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RESEARCH ARTICLE

One Stage Solvent Extraction Synergism for the Purification of Industrial Wet Process Phosphoric Acid to the Food Grade Quality.

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Abstract

Different organic solvents were investigated, separately or in mixture for example methanol, ethanol, butanol, hexanol, octanol, TEP,D2EHPA, TBP,TOPO and a mixture of TBP plus butanol. Among these solvents, TBP plus butanol proved to be the most efficient solvents mixture. The effect of organic/aqueous phase ratio, temperature, shaking time, settling time and phosphoric acid concentration were studied. Scrubbing of the loaded organic acid was done using 4.2M pure phosphoric acid at an O/A phase ratio of 1:1 while stripping of H_3PO_4 was performed using distilled water of an O/A phase ratio of 3:1 in one stage. The final recovery of the process is 97.8%.

Introduction:-

The necessity of very pure phosphoric acid has been increased in recent years in the use of chemical industries, metal surface, feed and food industries beside the possibility of by product extraction of vandium, molybdenum, nickel, chromium, uranium and rare earth elements .

In general phosphoric acid is manufactured by these methods, the dry and wet methods. Acid produced by the dry process, has a much higher purity, essentially containing only the phosphtic value. However, because of the large quantities of energy that are required to manfacture thermal phosphoric acid, its cost has risen considerally in the last ten years or so. Consequently a number of companies have devolped technique to replace the purer thermal acid.

