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## Overview on the Removal of Iron from Phosphoric Acid: A Comparative Study

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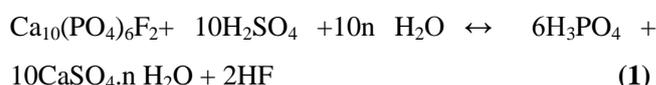
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### ABSTRACT

Wet process phosphoric acid (WPA) represents the main route for phosphate fertilizers world's production using sulfuric acid as leaching agent. The produced acid is contaminated with various metal ions as iron, aluminum, cadmium, arsenic, uranium, etc. that limit its use in metal finishing, food, cosmetics and electronic industries. Hence, purification of the wet phosphoric acid is a challenge task. The presence of high concentration of iron in phosphoric acid leads to many problems that affect the production process as increasing the viscosity, decreasing the filtration ration rate, formation of precipitates during concentration, clarification and storage, P<sub>2</sub>O<sub>5</sub> loss in addition to decreasing the solubility of fertilizers, The present review gives an overview on the removal of iron from crude phosphoric acid by some commonly used techniques including precipitation, sorption and solvent extraction to evaluate the efficiency and drawbacks of each process. The pre- treatments of phosphoric acid are also discussed.

### INTRODUCTION

Pure phosphoric acid is used in many applications as metal finishing, food products, detergents and pharmaceuticals. The world production capacity for phosphoric acid reaches about 33 million per year tons of P<sub>2</sub>O<sub>5</sub>. ninety percent per year of the world P<sub>2</sub>O<sub>5</sub> consumption participates in the fertilizer industry [1, 2]. The major of phosphate ores are sedimentary rocks which are composed of apatite in addition to fluorides, carbonates, clays, quartz, silicates, and metal oxides and are found in Morocco, Egypt, Jordan etc., and may be found also in igneous sediments in Russia, Brazil, South Africa, etc. [3] Phosphoric acid can be manufactured by three processes namely, wet, thermal and dry kiln process. Wet process (WPA) is the most common method for phosphate fertilizers production, thermal process gives higher purity and is used in non fertilizer products, rotary kiln process is a promising method as it reduces the environmental footprint [4]. In the wet process, the mineral is treated with mineral acids that may be nitric, hydrochloric or sulfuric according to:



Globally, most of phosphoric acid is manufactured by the wet process using sulfuric acid as leaching agent that has the advantage of forming an insoluble precipitate of calcium sulfate dihydrate (phosphogypsum, (10CaSO<sub>4</sub>·2H<sub>2</sub>O)) in addition to radionuclides and lanthanides that are coprecipitated [5-8]. Three fractions of phosphoric acid are produced depending on the process conditions namely: Dihydrate acid, WPA [20-30% P<sub>2</sub>O<sub>5</sub>], Hemihydrate Acid [40-45% P<sub>2</sub>O<sub>5</sub>], Merchant Grade Acid (MGA) [50-55% P<sub>2</sub>O<sub>5</sub>] [9-11]. Fig. 1, represents a flow chart for a wet process facility.

WPA contains many impurities that depend on the origin of phosphate ores and which render the phosphoric acid unsuitable for certain uses, such as, metal treatment, food ingredients and electronic applications, therefore, it must be purified before use. Iron in particular, leads to many problems that affect the production process as increasing the viscosity, decreasing the filtration rate, formation of precipitates during concentration, clarification and storage,  $P_2O_5$  loss in addition to decreasing the solubility of fertilizers. The constituent of phosphoric acid from different origins are given in Table 1. The concentration of iron should be  $<1.5\%$   $Fe_2O_3$  as standard for fertilizer grade phosphoric

acid of  $50\%$   $P_2O_5$  [16-19]. Many trials were performed by various techniques in order to purify the WPA via precipitation [4], adsorption, ion exchange [20-22], reverse osmosis, ultrafiltration [23-28], electrodeposition [29], solvent extraction [30-32] and magnetic separation [33] The concentration of iron in phosphate rocks varies from  $0.1\%$  -  $4.0\%$  as  $Fe_2O_3$  depend on their origin [34, 35]. The present overview discusses some of the techniques used for iron removal from WPA mainly, precipitation, adsorption and solvent extraction, magnetic separation, crystallization, reverse osmosis, nanofiltration as well as electro dialysis.

