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Nitrate removal from aqueous solutions by nanofiltration

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ABSTRACT

Due to excessive usage of nitrate fertilizers in agricultural sectors and dumping of domestic wastewaters, nitrate levels of water resources are increased in aqueous environments. Increased nitrate-containing compounds in the water resources, could lead to serious problems including eutrophication, and cause potential hazards for human and animal health. The aim of the present study was to investigate the effectiveness of nitrate removal from aqueous environments using nanofiltration (NF) membranes. In this study, the effect of different factors such as initial nitrate concentration, flow rate and associated cation and co-existing anions on the retention of nitrate by NF was examined. The results showed that with increased initial concentration of nitrate, flow rate and associated anions, the removal efficiency of nitrate decreased. The experiment indicated that many of negative charge groups on the membrane surface are covered by cations. The divalent cations covered membrane charge more effectively than monovalent cations. The result showed with high removal of sulfate ion, many nitrates are forced to pass through the membrane. The highest nitrate removal efficiency was 80.5%. According to the findings of this study, NF membrane usage could be recommended as an effective and reliable method for removing nitrates from aqueous environments.

Keywords: Water treatment; Flow rate; Co-anion; Associated cation; Membrane; Kerman water

1. Introduction

Because of strict standards for drinking water and increased pollution of waters, groundwater treatment for drinking is increasingly becoming an even more complex matter [1]. In treatment of waters, some components such as nitrate, pesticide, water hardness, water color, natural organic matter (NOM), etc. must be removed [1–3]. Due to excessive usage of nitrate fertilizers in agriculture and disposal of domestic wastewater effluents, the amount of nitrates in water resources is increased [4–8]. When nitrogen containing complexes enter into water resources, they can cause serious problems including eutrophication, lower water quality and potential hazards for human and animal health [9]. Increased intake of nitrate affects human health through methemoglobinoma in children, hypertension, thyroid malfunctioning and the risk of carcinogenicity of nitrosamine and nitrosamide [9–12].

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The WHO guideline is 50 mg/L as NO_3 for nitrate [5,9,13]. Conventional methods for nitrate removal include ion exchange, biological treatment, reverse osmosis(RO), coagulation process, activated carbon absorption and nitrification by ozonation [2,6–8,14–16].

As of recently, nanofiltration process (NF) has been widely being used in water treatment, food, pharmaceutics and chemical industry and wastewater treatment [1,17,18]. Charged groups and pore diameters > 1 nm are some of NF characteristics [19]. NF has shown its effectiveness in the removal of great variety of undesirable components from water. Its separation mechanisms are sieving effect, differences in diffusivity and solubility of solutes and electrostatic interactions between the membrane surface groups and ions [20,21]. The advantages of NF processes are operational simplicity , reliability, no additive requirements and modular construction [1].

Kerman province located in the south-eastern part of Iran with longitude 54°21′–59°34′ and latitude of 26°29′–31°58′, is characterized by warm and arid climate and considerable temperature variations between day and night [22]. In most parts of the province groundwater as a drinking water resource is being used. Due to the occurrence of drought in Kerman province, the quality of groundwater is affected. The aim of this study was to investigate nitrate removal process from aqueous solutions by NF membranes under different circumstances.

2. Material and methods

2.1. Experimental procedure

In this study, a commercial NF membrane similar to pilot scale was used. Table 1 shows the characteristics of an NF membrane and Fig. 1 illustrating the schematic design of the NF system. Only new membranes were used for the experiments. The membrane was soaked in the deionzed water for at least 48 h prior to use. The feed water is pumped onto the NF membrane by a peristaltic pump. In all stage, experiments were conducted at a pressure of 8 bar and a 45% recovery rate.

2.2. Effect of nitrate initial concentration

To examine the effect of nitrate initial concentration, synthetic sample was prepared with 100, 150, 200, 250 and 300 mg NO_3^-/L as KNO_3 and the system was run at a flow rate of 0.4 L/min. Standard nitrate solutions were prepared by dissolving the potassium nitrate (KNO_3) with appropriate amounts of distilled water.