Wet process phosphoric acid is obtained on subjecting and phosphate ores to wet processing with mineral acid, commonly sulfuric acid. The crude acid which is obtained contains in organic and organic impurities which originates from phosphate ores and appear therein avariable concentrations depending on the crude phosphate origin and its pretreatment. [1] Many of these impurities particularly are removed from the acid whatever its use ,by various technique such as clarification. Other purification techniques are employed depending on the use for which the acid is intended food and technical grade acid ,the levels of the following impurities on the acid must be considered, calcium,magnesium,sulphate,iron,lead,cadmium,rsenic,uranium,thorium,rare eaths and organic acids, many different techniques have been considered for purification of wet process phosphoric acid to food and technical grades such as solvent extraction, ion exchange, para magnetism, electrodialysis, electro deposition and electrode ionization on ion exchange textiles. However solvent extractionhas been widely employed, forms the basis of the of the majorly of commercially operated purification units, moreover it's easier to recover any of the valuable elements from the raffinate as an added value to the solvent extraction process. The recovery of uranium industrial phosphoric acid of abu Zaable Fertilizer and Chemical company have 28-30% P_2O_5 done by a synergic effect of DDEPA-TOPO, the process needs acid pretreatment and to a cycle extraction, stripping are very complicated [2] while extraction of uranium from the concentrate phosphoric acid by hemi dehydrate process is done by 2.5% capryl pyro phosphoric acid(CPPA) stabilized by 2.5% TBP in kerosene as diluent from the pre treatment acid way ($13.5P_2O_5$ and55 ppm U) Uranium extraction 97.8% while uranium stripping is carried out by0.3M (NH4)2CO3 at a phase ratio of 3:1 O/A[3] . [4] Moreover Laila.A.Gurguis studied the extraction of uranium from H_3PO_4(45%P_2O_5 and 74ppm U) by N- butanol at an O/A phase ratio of the stripping the impurities with ortho phosphoric acid at aphase ratio of 1:4 O/A at room temperature and stripping the acid with distilled water at O/A 3 at room temperature . food grade phosphoric acid is obtained from this method needs a pretreatment step cooling,desaturation followed by deflouration, clay treatment and carbon column treatment to obtain acid for extraction(45% P_2O_5, 74ppm U) Moreover the acid after extraction is vaccum distilled and treated with activated carbon as a post purification Laila.A.Gurguis et al [5] purify H_3PO_4 by a mixture of hydrophobic and hydrophilic extraction in a single stage from crude phosphoric acid57-75% P_2O_5 with a mixture of low and high molecular weight alcohols one of which is hydrophobic i.e ethanol and hexanol. The phosphate values segregate to high molecules weight alcohol fraction and the impurities segregate to high molecules weight alcohol fraction. The optimum ratio for the extraction is formed to be 0.5 part methanol , one part impurer acid and four parts hexanol 95% extraction percent is achieved. Laila.A.Gurguis et al [6] Laila.A.Gurguis et al [6] Pre extraction of phosphate 95% extraction percent is a chieved- pre extraction of phosphate value by 6% H_3PO_4 ,the purified acid is concentrated under reduced pressure and formed through activation carbon column, whereas the alcohols are recirculated. purify industrial phosphoric acid by a mixture of hydrophobic and hydrophilic extraction in a single stage in fact a mixture of low and high molecules weight alcohols is used i.e methanol and hexanol. Ahmed Abd El Magied et al. [7] used synergistic organophosphorus solvent mixture of DNPPA and TEP to extract uranium from hemi-dihydrate wet process phosphoric acid (9.2M) relvant factors of extraction who studied, and extracted uranium is further subjected to a second cycle extraction by(0.3M DEHPA+ 0.075 M TOPO) scrubbing impurities by (5 M sulfuric acid) and stripping with 1 M $(NH_4)_2CO_3$ solution nd precipitation of uranium as UO_3. Synergism of solvent extraction and solvent extraction kinetics of different metal ions $Fe^{2+,}$ Cd^{2+}, Cr^{3+}, $Ni^{2+}$and U^{6+} using different extractants in different extracting conditions have been reviewed[8] extraction of uranium from fertilizer grade phosphoric acid with a novel synergistic mixture of DNPPA and TBP is reported. The extraction of uranium is subjected to a second cycle using D2EHPA-TBP. The uranium is finally converted to a high purity UO_3 using precipitation with hydrogen peroxide and heat treatment at 200^0C [8]. The purification of the wet process phosphoric acid with MIBK and TBP was investigated. The purification is obtained from the higher solvent mixture rates. While TBP has the highest selectivity, compared with MIBK the solvent mixture is more selective for extracting phosphoric acid [9]. The synergistic effect of some alcohols such as iso amyl alcohol, pentanol, hexanol and heptanol on the extraction of $H_3PO_4$from syrian phosphoric acid by TBP. The results show that the alcohols have higher extraction yield than TBP diluted in kerosene. The alcohol have an important synergistic effect while they were used as diluents instead of kerosene, Extraction of uranium, fluoride , sulphate and heavy metals is relatively small[10]. Harvinderpal Singh, has developed a novel solvent extraction based on DNPPA[11]. Selective synergistic extractant mixture of an organo phosphorous acid and a neutral extracting agent ie DNPPA+TOPO or DNPPA+DBBP the process is suitable for weak and strong acids.Ahmed.A.,Abdel khalek et al[12] extract uranium from Egyptian phosphoric acid with a synergistic mixture of D2EHPA and DBBP. Uranium extraction is further subjected to a second cycle of extraction and scrubbing impurities.The uranium is finally converted to UO_3 .

Experimental:-

Materials

- The starting materials for the present work is a commercial wet process phosphoric acid (43% P_2O_5) which is kindly supplied by Polyserve for Fertilizer Company, Cairo, Egypt (from the evaporator unit after filtration).
- TBP from BDH chemical company.
- Butanol 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 . Anion exchange method is used in the present study for the analysis of phosphoric acid. This method was applied 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 the 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 into 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:-

