



Wet Process Phosphoric Acid Purification using Nanofiltration Membrane Technology

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ABSTRACT

Herein we report the purification of pre-treated industrial phosphoric acid using pre-modified nanofiltration membranes. We demonstrated that the prior pre-treatment steps of industrial phosphoric acid allow the elimination of sulphate, fluorine and arsenic. Further purification of the obtained pre-treated phosphoric acid using membrane cells reduce the concentrations of Cd, As, Al, Fe and rare earth elements by 94.47%, 82.35%, 99.40%, 99.64% and 96.67%, respectively. We found that this purification process relies on electrostatic repulsion between the membrane and highly charged ions and the reduction rate of metals is a cation charge dependent parameters. The laboratory and pilot scale results show that this process allows the production of food-grade phosphoric acid.

Keywords: Nanofiltration; Phosphoric acid; Membrane; Functionalization; Purification; Pilot scale

INTRODUCTION

Phosphoric Acid (PA) is the second produced acid worldwide after sulfuric acid. It is an indispensable intermediate product in the synthesis of fertilizer. In addition, it is extensively used as an additive in food, detergent and pharmaceutical industries [1]. Mainly, PA stems from the wet attack of phosphate rocks by concentrated sulfuric acid. However, industrial PA contains numerous impurities such as Fe³⁺, Fe²⁺, Al³⁺, Cu²⁺, Zn²⁺ etc. That restrict its use in food and pharmaceutical industry. Various methods have been used to eliminate or reduce those impurities. Among them precipitation, crystallization, liquid-liquid extraction and ion exchange are the most known processes. However, the use of additives and the generation of effluents limit the use of these conventional technics, promoting therefore the investigations of new green and sustainable alternatives [2]. In line with these considerations, membrane-based process, widely used in various purification processes, seems to be very interesting as it is energy efficient, needs no chemicals and is easy to scale up. However, one of the major limitations of this technology is the design and the development of stable and highly selective membrane mainly under harsh conditions *i.e.*, high temperature and low pHs.

The precipitation method is the most economical technic, but it is less selective and generates a large amount of precipitate that requires further separation procedure. G. Bone, et al. finds that PA treatment by ammonium reagents R(NH₄) during 1 h at a temperature range from 50°C-70°C, with a molar ratio of NH₄/Mg, Al/Mg and F/Mg varies between 0.5-2, 0.8-2 and 4-20, respectively, which favored the precipitation of (NH₄)_xMg_yAl_z(FOH)₆. X, Y and Z values depend on Mg, Al and F initial concentrations. The addition of fluoride F⁻ and if necessary aluminum ions at a molar ratio F/Al and Al/Mg range between 3.5-7 and 1.1-2 promotes the elimination of Mg and Al through MgAl₂F₈ and MgAlF₅ precipitation. Fluoride F⁻ and silicate Si⁴⁺ ions exists as a stable complex SiF₆²⁻ in PA are precipitated in the form of Na₂SiF₆ using sodium compound. Urea also has been used to precipitate P₂O₅ in the form of urea phosphate. The precipitation process consists of attacking 30%-50% P₂O₅ PA using 0.5% to 3% of urea in the presence of 2% to 7% NO₃⁻. The formed precipitate contains 40% P₂O₅, 4% NO₃⁻, 1% urea, 41 ppm Fe, 1 ppm As, 2 ppm Pb, 9 ppm Mg, 10 ppm F, 0.05 ppm SO₄²⁻ and 9 ppm Ca. Then a gas mixture of NO+NO₂ and air was used to treat the precipitate at volume ratio nitrous/air=108/300 in order to eliminate excess urea [3].

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Received: 17-Aug-2021, Manuscript No. JMST-24-12400; **Editor assigned:** 20-Aug-2021, PreQC No. JMST-24-12400 (PQ); **Reviewed:** 03-Sep-2021, QC No. JMST-24-12400; **Revised:** 02-Sep-2024, Manuscript No. JMST-24-12400 (R); **Published:** 30-Sep-2024, DOI: 10.35248/2155-9589.24.14.400

Citation: Khaless K, Chanouri H, Amal S, Benhida R (2024) Wet Process Phosphoric Acid Purification using Nanofiltration Membrane Technology. J Membr Sci Technol. 14:400.

