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Nanofiltration Efficiency in Nitrate Removal from Groundwater: A Semi-Industrial Case Study

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Abstract. Nanofiltration is a promising technology which has many applications in water and wastewater treatment. This work studies the efficiency of a semi industrial nanofiltration pilot plant (plant capacity: 60 m3/d) in nitrate removal from groundwater. An activated carbon filter and an ultrafiltration system with 90% recovery were used for pretreatments. Nanofiltration had a great efficiency in sulphate and chloride removal, but nitrate removal was less than expected. Also it showed good ability in cations rejection and it was effective in hardness and alkalinity removal. The effect of the pressure and permeate flux on nitrate removal is investigated.

Keywords: Nanofiltration, Nitrate, Groundwater, NF90.

1. Introduction

Nanofiltration (NF) is defined as a process with characteristics between reverse osmosis and ultrafiltration. It was introduced in the late 1980s, mainly applied in softening, but it has been used for combined removal of micropollutants, nitrate, arsenic, fluoride, viruses, NOM [1]. Nanofiltration can remove mentioned components completely or partly. Nanofiltration has been reported as a suitable method for groundwater treatment [2]. Retentions higher than 90% were found for multivalent ions, whereas monovalent ions were retained for about 60- 70% [3]. Nanofiltration has many advantages: low operation pressure, easy operation, good quality product, and low investment cost [4].

The nitrate concentration level in groundwater for human consumption is one of the most important problems related with the quality of the groundwater in many countries and also in Iran [5]. The health effects of nitrate are generally a consequence of its ready conversion to nitrite in the body [6]. The Iranian legislation established a maximum allowed concentration of 50 mg- NO3- L-1 in drinking water [5]. In researches have done so far, it can be concluded that NF90 has a relatively high nitrate rejection [7-9].

In this paper the nanofiltration efficiency with two pretreatments is studied for groundwater treatment. The application of NF for the simultaneously removal of hardness, and some ions such as: sulphate, chloride, magnesium, sodium and calcium were examined. This study attempts to highlight the effects of the feed composition and operating parameters (the pressure and the permeate volumetric flux (Jv)) on the retention of nitrate ions. The membranes (NF90) were chosen based on the reported results from the literature [1,8]. Properties of NF90 are summarized in table 1.

Table 1. Properties of NF90 indicated by manufacturer [10].

Membrane	Nf90
Material	Polyamide
Operational pressure (bar)	5.4

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Approximate solute rejection NaCl (%)	85-95
Water flux ($L/m^2/h$)	43
pH range	4-11
Surface charge	Negative

2. Material and methods

Considering nitrate level, a well was selected for observation in Tehran, Iran. A nanofiltration pilot plant with two pretreatments (UF and ACF) was used for reducing nitrate. The water enters the ACF tank at the top and distributes evenly to flow downward through the media bed. Then it passes through the disc filter (100 microns) and enters the UF system. The product of UF is stored in a tank ($1m^3$) and then it is pumped into cartridge filters (5 microns). Which is followed by entering the nanofiltration system Consisting 3 stages (Fig. 1). Figure 1 shows that water is passed through the first two filters and the resulting concentrate exits through the other stage As it shows in Fig. 1, the water passes through the two first stages and then its concentrate goes into the other stage. The ultrafiltration and nanofiltration recoveries are 90% and 70%, respectively.

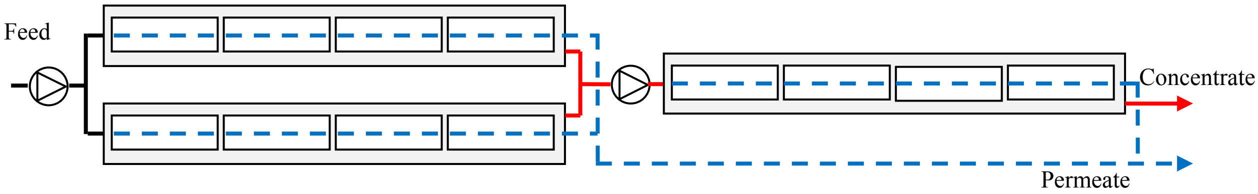

Fig. 1. Schematic diagram of the nanofiltration system.

