ABSTRACT

Purification of Industrial Phosphoric Acid by Synergistic Solvent Extraction Technique in One Step as Well as Preparation of Some Phosphatic Salts and Pure Uranium

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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 and settling time as well as 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%.

The extraction of uranium from phosphoric acid raffinate after purification by aliquateR336 in kerosene was investigated. Several factors were studied for the maximum extraction of uranium. Mainly aliquateR336 concentration, shaking time, aqueous\organic phase ratio. As well as the diluents and temperature on the extraction process. Different stripping agents were also investigated and the highest uranium extraction yields 98.4% were obtained. The uranium is finally precipitated as uranyl peroxide by hydrogen peroxide. Overall uranium recovery reached 98.4%.

Total rare earth elements is precipitated from purified phosphoric acid raffinate after uranium extraction by oxalic acid at pH 2-2.5 using ammonia then after Cerium is extracted by 15% TBP in hexane and stripped by 1.5M H_2O_2 in 0.015M HNO_3 acid. Lanthanum is extracted by 5% D2EHPA in kerosene and stripping by 1.3M HNO3 acid. Total recovery of Ce and La is 82%, 92% respectively.

Finally some phosphatic salts were prepared from the purified industrial phosphoric acid. namely sodium ammonium phosphate, sodium aluminum phosphate and potassium magnesium phosphate. The structure of each product was confirmed by means of infrared spectroscopy (FT-IR), X-ray diffraction (XRD), EDAX and complete chemical analysis. Moreover the obtained results indicate that the prepared salts matches that produced. It was found that chemical analyses of these products in close agreement with their theoretical value

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INTRODUCTION

I.1. General Outline

The necessity of very pure phosphoric acid has been increased in recent years because of its increased use in certain non–fertilizer applications, such as its use in food stuffs, animal feed additives and detergent industries. In general, phosphoric acid is manufactured by two methods. One method is the “dry method” the other is the “wet process” method. Acid produced by the dry process, has a much higher purity, essentially containing only the phosphatic values, since the phosphorus is separated from phosphate rock before acid manufacture. However, because of the large quantities of energy that are required to manufacture thermal phosphoric acid, its cost has risen considerably in the last ten years or so. Consequently a number of companies have developed techniques to replace the purer thermal acid in certain situations.Wet processed phosphoric acid is obtained on subjecting crude phosphate ores to wet-processing with a mineral acid, commonly sulfuric acid. The crude acid, which is so obtained, contains inorganic and organic impurities which originates from the phosphate ores and appear therein in variable concentrations, depending on the crude phosphates origin and it’s pre-treatment. Many of these impurities particularly are removed from the acid whatever its use, by various techniques such as clarification. Other purification techniques are employed depending on the use for which the acid is intended. For food and technical grade acid, the levels of the following impurities in the acid must be considered, calcium, magnesium, sulfate, iron , lead , cadmium ,arsenic ,uranium ,thorium , rare earths and organics. Many different techniques have been considered for purification of wet process phosphoric acid to food and technical grades. However solvent extraction has been most widely employed, forms the basis of the majority of commercially operated purification units moreover, it is easier to recover any of the valuable elements from the raffinate as an added value to the solvent extraction process.

Synergism in Solvent Extraction and Solvent Extraction kinetics

The phenomenon in which two extractants when present together, extracted species, mostly metal ions with greater efficiency than that corresponding to their additive action is called synergism. The first careful studies of this phenomenon found that U (VI) is extracted synergistically by a mixture of dialkyl- phosphoric acid and a neutral organo phosphorous reagent. **(Roshni Sarkar *et al., 2014).***

Synergistic extraction: Synergism can be defined as cooperation of two extractant molecules to transfer metal ions from aqueous medium to organic phase in order to satisfy both the solvation and co-ordination sites of the cation and neutralizes charge, while another less sterically demanding extractant or synergist may serve to replace water or to occupy open co-ordination sites. In this way two extractants cooperate to increase the extraction, which is greater than the sum values obtained with each extractant operating independently., D12 >> D1 + D2.

The synergist should have to fulfil the following conditions:

(i) It should have capability of displacing water molecules from the metal complex rendering it less hydrophilic.

(ii) It should form less stable complex than the primary ligand.

(iii) It should favour the maximum co-ordination number of the metal.

Synergism reaction may be of various types:

(i) Synergist co-ordinates with metal ion due to complete dissociation of the ligand.

(ii) Interaction between the synergist and coordinated ligand molecule.

