# Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration

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## HIGHLIGHTS

- Analysis of separation process of lead ions from synthetic wastewaters by NF using the AFC 80 membrane
- Effective removal of heavy metals concomitantly with obtaining non-toxic permeates
- Concentration by NF of aqueous solutions simulating the real wastewaters
- Modeling of the concentration process of synthetic wastewaters containing heavy metals

## ARTICLE INFO

## ABSTRACT

The focus of this paper is to test the ability of a commercially available nanofiltration membrane (AFC 80) to remove polluting and toxic Pb(II) ions from aqueous solutions in order to meet the USEPA guidelines regarding the toxicity threshold limits. The investigation has been conducted for aqueous solutions containing lead in a wide concentration range and also with similar composition with real wastewaters, both in batch circulation and in concentration mode. The influence of the operating variables on the membrane performance was investigated. Experimental results show that the rejection of lead ions slightly increases when increasing the cross-flow velocity and operating pressure, and slightly decreases when increasing the metal concentration in feed. The metal rejection and the permeate flux were found to slightly decrease and strongly increase, respectively, when increasing the feed pH. Generally, the rejection of lead ions is greater than 98% even for very concentrated feed solutions. Additionally, the membrane is able to concentrate lead containing aqueous solutions with pH 5.8 at a medium operating pressure of 25 bar, and concomitantly obtains non-toxic permeates. The metal concentration in permeate and the metal rejection during the concentration process were successfully predicted with high accuracy by a simple model.

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## 1. Introduction

Heavy metals of the greatest concern in the treatment of wastewaters are copper, cadmium, iron, lead, zinc, mercury, chromium and silver, as they are highly toxic, non-biodegradable and have the tendency to accumulate in living organisms [1]. The main sources of heavy metals are tanning, petroleum refining, chemical manufacturing, electroplating, mining, textile industry, fertilizer plants, photographic process industry, battery manufacturing, metal and steel working and finishing, and landfill leachates. Lead concentrations in wastewater from battery manufacturing, acid mine drainage and steel production plants range from 0.5 to 25 mg/L [2]. Wastewaters containing heavy metals resulting from various industrial activities must be finally discharged into the environment. As heavy metals are extremely dangerous for human health and for living organisms, due to the current environmental legislations, the treatment of wastewaters for the removal of heavy metals is a problem of critical importance [3].

Among heavy metals, lead is an extremely toxic and highly polluting agent, which can have side effects on the human body even at very small concentrations. According to the USEPA regulations, the toxicity threshold level of Pb(II) in wastewaters is 5.0 mg/L [4]. Conventional methods used to remove Pb(II) ions from various industrial effluents usually include liquid–liquid extraction [5], precipitation [6,7], ion exchange [8], adsorption on various sorbents [4,9–13] and filtration through membranes [14–26]. The techniques involving chemical reactions require the use of large amounts of expensive organic solvents and other polluting chemicals, they are slow and laborious, and the recovery of the components is seldom complete. Due to the necessity of finding cheaper, efficient, and non-polluting separation methods, the membrane processes like reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) have gained increasing popularity in wastewater treatment [3]. The membrane processes used for the removal of heavy metals from aqueous solutions are liquid

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membranes [14–17] and pressure driven membrane processes like reverse osmosis (RO) [18,19], nanofiltration (NF) [19–26], and membrane hybrid processes [27]. Among these methods, nanofiltration is a relatively recent water treatment technique which uses membranes with very small pores (<1 nm) and requires operating pressures in the 10–50 bar range. Thus, NF membranes are able to retain neutral species with MW < 200–300 g/mol, and also to reject inorganic ions by a size exclusion mechanism combined with electrostatic interactions between the ions and the charged membrane. Nanofiltration has some advantages over other membrane techniques, for example higher rejection of divalent ions and lower rejection of monovalent ions, lower operating pressure, higher flux and lower energy consumption compared with RO. These features recommend NF as a promising and innovative technology which can be widely applied in drinking water and the treatment of industrial effluents [28].

To the best of our knowledge, only a small number of studies have been devoted to Pb(II) removal by NF [13,19–26]. In a previous work [21], we investigated for the first time the removal of lead ions by using AFC 80 membrane. This work was centered on membrane characterization by using the DSPM model and zeta potential measurements, and also on the investigation of the transport mechanism by using the Spiegler–Kedem model.

The main emphasis of the present work is on the investigation of lead removal by this commercial thin-film composite polyamide NF membrane from aqueous solutions with very low to very high concentration ranges, as often occur in real wastewaters from various industries and in their reclamation processes. The removal of heavy metals from wastewaters by nanofiltration (NF) offers the possibility of permeate reuse or discharge and the metal recovery from the retentate (concentrate). Thus, the investigation was focused on obtaining permeates with lower metal concentrations than the EPA guidelines regarding the toxicity threshold limits. The performance of the NF membrane for the removal of Pb(II) and the rejection mechanism are investigated under various operating conditions: feed cross-flow velocity, feed solution pH and applied pressure, and the presence of other heavy metals (cadmium) as occurring in the real industrial effluents. The ability to concentrate the lead-containing aqueous solutions for metal recovery and for concomitantly obtaining a non-toxic permeate is also tested here by performing NF experiments in concentration mode. The performed experiments allow to be indicated the operating conditions which can assure an excellent performance of the AFC 80 membrane for removal of the highly contaminant heavy metal ions studied in order to meet the EPA guidelines regarding the toxicity threshold limits. A simple model is used to predict the rejection rate and the metal concentration in permeate during the concentration process, as it can be a useful tool for predictive purposes in possible practical applications.