The nanofiltration system is equipped with 12 NF90-4040 (DOW-filmtec) modules, Including 4 membranes in each stage. The experiments were performed at 298 K over the pressure range of 4 to 6 bar. The volumetric flux Jv was determined by measuring the volume of permeate collected in a given time interval. The observed retention (R) derives from the following relation:

$$R = \left(1 - \frac{C_p}{C_0}\right) \quad (1)$$

Where C_p and C_0 are the concentration in the permeate and feed solution, respectively. An ionic chromatography method was used for measuring the anions concentrations The anions concentrations were measured by ionic chromatography (Metrohm 6.2041.430) and the An atomic absorption spectrophotometry method was utilized for measuring cations concentrations cations concentrations were measured by atomic absorption spectrophotometry. The pilot plant was being operated for 3 months.

3. Results and discussion

The feed water composition are shown in table 2. As it is shown in table 2, the nitrate concentration level is higher than standard. Also the permeate observed parameters levels(for the permeate of all stages) are reported in this table as the result of two pretreatments (with ACF and UF) and a main treatment (NF). Fig. 2 is drawn according to the table 2.due to the rejection amounts in table 2, it is obvious that the nanofiltration in E.C, TDS, Hardness, Alkalinity removal is more than 84% efficient.

It can be seen that certain ions removals are efficient using nanofiltration (Fig. 2). The sulphate shows the largest rejection value among the anions and the nitrate rejection resualts the lowest level the anions.

Cause of this result is the influence of the chloride and sulphate ions on the retention of nitrate. The sulphate ion retention has the highest rejection level because of its high hydration energy and large size and also its charge (table 3). So sulphate cannot pass the membranes, and the nitrate ions rejection decrease which electroneutrality conditions interpret having to be established on both sides of membranes [11, 12].

Table 2. Characteristics of groundwater quality.

parameters	unit	Mean value in the feed water	Permeate values	Rejection (%)
temperature	˚C	25	25	----
pH	------	7.6	6.6	----
E.C.	µ s/cm	871	108	87.6
TDS	mg/l	553	82	85.2
Hardness	mg/l	195	22	88.7
Alkalinity	mg/l	233	36	84.5
SiO_2	mg/l	22.9	3.5	84.7
Cl^-	mg/l	55	6.5	88.2
SO_4^{2-}	mg/l	84.8	0	100
NO_3^-	mg/l	61	24.3	60.2
Na^+	mg/l	116.5	17.3	85.2
Ca^{2+}	mg/l	62.2	6.7	89.2
Mg^{2+}	mg/l	9.2	1.3	85.9

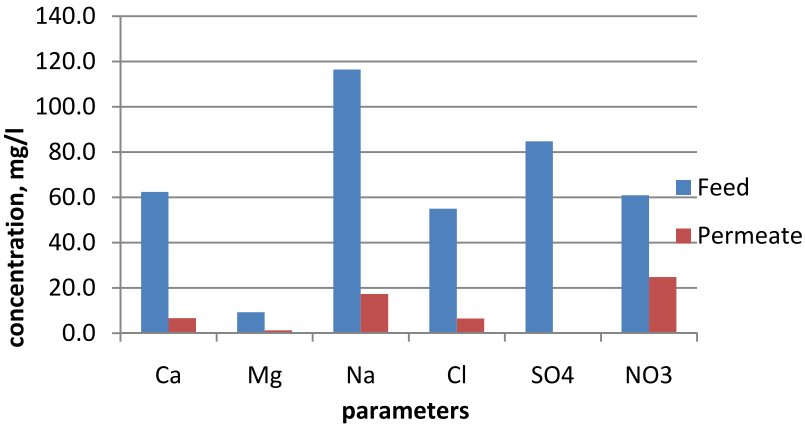

Fig. 2. The concentrations for different components in feed and permeate flow.

