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The impacts of operational conditions on phenol removal by nanofiltration membranes

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ABSTRACT

The main purpose of this study was to investigate the effectiveness of various nanofiltration (NF) membranes in rejecting phenol from waters. The impacts of operational conditions and water chemistry on phenol rejections in model solutions were studied. Single-solute phenol model solutions were prepared in distilled and deionized water. All membrane tests were conducted using a lab-scale cross-flow flat-sheet configuration test unit. For all the tested NF membranes, the main factor affecting phenol rejections was solution pH. Increasing solution pH from 7.0 to 10.5 significantly increased phenol rejections. Both the enhanced negative membrane surface charge at higher pH and the dominance of negatively charged phenolate species led to higher phenol rejections at pH 10.5 compared to neutral pH. No significant changes in flux values were observed at neutral pH and pH of 10.5. There was not a correlation among salt and phenol rejections by the tested polyamide NF membranes. The initial phenol concentrations (50 and 200 mg/l) did not affect permeate flux and phenol rejections. Phenol rejections increased by increasing the pressure from 100 to 200 psi. The results overall indicated that although both size exclusion and electrostatic repulsion mechanisms play role in phenol rejections by NF membranes, electrostatic repulsion mechanism contributes more to rejections than size exclusion mechanism. Supporting the electrostatic repulsion mechanism through pH increase in NF applications may result in both enhanced phenol rejections and prevention of phenol adsorption and further diffusion inside the membranes. On the other hand, the pH adjustments should be within the range of manufacturer specifications since increased membrane degradation could occur at higher pH values in polyamide membranes.

Keywords: Membrane; Nanofiltration; Phenol; Water treatment

1. Introduction

Industrial structures demand greater amount of process water nowadays due to the increased production capacities. However, such a demand creates a stress on water sources and has become a worldwide concern. Recovery and reuse of industrial wastewaters through effective pollutant removal arouse as a must in order to keep the balance of water budget. The contamination of ground and surface waters with organic pollutants emerges as a critical problem. A research conducted in USA about the presence of organic contaminants in streams showed that 80% of those streams contained organic contaminants [1]. Phenol and phenolic compounds are among the most prevalent forms of organic chemical pollutants in industrial wastewaters [2].

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Phenols are pollutants of high priority concerns because of their toxicity, low biodegradability and possible accumulation in the environment. Phenol and its derivatives appear to be the major organic pollutants globally in this century [3].

Phenolic compounds are found in the wastewaters of various industries including coal conversion processes, coke ovens, petroleum and oil refineries, phenolic resin manufacturing, herbicide and pesticide manufacturing, fiberglass manufacturing, synthetic chemical production, ceramic, steel, pharmaceutical, leather, paper, food, textile [2, 4–7]. Typical phenol concentrations in such wastewaters are as following: refineries (6–500 mg/l), coking operations (28–3900 mg/l), coal processing (9–6800 mg/l), and petrochemical manufacturing (3–1220 mg/l). One major phenol-related problem especially in the Mediterranean area is the voluminous amounts of olive oil mill wastewaters, which may cause phytotoxicity if not treated properly prior to discharge to receiving environments [8]. Another issue is that when phenol-containing water is chlorinated, toxic polychlorinated phenols can form and thus contribute to off flavors in drinking and food processing waters [9].