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

Where $[P_2O_5]$ = weight percent of P_2O_5

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

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

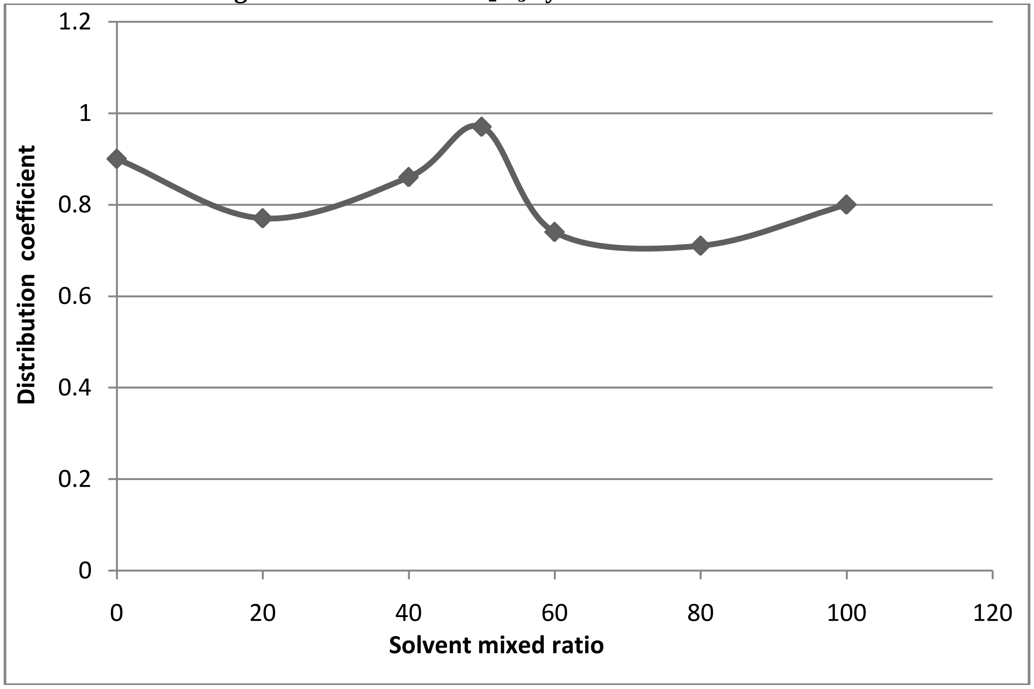
Major and Minor elements		Trace elements (ppm)	
Component	**Assay (%)**	**Component**	**Assay (ppm)**
P_2O_5	43.00	U	74
Fe_2O_3	2.80	Cr	121
TiO_2	0.025	V	101
Al_2O_3	1.08	Ni	58
CaO	7.20	Cu	11
MgO	8.40	Zn	319
SiO_2	UDL	Mo	243
MnO	0.011	Cd	U.D.L
SO_4^{--}	5.80	Pb	U.D.L
Cl^-	0.006	Co	U.D.L
K_2O	0.25	REE	626
Na_2O	0.34		
Combined water	48.09		
Total	102.05		

U.D.L = under detection limit

Extraction of P_2O_5 by mixture butanol and TBP (synergistic effect):-

Mixture between TBP and butanol indicate that the distribution ratio(D) increases due to synergistic effect between neutral alkyl phosphate(TBP) and alcohol(butanol) reaching maximum when the percent of TBP in the mixture reaches 50% and then decreases by increasing the TBP which illustrated in **Figure (1)** The decrease in the value of D by increasing the percent of TBP is due to the increase in hydrogen bond formation between reagents to percent of TBP. The obtained results also show that at 100% TBP the distribution coefficient is 0.8. However the imbedded uranium is very high i.e no selectivity on separation occurs as the amount of uranium at 100% Butanol is decreased.

Figure.1:Extraction of P_2O_5 by mixture butanol and TBP



Effect of organic/aqueous phase ratio on the extraction process:-

Different organic to aqueous phase ratio namely 1/1, 1/2, 1/3, 1/4 and 1/5 were used to get the optimum phase ratio for extraction P_2O_5 while the other extraction factors are kept as before. From the results illustrated in **Figure (2)** the best organic to aqueous phase ratio could be taken as 4:1.

Figure. 2: Effect of aqueous/organic phase ratio on the extraction process.