(iii) Co-ordination of the synergist to the metal ion such that it occupies the empty coordination

Sites made available as a result of dissociation of one end of the ligand. The extent of synergism is determined by synergistic coefficient (S.C) for the combination of two extractants defined by equation S.C = log [D mix / (DI + DII)].

where D mix, DI and DII denote the distribution ratios of a metal ion with a mixture of extractants, extractant I and extractant II, respectively in binary liquid system.The extent of synergism is given by ΔD = D mix – (DI + DII).

Thus, when S.C and ΔD values are positive then it is said that synergism occurs. If both are negative i.e. extraction decreased due to combination of some reagents, the phenomenon is known as antagonism.

The synergistic extractions can be carried out with any of the following combinations of the extractants.

(i) Acidic and neutral extractants like (β-diketone, carboxylic acids,Sulfonic acids etc. which may behave as chelating extractants. the neutral donors include ketones, amides, ethers, alcohols, sulphoxides, organo phosphorous, esters, etc.)

(ii) Two acidic extractants like (two β-diketones or two organic acids)

(iii) Two neutral extractants like (ketones, amides, ethers, alcohols, sulphoxides, organo phosphorous, esters).

(iv)Anionic and neutral extractants like (mixture of amine salts which act as anionic extractants and neutral organo phosphorous extractants).

(v) Cationic and anionic extractants like (amines and cationic extractants)**.**

(vi) Two anionic extractants like (mixture of two amines).

(vii) Chelating agent and crown ether: like (mixture of picrolinic acid & benzo crown-5 in CHCl3)

(viii) Synergism in RTIL: Extractions of alkali & alkaline earth cations by crown ether at room temperature. Ionic liquid (RTIL) have been carried out and synergistic effects in the facilitated transfer of metal ions in to RTIL is observed. This results minimum amount of disposable waste.

(ix) Miscellaneous combination : The enhancement of extraction efficiency was observed whenextraction of copper(II) was carried out with bidentate mono-schiff base extractants(HL), namely, NNsalicylideneaniline (SA), N-(2-hydroxy- 1-naphthalidene)aniline (HNA), N-salicylidene-1-naphthylamine (SN), and N- (2-hydroxy-1-naphthalidene)-1-naphthylamine (HNN), from a weakly acidic sulphate media into chloroform in the presence of acyclic polyether non-ionic surfactant Again, when lanthanides (III) were extracted with HTTA and Cu(Saltn) [Saltn = N Ndisali cylidene trim ethylene diamine] a large synergistic effect was observed into chloroform due to formation of binuclear complexs.

(x) Self-adducts: If the system does not contain any donor molecule *B*, the water of hydration may be replaced by undissociated HA (assuming the ligand A− to be a dissociation product of HA), at least at high HA concentrations; the MA*z*(HA)*x* complexes are refered to as *self-adducts*. Such type of extraction was first noted during the extraction of Sr^{2+} with 8-hydroxyquinoline in CHCl3 and species was identified as Sr(A)2 2HA. Recently this type of extraction on the transition divalent metal (like Cu (II), Co (II) and Ni (II)) by Schiff base salicylideneaniline (SAN) in chloroform from aqueous sulfate medium have been reported.

Pathways of synergism: The phenomenon have been reported of synergistic extraction of mixed ligand complexes has been explained in terms of the enhancement of hydrophobic character of extracted complex at first the metal ion is coordinated by the ligand and if the coordination number of the metal ion is not fulfilled then water molecules enter into inner sphere. Later the water molecules are replaced by the addition of donor. In other cases, an expansion of the coordination sphere of the metal ion takes place in order to allow bonding with the donor molecules. Alternatively, the second ligand or donor is attached to the metal-chelate complex via hydrogen bonding with the water molecules of metal chelate complex, e.g,

M (L) 2(H2O) 2 + (donor) = M (L) 2(donor) (H2O) + H2O (Replacement of water from inner sphere)

M (L) 2(H2O) 2 + (donor) = M (L) 2 (H2O) 2(donor) (Expansion of co-ordination shell of metal e.g, rare earths)

M (L) 2(H_2O) $_2$ + (donor) = M (L) $_2$(HO—H—donor) (Hydrogen bonding) Assuming the metal ion is hexa coordinated in simple aqua complex ML2 (H_2O) $_2$, where L= bidentate ligand. Formula and structures may vary from system to system but basic idea of incorporation of donor into ternary adduct is the same and can take place either of the alternate pathways. **(Roshni Sarkar *et al.*, *2014*).**

