



Procedia Environmental Science, Engineering and Management **8** (2021) (1) 137-145

Environmental Innovations: Advances in Engineering, Technology and Management,
EIAETM, 21st-27th September, 2020

APPLICATION OF A SUPPORTED LIQUID MEMBRANE FOR THE PURIFICATION OF WET-PROCESS PHOSPHORIC ACID USING CENTRIFUGAL EXTRACTORS*

Natalya Bagnavets¹, Sergey Belopukhov¹, Margarita Ivanova^{2},
Svetlana Klimenkova², Andrey Ivanov²**

¹ *Russian State Agrarian University, Moscow, Russia*

² *Irkutsk National Research Technical University, Irkutsk, Russia*

Abstract

Application of organic solvents for the purification of wet-process phosphoric acid produced by acid decomposition of natural phosphates is one of the most common methods for obtaining purified phosphoric acid, the latter being a high-demand chemical in numerous industries. Usually, wet-process phosphoric acid is purified in cascade plants consisting of several process stages of extraction, stripping and, in some cases, extract scrubbing stage.

Membrane extraction processes offer an alternative to the conventional purification technology. They are characterized by simultaneous participation of three liquid phases in mass transfer: donor, acceptor and transport (membrane). In the process of extractive phosphoric acid purification, an organic extractant acts as a “liquid membrane” circulating between two aqueous solutions. The feed solution of wet-process phosphoric acid at the extraction stage is the donor solution, and distilled water at the stripping stage is the acceptor solution. The extractant in the membrane phase is only a carrier interacting with the extracted substance during its transport from the donor phase to the acceptor phase. The paper presents the results of application of a membrane extraction process for the purification of wet-process phosphoric acid in a single-stage plant consisting of two centrifugal extractors.

Keywords: centrifugal extractor, energy saving, extraction and purification, membrane extraction processes, phosphoric acid

* Selection and peer-review under responsibility of the EIAETM

** Corresponding author: e-mail: rita-iva@yandex.ru

1. Introduction

Orthophosphoric (phosphoric) acid (PA) is a common inorganic acid that has a wide range of applications in food, chemical, woodworking, paint and varnish and other industries due to its physical and chemical properties. It is most widely used in chemical industry as a catalyst, including for acid hydrolysis of cellulose, lignocellulosic biomass, food waste. Another important area of phosphoric acid consumption is production of mineral fertilizers for agriculture (Salas et al., 2017).

The growing demand for eco-friendly phosphate fertilizers, feed and food phosphates leads to increasing requirements to the quality of phosphoric acid as a feedstock for their production (Chashchina and Bagnavets, 2010). The high cost of production of thermal phosphoric acid (TPA) is due to the fact that the primary feedstock for the production of purified phosphoric acid (PPA) is wet-process phosphoric acid (WPPA) obtained from natural phosphate rocks (phosphorites, apatite) by decomposing them with mineral acids (e.g. sulfuric acid) (Artamonov, 2016).

However, WPPA has a significant impurity content. Some of them are solid finely dispersed substances (e.g. calcium sulfate), and others are dissolved cation and anionic impurities (Fe^{3+} , Al^{3+} , Ca^{2+} , SO_4^{2-} , F^- , etc.). The presence of these contaminants prevents using WPPA for feed and food purposes.

One of the proposed approaches of purified phosphoric acid production is the use of organic solvents for this purpose. In this case, wet-process phosphoric acid is brought into close contact with organic solvent (extractant), which is partly or completely not mixed with water and in which most of the PA is extracted. After that, the organic and aqueous phases are separated. The aqueous phase (raffinate) contains a certain amount of PA and most of the impurities, is often used to produce fertilizers, such as simple superphosphate. The organic phase (extract) contains most of the target component and a small amount of impurities. After phosphoric acid has been stripped from the extract, it has a much higher purity than the feed WPPA. The extraction and stripping phases are often separated by the scrubbing phase of the extract for additional impurity purification.

Purification of phosphoric acid with organic solvents has been becoming increasingly common across the world: it is used in France, Israel, USA, Belgium, etc. A variety of extractants and equipment are used in this process. Columns, settling mixers and centrifugal extractors are used as equipment for continuous countercurrent extraction (Grinevich et al., 2008). Various organic solvents, in particular, tributyl phosphate (TBP), a chemical that is poorly soluble in aqueous solutions of phosphoric acid, can be used as extractants. The strengths of TBP include its rather high selectivity to PA, as well as its commercial availability and relatively low cost (Nurmurodov et al., 2018).