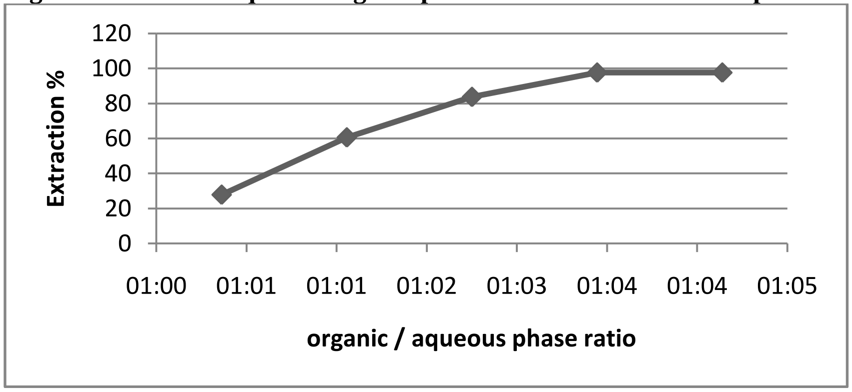


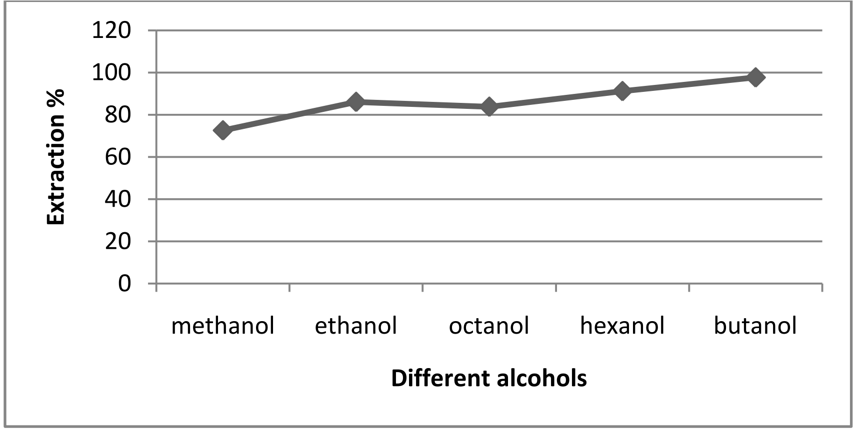
Table.2:Extraction of P_2O_5 by different solvent mixture

Mixed solvent	**P_2O_5 Extraction %**
TBP+butanol	97.6
D2EHPA+butanol	95.5
TOPO+butanol	46.9
TBP+MIBK	88.3
TEP+butanol	90.6
TEP+TBP	41.8

Table 3:Effect of different acids concentration on the extraction process.

% P_2O_5 Acid: ethanol: MIBK	**P_2O_5 Extraction %**
26	92.3
39.5	97.2
43	97.6
57	96.1

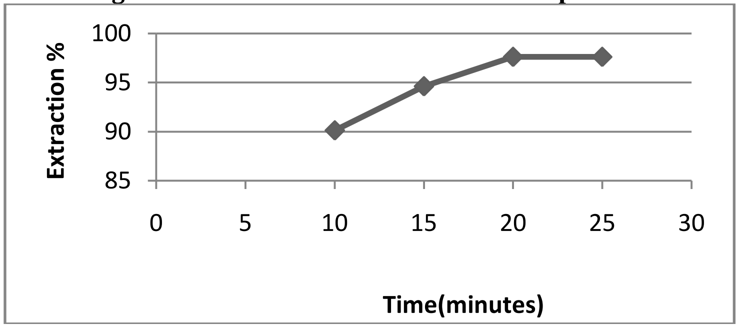
Figure.3:Effect of different alcohols on the extraction process.



Effect of contact time on the extraction process:-

The effect of contact time on the extraction process was investigated. The extraction was carried out at optimum previously determined values and at room temperature. The contact time was varied from 10 to 30 minutes. The results are represented in **Figure (4**). It was observed that the mixing time is 20 minute and this mixing time was adopted for further experiments.