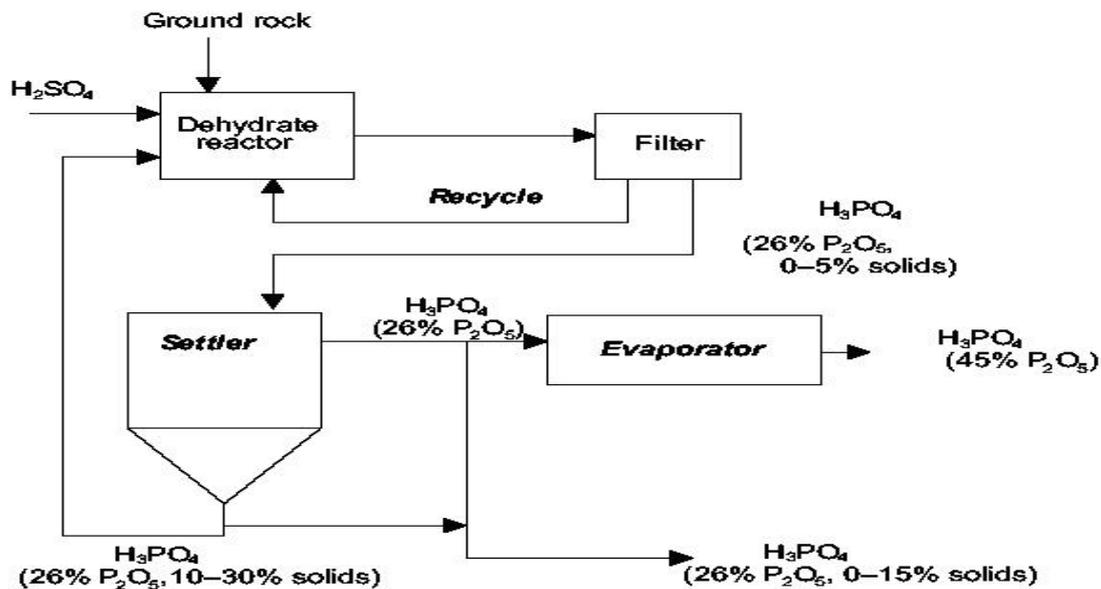


Fig. (1): Flow chart for a wet phosphoric acid process facility [12]

Table (1): gives the properties phosphoric acid from different origins [13-15]

Contents	Morocco	Togo	Senegal	Jordan	Egypt
$U_3O_8$ mg/L	260	142	215	-	55.0
$P_2O_5$ %	53.2	50.5	47.8	50-52	40.2
MgO g/L	10.8	1.5	1.9	4.1	5.0
$K_2O$ g/L	0.4	0.8	0.3	-	0.2
$Na_2O$ g/L	2.3	1.9	0.2	-	0.45
CaO g/L	-	-	0.2	0.8	3.0
$SO_3$ g/L	47.9	34.1	18.4	30.5	13.0
Fe g/L	4.4	9.3	11.6	3.01	16.6
Cl g/L	Trace	Trace	Trace	Trace	Trace
F g/L	25.6	20.8	19.7	-	50.0
Sp. gravity	1.6	1.26	1.58	1.63	1.54

### Precipitation

Precipitation is a simple, cheap and ease operation process for the removal of metal ions but its disadvantages are the formation of a large amount of sludge that is associated with disposal problems. Precipitation as sulphides has an important role in hydrometallurgy but the main advantages of sulphide precipitation are the fast reaction rates, selective metal ions removal, better settling; the lower solubility of metal sulphide precipitates and the sulphide precipitates can be recycled by smelting to more value added product [36]. The sulphide species, ( $H_2S$ ,  $HS^-$  or  $S^{2-}$ ) are dependent on the pH value. Fig.2 gives the speciation of sulphide species as function of pH of the solution.

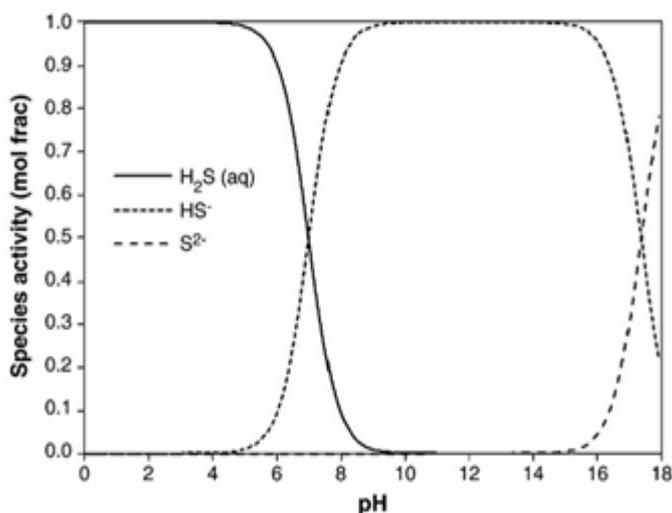
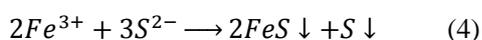


Fig. (2): Speciation of sulphide as a function of pH [36]

However, the drawback of this process arises from the difficulty in controlling the sulphide concentration and the corrosive behavior of sulphide. El-Nadi and Daoud [37] investigated the removal of iron and uranium from WPA using sodium sulphide. The removal of iron increased with increasing the sulphide concentration; the amount of sodium sulphide added seemed to be much more than the stoichiometric ratio that may be due to the partial consumption of sulphide in reaction with phosphoric acid in the form of hydrogen sulphide. The precipitation reaction can be represented by the following reaction :



On the other hand, oxalic acid exists in solution in many species ( $H_2C_2O_4$ ,  $HC_2O_4^-$ ,  $C_2O_4^{2-}$ ) depending on

the pH. The oxalic acid speciation curve is shown in Fig. 3,

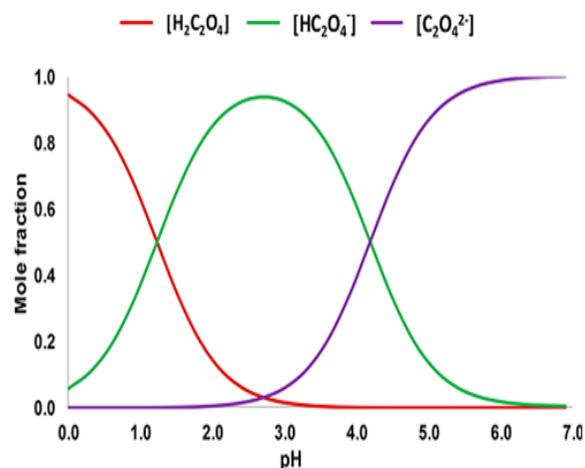


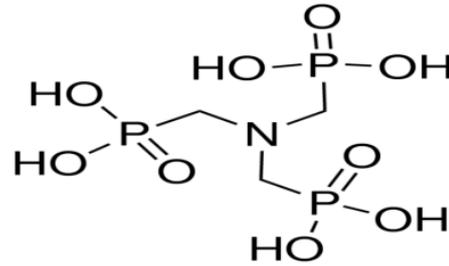
Fig. (3): speciation of oxalic acid as a function of pH [38]