PARAMETERS CONTROLLING SYNERGISM

(a) Role of bases or synergists

(b) Role of ligand

(c) Temperature

(d) Diluent effect in synergistic extraction

(E) Kinetics of synergistic solvent extraction

In Egypt, the first commercial plant of wet process phosphoric acid by the dehydrate process (Norske-Hydro Fission process) using Sebaiya ore, has come into stream in late 1984 year by Abu Zaabal Fertilizers and Chemicals Company. The nominal production of this plant is 600,000 ton P_2O_5. In the Norseke-Hydro fission dehydrate process, the input ore should be ground so that 65% of it passes-100 mesh size, the temperatures of the reaction of sulfuric acid with the ore should be between 80°C-82°C while the filtrate acid temperature should be between 56^{o}C-70°C. The free amount of the sulfuric acid should be between 3% and 5%. The produced dilute acid 30% could be concentrated to 45.50% by an evaporator whereby most of the impurities, namely fluoride are precipitated **(Moldovan et al., 1969).**

I.2 Literature Survey

There are many methods used to purify phosphoric acid from impurities such as solvent extraction, solvent precipitation, indirect purification, clarification, ion exchange **(Mcullougteh, 1976)**.

I.2.1 Purification of wet process phosphoric acid by organic solvents

The use of organic solvents has probably received most attention for the purification of wet process phosphoric acid; they may be used in either of two ways for extraction or precipitation.

In the former technique wet process phosphoric acid is brought into initial contact with a practically or substantially water immiscible organic solvent, into which a majority of the phosphoric acid is extracted. After the two phases have been separated, the aqueous phase or raffinate, which contains some phosphoric acid and most of impurities, can be used for the manufacture of fertilizer such as single super phosphate. The organic phase, however, contains very few of the impurities and the phosphoric acid that is subsequently re-extracted from the solvent and has a much higher purity than the original acid **(Blumberg, 1971).**

Obviously the process is not that simple, though it is necessary for example to ensure that all the solvent is recovered from both the raffinate and the purified acid. But there are two aspects that are of major importance: choice of solvent and the impurities present in the acid. In the later technique a water miscible solvent, usually with an alkali metal or ammonium ions, is mixed with the acid and tends to through many of soluble impurities out of solution. A considerable amount of solvent has been studied, as an extractant of wet phosphoric acid, to be purified by using partially immiscible solvents including alcohols, esters, ethers, ketones, and amines **(Randa M. El Rakiby, 2005).** The rejection of cationic impurities is marked, moreover when operating with a concentrated acid feed the selectivity is poor. When ethers are selected as solvent, the effect of temperature is very important, while with alcohols and ketones it is not important.

I.2.1.1 Purification of wet process phosphoric acid by ethers

The results obtained when studying the purification of wet process phosphoric acid with dibutyl ether are reported **(Marcilla et al.,**

1989). Percent PA and impurities; Fe, Al, Mg, SO_4^{2-} and F^- extracted into the organic phases are given. The variation of the percent extracted into the organic phase for the different components has been studied as function of the phosphoric acid weight percent in the organic phase. Results have been compared with those corresponding to other solvents previously studied. Dibutyl ether shows good purification behavior on metallic impurities and SO_4^{2-}, but it seems to be not very suitable for F^- purification due to its high F^- extraction capacity.

Solubility and liquid-liquid phase equilibrium data have been determined for the ternary system water-phosphoric acid- isobutyl ether at 25ºC. Data for the bimodal curve have been obtained by analyzing the phosphoric acid percentage in both organic and aqueous phases. The phosphoric acid extraction of dibutyl ether has been compared to that of several solvents previously studied showing that dibutyl ether has a phosphoric acid extraction capacity similar to propyl ether and lowers than isoamyl alcohol **(Marcilla et al., 1989).**

At low temperature the isopropyl ether extracts substantially more P_2O_5 than at higher temperature. The impurities distributing ratio between the extracted organic phase and the residual acid phase in this solvent is very advantageous since very few impurities go over to the organic phase together with the P_2O_5 and this is substantially less than for an alcohol –type solvent having 5-6 carbon atoms. P_2O_5 extracted from acid by mixed solvents formed by 95% to 50% isopropyl ether and 5% to 50% tributyl phosphate by volume at temperature of 10ºC and one volume of phosphoric acid extracted with four volumes of used solvent. The P_2O_5 is re-extracted from the organic phase by water **(Wilhelm, 1976).**

I.2.1.2 Purification of wet process phosphoric acid by tributyl phosphate (TBP)

