Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1044914

57 (2016) 11782–11788
May

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Application of nanofilter in removal of phosphate, fluoride and nitrite from groundwater

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Received 13 July 2014; Accepted 18 April 2015

ABSTRACT

At present, nanofiltration (NF) technologies find the ever greater use in the water industry, particularly, drinking water supplies. The concentrations of most anions in the groundwater sources are much higher than surface water and in some cases are higher than drinking water standards. In this regard, the aim of this study was to investigate the possibility of application of nanofilters in removing phosphate, fluoride, and nitrite from aqueous solutions. In this research, the effect of different factors including initial concentrations of nitrate, phosphate, and fluoride along with the flow rate were investigated. The results showed that with an increase in the initial concentrations of phosphate, fluoride, and nitrite, along with an increase in flow rate, the removal efficiencies decreased. The maximum removal efficiencies for phosphate, fluoride, and nitrite were 98, 82, and 87%, respectively. According to the findings, NF membrane could be recommended for removing nitrates, fluoride, and phosphate from aqueous solutions.

Keywords: Nanofiltration; Eutrophication; Fluorosis; Blue baby; Groundwater

1. Introduction

The unforeseeable impact of global warming on the overall water scarcity and identification of a potential water shortage assume that the first and second decades of the twenty-first century could be called as the “water crisis decades” [1]. Many parts of the world, especially in the arid and semiarid regions are facing with water scarcity [2]. This water shortage can be associated with global population growth, limited natural resources, global warming, increasing industrial activities, water resources pollution, and improvement of life standards [3]. As a result, in many regions in the United States [4,5], drought-prone zones such as Middle East [6,7], and in areas where safe water resources are rare, such as Singapore [8], seawater is considered as a proper source for water

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supply [9]. In addition, in these areas, the reduction of underground aquifers, and the increasing salinity of non-renewable sources will continue to exacerbate the water shortage problems [10]. The environment and health regulations are turning into more stringent with increasing water demand, so, more research studies have been conducted for upgrading the membrane processes. A variety of membranes have been improved in the field of water treatment during the past decade [11,12].

The presence of toxic contamination in drinking water resources has adverse effects on human and animal health as well as the aquatic life. Among these contaminants, the excess of fluoride ion causes major effects such as dental and skeletal fluorosis [13–16]. The excess concentration of fluoride (>1.5 mg/L) causes serious health effects. In addition, many adverse effects were found in different countries, such as China [17,18], India [19–21], Mexico [22], Africa [23], and Iran [24–26].

According to Sweden rules and regulations, at least 75% of the phosphorous must be recovered from wastewater [27]. Moreover, the phosphorous rate in discharging wastewater should be according to environmental and human health guidelines [28,29]. For instance, the phosphate concentration in wastewater discharge to surface water bodies in Dutch should be less than 0.15 mg/L [29].

Membrane filtration is an attractive and efficient process for phosphate removal [30]. Nanofiltration (NF) process is similar to reverse osmosis, but with a high permeability of NF membranes, the pressure required for phosphate recovery can be decreased [31].

Nitrate in drinking water is dangerous due to its reduction to nitrite in human body, which is more toxic and affects health by creating methemoglobinoma (baby blue syndrome) in children under six months of age, causing reduced oxygen transfer to body tissues [32,33]. WHO drinking water guideline value for nitrite is 3 mg/L as NO_2 based on chronic effects. Many techniques have been applied for nitrate removal from aqueous solution including, ion exchange, biological denitrification, electrocoagulation, adsorption, and source management.

Many methods are available for removal and reduction of pollutants from aqueous solutions. Chemical oxidation with chlorine or ozone and other oxidants is efficient, but require higher oxidant dose which is very expensive. Photochemical degradation of some compounds in aqueous solution is slow due to these materials having high stability to light. Hence, a new method in treatment of drinking water is highly desirable. Membrane separation technologies have been considered as an effective and efficient method [34–37]. Pollutants and dissolved ions such as low molecular weight organic compounds, the divalent ions (such as Ca^{2+}, Ni^{2+}), and large monovalent ions can be separated from aqueous solution by NF process, at a moderate operating pressure [38]. Usually, the concentrations of most anions are high in groundwater aquifers with respect to surface waters, and therefore, removal of them from drinking water is recommended.