Most oxalate compounds are insoluble in water, thus act as a precipitating agent for alkaline earth metals, transition elements and rare Earth elements [39, 40]. The excess of oxalate may form various soluble oxalate complexes that find numerous applications in the leaching processes for the removal of iron from illmenite [41], nickel from Greek laterite ore [42], manganese and tungsten from their ores [43, 44].

Abdel Ghafar et al., [45] reported that the removal of iron from synthetic dilute phosphoric acid (28%  $P_2O_5$ , 2.8%  $Fe_2O_3$ , 390 g/L  $H_3PO_4$ ) similar to that from the dihydrate wet process. The iron was precipitated as ferrous oxalate dihydrate ( $FeC_2O_4 \cdot 2H_2O$ ) as its solubility in phosphoric acid is (0.078 g/100 mL) [46]. It is worth note to mention that iron in phosphoric acid is found as Fe(III) and iron scrap was used to reduce it to Fe(II) prior the treatment with oxalic acid. The optimum conditions for the precipitation were 7.5 g oxalic acid/100 g; 28%  $P_2O_5$  acid at 60 °C for 2.0 hrs. The efficiency of removal reached 91.0% with less than 1.0%  $P_2O_5$  loss and oxalic acid was recovered as a precipitated calcium oxalate  $CaC_2O_4 \cdot 2H_2O$  using  $CaCl_2$ ; the precipitated calcium oxalate was then leached with hot solution of 40%  $H_2SO_4$  to recover the oxalic acid as gypsum. Amin et al., [47] discussed the removal of iron content from crude phosphoric acid of concentration, 2.6% iron using oxalic acid and potassium hexyl xanthate to give ferrous oxalate dihydrate and iron xanthate precipitates, respectively [48].

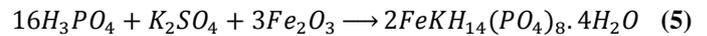
The removal of iron from WPA of 20 %  $P_2O_5$  was examined by Abdel Ghafar et al., [49]. In this respect, WPA was treated with calcium bentonite clay (11.67 g/L) with polyacrylamide type as a flocculating agent, 0.5 mg/L for 60 min. to reduce the iron content. The authors studied in details the iron removal using oxalic acid as a precipitating agent. The results showed that the removal reached 80.0% using 24.0 g oxalic acid/100-mL acid within 30 min., while the effect of temperature was found to be negligible. The removal percentage decreased on using potassium hexyl xanthate (PHX). The removal reached 59.3% of the iron content could be achieved using 0.8 g PHX/100 mL with pre-treated of WPA (44%  $P_2O_5$ , stirring time 1.0 h,  $P_2O_5$ % increases due to increasing the viscosity of the acid that may oppose the precipitation. The method was found to be promising for precipitation of iron from WPA with a negligible loss of  $P_2O_5$  without the necessity of dilution step.

Phosphoric acid containing  $> 2.5$  g/L of Al and Fe was purified with an organophosphorus reagent, nitrilo-tris (methyene) triphosphonic (NTMTP). The removal of iron and aluminum from 1.0 M WPA at ambient temperature was 99 and 85%, respectively. The precipitated organo-metallic complex was elucidated by IR and XRD analysis. The disadvantage of this process, in spite of its efficiency, is the use of relatively low acid concentration [4].



**Nitrilo-tris (methyene) triphosphonic (NTMTP).**

El-Asmy, et al., [50] discussed the removal % of iron, cadmium, copper, fluoride and organic matter from WPA of  $P_2O_5$  44% and iron 2.6% by bentonite as flocculent; the removal percentage of iron ranged from 2.7 to 19.2 % using 0.24-2.0 g of bentonite/150 mL of WPA. The removal was enhanced by the addition of potassium sulphate due to formation of Lehr's salt  $[FeKH_{14}(PO_4)_8(H_2O)_4]$



The drawback of this method is the high  $P_2O_5$  loss. Decreasing the iron content by 1.0% in phosphoric acid led to 3% loss in  $P_2O_5$ . The authors used potassium amyl xanthate that is usually used as flotation collector in the concentration of ores for minimizing the iron content by using a dose of 10.0g/L that decreased the iron to 52.4% with 0.5% loss in  $P_2O_5$ .