Figure. 4: Contact time on the extraction process.



Effect of temperature on the extraction process:-

This effect was studied at different temperatures from (10 ºC to 60 ºC) at the previously determined optimum extraction conditions. The percent P_2O_5 extraction achieved was 97.6 i. e temp. has a slightly negative effect on the extraction of the phosphate value. therefore, it is practically to carry out the extraction process at room temperature, results are illustrated in **Figure (5).** The relation between the equilibrium constant K and the temperature is given by Van Hoff's equation:

$$D \ln K / dT = \Delta H / R . T^{2}$$

By integration

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

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

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

The results are plotted in the form of ln D versus1/T(^{0}K). The results fit a straight line equation with a slope value 0.306. Comparing the two slopes (-ΔH / R) and (0.206) it is possible to calculate ΔH = -12586 J / mol

Figure. 5:Effect of temperature on the extraction process.

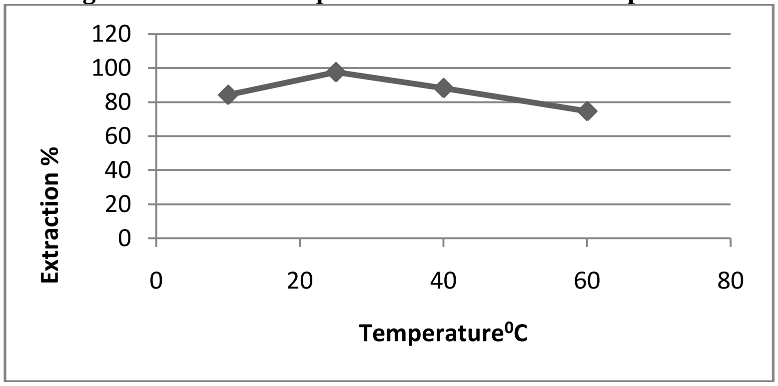
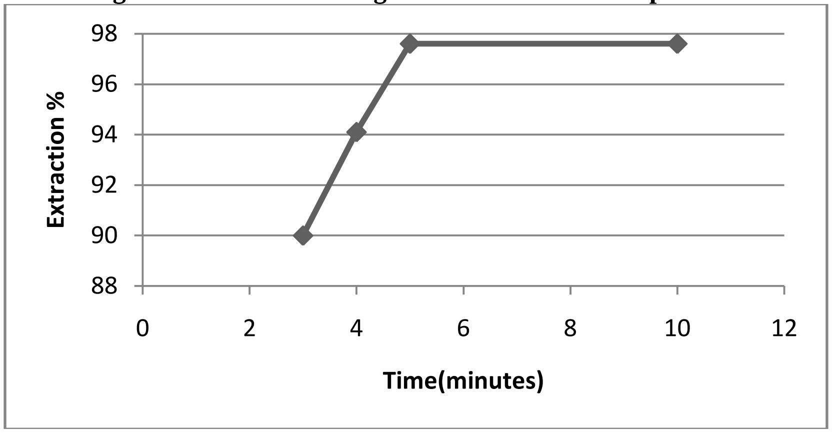


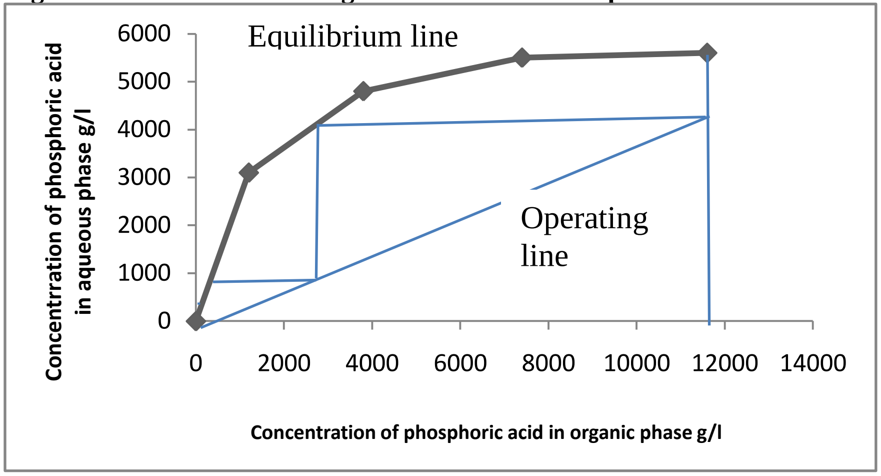
Figure. 6:Effect of settling time on the extraction process.