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The purification of PA by crystallization and solvent extraction allows to reduce the amount of Mg, Fe and F. Although, crystallization is not suitable for industrial scale applications, since it purifies partially the PA and must be accompanied with the addition of oxidants to remove metallic and organic impurities such as calcium phosphate, chromium, cadmium and manganese. However, other crystallization processes have been developed to avoid the use of additives. The technique relies on PA (60% to 66% P₂O₅) cooling under -5°C and then feeding continuously a crystallization container to prepare crystals. Results demonstrate a high performance for this process since more than 90% of metallic (Fe, Al, Mg, etc.) and non-metallic (F, SO⁴...) impurities are removed.

Currently, Moroccan phosphate plant use solvent extraction process to purify PA. A mixture of Tri-n-Butyl Phosphate (TBP) and Isopropyl Ether (IPE) is applied in a counter current process. Afterwards, the solvent discharged and recycled with water at counter-current.

Ion exchange resins also was studied to extract lanthanides. Literature results demonstrate that Rare Earth Elements (REEs) are removed from PA and phosphogypsum by resin treatment during phosphoric acid manufacture using cationic resins with a sulfonic acid function (DOWEX C_500).

Reverse Osmosis (RO) and Nanofiltration (NF) are a downstream finishing process. Membranes technology is newly emerging the phosphate sector to purify acid and reduce metal ion impurities without reducing the PA concentration. Gonzalez, et al., demonstrate that reverse osmosis is effective at concentration lower than 2 mol/L, while nanofiltration has good performance at concentration up to 8 mol/L. However, details about membranes lifetime and performance over time has not mentioned in this study. The examination of commercial nanofiltration membranes shows that Desal KH membrane could retain 92%-95% of cooper [4].

This work presents the purification of industrial PA obtained from Jorf Lasfar PA plants using membrane technology. Unlike discussed technologies, this process relies on the reduction of the totality of undesirable impurities. The PA contains significant amount of F, SO₃, SiO₂ and wide range of metals. Typically, related to percentage weight, it contained about 1.6%-2% of SO₃, 0.5%-1% F, 0.4%-1% SiO₂, 0.1%-0.2% Al₂O₃, 0.3%-0.4% Fe₂O₃, 0.2%-0.5% MgO and some other metals at a lower level. The purification was carried out on a laboratory and pilot scale in two steps:

- Purification of PA from metals by membrane treatment.
- Concentration of treated PA up to 54% PO

MATERIALS AND METHODS

The PA (25% P₂O₅) studied in this work was provided from Moroccan phosphoric acid plant in Jorf-Lasfar. The purification process consists of two major steps.

- PA purification by modified nanofiltration membrane to remove impurities and heavy metals.

- Concentration of purified PA by evaporation.

Firstly, the membrane was washed with ethanol at least for one hour, then compressed at 40 bar prior to the modification step. The functionalization of the nanofiltration membrane NPS36 (4 inch spiral diameter with a molecular weight cut off "MWCO" of 1000 g/mol) chemically stable in concentrated PA was conducted by a deposit of a high molecular weight polycationic polymer of polyethylimine. The adsorption step was carried out at a temperature of 60°C under 10 bar within a solution of polymer containing 250 ppm polyethylimine. The hydraulic permeability (L_p) of the modified membrane varies between 20 and 40 L/h/m² at 40°C [5].

The membrane chamber in NF cell is made of spiral 316L stainless steel. NF standard circulation speed and transmembrane pressure at ambient temperature are 600 L/h and 30-40 bar, respectively. Figure 1 shows a schematic representation of the experimental setup.

