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Hybrid precipitation-nanofiltration treatment of effluent pond water from phosphoric acid industry

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HIGHLIGHTS

- A novel hybrid precipitation- NF treatment was applied to wastewater for purification and the potential recovery of H_3PO_4.
- Most silicon was precipitated leaving almost 60% of H_3PO_4 in the effluent wastewater at $Ca(OH)_2$ dosage of 130 g/L.
- Three types of membranes (NF90, NF270, and BW30) were tested for potential treatment of effluent acidic wastewater.
- NF90 gave a high rejection, while NF270 showed a reasonable rejection with high flux.
- NF270 showed a potential selective recovery of H_3PO_4. NF90 and BW30 have high rejections for almost all species.

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ABSTRACT

Wastewater generated from phosphoric acid industry poses a real environmental challenge. This water contains valuable components the utilization of which can contribute to the conservation of natural resources. Water sample from an effluent pond of a phosphoric acid plant was collected and characterized for its physical and chemical properties. The collected samples were subjected to a hybrid process of chemical precipitation followed by nanofiltration. Both sulphate and fluoride ions were separated by precipitation using $Ca(OH)_2$. Silicon exhibited complex behaviour during the precipitation stage.

The observed flux using the different tested membranes (NF90, NF270, and BW30) indicated the success of the pre-treatment method in preventing heavy fouling. Very high rejections were obtained using the NF90 and BW30 membranes and, generally, the rejection increased with pressure. As expected, higher flux and lower rejections were observed with NF270 for Si and H_3PO_4 species. At a pressure of 20 bar the rejection increased with feed concentration which can be attributed to Donnan effects. It is concluded that NF270 could be potentially applied to separate PA from the rest of the species present in water. However, the main challenge is the low rejection of Si.

1. Introduction

The development of the industrial sector result in the generation of large amounts of industrial wastewater. Such water may contain heavy metals, acids, in addition to other toxic substances. Wastewaters may also contain materials that can be recovered to produce valuable products. An example of such water is that generated from phosphoric acid (PA) industry. Normally, such water is dumped into effluent ponds and left for evaporation or is neutralized with calcium based agents such as calcium carbonates, oxide or hydroxide. Effluent pond water from PA industry contains appreciable amounts of acids including H_3PO_4, H_2SiF_6, HF and H_2SO_4 as well as variable concentrations of heavy metals [1–3]. A simplified description of effluent pond water generation from PA plants was reported elsewhere [2].

Effluent pond wastewater forms a real challenge to PA industry due to its high acidity and toxicity. Therefore, many researchers have attempted to tackle the possible treatment options [4–11]. One of these options is to neutralize this water by alkaline medium [8,9,11]. However, this does not consider the recovery of valuable materials in the effluent water. Recently, there was an attempt to utilize nanofiltration (NF) technology for the treatment industrial wastewater. NF has wide range of applications in wastewater treatment and desalination processes [12,13]. For the case of PA effluent water, the main challenge was to find NF membranes that are capable of withstanding the highly acidic and fouling conditions. The development of membranes that can operate at low pH levels (as low as 1) made NF applications to such water possible.

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Table 1
Characteristics of the membranes used in the current work.

Membrane	MWCO (Da)[a]	Flux (L/m^2·hr·bar)[b]	IEP[c]	NaCl rejection (%)[d]	$MgSO_4$ rejection (%)[d]	Pore size (nm)[e]
BW30	~100	1.7	4	99.5%	99.5	NA
NF90	<200	6.4	4.3	90–96%	>97.0	0.99 [17], 0.51 [18]
NF270	>200	13.5	3.3–4	50%	>97.0	0.68 [18]

[a] Exact numbers not reported due to variations. NF membranes have MWCO between 200 and 400 Da, while RO membranes have MWCO of ~100 Da.
[b] Flux values as reported in literature [19]. Large variations in these values are found in literature [20,21].
[c] Isoelectric point (membrane has +ve charge below IEP and −ve above IEP).
[d] Permeate flow and salt rejection as reported by the manufacturer based on the following test conditions: 2000 ppm salt, 25 °C at 4.8 bar for NF and 15.5 bar for RO.
[e] The reported pore size of NF90 was measured using atomic force microscopy (AFM) and its value was 0.99 nm [17], while another work found its value around 0.51 nm and NF270 around 0.68 nm [18].

Al-Harahsheh et al. [2] proposed a process for the treatment of effluent pond water by chemical precipitation followed by NF. In the reported study, however, only chemical precipitation was considered whereby the effluent pond water was subjected to two stage precipitation treatment. In the first stage, only sulphuric acid was precipitated in the form of gypsum. The second stage involved the precipitation of H_2SiF_6 and HF in the form of CaF_2 at a pH of 2–2.5. At this pH about 60% of PA is left in water. It was suggested that the resulting solution can be treated by NF to recover PA or to produce process water that can be used in the plant. The current paper considers the treatment of water obtained from the precipitation treatment by NF. The need for chemical precipitation is two folds; effluent pond water is of high acidity (pH < 1) and the known NF membranes cannot withstand such acidity without fouling; additionally, chemical precipitation can offer a potential method for production of CaF_2 from this water that can be used in the metallurgical industry as fluxing agent [2].