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 raffinate 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 (butanol:TBP) (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 constructing the extraction isotherm of P_2O_5 with an organic mixture of TBP:butanol from phosphoric acid 43 % P_2O_5, the phase ratios range from 1:4 (phosphoric acid: TBP:butanol), the extraction was carried out at the same previous conditions. The results are represented in **Figure (7)** where P_2O_5 concentration in the solvent is plotted versus P_2O_5 concentration in the raffinate.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 raffinate 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 extreme of the operating line is intersected.The separation curve (equilibrium line) is then constructed as in **Figure (7),** the next step in construction of McCabe-Thiele diagram was to try a number of operating lines. The slope equal to the ratio of aqueous/organic volumes. The theoretical number of stages could be stepped off upon the diagram in **Figure (7).** 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 4/1.

Figure. 7:Mc Cabe Thiele diagram on the extraction process.



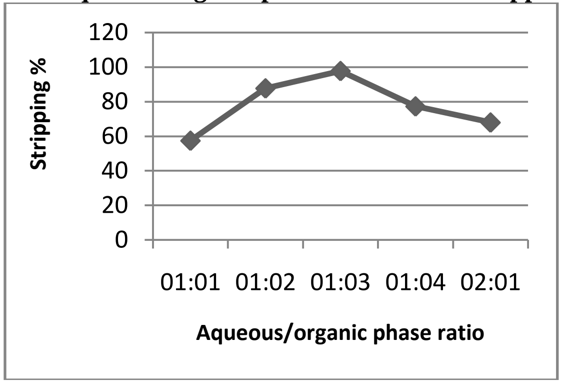
Stripping Process:-

Having determined the optimum conditions for the extraction process a stock solution about five liters was prepared for stripping at optimum condition extraction for A/O ratio 1:4 at room temperature and contact time 15 minute).

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 (8)** the best organic to aqueous phase ratio could be taken as 3/1.

Figure. 8: Aqueous/Organic phase ratio on the stripping process.



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 (4)** that distilled water can be used as a stripping agent.

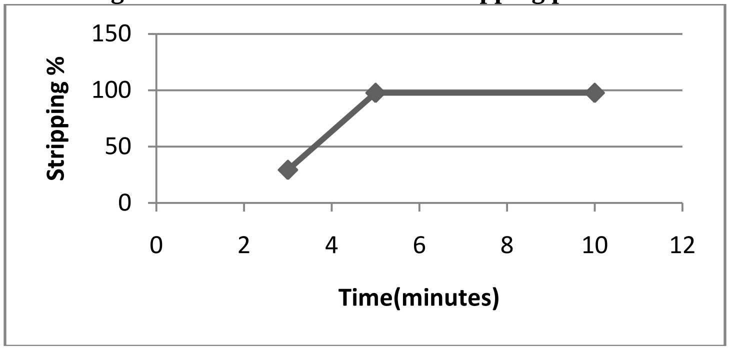
Table 4: Effect of different reagents on the stripping process.

Reagent	P_2O_5 Stripping %
Distilled water	97.6
3% diluted phosphoric Acid	94.1
6% diluted phosphoric Acid	92.3

Contact time for the stripping process:-

The effect of contact time on the attainment of equilibrium state has been studied at different time intervals from 3 to 10 minutes. The obtained results illustrated in **Figure (9).** It is clear that 5 minutes contact time is the best; whereas the settling time is about 5 minutes.

Figure. 9: Contact time for the stripping process.