The chloride ion rejection shows higher levels than nitrate (table2). However, size (steric) or charge (Donnan) effects cannot explain that, (table3). One assumption in order to explain this phenomenon considered to be the nitrate ion with a larger molar volume corresponding to a larger surface area would have a lower surface charge density around the molecule compared to smaller molar volume of the ion. Thus the donnan effect between nitrate and membrane (which is negatively charged) is weaker and because of electroneutrality condition its rejection is lower than chloride [4].

For cations , the difference in ion diffusivity (Ds) could affect the rejection sequence, an ion is retained more if it has a smaller diffusivity. So the sodium rejection is lower than magnesium and calcium, because its diffusivity is the largest [4]. But this theory cannot explain the rejection of calcium and magnesium, their charges are similar, but $r_s(Mg^{2+}) > r_s(Ca^{2+})$, $D_s(Mg^{2+}) < D_s(Ca^{2+})$ and $R(Mg^{2+}) < R(Ca^{2+})$. The effect of concentration can explain the mentioned, that is shown to be higher for calcium.

Table 3. Characteristics of studied ions [4,11].

Ion	$r_{s(nm)}$	Hydration energy ($kJmol^{-1}$)	D_s ($10^9 m^2 s^{-1}$)
Cl^-	0120	376	2.032
SO_4^{2-}	0.229	1138	1.065
NO_3^-	0.128	329	1.902
Na^+	0.183	407	1.333
Ca^{2+}	0.307	1584	0.718
Mg^{2+}	0.345	----	0.706

In this work the influence of the pressure on nitrate removal is studied, too (Fig. 3). it can be shown, the nitrate retention rises with an increase in the pressure. This can be explained by the influence of the pressure on the permeate flux (Fig. 4) and also its effect on concentration polarization. The permeate volumetric flux increases linearly with the pressure (Fig. 4), so the concentration polarization which leads to a resistance to the transfer through the membrane is not significant [8,11].

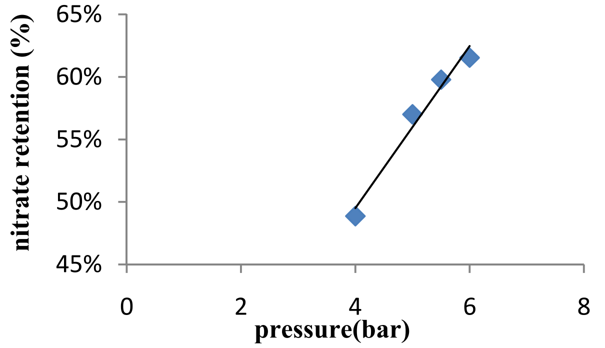

Fig. 3. Nitrate retention as a function of the pressure

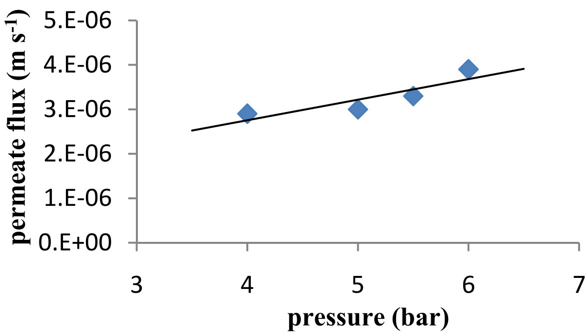

Fig. 4. Permeate flux as a function of the pressure

4. Conclusion

Nanofiltration has shown its effectiveness in the removal of a great variety of undesirable components from water. In this work the rejection of nitrate with NF90 was studied and it was 60%. However, in the literature it mentioned that NF90 can remove nitrate in the range of 85- 95% [1,8,13]. This difference can be explained by this fact that all of the other works have been done in the batch scale, the feed was synthetic and prepared in the under control circumstances.