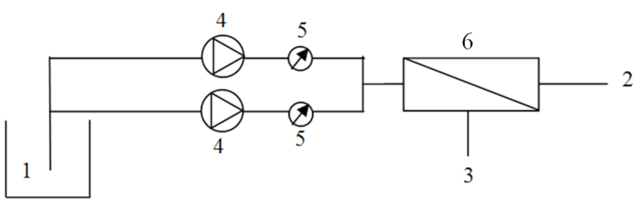

Fig. 1. Schematic of a nanofiltration membrane (1: feed tank, 2: permeate flow, 3: concentrate flow, 4: pump, 5: barometer, 6: NF membrane).

Table 1
Characteristics of a nanofiltration membrane

Membrane type	Polypiperazine amid thin-film composite
Maximum operational pressure, bar	8–16
Maximum operational temperature, °C	45
pH range	4–11
Surface charge	Negative
Nominal cut off, Da	270
Surface, m^2	0.002
Nominal capacity, L/min	0.8

2.3. Effect of flow rate

To study the effect of flow rate on nitrate removal efficiency, the nominal capacities of 0.4 and 0.8 L/min were used.

2.4. Effect of associated cations

In this stage, the effect of associated cations was investigated. For this purpose, $NaNO_3$, KNO_3 and $MgNO_3$ were used to provide stock solutions. The solutions with initial concentration of nitrate equal to 100, 150, 200, 250, 300 mg/L were provided and the system was set with a flow rate of 0.4 L/min.

2.5. Effect of co-existing anions

The effect of co-existing anions on nitrate removal efficiency was determined by using NaF, NaCl and $NaSO_4$. In this stage, the solutions were first prepared with nitrate initial concentration of 100 mg NO_3^-/L of KNO_3 and then different concentrations of the mentioned anions were added to the solution and finally the combined solution was passed through NF. In this stage, the experiments were conducted at a flow rate of 0.4 L/min.

2.6. Effect of TDS on actual flux crossing

In this stage, we used two types of salts (i.e., NaCl and Na_2SO_4) to prepare the TDS solution. Afterwards, different concentrations of each salt and the required time for passing the 5 L solution from NF were calculated as:

Actual flux = solution volume (L) / crossing time (min)

This stage was carried out by 2 pumps. Finally, this process was tested on Kerman groundwater which chemical quality was previously been tested. The entire required chemical materials were purchased from MERCK in analytical grade. All experimental methods for the study were chosen according to Standard Methods for Examination of Water and Wastewater [23].

3. Results

Fig. 2 presents the effect of nitrate concentration and flow rate on nitrate removal efficiency.

Fig. 3 shows the influence of associated cation on nitrate removal efficiency.

The effect of associated anion on nitrate removal efficiency is shown in Fig. 4.

The influence of TDS on actual flux of membrane is shown in Fig. 5.

Table 2 shows the results of treating Kerman groundwater by the NF membrane.

4. Discussion and conclusion

Fig. 2 shows that with increased initial concentration of nitrate, the nitrate removal efficiency was reduced. The highest and lowest nitrate removal efficiency was 80.5% and 70.3% which were obtained from 100 and 300 mg/L initial concentration of nitrate, respectively. These were due to the characteristics of the charged membranes and known as the screen phenomenon. With increased dissolved nitrate salts, concentrations of cations increased in the solution. The cations neutralized the negative charges on the membrane and increased passage of the nitrates ions through the membrane [24]. The result of this study have been confirmed by Paugam et al. in France, Kang et al. in Korea, Garcia et al. in Spain and also Santafé-Moros et al. in France [21,24–26].

As shown in Fig. 2, when the flow rate was 0.8 and 0.4 L/min, the nitrate removal average was 69.3 and 75.7% respectively. It means that at increasing flow rate, the nitrate removal efficiency is reduced. Indeed, this was due to the influence of amount of ion released over surface of

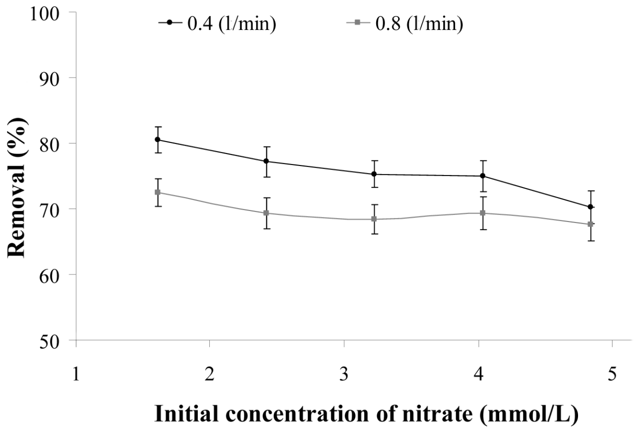

Fig. 2. Effect of nitrate concentration and flow rate on removal efficiency (nitrate salt: KNO_3, pH = 7).

