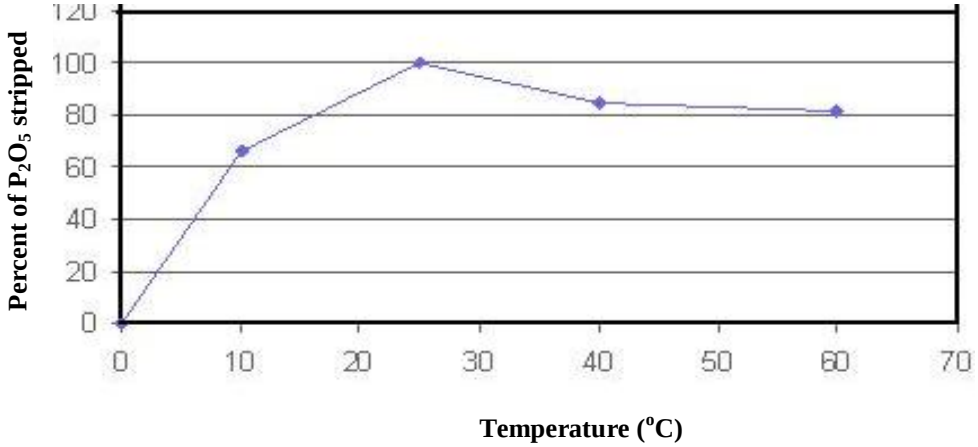

Figure (9): Effect of temperature on the stripping process

Equilibrium line and construction of Mc Cabe-Thiele diagram for the stripping process

McCabe-Thiele diagram is a composite plot of the distribution isotherm and the operating line. The latter readily is established by only one point, which corresponds to the final rafinate composition and the ratio of the aqueous to organic phases that determines the slope of the line, as it is a straight line. The diagram can be used to approximate the number of theoretical stages required for the given process. Another importance of the McCabe-Thiele diagram is the evaluation of the results. In this study, 50 gm of loaded organic (MIBK) and 50 gm of distilled water (stripping reagent) are contacted for 30 minutes at the previously determined optimum stripping conditions until equilibrium is attainted. The phases are allowed to separate (3 minutes). A measured portion of the aqueous phase is taken for analysis. Fresh loaded MIBK is added to the separating funnel containing the remainder of the aqueous phase, in amount to give the same phase ratio as the originally used. The phases are

again contacted until the equilibrium is attained and the same procedure is carried out. This process is carried out until saturation of the aqueous phase with P_2O_5 is obtained. Figure (10) illustrates the obtained results where one stage was found sufficient for the stripping of P_2O_5 from the loaded organic phase.

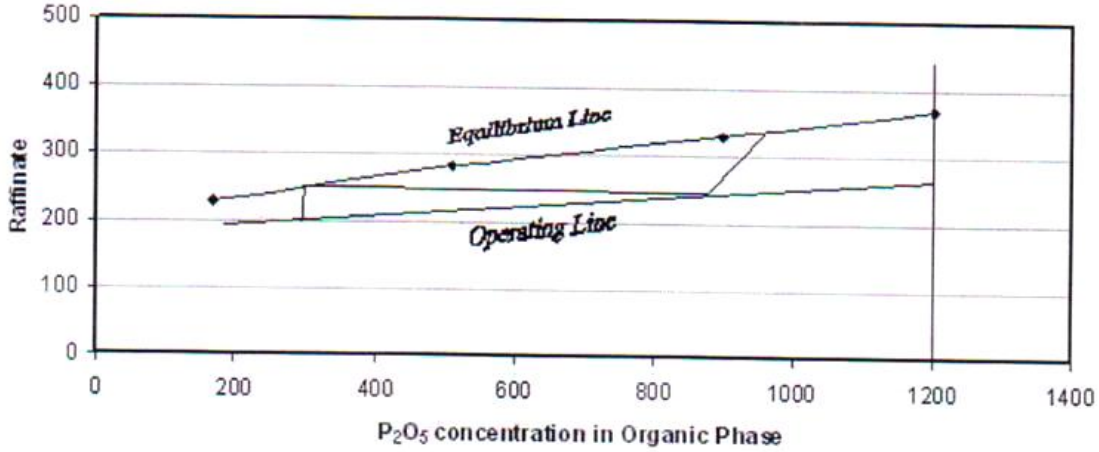

Figure (10): Mc Cabe Thiele diagram for the stripping process

Post Acid Treatments

The obtained purified acid after stripping is concentrated by evaporation under reduced pressure to a P_2O_5 concentration in the range from 85% to 86%. The obtained concentrated acid is passed through an activated carbon column at a flow rate of 60 ml/h to remove any residual contaminations. A complete chemical analysis of the purified acid together with a standard sample of food grade quality phosphoric acid is shown in Table(3).