The search for solutions to the problems of extraction, separation and concentration of substances by the extraction method resulted in the creation of processes alternative to traditional liquid extraction. Such processes make up a class of membrane extraction processes. The use of membrane technologies has made it possible to significantly reduce the number of purification stages, and at the same time to reduce the consumption of utilities. The problem of decreasing utility consumption is vital for the organization of the process of WPPA purification. This problem has not been sufficiently studied yet with respect to membrane purification technology. Thus, our assumption about the possibility of applying membrane technology for phosphoric acid purification should be considered not only in terms of purification from impurities, but also in terms of cost-efficiency indicators, one of which is low power consumption.

Membrane technologies have a great variety of applications in the chemical industry: separation, purification, changing the concentration of liquid mixtures; various laboratory tests; stripping of different volatile substances (Apel et al., 2019). Currently, a rather

superficial but already common classification of membrane extraction processes has been established. The main technology options of such processes are:

- the process with separation of the donor and the acceptor solutions by porous partition impregnated by membrane phase (Sanders et al., 2013);
- the process with separation of all three phases by porous partitions;
- the process with separation of all three phases with stabilized interphase interface in an extraction multiple emulsion (Danesi, 1984).

Membrane processes are characterized by simultaneous participation in mass transfer of the three liquid phases: donor, acceptor and transport (membrane). For this purpose, mass transfer is determined by difference of the current concentrations from the equilibrium ones in each of the components of two-phase systems. Membrane phase makes alternating (cycling) contact with donor and acceptor flows, and distribution of substance is determined exclusively by the type of isotherm of the component being distributed and the relative speed of membrane phase flow. In this case, the feed rate is limited by the rate of emulsion separation in the plant. Depending on the relative speed of the transport flow, there is a preferential transfer of one of the components of the donor flow to the acceptor flow (Cussler and Evans, 1980), where the parameter of dynamic separation is achieved.

The extractant in the membrane phase is only a carrier interacting with the extracted substance during its transport from the donor phase to the acceptor phase. Therefore, it is not necessary to demand large capacity and high distribution coefficients for the liquid membrane. The transporter extractant determines primarily the speed and selectivity of the process. The degree of substance extraction depends, first of all, on the compositions of the feed and acceptor solutions.

The equipment for carrying out such processes may include a membrane module assembled of two extraction stages of various designs (mixing and settling or centrifugal extractors of various designs).

The implementation of the membrane extraction technology offers a number of advantages compared to conventional extraction. One of the main advantages is the reduction of the number of process stages. With membrane extraction, it is possible to receive the same outcome after one stage of extraction and stripping that would require a multi-stage process with the conventional technology. Besides, by changing compositions of the phases according to the set objective, it is possible to achieve both nearly complete extraction of the target component from the donor solution and the highest possible concentration in the acceptor solution for this system.

The aim of this work is to test the possibility of using a liquid membrane for the process of WPPA purification in a single-stage plant. As of today, there is little information about the use of supported liquid membranes for PPA production.

ETs33F centrifugal extractors, which have a number of advantages in comparison with extraction columns and settling mixers, were used as the process equipment. The membrane plant is assembled of two extraction stages, see Fig.1.

In order to achieve the set aim, the following objectives were met:

- determination of the optimal phase ratio for phosphoric acid purification process for the membrane plant;
- determination of the degree of recovery of the target component (phosphoric acid) and the main impurities (sulfuric and hydrofluoric acids);
- determination of whether it is possible to use the kinetic factor to improve purification of phosphoric acid from impurities;
- determination of whether it is possible to achieve energy saving for the membrane plant as compared with the conventional cascade.