Removal of iron from phosphoric acid by different precipitating agent are illustrated in Table 2

**Table (2): Removal of iron from phosphoric acid by precipitation**

Precipitating Agent	Dose, g	[Fe], g/L	Clarification, Time, min.	$[H_3PO_4]$ , M	T, °C	R %	Ref
Oxalic acid	7.5/100 g acid	26.3	120.0	3.18	60.0	87.73	[45]
NTMTP	2.5/L acid	2.5	5.0	1.0	25.0	99.0	[4]
NTMTP	2.5/L acid	2.5	5.0	5.0	25.0	80.0	[4]
Sodium sulphide	35.0/100 g acid	10.0	25.0	5.0, pure	55.0	81.8	[37]
Sodium sulphide	35.0/100 g acid	10.0	25.0	5.0, native	55.0	72.8	[37]
Oxalic acid	24.0/100 mL acid	21.28	30.0	2.27	50.0	80.0	[47]
Potassium hexylXanthate	0.8/100 mL acid	40.56	60.0	5.0	25.0	59.0	[47]

### Sorption

Among purification and recycling technologies, adsorption on organic and inorganic materials is characterized by its simplicity, efficiency and applicability [51]. Factors affecting the adsorption process include pH, contact time, adsorbate-adsorbent interaction, temperature, adsorbent particle size, surface area, complexing agents, adsorbent to adsorbate ratio, and ionic strength. Generally, the sorption at initial stage is fast and this could be referred to plenty of active sites on the surface of adsorbent; after the diffusion of adsorbate from the solution to the surface of adsorbent, the reaction slow down gradually until reaching equilibrium. In this concern, the order of the sorption process can be described by various kinetic models. The pseudo-first order model is illustrated by Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (6)$$

The pseudo- second-order kinetic equation is expressed as:

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (7)$$

The intraparticle diffusion model can be represented as:

$$q_t = K_i t^{0.5} + C \quad (8)$$

Elovich model describes the activated chemisorptions, the Elovich equation is expressed as:

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (9)$$

Where,  $k_1$  is the rate constant of pseudo- first- order ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the second-order adsorption,  $K_i$  ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) is the intraparticle diffusion rate constant and C is proportional to the boundary layer thickness, constant (a) is the initial sorption rate ( $\text{mg/g min}$ ) and (b) is a constant characteristic of the process.

The effect of concentration of the adsorbate is critical where the amount adsorbed  $q_e$  increases with the increase in initial concentrations as the adsorbates are sorbed by specific sites on the adsorbents until the surface area of the adsorbent is filled [52]. Hydrogen ion concentration, PH, is a key factor affecting the sorption process as it influences the charge of both adsorbent and adsorbate. Acidic conditions where  $\text{pH} < \text{pH}_{\text{ZPC}}$  at zero point charge,  $\text{pH}_{\text{ZPC}}$ , develop a positive charge on the

surface of the adsorbent that favors higher sorption of anionic species while at  $\text{pH} > \text{pH}_{\text{ZPC}}$ , it carries a negative charge. The sorption may refer to the involvement of physical forces such as, Van der Waals force, hydrogen bonding, electrostatic forces etc. or chemical covalent bonding [53, 54]. The sorption is dependent on temperature changes, the endothermic nature of the sorption process; the increase in temperature decreases the viscosity of the solution, fastens the rate of diffusion of adsorbate molecules toward the external boundary layer of the adsorbate and facilitates the formation of surface monolayer. Moreover, the thermodynamic parameters of the sorption process can be evaluated.

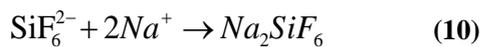
The sorption of heavy metals using natural zeolite showed high sorption capacity for iron but is very poor towards the other heavy metals as copper and lead cations. The possibility of its modification and its high acid resistance enables the sorption of heavy metals from WPA. The sorptive removal of  $500 \text{ mgL}^{-1} \text{ Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  from phosphoric acid of 20%  $\text{P}_2\text{O}_5$  (pH 2) by zeolite modified with 1.0 M  $\text{Na}_2\text{CO}_3$ , mechanically activated zeolite where the zeolite is firstly separated according to mesh size and treated with 1.0 M  $\text{Na}_2\text{CO}_3$  at room temperature. Composite sorbent based on a mixture of modified zeolite and bentonite treated with 1.0 M  $\text{Na}_2\text{CO}_3$  solution in the ratio 7:3 has been investigated. The modification of zeolite by sodium carbonate solution increased the removal percentage of iron to 60.2% within 5 min. at  $30^\circ\text{C}$ , the mechanical activation of natural zeolite showed no influence on the removal of iron while the composite (Zeolite+ bentonite) enhanced the removal efficiency [55].

Reducing the concentration of ferric ions in crude phosphoric acid ( $\text{P}_2\text{O}_5\% = 48.4\%$ ),  $[\text{Fe} = 37.5 \text{ g/L}]$  was attained using silica extracted by sodium hydroxide of rice husk after oxidation of iron(II) using hydrogen peroxide. The adsorption of  $\text{Fe}^{3+}$  ions at  $\text{SiO}_2$  interfaces is referred to the surface complex formation with deprotonated silanol groups. The data obtained fitted with Langmuir isotherm and the maximum monolayer capacity was found to be  $386 \text{ mg/g}$  [56].

Removal of iron from WPA [5 M, pH 0.6,  $\text{Fe} = 25.0 \text{ g/L}$ ] as obtained from Abu-Tarture, Egypt was investigated using natural white silica sand, of 0.2 mm size particle after washing it with 0.1 M HCl for 24 hrs. The removal of Fe(III) reached 84% with adsorbent doses  $60.0 \text{ g/L}$ . The results were analyzed by the Langmuir and Freundlich adsorption isotherms where the maximum monolayer capacity,  $Q_{\text{max}}$  was found to be  $345.0 \text{ mg/g}$ . The thermodynamic parameters showed the

exothermic nature of the process and the negative free energy values indicated the spontaneous nature of the process [57].