Table (3): Chemical Analysis of the Purified Phosphoric Acid together with the International Standards

Element	Purified Phosphoric Acid, Present Work	International Sample of Food Grade Acid [5]
Purity	85.5	85 Max 85.3 typical
COLOR	10	35 Max 20.0 typical
Cl^-	UDL	5 Max 1.0 typical
SO_4^{2-}	10	50 Max 30.0 typical
F^-	UDL	20 Max 3.0 typical
Ni	1.93	
Cd	UDL	
Fe	12	
Zn	0.04	
Pb	UDL	
As	UDL	
Cr	0.05	
Heavy Metals as Pb	5	

Phosphoric acid is determined by transmission at 365 nm in 1 cm cell [5] where-as the content of volatile acid is calculated as acetic acid and is taken for its odor [6].

It is international in this regard that complete decolorization of purified phosphoric acid wet process is obtained. Finally a technological flow sheet is elucidated in Figure (11).

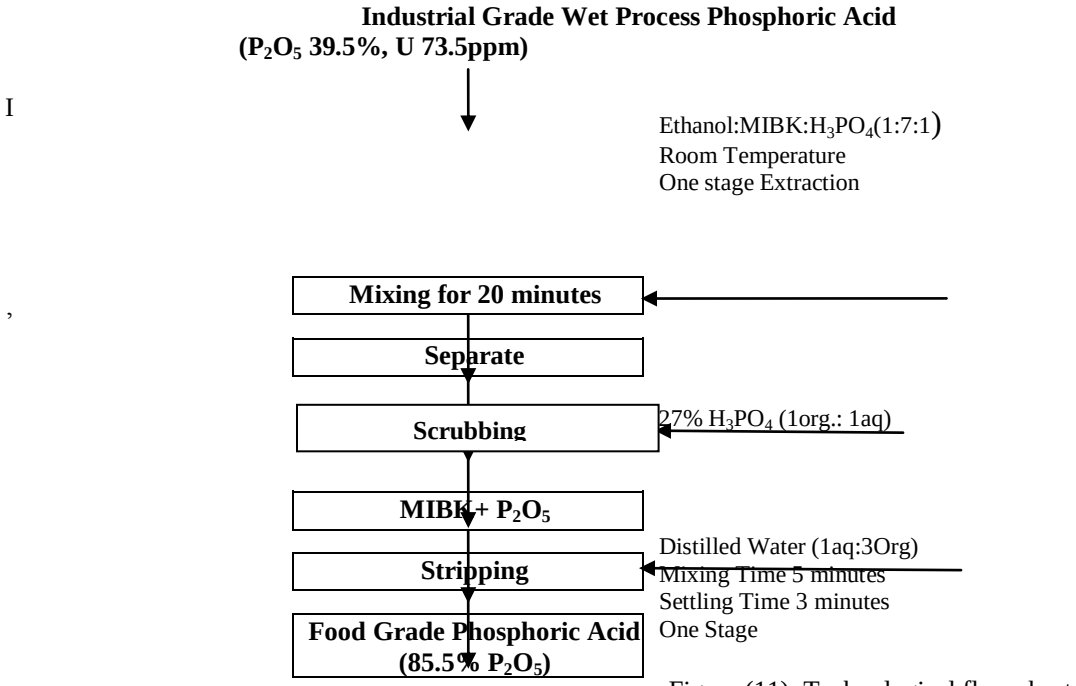

Figure (11): Technological flow sheet

Conclusions

1. The presented approach consists of a single stage extraction using one part ethanol (hydrophilic), 7 parts of methyl isobutyl ketone [MIBK] (hydrophobic) for each one part of impure acid feed (39.5% P_2O_5, U is 73 ppm).
2. The hydrophobic solvent MIBK prove to be selective to phosphoric acid. Extraction of embodiment impurities is negligible.
3. The temperature has a small negative effect on the process thus it could be carried out at room temperature.
4. The concentration of phosphoric acid has a positive effect on extraction where it is recommended to high strength acid (from 36.5 to 67.5 weight percentP_2O_5).
5. The time of mixing has a small effect on P_2O_5 weight percentage extraction which indicates that extraction is not diffusion control.
6. Stripping with diluted water at an A/O of 1:3 at a mixing time of 5 minutes and settling time of 3 minutes in one stage.

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