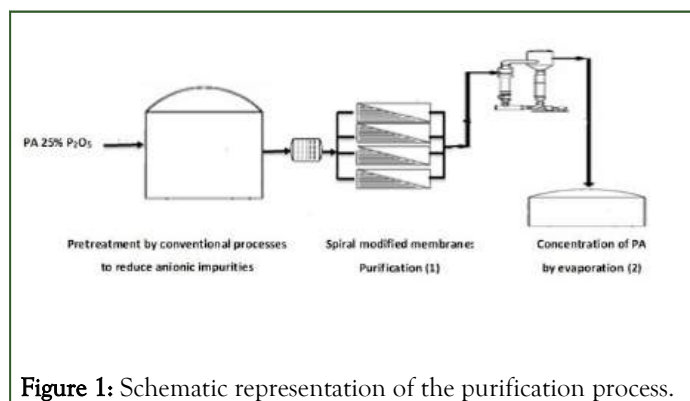


Figure 1: Schematic representation of the purification process.

The extraction of permeate was performed in a continuous mode and the reduction rate of each species is calculated by the follow equation:

$$ABT (\%) = \left(1 - \frac{C_p}{C_i}\right) \times 100$$

Where, C_p and C_i are the concentration of impurities in permeate and raw solution, respectively.

RESULTS AND DISCUSSION

The quality of PA depends on impurities in the phosphate ore. The mineral compositions present in the PA were determined (Table 1). The major elements content in PA are phosphorus, fluoride, silica, sulfate, iron, aluminum, calcium, magnesium, potassium and sodium. In addition, other trace elements such as cadmium, copper, manganese, chrome, vanadium, zinc, uranium arsenic, nickel and strontium are present in a low concentration, i.e., between 10 ppm and 400 ppm [6].

Table 1: Elemental content of raw PA, pretreated PA and nanofiltrated PA at 40 L/h/m² permeate flow.

	Raw PA	Pretreated PA	Final product	Reduction (%)
P ₂ O ₅ (%)	25.9	25.83	25	3.47
SO ₃ (%)	1.71	0.01	0.008	99.53
Al (%)	0.5	0.43	0.003	99.4
Fe (%)	0.28	0.27	0.001	99.64
Ca (%)	0.23	0.95	0.02	91.3
Mg (%)	0.39	0.41	0.004	98.97
K (%)	0.04	-	0.007	82.5
Na (%)	0.1	-	0.03	70
Si (%)	1.02	..	0.09	91.18
F (%)	1.57	0.1	0.05	96.82
Cd (ppm)	15	16	0.83	94.47
Co (ppm)	0.79	0.79	0.002	99.75
Cr (ppm)	240	215	0.78	99.68
Cu (ppm)	30	30	0.64	97.87
Mn (ppm)	14	14	0.15	98.93
Mo (ppm)	4	4	0.17	95.75
V (ppm)	208	187	1.35	99.35
Zn (ppm)	285	285	3.49	98.78
As (ppm)	17	3	3	82,35
REEs (ppm)	60	60	2	96.67

PA pretreatment prior to membrane purification allowed having a clarified solution in which the concentration of sulfate, fluoride and arsenic have decreased by 171, 157 and 5.6 fold, respectively, compared to raw PA. The measured absorbance of the clarified solution is 0.143 at $\lambda=408$ nm which explains the strong elimination of suspended matter that increases the clogging of the membrane and decreases its performance [7].

Table 1 clearly, shows that the application of tangential filtration with the modified membrane allows reaching quantitative a reduction rate above 99% for trivalent metallic ions including aluminum, iron and REEs and more than 91% for divalent metallic ions such as calcium, cadmium, copper and magnesium. However, monovalent ions showed a lesser reduction rate of 82.5% and 70% for potassium and sodium, respectively [8].

In general, transfer of ions through the membrane is controlled by the membrane charge rather than, pore size. Since the surface

of the membrane is positively charged it induced rejection of highly charged cations by electrostatic repulsion which may explain the higher reduction rate of trivalent rather than divalent and monovalent cations, respectively. It is well known that iron exists in PA as $\text{Fe}(\text{HPO}_4)^+$, $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ and $\text{Fe}(\text{H}_2\text{PO}_4)^+$ species. According, the overall reduction efficiency of iron is 99.64% indicating that iron phosphate complexes of $\text{Fe}(\text{HPO}_4)^+$ and $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ are more predominant than $\text{Fe}(\text{H}_2\text{PO}_4)^+$. Moreover, based on the obtained results we also expected that cadmium may exists as free aquo ionic form within $\text{Cd}(\text{H}_2\text{PO}_4)^+$ [9].