Awwad et al., [58] investigated the removal of iron and fluoride from WPA by silica extracted from rice husk. Firstly, the acid was treated with ilmenite clay to reduce the content of iron. The investigated silica minimizing the iron by 80%,  $P_2O_5$  loss is 1% while the fluoride reacted with silica to form  $SiF_4$  using a dose 50.0 g silica/L  $H_3PO_4$ , stirring time: 60 min at ambient temperature according to:



Ahmed et al., [59] used expanded perlite;  $SiO_2$  72.6%,  $Al_2O_3$  11.4% to investigate the removal of iron from phosphoric acid. The sorption process was performed using 50.0 g/L adsorbent with different iron concentration in the range 2-16 g/L from 7.0 M  $H_3PO_4$ , the uptake increased with increasing the initial metal concentration. The affinity of Fe(III) towards the removal on expanded perlite may be due to the deprotonation of silanol groups, Si-OH on the surface of perlite that enhances the ion exchange capacity with respect to the adsorbent. This can be explained by the following equation:



Removal of iron from phosphoric acid by different sorbents are illustrated in Table.3

### Solvent extraction

Solvent extraction is a powerful tool in separation and purification processes in hydrometallurgy. It is now commonly used in separation and purification of transition elements, rare earths, reprocessing of nuclear fuels, WPA and organic acids recovery, etc. The principle of solvent extraction separation is based on the difference in solubility of the species in two immiscible liquid phases. Solvent extraction is usually fast, simple, less expensive and lends to multi stage operation without increased consumption of heat and chemicals which make it particularly useful when either extreme purification is necessary or when the metals are so similar in their properties [60].

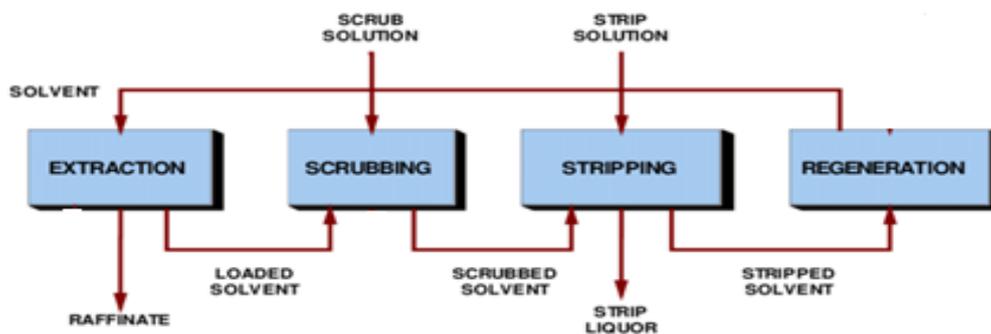
The distribution ratio (D) is calculated from the relation:

$$D = \frac{(C_o - C_e)V_a}{C_e V_o} \quad (12)$$

Where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of metal, respectively,  $V_o$  and  $V_a$  denote the volume of organic and aqueous phases. Fig.4 represents the flow sheet of solvent extraction process.

**Table (3): Removal of iron from phosphoric acid by different sorbents**

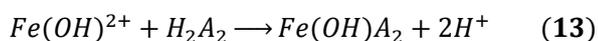
Adsorbent	Dose, g/L	[Fe] initial, %	% $P_2O_5$	T, oC	Fe Removal (%)	Ref
Bentonite	1.6	2.6	44	25	2.7	[50]
Bentonite+ $K_2SO_4$	13.3	2.6	44	25	19.6	[50]
potassium amyl xanthate	10	2.6	44	25	52.4	[50]
Modified zeolite	N/A	0.05	20	25	60.2	[55]
Natural zeolite	N/A	0.05	20	25	84	[55]
Silica from rice husk	60.0	3.75	48.4	30	87	[56]
White silica sand	60.0	2.5	52.0	30	84	[57]
Silica from rice husk	50.0	2.6	57.0	25	80	[58]
Expanded perlite	50.0	3.0	28.0	25	5.0	[59]



**Fig. (4): The flow sheet of solvent extraction process [61]**

The organophosphorus extractants are commonly used for the solvent extraction purification of phosphoric acid as di-(2-ethylhexyl)phosphoric acid (DEHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), a purified 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate, HEH(EHP), tri-butyl-phosphate (TBP), tri-n-octyl-phosphine oxide (TOPO or Cyanex 921) and Cyanex 923 which is a mixture of four trialkyl-phosphine oxides. The polarity of the phosphoryl group increases in the following order: Phosphine oxides > Phosphinates > Phosphonates > Phosphates, thus the solubility in water decreases in the same order [61] also, tertiary amines [19, 62, 63], sulphoxide [64-66] and alcohols [67- 69] were investigated.