## 2. Experimental

### 2.1. Materials

A commercially available tubular NF membrane, denoted AFC 80 by the manufacturer (PCI Membrane Systems), was employed in this study. The main experimental conditions and properties of this membrane are summarized in Table 1.

Lead nitrate $Pb(NO_3)_2$, cadmium nitrate $Cd(NO_3)_2 \cdot 4\ H_2O$ and $HNO_3$ were supplied by Penta Co., Czech Republic. All chemicals used for the preparation of the synthetic solutions were of analytical reagent grade or the highest purity available, and were used as received. The aqueous solutions were prepared by dissolving the reagents in highly demineralized water (conductivity < 1 μS/cm, pH 6.0 ± 0.1).

### 2.2. Experimental setup and methods

Nanofiltration experiments were performed with a cross-flow separation unit illustrated in Fig. 1. The membrane module used was

**Table 1**
Main characteristics of the NF membrane used.

| Membrane structural parameters | | Data origin |
|---|---|---|
| Membrane type | Thin-film composite, tubular | Supplier |
| Material | Aromatic polyamide skin layer on polysulfone substrate | Supplier |
| Operating pressure (bar) | 0–60 | Supplier |
| Operating temperature (°C) | 0–70 | Supplier |
| Feed pH range | 1.5–10.5 | Supplier |
| Membrane surface charge | Negative | Supplier |
| NaCl rejection (%) | 80 | Supplier |
| Mean pore radius (nm) | 0.262 ± 0.003 (slit-like pore geometry) | [21] |
| Thickness to porosity ratio $\Delta x/A_k$ (μm) | 6.32 ± 0.015 (slit-like pore geometry) | [21] |
| Water permeability $L_P$ at 25 °C (L/m² h) | 1.45 ± 0.1 | [21] |
| Isoelectric point (IEP) | 3.6 | [21] |

equipped with two tubular AFC 80 membranes of 1.25 cm internal diameter and 30 cm length, with the effective membrane filtration area being 240 cm². If not otherwise stated, experiments were carried out for applied pressures in the range of 10–50 bar. The temperature of the feed solution was maintained at a constant value of 25 ± 0.5 °C by using a heat-exchanger. The NF membranes were cleaned for 4 h by circulating demineralized water at 45 °C at the pressure of 30 bar. In order to avoid the compaction of the membranes during the experiments, the membranes used were stabilized for at least 2 h at the maximum pressure used in this study (50 bar). The membrane pure water permeability ($L_P$) was calculated from the plot of pure water flux ($J_w$) measured at different transmembrane pressures. After each experiment, the system was cleaned with demineralized water for 3 h at 30 bar and 45 °C, until the water flux and permeability of the membrane were restored. If necessary, chemical cleaning by recirculating a 0.3% $HNO_3$ solution was also performed. Synthetic lead polluted aqueous solutions were prepared by adding the required amounts of $Pb(NO_3)_2$ and $Cd(NO_3)_2$, respectively, into highly demineralized water. The pH of the aqueous solutions was adjusted with $HNO_3$.

A series of experiments were designed to measure the lead rejection in batch circulation mode at various feed flow velocities, operating pressures, pH and feed concentrations; the ability of the AFC 80 membrane to remove the heavy metals from a model solution simulating a mining plant effluent containing about 15 mg/L Pb(II) and 5 mg/L Cd(II) was also investigated [4]. In these experiments both permeate and retentate were returned to the feed tank in order to maintain a constant concentration in feed. Feed and permeate samples were collected at different applied pressures, after the recirculation of both solutions until the system reached a steady-state (constant permeate flux and composition, respectively). The constant composition of permeate corresponding to the steady-state was ascertained by reaching of a constant conductivity value in permeate solution. The various experimental conditions during these experiments are summarized in Table 2.

The influence of feed concentration was then also studied in concentration mode, both for a single salt solution containing lead nitrate (with an initial concentration of 250 mg Pb/L) and also for a solution containing lead and cadmium nitrates which simulates the concentration of a real mining effluent (initial feed concentration 150 mg Pb/L and 40 mg Cd/L). The experiments were conducted at feed pH of 5.8 ± 0.1, operating pressure of 25 bar and feed cross-flow velocity of 1.250 m/s. Both feed and permeate samples were collected after the removal of each 0.5 L of permeate during the concentration of the feed solutions from 11 L to 2 L.

The permeate flux was determined by weighing using an electronic balance connected to a personal computer, with the fluxes recorded automatically by software. In order to assure the reproducibility of the results, all experiments were performed in duplicate. The reported values