Phenols are introduced into aquatic ecosystems and adversely affect the indigenous biota, including algae, protozoa, invertebrates, and vertebrates [10]. Phenols are toxic, carcinogenic, mutagenic, and teratogenic even at low concentrations [11]. It is among the list of priority organic pollutants proposed by the US Environmental Protection Agency (USEPA) [12]. They are growth inhibitory to microorganisms in biological treatment processes. Owing to their toxic effects, including permeabilization of cellular membranes and cytoplasmic coagulation, phenolic contaminants can damage sensitive cells and thus cause profound health and environmental problems. Acute poisoning can lead to severe gastrointestinal disturbances, kidney malfunction, circulatory system failure, lung edema and convulsions. Key organs damaged by chronic phenol exposure include spleen, pancreas and kidneys [2,13]. Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis, and death can result from over exposure to it. The ingestion of 1 g of phenol is deadly for man [8]. Phenol concentrations of ≥1 mg/l affect aquatic life. Therefore, in most cases stringent effluent discharge limit of less than 0.5 mg/l is imposed [4,14,15]. The USEPA set a water purification standard of less than 1 μg/l of phenol in surface waters. In Italy, in agreement with the recommendations of the European Union, the limit for phenols in potable and mineral waters is 0.5 μg/l, while the limits for wastewater emissions are 0.5 mg/l for surface waters and 1 mg/l for the sewerage system [8]. All these stringent regulations trigger the efforts for more efficient phenol removal processes from waters [5,16].

Main technologies for the treatment of wastewaters containing phenol include chlorination, oxidation, adsorption, separation processes, coagulation-flocculation, and biological treatment. Specific phenol treatment technologies can be summarized as following: enzymatic treatment, separation technologies such as distillation, liquid–liquid extraction with different solvents, membrane pervaporation and membrane–solvent extraction, destruction technologies such as non-catalytic, supercritical and catalytic wet air oxidation, ozonation, non-catalytic, catalytic and enzymatic peroxide wet oxidation, electrochemical and photocatalytic oxidation, supercritical wet gasification, destruction with electron discharge or ultrasound [2,8,5,17]. Physicochemical methods have proven to be costly and have the inherent drawbacks due to the tendency of the formation of secondary toxic materials such as chlorinated phenols, hydrocarbons, etc [5]. Adsorption of phenol by activated carbon is the most widely used treatment method [18]. The main drawback is the capital intensiveness of activated carbon in wastewater treatment. The use of activated carbon have also some other drawbacks such as the need for regeneration of activated carbon and intraparticle resistance during the adsorption process [16]. Ozonation, Fenton's reagent, UV or hydrogen peroxide treatments are usually complex and expensive [19,20].

High-pressure membrane processes such as nanofiltration (NF) and reverse osmosis (RO) may also be effective in removing phenolic compounds from waters. For the removal of trace levels of dissolved organics such as methanol, ethanol, carbon tetrachloride, and phenols from waters, such processes are efficient only when the membranes have very small pores [21]. The applications of high-pressure membrane processes for the removal of low molecular weight organic compounds from wastewaters were analyzed in recent publications [22–25]. Despite excellent rejection of salts, high-pressure membrane processes may also provide low rejection levels for many small organic molecules [2]. It is apparent from the literature that the removal of synthetic chemicals through NF or RO processes from waters depends on various factors including membrane type and characteristics, operational conditions, background water chemistry, and obviously the characteristics of the chemical itself. In this context, phenol being one of the major pollutants in waters was selected in this work and the main purpose was to investigate the effectiveness of various NF membranes in rejecting phenol as single-solute in solutions. Furthermore, the impacts of operational conditions and water chemistry on phenol rejections in model solutions were studied. Single-solute phenol model solutions were prepared in distilled and deionized water (DDW). Single-solute tests were conducted to directly investigate the phenol rejection by NF membranes and sort out the impacts of tested factors. When phenol rejections are studied in natural waters or industrial wastewaters, background water chemistry (salts, other organics, etc) obviously may affect the extent and mechanisms of phenol rejection by polymeric NF/RO membranes. Such study will be performed in the next phase of the project.