The extraction of iron using HDEHP was investigated in the concentration range 0.005-0.1 M. The extraction of iron increased up to 0.05 M then became constant until it reached 0.08 M or above. The slope analysis method indicated that 3.0 moles of extractant are attached to one mole of iron [58]. Meles and Prostenik [70] proposed the mechanism of interaction between iron and HDEHP from phosphoric acid where Fe(III) hydrolyzes in aqueous phase then reacts with the extractant according to:



TBP as a neutral extractant is extensively used in WPA purification. In this concern, the extraction of WPA [5.0 M, Fe(III) 5.67 g/L] by undiluted TBP. The equilibrium was obtained after 30.0 min. then the extraction decreased with further increase in shaking time and extraction of Fe(III) increased with increase in TBP in the range 0.366 M to 3.66 M in kerosene [71].

The extraction of Fe(III) from WPA [5.0 M] by 0.2 M Cyanex 921 was studied in the range 5.0 to 60.0 minutes. The equilibrium was obtained after 20 minutes then decreased with further increase in the contact time and also increased with Cyanex 921 concentration in the range 0.05 M to 0.2 M in kerosene. The effect of isoamyl alcohol (iA) concentration was also investigated in the range 1.0 - 9.0 M; the extraction of Fe (III) was found to increase also with the increase in iA concentration and the extraction was found to be endothermic in the range of 10 to 45 °C [72].

Amin et al., discussed the use of aliphatic alcohols as n-butanol, n-hexanol and n-octanol for the recovery of impure H<sub>3</sub>PO<sub>4</sub>, 9.2 M. The recovery of phosphoric acid was 86%, 94% and 87% within 3.0 stages using butanol, hexanol and octanol, respectively while iron and other

cations were almost unextracted [73]. Li et al., investigated the extraction of phosphoric acid in addition to the interfering cations and anions that are commonly contaminating industrial WPA (56%) using TBP and cyclohexanol mixture. The results show that the acid was extracted efficiently and the cation impurities: Fe<sup>3+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, had higher separation factors than anion impurities F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> did. The values of the enthalpy change of extraction for Fe<sup>3+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> were 5.54, 24.54, 22.48, 18.84 and 7.40 kJ mole<sup>-1</sup>, respectively, indicating that the extraction of these impurities was endothermic [74].

The extraction and stripping investigation of 1.0 g/L iron (III) from 2.0 and 6.0 M phosphoric acid with D2EHPA alone and its mixture with 0.375 M TOPO and/or 0.2 M TBP were investigated [75]. In HDEHP system, the extraction of iron (III) decreased with increase in phosphoric acid concentration and this may be due to cation exchange mechanism. The presence of TOPO or TBP with D2EHPA showed antagonism. The extraction of iron (III) with D2EHPA alone and its mixture with either TOPO or TBP was found to be exothermic. The stripping of iron (III) using different mineral and organic acids indicated that the stripping was efficient using oxalic acid and found to be endothermic independent of the type of the reagent used. It is worth to mention that D2EHPA is found as a dimer in aliphatic diluents (H<sub>2</sub>A<sub>2</sub>) [76].

Singh et al., studied the stripping of iron (III) from a loaded mixture of 1.5 M D2EHPA + 0.2 M TBP + 10 g/L Fe(III) at (O/A) = 1. The stripping efficiency decreased in the following order : (COOH)<sub>2</sub> > (COO)<sub>2</sub>NH<sub>4</sub> > HCl > H<sub>2</sub>SO<sub>4</sub> > glacial CH<sub>3</sub>COOH while four stages were found to be efficient for stripping of iron from the loaded extractant that comprised 1.5 M D2EHPA + 0.2 M TBP + 14.8 g/L U<sub>3</sub>O<sub>8</sub><sup>+</sup>, 1.12 g/L Fe (III) + 1.0 g/L total REEs with 7.5% oxalic acid at (O/A) = 3 [77].

El-Khaiary [78] investigated the extraction of Fe(III) from 2.3 M phosphoric acid solution by didodecyl naphthalene sulphonic acid (HDDNSA). It was found that the extracted species were Fe(DDNSA)<sub>3</sub>, and FeHPO<sub>4</sub>-DDNSA. Both the ferric and its phosphate complex were extracted with HDDNSA, and the two complexes FeR<sub>3</sub> and FeHPO<sub>4</sub>R were formed in the organic phase. FeR<sub>3</sub> solvated by one HDDNSA molecule while FeHPO<sub>4</sub>R solvated by 8.0 molecules and the results were numerically analyzed by nonlinear regression.

Mahmoud and Qahtani [19] studied the effect of chloride medium on the extraction of Fe(III) and Cd(II) from 30% H<sub>3</sub>PO<sub>4</sub> contaminated with 3% Fe and 40 mg/L Cd using 20% trioctylamine (TOA) as extractant in presence of 10% octanol as phase modifier. The extraction of the two metal ions was found to be negligible in absence of chloride ions and it sharply increased by increasing HCl concentration in the range 1-3% HCl. More than 98% of Cd<sup>2+</sup> and Fe<sup>3+</sup> were quantitatively extracted under the experimental conditions. The extraction can be referred to the formation of anionic chloro- species, the speciation of Fe(III) in chloride medium is illustrated in Fig. 5. The reaction mechanism for the extraction of iron is referred to ion exchange mechanism according to:

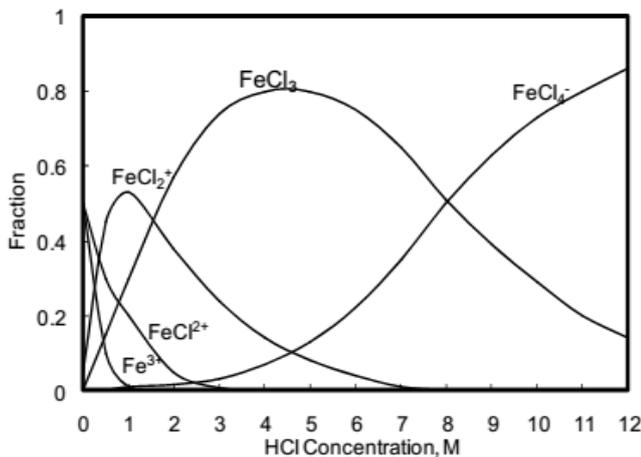


Fig. (5):.Speciation diagram of Fe<sup>3+</sup> at different HCl concentrations [19].