Effect of temperature on the strripping process:-

The effect of temperature was investigated for stripping phosphoric acid from TBP:butanol phase at the above obtained optimum conditions while varying the temperature from 10°C to 60°C. The results are illustrated in **Figure (10)** in the form of Ln D versus 1/T (ºK). The results obtained fit a straight line equation with a slope value of 0.345. The relation between equilibrium constant K and temperature T is given by van Hoff's equation :

$$D \, Ln \, K / dT = \Delta H / R.T^2$$

By integration

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

and since the distribution ratio D is related by definition to the equilibrium constant K, the previous equation could be written:

$$Ln \, D = (- \Delta H / R)(1/T) + a$$

Comparing the two slopes (-ΔH / R) and (0.345) it is possible to calculate ΔH = -12883 J/M. The results show that the temperature has a slight negative effect on the stripping of the acid. Therefore, it is decided 'for economic reasons 'to use room temperature in the stripping process.

Figure. 10:Effect of temperature on the stripping process.

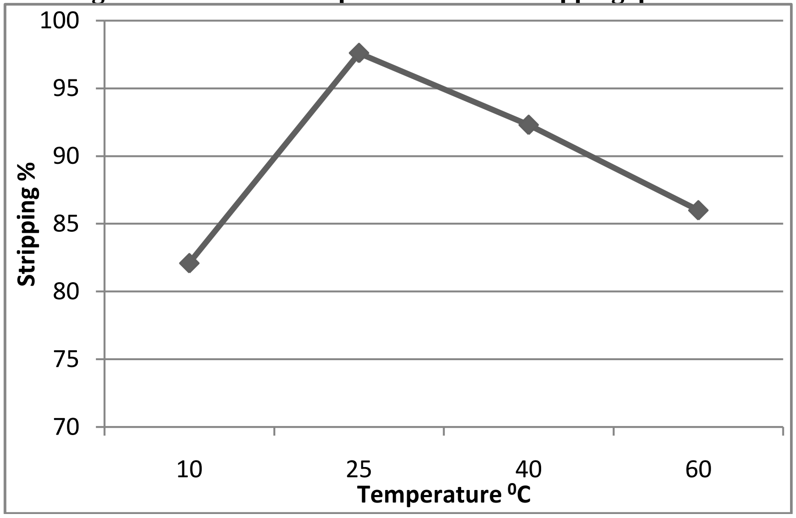
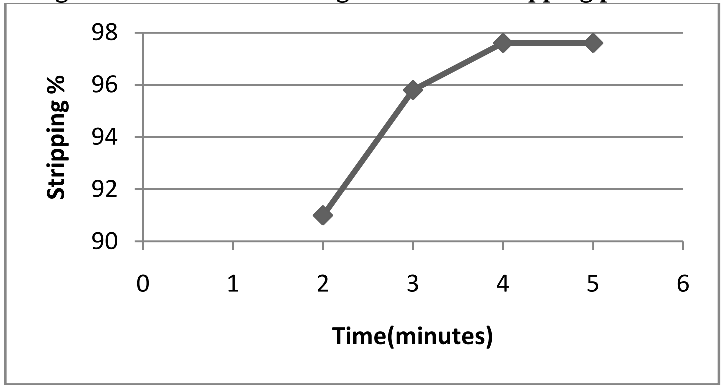