2. Materials and methods

2.1. Membrane test unit

A lab-scale cross-flow flat-sheet configuration test unit (SEPA CF II, Osmonics) was used for all membrane separation experiments, which simulates the flow dynamics of larger, commercially available spiral-wound membrane elements. The membrane test unit accommodates any 19 × 14 cm flat-sheet membrane for a full 140 cm^2 of effective membrane area. Maximum operating pressure of the unit is 69 bar (1000 psi). The membrane test system consists of a high pressure pump (Hydra-Cell G13) equipped with digital variable frequency drive (ABB ACS-140) to adjust feed flowrate and its 1.1 kW motor, pressure relief valve, membrane cell, membrane cell holder, high pressure concentrate control valve, hydraulic hand pump, pressure indicators in the membrane cell, cell holder and high pressure pump outlet, feed tank (37 l max. solution volume, stainless steel), and connections/tubings made of either stainless steel, nylon-seal plastic and/or teflon (Fig. 1). During the membrane tests, temperature of the feed tank was kept constant by circulating water from water-bath through the jacket around the feed tank outer walls. All experiments were performed at feed water temperatures of 20 ± 1 ºC.

The tested commercial NF membranes were obtained from Dow FilmTec, GE Osmonics and Koch Membrane Systems. Notations of “A”, “B” and “C” are used throughout this paper for FilmTec, Osmonics and Koch membranes, respectively. Membrane A is a polyamide thin-film composite membrane with maximum operating pressure up to 600 psi and has >97% $MgSO_4$ rejection. Membrane B is a thin-film composite membrane with maximum operating pressure up to 600 psi and has 98% $MgSO_4$ rejection. Membrane C is also a thin-film composite polyamide membrane with maximum operating pressure up to 600 psi and has 99.4% $MgSO_4$ rejection.

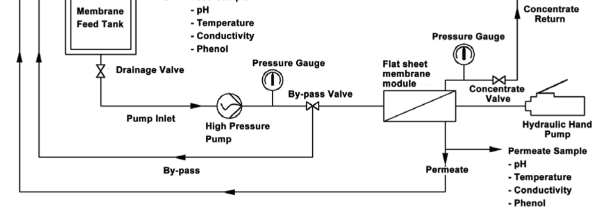

Fig. 1. Schematic of the membrane test system.

2.2. Membrane tests

Membrane operating pressures tested were 6.9 bar (100 psi), 13.8 bar (200 psi) and 20.7 bar (300 psi). The membrane feed flowrate was 3.3 l/min with corresponding cross-flow velocity of about 0.8 m/s. Two different pH values were tested: 7.0 (neutral) and 10.5 (high pH). Total recycle mode (permeate and concentrate streams were returned back to the feed tank) was applied during the tests. A new membrane was used for each test after conditioning the as received membrane for about 4–6 h of feeding with DDW at the conditions of the experiment to be conducted. After this conditioning step, the duration of each actual membrane test was 14 h. Samples from feed tank and permeate were taken each hour for total dissolved solids (TDS), conductivity, pH, and temperature measurements and each two hour for phenol analysis. To maintain constant pH in the feed tank depending on the experimental matrix, pH was monitored and adjusted with various concentrations of HCl and/or NaOH solutions, if necessary. Flowrates of concentrate and permeate streams, membrane unit and pump outlet pressures were also recorded each hour.

2.3. Model solution and analytical techniques

All experiments were carried out with model solutions (single-solute phenol in DDW). Target phenol concentrations in the feed water were 50 or 200 mg/l depending on the experimental matrix. Powder phenol (99.0%, Merck) and DDW was used to prepare model solutions. The conductivity and total organic carbon (TOC) levels of DDW were typically <2 µS/cm and <50 µg/l (detection limit of the TOC analyzer), respectively.

Phenol was measured using a spectrophotometer (Hach Lange DR5000). Conductivity and TDS was measured using WTW Inolab Cond. Level 1 conductivity meter. pH was measured using bench-scale Schott Handylab 1 pH meter. All chemicals used were reagent grade. DDW was used for stock solution preparations and dilutions. All analytical measurements were conducted in duplicates.