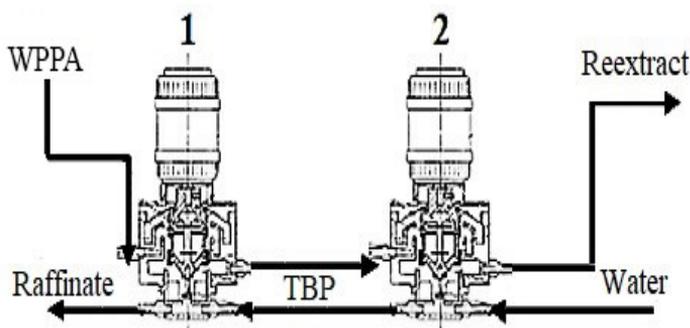


Fig. 1. Layout of a single-stage membrane plant. 1, 2 – ETs33F centrifugal extractors

2. Materials and methods

A physical experiment on WPPA purification on a single-stage extraction module with two centrifugal extractors was chosen as the main method of study. We used WPPA with reduced sulfate content (desulphated) as the feed (donor) solution with the following component concentrations: $C(\text{H}_3\text{PO}_4) = 12.32 \text{ mol/l}$, $C(\text{H}_2\text{SO}_4) = 0.10 \text{ mol/l}$, $C(\text{HF}) = 0.25 \text{ mol/l}$.

100% TBP was used as the extractant (membrane phase), and distilled water was used as the stripping solvent.

The process was organized as follows: the two machines are filled with water phase with the electric motor switched on: one machine with WPPA solution, the other one with distilled water until the water phase appears at the outlet. After that, the organic phase is supplied at a set flow rate.

The reagents consumption was monitored by the decrease of liquid in measuring cylinders every 30 minutes. The extractant circulates between two extraction units, and its level in the plant feed tank must remain constant.

At the same time, the following process parameters were monitored:

- volumes of raffinate and reextract at the outlet of the machines by means of measuring cylinders,
- temperature of solutions using a thermometer;
- density of solutions using a hydrometer.

The indicator of the process transition to the stationary mode of operation was the density levels of both raffinate and reextract remaining constant over time. After the transition of the process to the stationary mode, samples of raffinate and re-extract were taken for analysis on phosphoric acid and impurities content. This work presents the results on the content of the main impurity acids in aqueous phases, sulfuric acid (H_2SO_4) and hydrofluoric acid (HF).

Chemical analysis of raffinate and reextract composition for acid content was carried out as follows:

- phosphoric acid concentration was determined by photometric analysis by phosphorus vanadium molybdenum complex;
- sulfuric acid concentration was determined by turbidimetric analysis using 1% starch solution as stabilizer.

The optical density of the solution was determined at $\lambda = 490 \text{ nm}$ in a cuvette with the thickness of the absorbing layer $l = 10 \text{ mm}$. Distilled water was used as the blank solution.

The determination of the content of phosphates and sulfates was carried out by KFK-2 photoelectric colorimeter produced by Zagorsky Optical and Mechanical Plant (ZOMZ), Russia (instrumental error not exceeding $\pm 1\%$) (Spectrophotometer KFK). Each

measurement was performed in triplicates. The relative error of the method does not exceed $\pm 5\%$.

The determination of the content of hydrofluoric acid was determined by potentiometric analysis by fluorine selective electrode on Ecotest-2000 ion meter produced by Econix, Russia (instrumental error not exceeding $\pm 1\%$) (Ecotest-2000). The relative error of the method does not exceed $\pm 5\%$.

A certain equilibrium is established between the organic phase circulating at a certain rate and the aqueous solutions (donor and acceptor), depending on the phase composition and the membrane flow rate.

In order to write the mass balance of the membrane process, we denote the concentration of each component in the aqueous phase C_w , the aqueous phase flows Q , the concentration of the component in the organic phase C_o and organic phase flow rate V . The acceptor phase is distilled water, which does not contain any extractable components, therefore $C_{H_2} \cdot Q_{H_2} = 0$. Thus, the mass balance for the two stages of the extraction process will be represented by the following system of equations:

$$\begin{cases} C_{wH1} \cdot Q_{H1} + C_{oH1} = C_{wK1} \cdot Q_{K1} + C_{oK1} \cdot V_{K1} \\ C_{oK1} \cdot V_{H1} = C_{wK1} \cdot Q_{K1} + C_{oK1} \cdot V_{K1} \end{cases} \quad (1)$$

where:

Q_1, Q_2 are the flow rates of donor and acceptor aqueous phases, L/h;

V is the membrane organic phase flow, L/h;

C_w and C_o are the concentrations of the component in aqueous and organic phases, respectively, in mol/l.

