NITRATE REMOVAL FROM WATER USING SURFACE-MODIFIED ULTRAFILTRATION MEMBRANES

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Abstract: Elevated nitrate concentrations in natural water sources are a worldwide concern due to the extensive levels of soil N-fertilization. This study investigates three commercially available polyethersulfone (PES) ultrafiltration (UF) membranes with different molecular weight cut-offs (5, 10, and 30 kDa), which we modified with a cationic surfactant, cetylpyridinium chloride to improve their nitrate removal. The nitrate removal efficiency of these membranes was examinated as functions of initial nitrate concentration, pH, and permeate flux. The best nitrate removal efficiency was obtained with a 5 kDa surface-modified UF membrane.

Key words: nitrate removal, UF membrane, permeate flux, cetylpyridinium chloride, membrane surface-modificaton

UKLANJANJE NITRATA IZ VODE POVRŠINSKI MODIFICIRANIM ULTRAFILTRACIJSKIM MEMBRANAMA

Sažetak: Pojava povećanih koncentracija nitrata u prirodnim vodama diljem svijeta najčešće je posljedica prekomjerne uporabe mineralnih gnojiva u poljoprivredi. U ovom radu ispitana je mogućnost primjene tri komercijalno dostupne površinski modificirane polietersulfonske (PES) ultrafiltracijske (UF) membrane s različitim graničnim molekulskim masama (5, 10 and 30 kDa). Površinska modifikacija UF membrana načinjena je primjenom surfaktanta cetilpiridin klorida. Učinkovitost uklanjanja nitrata ispitana je ovisno o početnoj koncentraciji nitrata, pH vrijednosti otopine i fluksu permeata. Najbolji učinak postignut je primjenom površinski modificirane membrane s graničnom molekularnom masom od 5 kDa.

Ključne riječi: uklanjanje nitrata, UF membrane, fluks permeata, cetilpiridin klorid, površinska modifikacija membrane

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1 Introduction

Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, seriously threatening supplies of drinking water and promoting eutrophication [1]. Oxides of nitrogen, such as nitrate and nitrite, are common pollutants in water resources and various types of agricultural, domestic, and industrial wastewater [2]. High nitrate levels in drinking water have been associated with increased N-nitrosoproline levels in urine, and nitrate administered via drinking water has been shown to be directly related to the concentrations of N-nitroso compounds (NOC) in feces. Water containing significant concentrations of nitrate can cause methemoglobinemia in infants, also known as "blue baby syndrome", while some studies have emphasized the relationship between nitrate levels in drinking water and cancer incidence [3, 4]. For these reasons, the US Environmental Protection Agency (EPA) and the World Health Organization (WHO) have defined a maximum contamination level (MCL) of 10 mg $N\text{-}NO_3^-$/L in water [5, 6]. Figure 1 shows the average nitrate concentrations in groundwater from 27 water-wells in eastern Croatia, a site of intensive agriculture over recent decades. These nitrate concentrations were measured throughout 2011 under different hydrological conditions.