3. Results and discussion

Fig. 2 shows the phenol rejections achieved by the tested NF membranes at pH 7.0. Membrane A provided around 45–47% phenol rejections, which is consistent with the work of Arsuaga et al. [7]. Other membranes showed poor rejections (around 4–5%) compared to membrane A although all the tested three membranes have similar salt rejection specifications. Size exclusion mechanism seems to be one of the reasons of this trend since the molecular weight cut-off (MWCO) of membrane A is around 180 Da [24] compared to 150–300 Da of the membrane B [26]. It is known that the removal of organic solutes is influenced by operating variables and membrane sieving effect. In addition, certain membrane-solute interactions, molecular characteristics of organic molecules (size, charge, solubility, acidity, ability to hydrogen bonding, etc.), membrane properties (surface charge, hydrophobicity and pore size) affect the retention of organics by NF membranes [2,7,22,27,28]. Therefore, rejection differences among different membranes for an organic compound at constant operating condition could be expected even their salt rejection performances are similar. Agenson et al. [22] tested the removal of various organic pollutants by NF membrane and reported that membranes with higher salt rejections also retained more of the target solutes. The patterns of retention noticeably varied with membranes and solute type.

As indicated above, size and charge of organic molecules could affect their rejection by polymeric membranes. Phenol is an aromatic compound with a pKa value of 9.98. Above pH of 9.98, phenol starts to ionize and charged phenolate anion become dominant in waters. To determine the impacts of solution pH on phenol rejections, membrane tests were also conducted at a pH of 10.5. The phenol rejections obtained at pH 7.0 and 10.5 are compared in Fig. 3. While membrane A provided around 45–47% phenol rejections at pH of 7.0 rejections significantly increased to 82–85% levels at pH of 10.5. Similarly, membrane B rejected about 73–75% phenol at pH 10.5 while this membrane rejected phenol only less than 10% at neutral pH. Membrane C was unable to show a stable rejection path at pH 10.5. It is generally suggested that most NF membranes show a potential amphoteric behavior [24]. A typical polyamide membrane has an isoelectric point between pH 2 and 4. At pH below the isoelectric point, the membrane is expected to be positively charged due to the protonation of the amine functional group. On the other hand, at pH above the isoelectric point, the membrane surface becomes negatively charged due to the deprotonation of the carboxylic acid and amine functional groups of the membranes [29]. Therefore, the polyamide membranes have higher degree of negative surface charge at pH 10.5 compared to neutral pH. Hence, for all the tested NF membranes, both the enhanced negative surface charge at higher pH and the dominance of negatively charged phenolate species led to higher phenol rejections at pH 10.5 compared to neutral pH. This result further proves the importance of electrostatic repulsion mechanism for organic removals by NF processes. Based on our results on the tested NF membranes, it may be suggested that electrostatic repulsion mechanism has more impact than size exclusion mechanism on phenol rejection performances. However, it should also be noted that only three types of NF membranes were tested in this work and this result may not be generalized for all types of polymeric NF membranes.

Another important role of the electrostatic repulsion mechanism is the prevention of organic solute

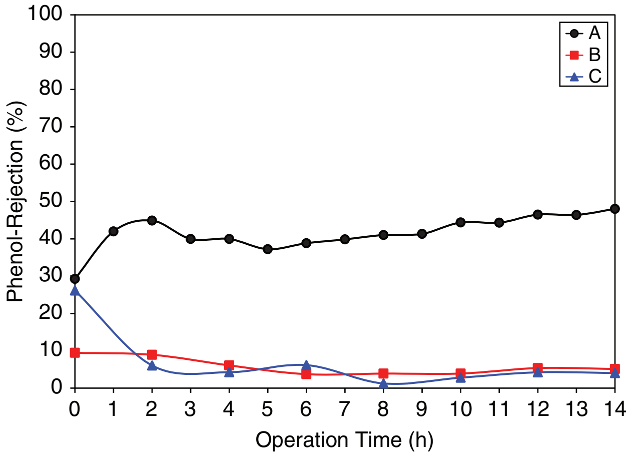

Fig. 2. Impact of membrane type on phenol rejection (pH=7.0; pressure=100 psi).