The main parameters in the membrane process organization are the ratio of donor and acceptor aqueous phase flows $Q_{w1}:Q_{w2}$ on the one side and the ratio of organic and water flows $Q_o:Q_w$ on the other side. The optimization of these relations is reduced to obtaining reextract being concentrated as much as possible with the sufficient degree of target component extraction exceeding the degree of extraction of the main impurity acids: sulfuric acid (SA) and hydrofluoric acid (HFA) (Klinsky et al., 2002).

Acid extraction was calculated by the formula:

$$\Psi = (C_r \cdot V_r) / (C_{wppa} \cdot V_{wppa}), \quad (2)$$

where C_r is the concentration of the component in the reextract;

V_r is the volume of reextract;

C_{wppa} is the concentration of the component in the initial WPPA solution;

V_{wppa} is the volume of WPPA.

As a result of WPPA purification, we obtained PPA of "technical PPA" grade, according to the international classification (e.g. to grades established by Phone Poulenc and Prayon companies).

3. Results and discussion

We have conducted three experiences with different ratios of phase flow rates. The experimental data and the values calculated for the three experiments are presented in Table 1.

In experiments 1 and 2, different ratios of feed WPPA and reextracting water flows ($Q_{w1}:Q_{w2}$) were maintained at almost constant ratio of volumes of organic and aqueous (donor) phases $V:Q_{w1} \approx 9$. When the ratio of volumes of donor and acceptor water phases ($Q_{w1}:Q_{w2}$) increases from 1.06 (experiment 1) to 1.5 (experiment 2), the extraction rate increases by 10.7% and the concentration of the final product increases from 5.80 mol/l

(experiment 1) to 6.25 mol/l (experiment 2). At the same time, in the second experiment the concentration of the extracted sulfuric acid increases, but the concentration of hydrofluoric acid in the reextract decreases.

Fig. 2 shows the composition of reextract in terms of phosphoric acid and impurities in three experiments.

At the same time, the degree of extraction of phosphoric acid and impurity acids (Fig. 3) was higher in the first experiment than in the second one. The extraction of hydrofluoric acid in the first experiment was 2 times higher than in the second one. This can be explained by a number of reasons: first, by displacement of HFA at higher PA content in the reextract and, secondly, by entering the concentration range of the target component ($C_{H_2PO_4} = 5.6 \div 6.0$ M) where the stripping of HFA becomes the highest possible (Klinsky et al., 2003).

In experiments 2 and 3 with the same ratio of flows of the donor and acceptor phases $Q_{w1}:Q_{w2} = 1.5$ the ratio of flows of the organic and aqueous phases $V_o:Q_{w1}$ was reduced at the extraction from ≈ 9 in the second experiment to 5.8 in the third one. At the same time, the rate of PA extraction decreased (by 3.9%), as well as its concentration in the reextract (by 0.23 mol/l). The extraction of impurity acids in experiments 2 and 3 remained practically the same.

It is known that certain consistent kinetic behavior is observed in joint stripping of phosphoric acid and impurity acids with water (Klinsky et al., 2003). For experiment 1, the kinetics of acid stripping was studied on membrane plant. The results are presented in Table 2.

As it follows from the experimental data presented in the table, the transition of the target component (phosphoric acid) occurs in the first seconds of phase contact, while hydrofluoric acid somewhat “lags behind” phosphoric acid extraction and its final transition to reextract occurs after 20 to 25 seconds (Fig. 4).

It is obvious that reduction of phase contact time at stripping will make it possible improve HFA purification, as the rate of its stripping in the first 10÷15 seconds is lower than that of phosphoric acid.

Since the use of the extraction membrane plant with the use of 2 extractors gives satisfactory results for WPPA purification, conclusions can be safely drawn about energy saving for the process in comparison with the conventional 12-stage cascade of centrifugal extractors. Thus, the consumption of electric power for the membrane plant is 19 Wh per 1 kg of PPA product, while conventional extraction cascade consumes 84 Wh per 1 kg.