This study examines the potential of nanofilter membrane for the removal of phosphate, fluoride, and nitrite from aqueous solutions as a function of flow rate and as well as associated anions.

2. Material and methods

In this study, a commercial NF membrane was used. The characteristics of NF used is shown in Table 1. The experiments were done as batch filtration and experimental processing about NF were conducted by flat sheet membrane. Before the preparation of experiments, the nanofilter membrane was soaked into the deionized water for at least 48 h. The peristaltic pump (Milton Roy Pvt. Ltd.) was used for pumping feed water onto the NF membrane. The membrane was polypiperazine amid thin film composite commercial membranes. In all samples, the feed solutions were synthesized from deionized and carbon-filtered water. The operations were conducted in a cross-flow membrane module (see Fig. 1, the schematic of the Nanofiltration system). Permeate samples were collected, and the water parameters (fluoride, nitrite, and phosphate) were measured analytically according to standard methods. In all stages, experiments were conducted at a pressure of 8–16 bar with a 45% recovery rate. All chemicals used in this study were analytical grade and used without further purification and were purchased from Merck Company (Germany). Double distilled water was used throughout this study. HCl and NaOH (1 N) were applied for pH adjustment and all the experiments were carried out at 25℃. All analyses were done using the Matlab software.

Removal efficiency was calculated using the following equation:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

where R is removal efficiency, and C_0 and C_e are concentrations of fluoride, nitrite, and phosphate in the initial and permeate solutions, respectively.

To examine the nanofilter efficiency on nitrite removal, stock of nitrite standards was prepared by

Table 1
Characteristics of nanofilter membrane

Membrane type	Polypiperazine amid thin film composite
Operational pressure, bar	8–16
Maximum operational temperature °K	313
pH	4–11
Surface charge	Negative
Surface, m^2	0.002
Nominal capacity, L/min	0.8
Nominal cutoff, Da	270

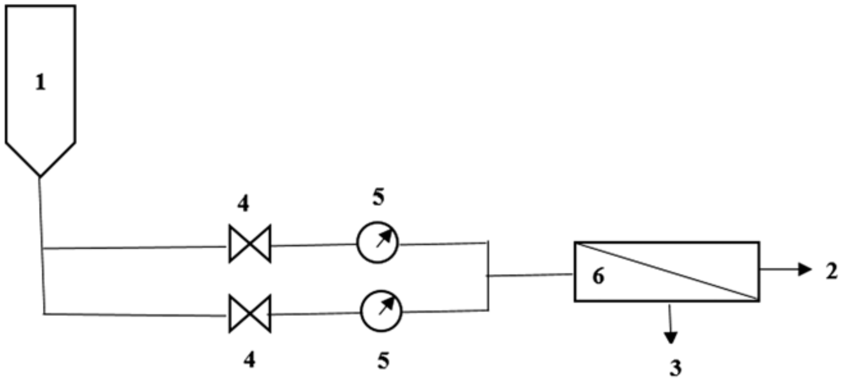

Fig. 1. The schematic of the NF system ((1) feed tank, (2) permeated flow, (3) concentrated flow, (4) pumps, (5) barometers, and (6) NF membrane).

dissolving the sodium nitrate ($NaNO_3$) in proper amounts of distilled water. Synthetic samples were provided with concentrations of 2–12 mg NO_2^-/L, and then system was run at a flow rate of 0.4 and 0.8 L/min. The nitrite concentration was measured by DR/5000 (HACH, Germany) spectrophotometer using the Diazotization standard method.

To survey the effect of nanofilter membrane on fluoride removal, stock of nitrite standards was provided with dissolving the sodium fluoride in deionized water. Synthetic samples also were prepared with concentrations of 4–12 mg F^-/L. Then, the system was conducted at flow rates of 0.4 and 0.8 L/min. The fluoride concentration was analyzed by DR/2000 (HACH, Germany) spectrophotometer using the standard SPADNS method.