The rejection sequence of NF90 to cations can be written as follows: $\mathrm{R(Na^{+})} < R(\mathrm{Mg^{2+}}) < R(\mathrm{Ca^{2+}})$ and for anions it is: $\mathrm{R(NO_3{}^{-})} < R(\mathrm{Cl^{-}}) < R(\mathrm{SO_4{}^{2-}})$. The reason for these sequences can be explained by the electrostatic phenomenon which is the major factor at low salt concentration. The sequence of cations rejection can be explained by the differences in charge, such as diffusivity (for the same valence ions, an ion is retained more if it has a smaller diffiusivity) and concentration. For anions removal, the sequence is a function of charge, size and hydration energy (the more the ion is hydrated, the more it can be rejected by the membrane).

It has expressed that nitrate removal rises with an increase in the pressure [11] (increasing the pressure from 4 bar to 6 bar leads to 10% increase in nitrate removal, approximately). In addition to pressure the nitrate removal is a function of permeate volumetric flux. The effect of the permeate flux is similar to the pressure, it means by increasing the permeate flux; more nitrate rejection can be reached.

Nanofiltration efficiency in hardness removal was 88.7 % which is less than expected but it is acceptable. It also has a good result in E.C reduction (87.6%), SiO2 removal (84.7%) and alkalinity (84.5%) rejection.

5. Acknowledgements

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6. References

[1] B. Van der Bruggen, M. Manttari, M. Nystrom. Drawbacks of applying nanofiltration and how to avoid them: A review. *Sep. Purif. Technol.* 2008, **63**: 251–263.

[2] B. Van der Bruggen, C. Vandecasteele. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environ. Pollut.* 2003, **122**: 435–445.

[3] N. Hilal, H. Al-Zoubi, N.A. Darvish, A.W. Mohammad, M. Abu Arabi. A comprehensive review of Nanofiltration membranes: treatment, pretreatment, modeling, and atomic force microscopy. *Desalination* 2004, **170**: 281–308.

[4] D.X. Wang, M. Su, Z.Y. Yu, X.L. Wang, M. Ando, T. Shintani. Separation performance of a nanofiltration membrane influenced by species and concentration of ions. *Desalination* 2005, **175**: 219-225.

[5] M. A. Amouha, B. Hooshyari, G. N. Bidhendi, review and determine the efficiency of nanofiltraion membranes in

removing contaminants from groundwater , *ICWW Press*, 2011, Iran.

[6] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García. Performance of commercial membranes in the removal of nitrate ions. *Desalination* 2005, **185**: 281-288.

[7] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García. Applicability of the DSPM with dielectric exclusion to a high rejection nanofiltration membrane in the separation of nitrate solutions. *Desalination* 2008, **221**: 268–276.

[8] F. Garcia, D. Cicerone, A. Saboni, S. Alexandrova. Nitrate ions elimination from water by Nanofiltration: membrane choice. *Sep. Purif. Techno.* 2006, **52**: 196-200.

[9] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García. Nitrate removal from ternary ionic solutions by a tight Nanofiltration membrane. *Desalination* 2007, **204**: 63-71.

[10] DOW Chemical Company. Filmtech membranes official website: http://www.filmtec.com.

[11] L. Paugam, S. Taha, G. Dorange, P. Jaouen, F. Quéméneur. Mechanism of nitrate ions transfer in nanofiltration depending on pressure, pH, concentration and medium composition. *J. Membr. Sci.* 2004, **231**: 37–46.

[12] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García. Nanofiltration study of the interaction between bicarbonate and nitrate ions. *Desalination* 2010, **250**: 773-777.

[13] A. Santafé-Moros, J.M. Gozálvez-Zafrilla, J. Lora-García. Nitrate removal from ternary ionic solutions by a tight Nanofiltration membrane. *Desalination* 2007, **204**: 63-71.