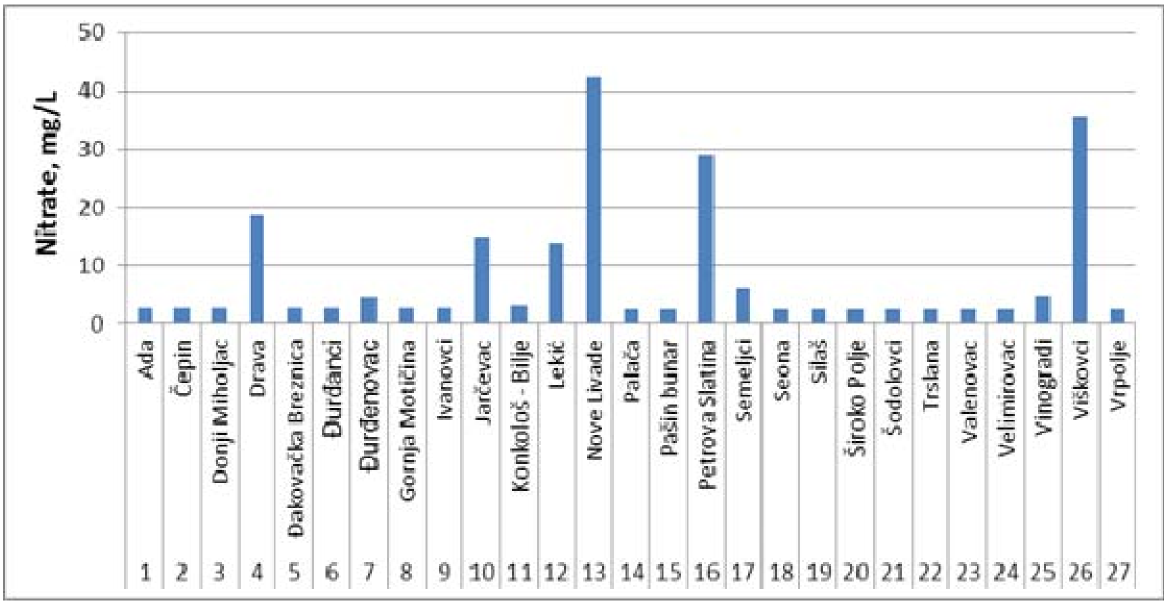

Figure 1. Nitrate concentrations in groundwater from 27 water-wells in eastern Croatia

Various technologies have been used to remove nitrate from drinking water, including reverse osmosis, ultrafiltration, ion exchange, ion-exchange-membrane bioreactors, catalytic reduction, electrodialysis, activated carbon, land disposal, chemical denitrification, and microbiological treatment [1, 2, 7]. Although these techniques effectively remove nitrate from contaminated water, they are very expensive to implement in pilot-scale programs, limiting their potential application. Of these technologies, the most versatile and widely used is biological denitrification [8] which uses an anoxic environment to completely remove nitrate; the chemically bound oxygen in nitrate acts as a terminal electron acceptor, liberating nitrogen (N_2) gas without generating brine as a by-product [9, 10, 11]. However, membrane filtration has been increasingly used to remove various contaminants from water [12-16]. Tight membrane filtration methods such as reverse osmosis (RO) filtration and nanofiltration (NF) can effectively remove nitrate from contaminated water, but such dense membranes are relatively costly and require electricity.

Several studies have shown that micellar-enhanced ultrafiltration can effectively remove organic and inorganic pollutants from aqueous phases [12, 14, 17-21]. In the present article, we investigate nitrate removal by using three commercially available cross-flow polyethersulfone UF-membranes with different molecular-weight cut-offs (MWCOs). We found that the selectivity of the UF membranes could be improved by filtering a cationic surfactant cetylpyridinium chloride (CPC) solution through them.

2 Materials and Methods

Cetylpyridinium chloride (CPC; 99% pure) was obtained from Sigma-Aldrich (USA), and KNO_3 was obtained from Alkaloid (Republic of Macedonia). A model nitrate solution was prepared with deionized (DI) water and KNO_3 as follows: 1.6305 g KNO_3 was dissolved in 1000 mL deionized water to obtain 1 mg/mL NO_3^-. This stock solution was diluted with DI water to concentrations of 60, 90, and 120 mg/L. The pH was adjusted using 0.1 M NaOH and KCl. The CPC solutions were prepared to concentrations of 1.0 mM, above the critical micelle concentration (CMC) when the surfactant forms micelles comprising up to 100 surfactant molecules. 1000 mL of the CPC solution was filtered through each membrane prior to filtering the nitrate solution. Three cross-flow polyethersulfone UF membranes (Biomax 5, Biomax 10, and Biomax 30; Millipore, USA) were used. These membranes had effective areas of 0.050 m^2 and molecular weight cut-offs (MWCOs) of 5, 10, and 30 kDa, respectively. Each membrane was fitted to a Pellicon XL laboratory-scale UF cell (Fig. 2), which had a peristaltic pump with adjustable speed (60–600 rpm/min) and adjustable capacity (optimal range of 30–50 mL/min). Before ultrafiltration, the permeate flux (J) of the feed was adjusted to 35, 65, or 85 L/m^2h. The permeate flux was adjusted by measuring the time needed to collect 25 mL of permeate by filtering DI water. The permeate flux was calculated by the following equation:

$$J=Q_p/S \qquad (1)$$

where Q_p is the permeate flow rate (L/h) and S is the membrane surface area (m^2).