Table 1. Process indicators for a single-stage membrane process

Experiment no.	Feed consumption rate, mL/h			Reextract composition, mol/l			Extraction Ψ , %		
	WPPA	H ₂ O	TBP	H ₃ PO ₄	H ₂ SO ₄	HF	H ₃ PO ₄	H ₂ SO ₄	HF
1	90	85	800	5.80	0.0065	0.028	44.5	6.1	10.6
2	90	60	820	6.25	0.0075	0.020	33.8	5.0	5.3
3	90	55	520	6.02	0.0075	0.021	29.9	4.6	5.1

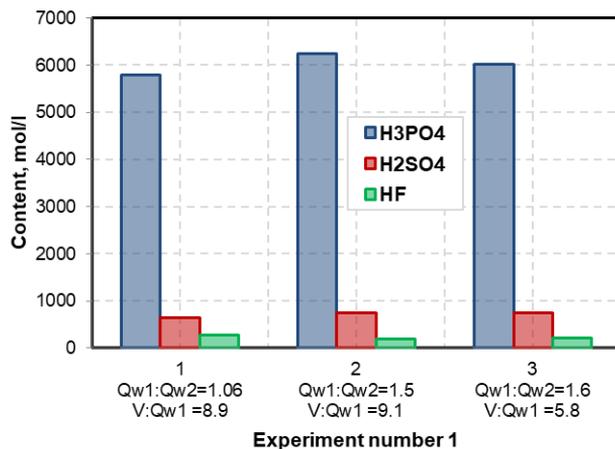


Fig. 2. Composition of reextract with the content of phosphoric, sulfuric and hydrofluoric acids (mol/l) in the three experiments

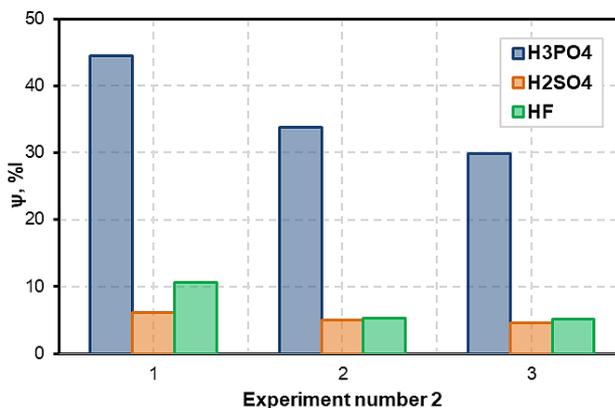


Fig.3. Extraction of phosphoric, sulfuric and hydrofluoric acids (experiment 2)

Table 2. Kinetics of phosphoric, sulfuric and hydrofluoric acids stripping

Time, s	Acid concentration in reextract, mol/l		
	H ₃ PO ₄	H ₂ SO ₄	HF
6	5.92	0.0070	0.010
9	5.90	0.0070	0.011
14	5.82	0.0068	0.020
20	5.80	0.0065	0.028
25	5.80	0.0065	0.028

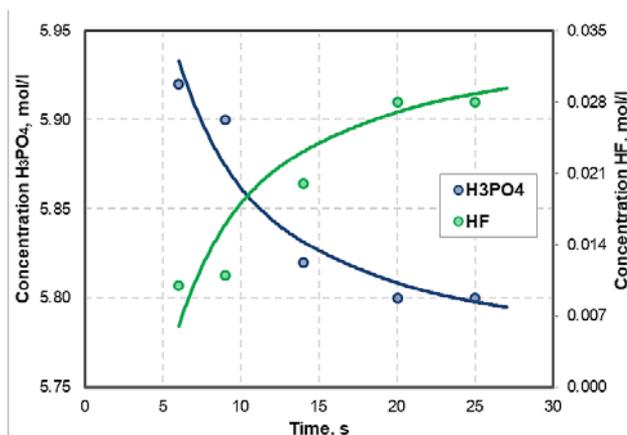


Fig.4 Comparative kinetics of phosphoric and hydrofluoric acid stripping

4. Conclusions

Among the three experiments on the membrane plant, experiment 1 should be considered to be the most successful in terms of the extraction rate of the target component (phosphoric acid) and the minimum relative content of sulfuric acid in the reextract. It is possible to improve the purification from hydrofluoric acid by keeping the phosphoric acid concentration in the reextract outside the range from 5.6 to 6.0 mol/l. In any case, the most significant purification from hydrofluoric acid occurs at the stage of reextract evaporation.