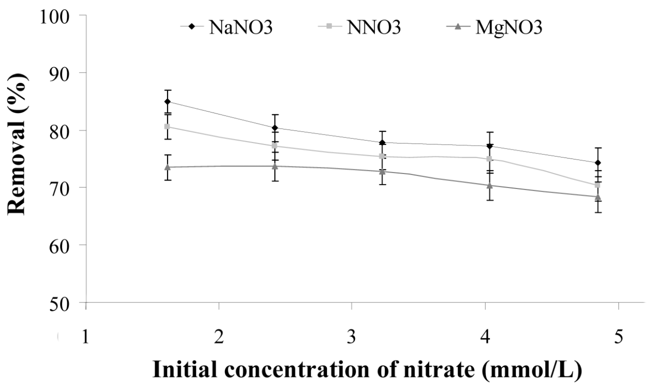

Fig. 3. Effect of associated cation on removal efficiency (0.4 L/min, pH = 7).

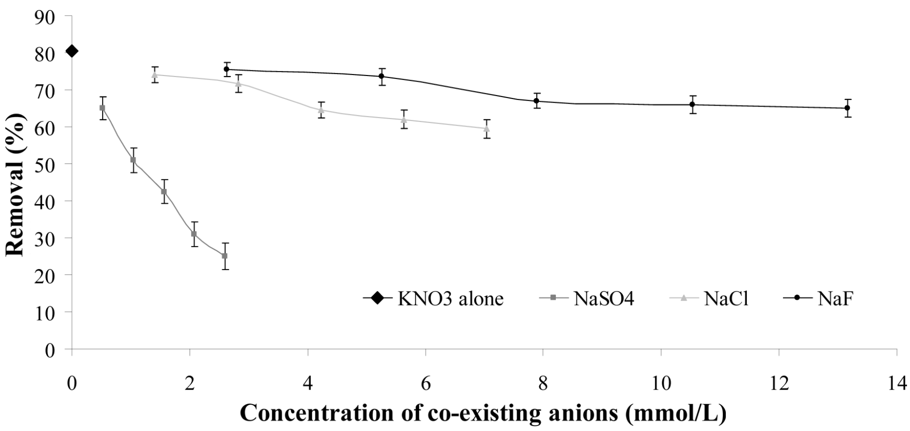

Fig. 4. Effect of co-existing anions on removal efficiency (nitrate salt: KNO_3, 1.6 mmol NO_3^-/L, 0.4 L/min, pH = 7).

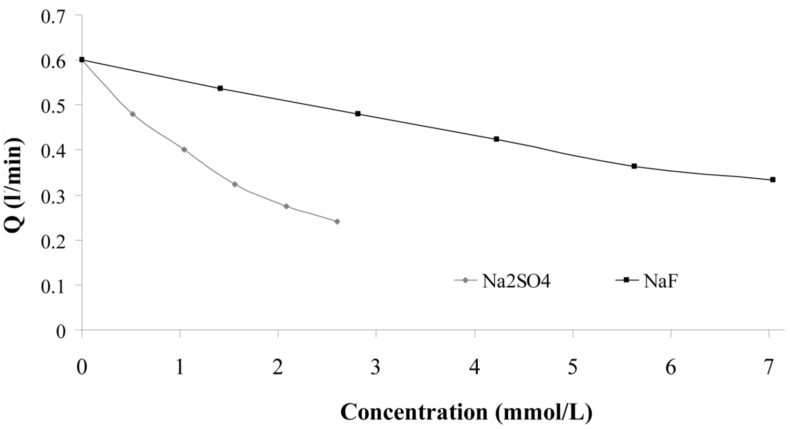

Fig. 5. Effect of TDS on actual flux crossing (two pumps, pH = 7).