To investigate the phosphate removal by NF process, stock of phosphate standards was purveyed with dissolving the anhydrous potassium phosphate in the distilled water. Then, the solutions with phosphate concentration of 10–30 mg/L were provided. Finally, the prepared solution was passed from nanofilter membrane at flow rates of 0.4 and 0.8 L/min. The phosphate concentration was determined by DR/5000 (HACH, Germany) spectrophotometer using the Molibdovanadate standard method.

3. Results

3.1. Removal of nitrite

Fig. 2 presents the effect of nitrite concentration and flow rate on nitrite removal efficiency by nanofilter. According to obtained results, by increasing the nitrite concentration and the flow rate, the nitrite removal efficiency decreased. With initial nitrate concentration of 2 mg/L, the maximum efficiency of nitrite removal was 92.8% at a flow rate of 0.4 L/min. With initial nitrate concentration of 12 mg/L, the obtained minimum efficiency of nitrite removal was 83.3% at a flow rate of 0.8 L/min.

3.2. Removal of fluoride

In this study, the removal of fluoride ion by nanofilter membrane was explored at different concentrations of fluoride ion and flow rates (Fig. 3). According to obtained results, the fluoride removal efficiency

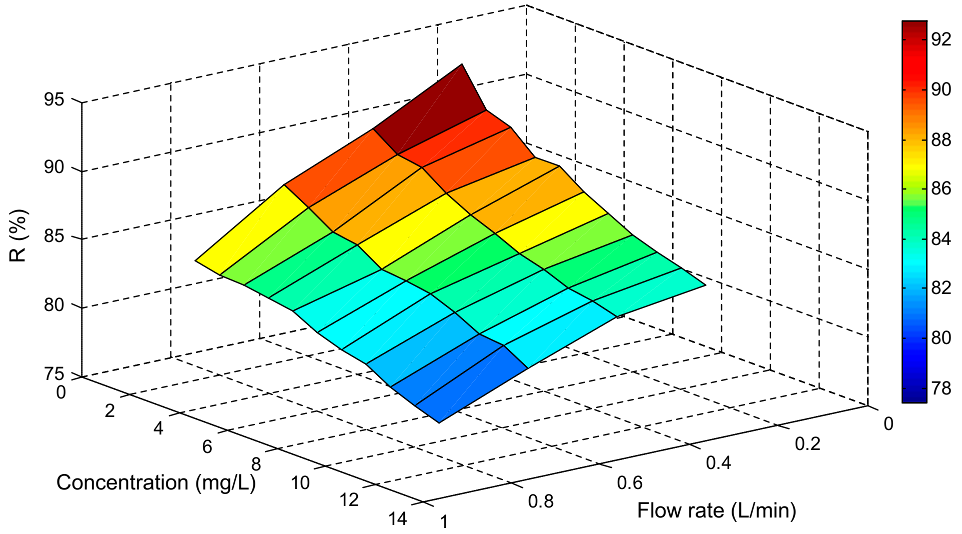

Fig. 2. Nitrite removal efficiency by NF process (flow rate: 0.4 and 0.8 L/min, initial concentration: 2–12 mg/L).