The solvent extraction of Fe<sup>3+</sup> from phosphoric acid in presence of chloride ion by D2EHPA in kerosene was studied. The extraction equilibrium was attained after 3 min. The extraction process was exothermic. The extraction of Fe<sup>3+</sup> increased with increase in D2EHPA concentration and decreased with phosphoric acid, calcium chloride and Fe<sup>3+</sup> concentrations. The extracted species was proposed to be FeClA<sub>2</sub>.4HA.D2EHPA. The extraction efficiency of Fe<sup>3+</sup> extraction either from the synthetic and actual HCl-route phosphoric acid reached 98.61 and 96.50% within 3 extraction stages and quantitative stripping was attained using 6.0 mol/L HCl [79]. Removal of iron from phosphoric acid by different organic extractants are illustrated in Table.4

#### Magnetic Separation

Magnetic separation is generally used to separate paramagnetic material from diamagnetic matrix. In magnetic filtration, a diamagnetic liquid containing magnetic particulate is passed through a magnetic steel wool where the magnetic particulate is entrapped. Chelating agent- coated paramagnetic were developed for the selective separation of metal contaminants as cesium, strontium and transuranics. A process was

proposed to remove the paramagnetic impurities from wet-process phosphoric acid where phosphoric acid (P<sub>2</sub>O<sub>5</sub> 54 %) suspension was passed through a hydrocyclone, the underflow portion was the solids and the overflow portion was the recovered phosphoric supernatant and the removal of iron reached 78.5% without any loss in the phosphate content [80, 81].

#### Crystallization

The presence of sludge in the WPA affects its quality and productivity; this sludge consists mainly, as x-compound [(Fe,Al)<sub>3</sub>KH<sub>14</sub>(PO<sub>4</sub>)<sub>8</sub>.4H<sub>2</sub>O] in addition to gypsum and hexafluorosilicates. Arlow [82] investigated the formation of sludge in the system. Many factors affected the precipitation process as agitation and adding magnesium ion as a seeding agent which increased x-compound precipitation while the addition of sodium hexafluorosilicates, gypsum or fluorosilic acid reduced the precipitation. Low acid concentration, favors the formation of iron and aluminium complexes with H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and as the acid concentration increases these complexes become less predominant. Fig. 6 gives the speciation of phosphoric acid at different pHs. The authors investigated the role of surfactants in the nucleation and crystal growth that indicates the possible absorption of surfactant on the crystal faces of the newly nucleated crystals and on the seed crystals and this caused growth variations.

#### Reverse osmosis (RO) and Nanofiltration (NF)

Gonzalez et al., [26] studied the use of reverse osmosis (RO) and nanofiltration (NF) in the purification of phosphoric. RO is suitable to purify up to a concentration of 2 M. on using SX01- RO membrane, 1800 psi, the iron concentration decreased from 4920 ppm to 10.5 ppm while on using DS5DL NF membrane, 1000 psi; the iron concentration decreased from 4920 ppm to 16.2 ppm a feed solution of concentration 7.9 M. Both systems decreased the cationic impurities but NF membranes showed a better performance than RO. The process of purification of phosphoric acid can be explained with the help of the ion exclusion model. This model considers that the ions contained into the feeding solution are rejected by the membrane, while small neutral molecules pass through it.

#### Electrodialysis

Machorro et al., [29] investigated the purification of industrial-grade phosphoric acid [P<sub>2</sub>O<sub>5</sub> = 54%] by conventional electrodialysis using a three-compartment cell with anion and cation membranes, where the acid was introduced into the central compartment. The results show that Na<sup>+</sup>, Mg<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> were reduced and the ratios of the concentration of the above mentioned ions were unchanged, also the anions as sulfates and chlorides would also migrate, i.e, electrodialysis could not purify the acid. The authors calculated the speciation of divalent and trivalent cations in the investigated acid as shown in Fig. 7.

Table (4): Removal of iron from phosphoric acid by different extractants

Extractant	Diluent	[Fe], g/L	Equilibration, Time, min.	[H <sub>3</sub> PO <sub>4</sub> ], M	T, °C	R %	Ref
1.5 M HDEHP	Paraffin	1.0	2.0	6.0	30.0	31.03	[75]
1.5 M HDEHP/0.2 MTBP	Paraffin	1.0	2.0	6.0	30.0	25.37	[75]
1.5 HDEHP/ 0.375MTOP	Paraffin	1.0	2.0	6.0	30.0	18.02	[75]
1.9 M Cyclohexanol	Kerosene	3.55	15.0	5.07	35.0	99.0	[76]
20% TOA+10% Octanol	Kerosene	30.0	10.0	6.0	25.0	86.0	[19]
0.58M HDDNSA	Kerosene	4.0	30.0	2.3	25.0	35.48	[78]
1.48 M HDEHP	Kerosene	1.68	3.0	1.45	25.0	73.33	[79]
0.3 M HDEHP	Mobil 190	2.0	10.0	5.1	20.0	23.07	[70]
0.3 M HDEHP+0.075 M TOPO	Mobil 190	2.0	10.0	5.1	20.0	23.07	[70]
0.5 M HDEHP	Mobil 190	2.0	10.0	5.1	20.0	28.57	[70]
0.1 M HDEHP	Kerosene	5.2	15.0	8.5	25.0	99.0	[37]
85.96% DBSO	-	5.5	30.0	2.27	20.0	90.54	[64]