On the basis of the work performed, it can be stated that tests of membrane extraction technology options have demonstrated the effectiveness of its application for purification of WPPA. One of the conditions of the most effective purification process is the ratio of flows of donor and acceptor aqueous phases $Q_{w1}:Q_{w2}$ close to 1.

An increase of the ratio of membrane and aqueous phase flows results in an increase of the extraction rate of the target component. A decrease in phase contact time due to the increase of total flow contributes to kinetic selectivity in phosphoric acid purification, especially from hydrofluoric acid impurity.

After evaporation, the reextract of the single-stage process corresponds to the quality of Grade B of technical phosphoric acid. Phosphoric acid of this grade is used for production of reactive and food phosphoric acids, technical phosphate salts, feed phosphate fertilizers, synthetic detergents, in metalworking, textile, oil, glass and ceramic industries. It is also widely used for metal phosphating and as a catalyst in organic synthesis

The prospect of significant reduction in energy costs by using a membrane extraction plant for phosphoric acid purification is an extremely important indicator for process optimization.

References

- Apel P.Yu., Bobreshova O.V., Volkov A.V., Volkov V.V., Nikonenko V.V., Stenina I.A., Filippov A.N., Yampolskii Yu.P., Yaroslavtsev A.B., (2019), Prospects of membrane science development, *Membranes and Membrane Technologies*, **1**, 45-63.
- Artamonov A.V., (2016), An integrated approach to purification of extraction phosphoric acid obtained by sulfuric acid decomposition of apatite concentrate, (in Russian), In *Proceedings of the All-Russian Scientific and Practical Conference*, Cherepovets, Russia, 15-16.
- Chashchina E.S., Bagnavets N.L., (2010), Use of phosphoric acid purified by extraction to obtain phosphoric fertilizers, (in Russian), *News of the Timiryazev Agricultural Academy*, 151-155.

- Cussler E.L., Evans D.F., (1980), Liquid membranes for separations and reactions, *Journal of Membrane Science*, **6**, 113-121.
- Danesi P.R., (1984), Separation of metal species by supported liquid membranes, *Separation Science and Technology*, **19**, 857-894.
- Ecotest-2000, (in Russian), http://econix.com/catalog/ph-metry_ionomery_serii_ekotest-470/ph-metr_ekotest-2000-ph-m_s_kombinirovannim_ph-elektrodom-2035.
- Grinevich A.V., Kerzhner A.M., Moshkova V.G., Grinevich V.A., Kuznetsov E.M., Kiselev A.A., (2008), A method of purification of wet-process phosphoric acid, RU2323875C1, (in Russian), Research Institute for Fertilizers and Insectofungicide.
- Klinsky G.D., Kesoyan G.A., Bagnavets N.L., (2002), Co-extraction of phosphoric, sulfuric and hydrofluoric acids, (in Russian), *Izvestiya of Timiryazev Agricultural Academy*, 135-143.
- Klinsky G.D., Kesoyan G.A., Bagnavets N.L., (2003), Kinetics of extraction and stripping of phosphoric acid and impurity sulfuric and hydrofluoric acids using a centrifugal extractor., (in Russian), *Chemical Technology*, **4**, 5-9.
- Nurmurodov T.I., Tursunova S.U., Khurramov N.I., Utamurodov E.A., (2018), Study of the purification of extraction phosphoric acid obtained from the phosphorites of the Central Kyzyl Kum., (in Russian), *Universum: technical sciences*, **7**, 43-46.
- Salas B.V., Wiener M.S., Martinez J.R.S., (2017), Phosphoric Acid Industry: Problems and Solutions, In *Phosphoric Acid Industry - Problems and Solutions*, Wiener M.S., Valdez B. (Eds.), InTech, 172.
- Sanders D.F., Smith Z.P., Guo R., Robeson L.M., McGrath J.E., Paul D.R., Freeman B.D., (2013), Energy-efficient polymeric gas separation membranes for a sustainable future: A review, *Polymer*, **54**, 4729-4761.
- Spectrophotometer KFK, (in Russian), *Spectrophotometers*, <http://zomzplus.ru/catalog/laboratornoe-oborudovanie/spektrofotometriy-fotokolorimetriy/fotometr-kfk/>.