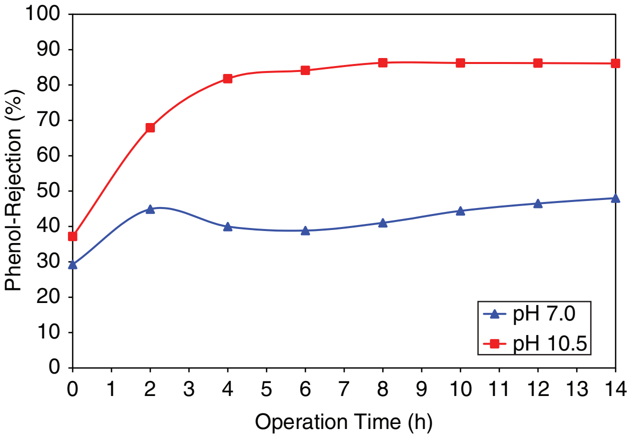

Fig. 3. Impact of pH on phenol rejection (membrane A; pressure=100 psi).

adsorption onto polyamide membranes [7]. Van der Bruggen et al. showed that compounds with molecular weights around 100 g/mol exhibit a high tendency to adsorb on polyamide NF membranes [30]. The molecular weight of phenol is 94 g/mol. Thus, a high degree of phenol adsorption and further accumulation on polyamide membrane surfaces is expected especially in the long term membrane operations. This accumulation may result in the breakthrough effect which is the diffusion of the adsorbed molecules through membranes after saturation of the membrane [31]. Therefore, supporting the electrostatic repulsion mechanism through pH increase in NF applications may result in both enhanced phenol rejections and prevention of phenol adsorption and further diffusion. On the other hand, the pH adjustments should be within the range of manufacturer specifications. It should also be noted that increased membrane degradation could occur at higher pH values in polyamide membranes. Therefore, the advantages of increased solution pH values should be balanced with its disadvantages in terms of membrane life when NF membranes are to be used for phenol removal from waters.

Permeate flux values obtained by the tested NF membranes are shown in Fig. 4. At a membrane pressure of 100 psi, the steady flux values obtained by membranes A, B and C were about 70, 20 and 40 l/m^2-h (LMH), respectively. Flux of membrane A was somewhat higher than the manufacturer specification since 100 psi pressure was applied in our tests to compare all membranes at constant pressure. Manufacturer flux specification was given at 70 psi pressure. For membranes A and B, no significant changes in flux values were observed at neutral pH and pH of 10.5. However, for membrane C, a slight flux decrease at higher pH was found. This may be partly explained by the hydration swelling of the membrane which could result in shrinking of membrane pore sizes. A significant swelling effect may also be observed at concentrated salt solutions [32]. Since the tests in this work were conducted in single-solute phenol solutions scaling due to Mg, Ca compounds at higher pH values was not a concern. However, in real waste-waters with high alkalinity and salt concentrations, operating membranes at pH 10.5 levels may cause scaling problems. Permeate flux values increased by increasing operating pressure for all the tested membranes, as expected. Improved flux values are important in terms of the capital costs of an application. On the other hand, increased pressures lever the energy consumption, thus the operating costs. So a detailed analysis for both total costs and "flux per unit energy spent" should be conducted in each specific application in addition to the contaminant rejection performances of the membranes [33].

Comparison of the phenol rejections at different pressure values is shown in Fig. 5. Phenol rejection increased by increasing the pressure from 100 to 200 psi, as may be expected from the diffusion-solution models. However, no further improvement in phenol rejection was found when the pressure was increased to 300 psi. Phenol rejections were similar for 200 and 300 psi (92–93%). Conductivity rejections were in the range of 80–90% by all the tested membranes. Conductivity was originated from NaOH and/or HCl solutions which were used for pH adjustment before and/or during the tests. No significant effect of pH on conductivity rejections was observed for the tested membranes. In order to determine the effect of feed phenol concentration on phenol rejections and permeate flux, 50 and 200 mg/l feed phenol concentrations were applied. No significant effect of initial phenol concentration was observed on permeate flux and phenol rejections.