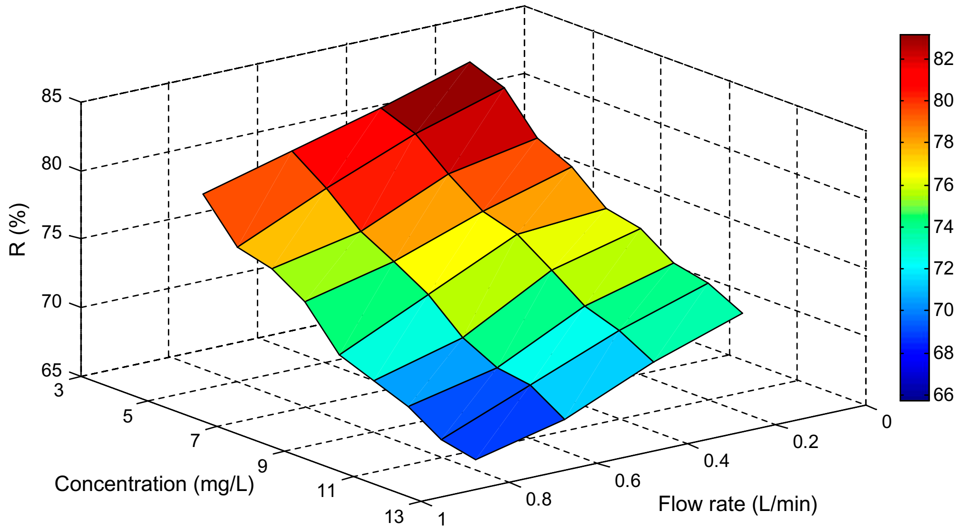

Fig. 3. Fluoride removal efficiency by NF process (flow rate: 0.4 and 0.8 L/min, initial concentration: 2–12 mg/L).

declined with raised initial fluoride concentrations and flow rates, as the highest removal efficiency (83.3%) was obtained at a flow rate of 0.4 L/min with initial concentration of 4 mg/L. The lowest removal efficiency (65.75%) was resulted at a flow rate of 0.4 L/min with initial concentration of 12 mg/L.

3.3. Removal of phosphate

The amounts of phosphate removal by nanofilter membrane are given in Fig. 4. As shown, when the flow rate and initial phosphate concentration were 0.8 L/min and 30 mg/L, respectively, the nitrate removal efficiency was 98.5%. While, when the flow rate and initial phosphate concentration were 0.4 L/min and 10 mg/L, respectively, the nitrate removal efficiency was 92.3%. It means by increasing flow rate and initial phosphorous concentration, the phosphate removal efficiency decreases.

4. Discussion

With increased nitrite concentration and flow rate, the nitrite removal efficiency decreased. The

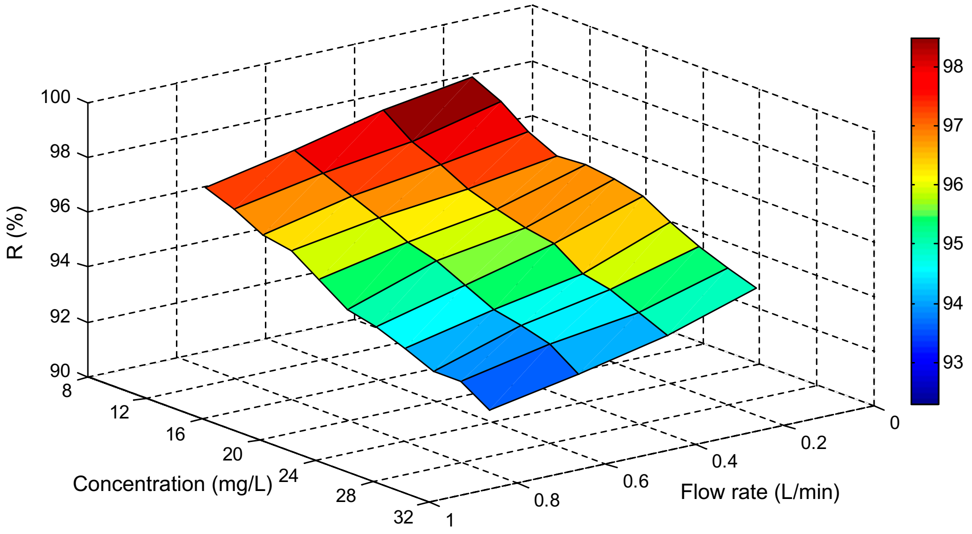

Fig. 4. Phosphate removal efficiency by NF process (flow rate: 0.4 and 0.8 L/min, initial concentration: 2–12 mg/L).

maximum efficiency of nitrite removal was 92.8% at a flow rate of 0.4 L/min. The results of this experiment indicated that a nano-membrane could considerably reject the monovalent ions. These results can be mainly described by its tight pore structure and the characteristics of the charged membranes. It can be contributed to the transfer mechanism, including sieving and electrostatic interaction effects [39,40]. The results of this study have been confirmed by some previous studies [40–42].