Purification of wet phosphoric acid was studied by liquid-liquid extraction with a mixture of diisopropyl ether (DIPE) and tributyl phosphate (TBP) in kerosene dilent **(Davister and Peterbroroeck, 1982).** Two thirds of P_2O_5 were extracted in four counter current stages at 5-25°C. Sulfate was removed from the acid by adding fine phosphate powder while fluoride was removed by adding silica during concentration of the acid by evaporation in vacuum. The pure phosphoric acid was recovered from the solvent by stripping with distilled water under higher temperatures. The color was adjusted by active carbon. Extraction, scrubbing and stripping of phosphoric acid from the Syrian wet phosphoric acid was carried out using micropilot plant of mixer-settler type of 8L / h capacity. Tributyl phosphate (TBP) /di-isopropyl ether (DIPE) in kerosene was used as extractant. Extraction and stripping, equilibrium curves were evaluated. Detailed flow sheet was suggested for the proposed continuous process. The produced phosphoric acid was characterized using different analytical techniques as food grade **(Shlewit and Alibrahim, 2008).**

Liquid liquid solvent extraction technology is used in several industrial processes such as petrochemical processing, pharmaceutical production, food and hydrometallurgy. It is successfully applied for purification of wet phosphoric acid with fairly good purification performances. The purification process is basically carried out in three steps: extraction, washing and recovery, each of these steps is a liquid liquid extraction operation. The aim was was develop a computer code that helps predicting the overall performance of purification process for agivnen set of operation conditions. The adopted approach is based on determining the necessary theoretical stages for each step purification process using a numerical technique. Some simulation results for the WPA purification process with TBP at 450C, MIBK at 25^0C and a mixture (TBP+MIBK) at 30^0C are presented**. (Hamdi and Hannachi, 2012).**

Strong wet process phosphoric acid is pretreated and extracted with 80% of tributyl phosphate (TBP) and 20% of saturated hydrocarbon by volume **(Lanoe et al., 1992).** In counter-current extraction at ambient temperature.

Extraction with tributyl phosphate (TBP) is one way of purifying phosphoric acid. The distribution of phosphoric acid between the organic and aqueous phases in the system H_3PO_4-Fe_2O_3-H_2O-TBP and H_3PO_4-Al_2O_3-TBP was investigated at 295°K. An equation was developed for the phosphoric acid distribution coefficient. The empirical phosphoric acid distribution coefficient depends on the concentration of Mg (II), Fe (III) and Al (III), impurities in the solution **(Konyakhina et al., 1991).**

The synergistic effect of some alcohols such as isoamyl alcohol, pentanol, hexanol and heptanol on the extraction of H_3PO_4 from Syrian phosphoric acid by (TBP) was studied. The possibility to use these alcoholic compounds as a diluent, instead of kerosene was also studied. The results show that the alcohols have higher extraction yield than (TBP) diluted in kerosene. The alcohols have an important synergistic effect, whenever they were used as a diluent instead of kerosene. On the extraction of H_3PO_4 by (TBP) they have a higher extraction yield and a quicker phase separation compared with kerosene. Extraction of uranium, fluoride, sulfate and heavy metals by these reagents is relatively small **(Abdulbake and Shino, 2004).**

Liquid-liquid extraction is a widely used unit operation in separation processes. It is present in all chemical, biochemical and food processing industries. This Technique has long been used for purifying the Wet Process Phosphoric Acid (WPA) with fairly good purification performances. The purification is carried out in three step Process: extraction, washing and recovery. Each of these steps is a liquid-liquid extraction operation. Because of the complexity of such operations, the choice of the best operating conditions has been a challenging task for engineers. In the present work, the simulation of the WPA has been conducted. The aim was to develop a computer code that helps predicting the overall performance of the purification process for a given set of operating conditions. The adopted approach is based on determining the necessary theoretical stages (NTS) and the contents of acid and impurities in the two phases for each step in the purification process using a numerical technique. The results of the simulation of the WPA purification process by the Tri butyl Phosphate (TBP) is shown by **(Rania and Hannachi, 2012).**

I.2.1.3 Purification of wet process phosphoric acid by Methylisobutylketone (MIBK)

MIBK was used for purification of phosphoric acid from major impurities of (Ca^{2+}, Al^{3+}, Fe^{3+}, SO_4^{2-}, F^-). Distribution of phosphoric acid (PA) and impurities as well as selectivity of MIBK for P, have been studied as a function of phosphoric acid concentration in the organic phase. The results are compared to other solvents (isoamyl alcohol, dibutyl ether and dipropyl ether). MIBK seems to have the best selectivity for phosphoric acid against SO_4^{2-}, and it shows an intermediate behavior between those of isoamyl