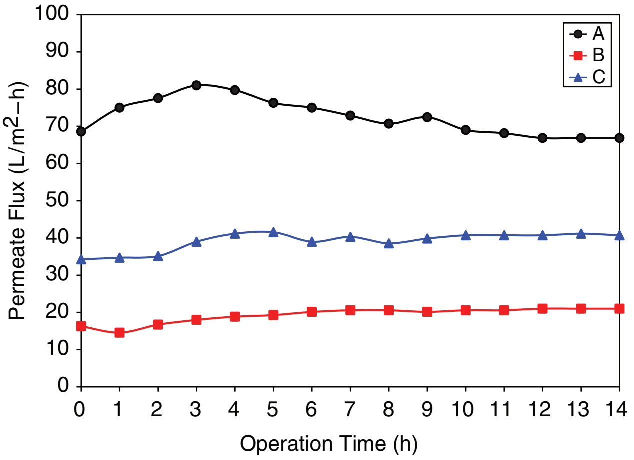

Fig. 4. Permeate flux values of the tested NF membranes (pH=10.5; pressure=100 psi).

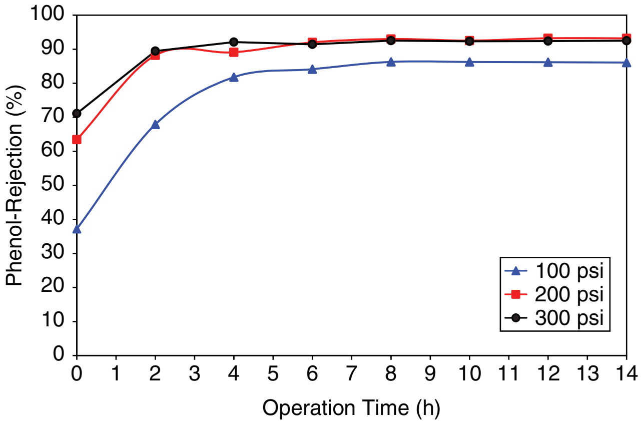

Fig. 5. Impact of pressure on phenol rejection (membrane A; pH=10.5).

4. Conclusions

For all the tested NF membranes, the main factor affecting phenol rejections was solution pH. While membrane A provided around 45–47% phenol rejections at pH of 7.0 rejections significantly increased to 82–85% levels at pH of 10.5. Similarly, membrane B rejected about 73–75% phenol at pH 10.5 while this membrane rejected phenol only less than 10% at neutral pH. This finding suggested that both the enhanced negative membrane surface charge at higher pH and the dominance of negatively charged phenolate species led to higher phenol rejections at pH 10.5 compared to neutral pH. Therefore, for the removal of phenol by polyamide NF membranes, it appears that electrostatic repulsion mechanism plays more role than the size exclusion mechanism. Supporting the electrostatic repulsion mechanism through pH increase in NF applications may result in both enhanced phenol rejections and prevention of phenol adsorption and further diffusion inside the membranes. However, the pH adjustments should be within the range of manufacturer specifications since increased membrane degradation could occur at higher pH values in polyamide membranes. If the process is to be conducted in high pH levels, selecting high pH-resistant membranes is important especially for long-term operations.

For membranes A and B, no significant changes in flux values were observed at neutral pH and pH of 10.5. Phenol rejection increased by increasing the pressure from 100 to 200 psi. No further improvement in phenol rejection was found when the pressure was increased to 300 psi. Phenol rejections were similar for 200 and 300 psi (92–93%). The initial phenol concentrations (50 and 200 mg/l) did not affect permeate flux and phenol rejections.

The results overall indicated that there was not a correlation among salt and phenol rejections by the tested polyamide NF membranes, which further proves that both size exclusion and electrostatic repulsion mechanisms play role in phenol rejections, the latter contributing more to rejections. However, it should also be noted that only three different NF membranes were tested in this work and the findings may not be generalized to all NF membranes. Since the rejections of organic contaminants by NF membranes depend on various factors including the characteristics of membrane and the contaminant itself, background water chemistry and operational conditions, lab- or pilot-scale tests should be conducted prior to each specific application to verify the rejections and operating performances.

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