The evaporation of purified PA (25% P₂O₅) allows the concentration and the preparation of high quality of PA (54% P₂O₅). The concentration was achieved without acid color changing or distressing its quality. Elemental analysis shows that metallic and nonmetallic elements in purified-concentrated PA are low (Table 2). Al, Fe, Mg, F and as are not detected in purified and concentrated PA, whilst Na, Cd and Cr

concentration are 0.06%, 2 ppm and 1.5 ppm, respectively. The concentration of all undesirable impurities is lower than the feed grade PA 54% P₂O₅ [10].

Table 2: Purified-concentrated phosphoric acid composition.

Elements	Purified-concentrated PA 54% P ₂ O ₅	Feed grade PA 54% P ₂ O ₅
P ₂ O ₅ (%)	54.55	54.7
Fe (%)	ND	0.4
Al (%)	ND	0.3
Mg (%)	ND	0.8
Na (%)	0.06	0.3
F (%)	ND	0.14
Cr (ppm)	1.5	-
Cd (ppm)	2	-
As (ppm)	ND	75.2

Pilot scale study

To evaluate the quality of produced PA by NF membrane process on a high scale level, a pilot scale unit with 0.16 m³/h was built. The raw PA 25% P₂O₅, industrial grade, was subjected to the same steps as in the lab scale procedure leading to the feed grade PA 54% P₂O₅. Nanofiltration pilot operates for 24 h per day. After 22 h of PA purification, a cycle of two-hour membrane cleaning is required to maintain the functionality of the membrane [11].

Results in Table 3 demonstrate that metals reduction at pilot unit are slightly higher than laboratory scale. However, we observed that the reduction of metals depends on the cationic charge of metals within the same pattern noticed at laboratory scale [12].

Table 3: Elemental content of nanofiltrated PA at pilot scale unit.

	Raw PA	Pretreated PA	Final product	Reduction (%)
P ₂ O ₅ (%)	25.9	25.83	25.15	2.9
SO ₃ (%)	1.71	0.01	0.008	99.53
Al (%)	0.5	0.43	0.001	99.8
Fe (%)	0.28	0.27	0.001	99.64
Ca (%)	0.23	0.95	0.01	95.65
Mg (%)	0.39	0.41	0.003	99.23
K (%)	0.04	-	0.005	87.5
Na (%)	0.1	-	0.02	80
Si (%)	1.02	..	0.05	95.1
F (%)	1.57	0.1	0.05	96.82
Cd (ppm)	15	16	0.5	96.67
Co (ppm)	0.79	0.79	0.002	99.75

Cr (ppm)	240	215	0.8	99.67
Cu (ppm)	30	30	0.7	97.67
Mn (ppm)	14	14	0.07	99.5
Mo (ppm)	4	4	0.17	95.75
V (ppm)	208	187	0.72	99.65
Zn (ppm)	285	285	1.65	99.42
As (ppm)	17	3	3	82.35
REEs (ppm)	60	60	1	98.33

CONCLUSION

Modified and conditioned nanofiltration membranes were used to purify industrial PA. Bench scale tests have shown promising results in reducing undesirable impurities. The use of membrane stages along with pretreatment steps to remove arsenic, fluorides and sulfates allows the production of food grade PA. The reduction of undesirable impurities of Cd, As, Al, Fe rather than valuable elements of REEs are 94.47%, 82.35%, 99.40%, 99.64% and 96.67%, respectively.

Moreover, we found that PA purification by modified membrane is controlled by the electrostatic repulsion between the membrane and highly charged cation. Moreover, the reduction rate of metals follows the order: Trivalent cation>divalent cation>monovalent cation.

Furthermore, pilot scale test for PA purification using membrane technology with an outflow of 0.16 m³/hr is currently ongoing at Jorf Lasfar fertilizer center. Altogether, the obtained results demonstrate the stability of the membrane at higher scale within an approved reduction rate of metals slightly higher than the reduction rate at laboratory scale.

ACKNOWLEDGEMENT

All the authors gratefully acknowledge UM6P and OCP innovation for their financial support to CBS.GPE program.

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