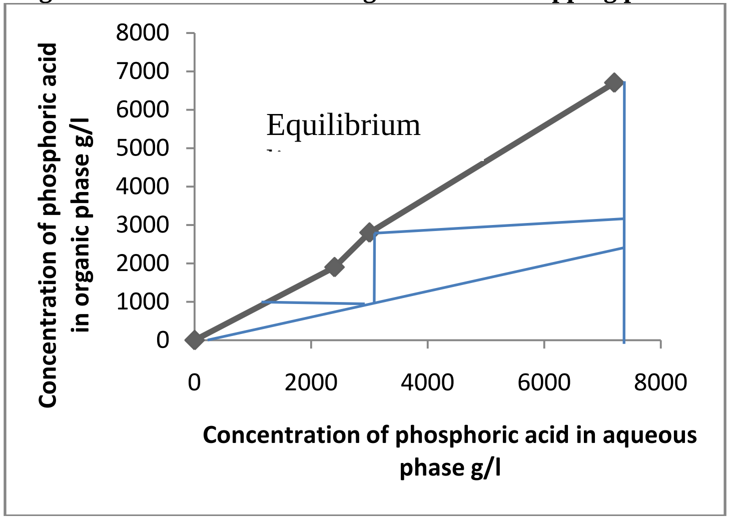
Figure. 11: Effect of settling time on the stripping process.



Equilibrium line and construction of McCabe-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 raffinate 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 in the evaluation of results. In this study, 50 gm of loaded organic (TBP:butanol) 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(TBP:butanol) is added to the separation 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 (12)** illustrate the obtained results where one stage was found sufficient for the stripping of P_2O_5 from the loaded organic/aqueous.

Figure. 12:Mc Cabe Thiele diagram for the stripping process.



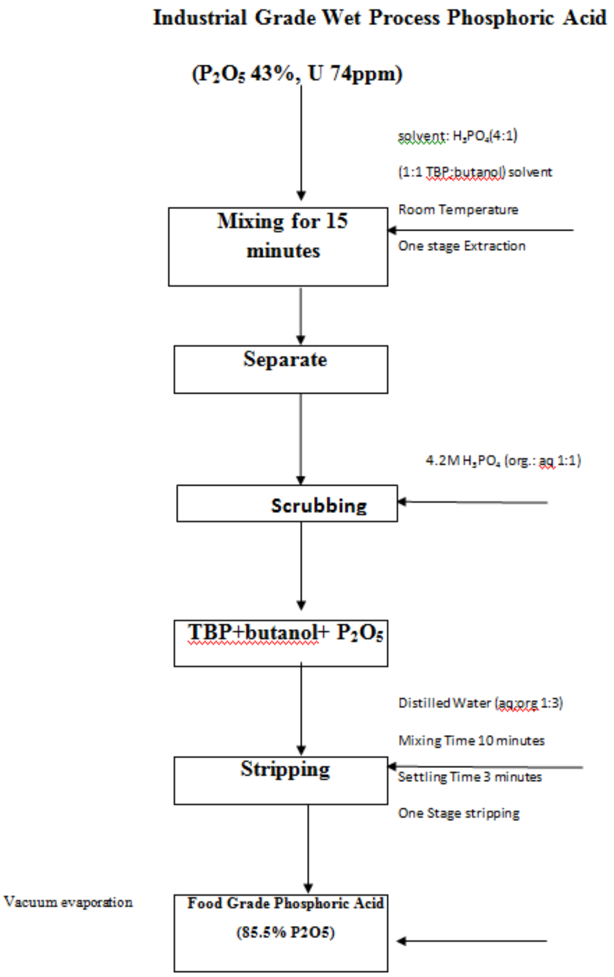
Post Acid Treatments:-

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(5).

Table (5): 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 where-as the content of volatile acid is calculated as acetic acid and is taken for its odor [13]. From obtained results relative to the international sample of food grade it is clear that complete decolorization of purified phosphoric acid wet process is obtained. Finally a technological flow sheet is elucidated Figure (13).



Conclusions:-

1. The presented approach consists of a single stage extraction using one part butanol one part TBP, then 4parts from mixture for each one part of impure acid feed (43% P_2O_5, U is 74 ppm).
2. The synergism effectTBP+butanol prove to be selective for phosphoric acid and uranium while of embodiment impurities are 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 nearly no effect on uranium extraction
5. The time of mixing has a small effect on $_{P2O5}$ weight percentage extraction which indicates that extraction is not diffusion control.
6. Stripping in one stage with distillated water at an A/O of 1:3 at a mixing time of 10 minutes and settling time of 3 minutes .

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