The fluoride removal efficiency declined with raised initial fluoride and flow rate, as the highest removal efficiency (83.3%) was obtained at a flow rate of 0.4 L/min and initial concentration of 4 mg/L. The evolution of rejection with flow rate showed a strong decrease by increasing flow rate from 0.4 to 0.8 L/min and initial concentration. This was due to screening phenomenon and increased concentration of ions in the solution. Increasing in ion concentration can be resulted to neutralization of negative charges on the membrane surface and decreased fluoride passage through the membrane [40,43]. This result has been observed by other authors who treating monovalent solutions with charged membranes [43,44].

With increasing flow rate and initial phosphate concentration, the phosphate removal efficiency is reduced. The highest and lowest phosphate removal efficiency was 98.5 and 92.3%, respectively. The results of this experiment illustrated that a nano-membrane could considerably reject the three-valent ions. As the rejection rate of phosphate was higher than the rejection rate of monovalent ions (fluoride and nitrite), the

Table 2
Comparison between the results of this study and other researches

Parameter	Methods	Removal efficiency	References
Nitrite	Polypiperazine amid thin film composite	92.8	This study
Fluoride		83.3	
Phosphorous		98.5	
Phosphate	NF200 membrane (NF)	85	[25]
Fluoride	Fe(III)-loaded ligand exchange cotton cellulose	96	[15]
Fluoride	Regenerated spent bleaching earth (RSBE)	75	[21]
Fluoride	Modified amberlite resin	80	[22]
Phosphate	Multilayer polyelectrolyte NF membranes	97	[28]
Nitrate	Electrocoagulation	92	[30]
Nitrate	Tight NF membrane (NF90)	97	[35]
Fluoride	Hybrid sorbent resin	63	[46]

experiments showed that nano-membranes strongly repulsed three-valent anions. However, phosphate ions were highly affected than nitrite and fluoride by the surface charge of the membrane. In addition, monovalent ions are hydrated in aqueous solution more than phosphate ions (multivalent ion), resulting in less rejection of monovalent ions [43,45]. The results of this study have been confirmed by other researchers [28,29]. Comparison between the results of this study and previously reported methods is shown in Table 2.

5. Conclusions

(1) With increased nitrite concentration and flow rate, the nitrite removal efficiency decreased. The maximum efficiency of nitrite removal was 92.8% at a flow rate of 0.4 L/min and initial nitrate concentration of 2 mg/L and minimum efficiency of nitrite removal was 83.3% that was obtained at a flow rate of 0.8 L/min and initial nitrate concentration of 12 mg/L.
(2) The highest fluoride removal efficiency (83.3%) was obtained at a flow rate of 0.4 L/min and initial concentration of 4 mg/L and the lowest removal efficiency (65.75%) was found at flow rate of 0.4 L/min and initial concentration of 12 mg/L.
(3) With the flow rate and initial phosphate concentration 0.8 L/min and 30 mg/L, respectively, the nitrate removal efficiency was 98.5%.
(4) With the flow rate and initial phosphate concentration 0.4 L/min and 10 mg/L, respectively, the nitrate removal efficiency was 92.3%.
(5) The results indicated that NF could considerably reject the monovalent ions due to the tight pore structure and the characteristics of the charged membranes and the transfer mechanism including sieving and electrostatic interaction effects.
(6) The evolution of rejection with flow rate showed a strong decrease by increasing flow rate and initial concentration.
(7) The results indicated that NF could considerably reject the three-valent ions. The rejection rate of phosphate was higher than the rejection rate of fluoride and nitrite.

According to our findings, the NF membrane is recommended as an effective and reliable method for removing nitrite, phosphate, fluoride, and other ions from aqueous solutions.

Acknowledgments

The authors would like to thank the Laboratory staff cooperation of environmental chemistry and financial support from the University.

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