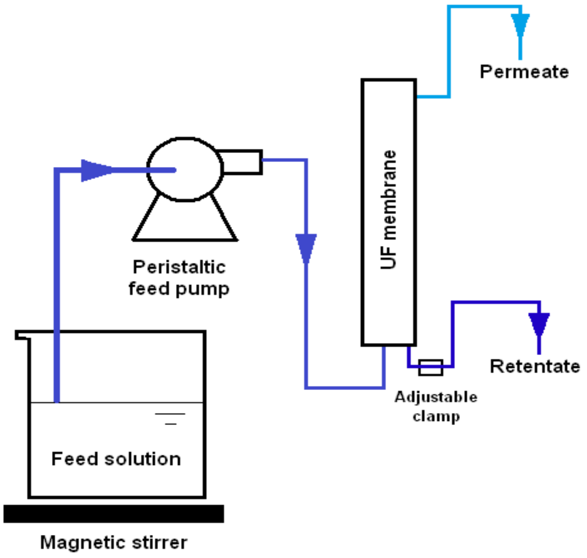

Figure 2. Schematic of the Pellicon XL ultrafiltration unit

In accordance with manufacturer instructions, the permeate flux through the membrane was adjusted with clamps attached on the retentate outlet conduit. After the permeate flux was established, 150 mL of nitrate feed solution was released, and then 300 mL of permeate was captured for analyses. Nitrate rejection was measured as a function of the initial nitrate concentration (60, 90, and 120 mg/L), pH (6–8), and permeate flux (J= 35, 65, and 85 L/m^2h). The nitrate concentrations were determined by the nitrate electrode method using an ion-selective electrode (Seven Easy, Mettler Toledo, USA) [22]. Nitrate removal (R) was calculated with the following equation:

$$R=\left(\frac{C_i-C_p}{C_i}\right)\times 100 \qquad (2)$$

where C_i is the feed concentration of nitrate and C_p the permeate concentration of nitrate.

3 Results and Discussion

3.1 Influence of pH on Nitrate Removal

Figures 3–5 show how nitrate removal varied with various membranes and at permeate fluxes of 35, 65, and 85 J/m²h, respectively. As the MWCO increased, the nitrate removal efficiency decreased. The nitrate was efficiently removed with a surface-modified Biomax 5 at a permeate flux of 35 J/m²h and an initial nitrate concentration of 60 mg/L. The greatest nitrate rejection of 34% occurred at pH 8 [Fig. 3(a)]. In general, when pH increased, the removal efficiency increased, except for an initial nitrate concentration of 120 mg/L [Fig. 3(c)]. In this case, the highest removal efficiency occurred at pH 7.5. The surface-modified Biomax 10 and Biomax 30 membranes exhibited lower nitrate removal efficiency than the surface-modified Biomax 5 membrane.

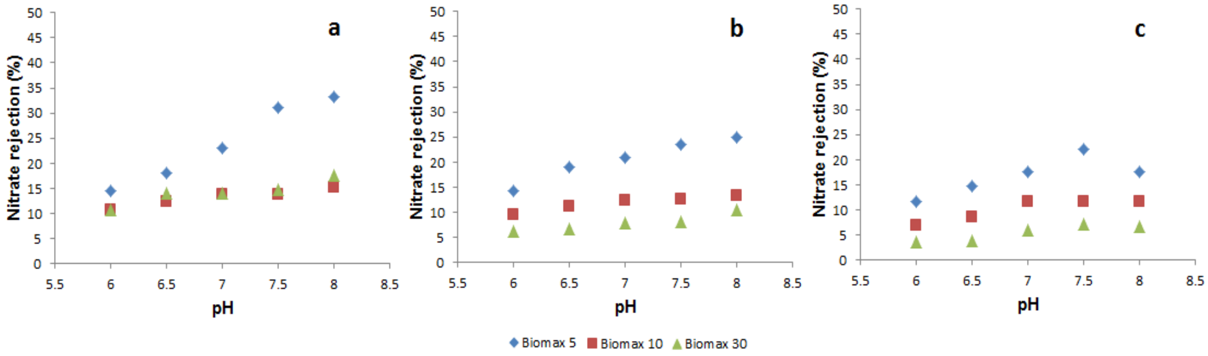

Figure 3. Nitrate rejection by UF membranes at permeate flux of 35 J/m²h and various nitrate concentrations: a) 60 mg/L, b) 90 mg/L, c) 120 mg/L

At a permeate flux of 65 J/m²h, decreasing the pH also decreased nitrate removal; the highest nitrate rejection was achieved at pH 7.5. At 85 J/m²h, the highest nitrate removal (19%) occurred at pH 7.5 with a Biomax 5 membrane at an initial nitrate concentration of 90 mg/L.

3.2 Influence of Initial Nitrate Concentration on Nitrate Removal

As shown in Fig. 3(a), at a permeate flux of 35 L/m²h, nitrate removal increased with decreasing concentration; the highest nitrate removal (33%) occurred at an initial nitrate concentration of 60 mg/L. At permeate fluxes of 65 and 85 L/m²h, nitrate rejection was almost independent of concentration in the studied range. At 65 L/m²h, the highest nitrate removal (over 37%) occurred at the highest nitrate concentration (120 mg/L), as shown in Fig. 3(c); at 85 L/m²h and the same initial nitrate concentration, only 13% of the nitrate was removed.