Table 2
Results of treatment Kerman groundwater by the NF membrane

Parameter	Initial concentration (mg/L)	0.4 L/min		0.8 L/min	
		Concentration after process (mg/L)	Efficiency (%)	Concentration after process (mg/L)	Efficiency (%)
EC, μS	1103.39	315.9	71.37 ± 2.1	348.9	68.38 ± 2.3
NO_3^-, mg/L	38.1	14.4	62.2 ± 2.2	17.1	55.12 ± 2.4
SO_4^{2-}, mg/L	194.1	41.1	78.83 ± 1.4	46.1	76.25 ± 1.5
Cl^-, mg/L	104.37	36.2	65.3 ± 2.1	44.73	57.14 ± 1.9
Alkalinity, mg/L	267	64	76.03 ± 1.5	80	70.04 ± 1.67
Ca, mg/L	60.8	16	73.68 ± 1.3	18.4	69.74 ± 1.4
Mg, mg/L	32.21	7.81	75.75 ± 1.5	10.25	68.18 ± 1.7
Na, mg/L	127.91	55.44	56.66 ± 1.6	59	53.87 ± 1.5
K, mg/L	3.5	1.5	57.14 ± 2.1	2	42.86 ± 2.4
pH	7.43	7.21	—	7.32	—

membrane on solute transfer. This behavior is characteristic of situations where concentration polarization still influences the solute transfer with, at the same time, a non-negligible contribution of diffusion in the pores and leads to dispersion and then to a poor observed retention [27]. These results have been adopted by Causserand et al. in 2005 in France [27].

As Fig. 3 shows, with the mixture of 3 conventional salts (i.e., $NaNO_3$, KNO_3 and $MgNO_3$) and equal concentration of nitrate, $NaNO_3$ and $MgNO_3$, had the highest and lowest removal efficiency, respectively. The presence of divalent ions as magnesium greatly reduced nitrate removal efficiency. Hydration energy of ions could also be affected on crossing ions, the more ions are hydrated so more it would be removed by membrane. Also at similar concentration of nitrate, the number of positive charge by dissolved magnesium salts are higher than sodium salts which caused the total charge of the membrane decreased and the repulsion between the latter and nitrate is reduced. Consequently, the nitrate more easily cross the membrane and the nitrate removal efficiency decreased [24]. The results are in line with Paugam et al. in France [24].

The effect of associated anions on nitrate removal efficiency is shown in Fig. 4. When other anions are added to the nitrate solution, anions forced nitrate ions to pass through the NF membrane. The results showed that with increased anions in the solution from 50 to 250 mg/L, the nitrate removal efficiency is reduced from 65.1 to 25.2% for $NaSO_4$, from 74.1 to 59.5% for NaCl and from75.5 to 65.1%. Because of high removal of sulfate ion, because of their high valence, nitrates are forced to pass through the membrane. The removal of monovalent ions such as nitrate was greatly decreased under the presence of sulfate ions. Retention of the negative sulfate ion in concentrate water disturbed the electrical equilibrium on both sides of the membrane that nitrate ions was forced through the membrane in permeate water to maintain electric equilibrium. The results have been matched with Paugam et al. in France, Santafé-Moros et al. in Spain and also Choi et al. in Korea [24,26,28].

Fig. 5 shows that, with increased ion concentrations in feed solution, the actual flux crossing of membrane is reduced at constant pressure. This reduction in flux crossing is increased when the divalent ion is added, probably due to increased solution osmotic pressure.

Although that "the standard limit for nitrate is 50 mg/L as NO_3^-, the recommended concentration was 25 mg/L" [1]. The initial level of nitrate concentration in Kerman water was 38.1 mgNO_3^-/L and with partial removal of nitrates, this value would be obtained. In some parts of Iran where there are high concentrations of nitrate and fluoride in ground waters, NF could be an appropriate technique for water treatment and removal of nitrate and fluoride from water and prevention of related disease [29–32].

According to our findings, the NF membrane is recommended as an effective and reliable method for removing nitrate from aqueous solutions.

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