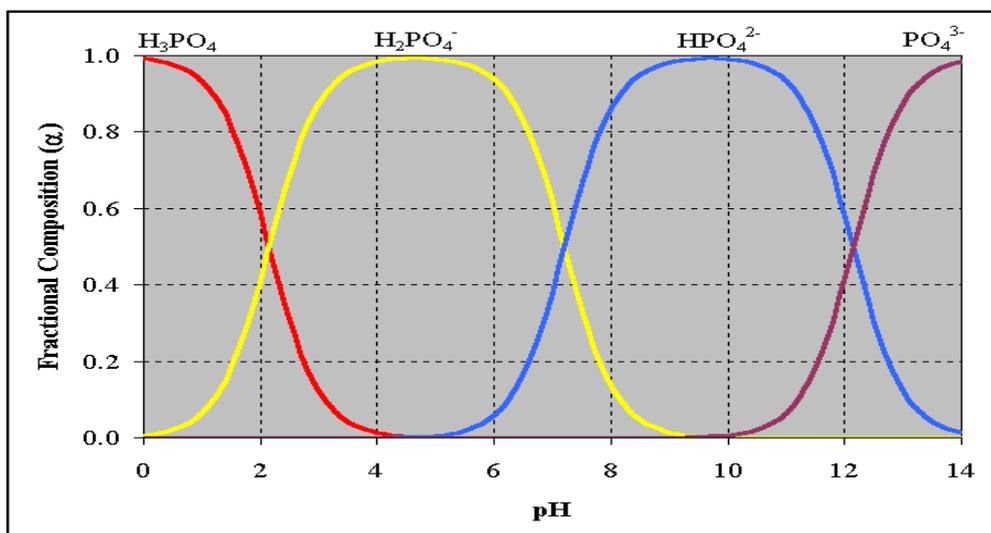


Fig. (6): The speciation of phosphoric acid at different pHs [83]

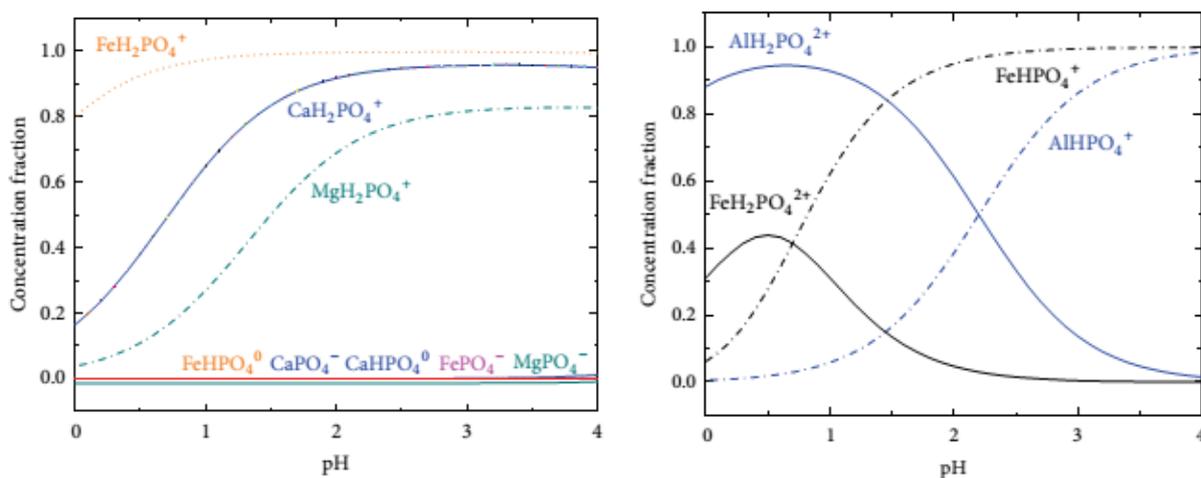


Fig. (7): Speciation of Metal (II) and (III) phosphate in industrial phosphoric acid [29]

## CONCLUSIONS AND PERSPECTIVES

The presence of iron in WPA is a technical problem, as it limits the use of phosphoric acid in several industrial sectors as food, metal finishing, cosmetics, electronics, etc., Consequently, it is essential to develop purification processes to overcome this problem. In this paper, some of the commonly used processes have been reviewed for the removal of iron from phosphoric acid, such as precipitation, adsorption, solvent extraction, magnetic separation, crystallization, reverse osmosis (RO) and nanofiltration (NF) and electrodialysis processes. These processes have been evaluated and compared based on technical aspects. For economic reasons, a low-cost technique, including modification in the existing processes based on combination of precipitation followed by adsorption and/ or solvent extraction, could be effective for removal or decrease in high iron ions concentration in WPA.

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