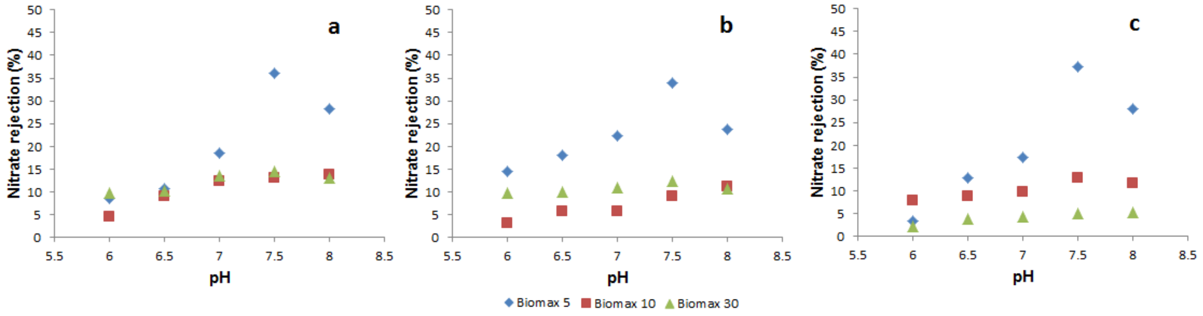

Figure 4. Nitrate rejection by UF membranes at permeate flux of 65 J/m²h and various nitrate concentrations: a) 60 mg/L, b) 90 mg/L, c) 120 mg/L

The highest removal efficiency was achieved with a Biomax 5 membrane at an initial concentration of 120 mg/L [Fig. 4(c)]. This membrane could be used as a household filter for drinking water to remove nitrate at concentrations slightly over the maximum concentration level (MCL).

3.3 Influence of Permeate Flux on Nitrate Removal

Our results show that the optimum permeate flux for nitrate removal was 65 L/m^2h. At 35 L/m^2h, the removal efficiency was somewhat lower, while at 85 L/m^2h all the examined membranes exhibited low removal efficiency. The highest nitrate removal (37%) occurred with the Biomax 5 membrane at a permeate flux of 65 L/m^2h [Fig. 4(c)].

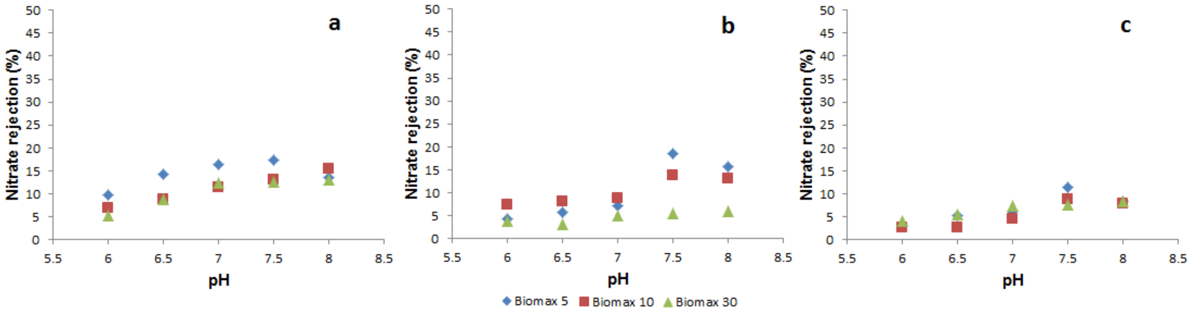

Figure 5. Nitrate rejection by UF membranes at permeate flux of 85 J/m^2h and various nitrate concentrations: a) 60 mg/L, b) 90 mg/L, c) 120 mg/L

4 Conclusions

In this article, we modified the surfaces of various ultrafiltration membranes with molecular weight cut-offs (MWCOs) of 5, 10, and 30 kDa using cetylpyridinium chloride cationic surfactant. We then tested the membranes for nitrate removal from water at various initial nitrate concentrations (60, 90, and 120 mg/L), pH values (6–8), and permeate fluxes (J= 35, 65, and 85 L/m^2h). The membrane with the highest nitrate removal efficiency (up to 37%) had an MWCO of 5 kDa; the membranes with MWCOs of 10 and 30 kDa exhibited much lower removal efficiency under the same conditions. The 5 kDa membrane achieved its highest nitrate removal efficiency at pH 7.5, specific flow of J=65 L/m^2h, and initial nitrate concentration of 120 mg/L NO_3^-. These results show that a surface-modified UF membrane with an MWCO of 5 kDa can be applied as home-filtration system to remove nitrates present in drinking water at slightly higher concentrations than the maximum concentration level.

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