Limited studies considered the recovery of from effluent pond water by NF. Such waters are composed of complex mixtures of ionic species and present a challenging study from the experimental and theoretical points of view. Some studies used synthetic model solutions to simplify the analysis. For example, Guastalli et al. [10] considered the separation of H_3PO_4 from industrial rinsing water by means of NF. They studied the separation of PA from synthetic solutions containing PA and Al using four types of NF membranes. Recoveries of up to 77% of PA were observed for some of the membranes. The important observation of that study is the charge role on the retention of the different ionic species. For example, H_3PO_4 rejection had lower retention than $H_2PO_4^-$. Both Donnan equilibrium and dielectric exclusion were proposed to explain such behaviour.

Abidi et al. [14] studied the selectivity of phosphate ions separation through Nanomax-50 NF membrane. They found the rejection of $H_2PO_4^-$ and HPO_4^{2-} to be 93 and 98%, respectively, and that the rejection depends on pH, feed concentration and ionic strength. Lee et al. [15] investigated the removal of phosphorous (P) by NF90 membranes from synthetic water containing 14.5 mg/L P which represents typical levels in the pulp and paper industry. The optimum conditions for P removal were found to be at 9.3 bar, 34 °C and pH of 7.2 giving 99.77% rejection at permeate flux of 88.74 L/m^2·h. Santos et al. [16] also studied the recovery of P from synthetic waters containing KCl, $CaCl_2$, and KH_2PO_4 using both NF90 and NF270 membranes. removal varied between 60 and 97% depending on the conductivity of the feed solution and type of salt added (KCl or $CaCl_2$); the rejection increased with feed conductivity.

Some important observations can be made from the above studies. For example, the rejection of phosphorous will depend on its dissociation state which, in turns, depends on the solution conditions. The exact rejection mechanism is strongly affected by the charge effects (Donnan equilibrium and dielectric exclusion). However, the role of these charge effects will depend on the membrane properties themselves. In tight membranes, size exclusion tends to overshadow the charge effects compared to more loose membranes.

The current study investigates a new hybrid process for the potential recovery of phosphorous and rejection of heavy metals from industrial PA wastewater composed of a chemical precipitation pre-treatment step followed by NF. The composition of such wastewater creates challenges in terms of using NF membranes and predictions of its operation. Therefore, the study focuses on addressing some of these issues. In addition, the rejection of heavy metals contained in this water is also reported.

2. Experimental work

2.1. Materials and chemicals

All chemicals used in the current work were of analytical grade (HF, H_2SiF_6, H_3PO_4, NaOH). Calcium hydroxide powder (Merck®) was used for precipitation experiments. Type I deionized water (18.2 MΩ) was used for the preparation of all solutions.

2.2. Effluent water samples

About 500 L of effluent wastewater sample was collected from the effluent pond of a PA plant located in the south of Jordan. The sample was characterized for its chemical composition, acids content, pH, and

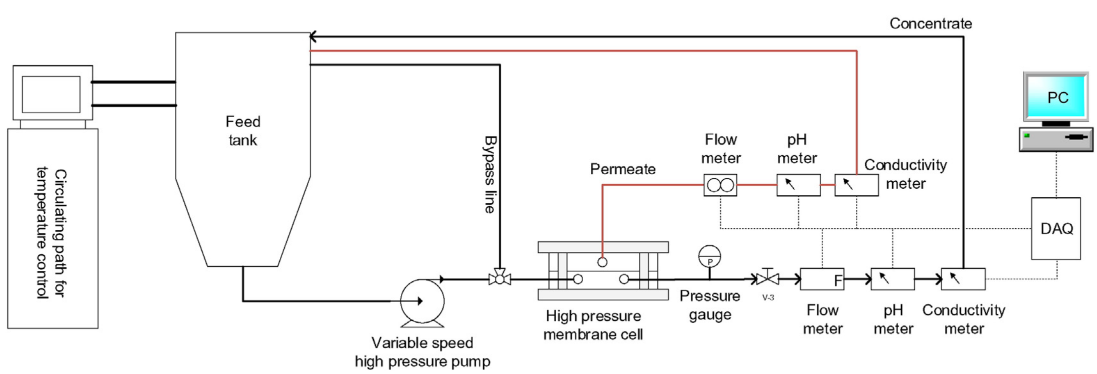

Fig. 1. Schematic diagram of the filtration setup used in this work.

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