Desalination of reclaimed water by nanofiltration in an artificial groundwater recharge system

Wu Lin Lin, Zhao Xuan, Zhang Meng and Cheng Xu Zhou

ABSTRACT

Desalination is important in artificial groundwater recharge with reclaimed water for minimizing the effect of salinity on groundwater and soil quality. In this study four kinds of nanofiltration membrane, as the compensatory process in soil treatment, are embedded into enhanced direct injection-well recharge (EnDir) for desalination purposes. The lab-scale experiments indicate that nanofiltration (NF) in the sequence of short-term soil treatment provides additional removal of organic and inorganic compounds. NF90 exhibits a marked superiority over the other types of membrane, with respect to the desalinization of reclaimed water. The removal efficiencies for total dissolved solids (TDS) and alkalinity amount to 89% and 96%, respectively. For the anions in the reclaimed water, NF90 exhibits 80% removal efficiency for nitrate, 94% for chloride and 99% for sulphate, which are removed to a limited extent in the soil treatment. The sodium adsorption ratio (SAR) value of NF90 permeate is the lowest among these membranes, which minimizes the risk of sodification associated with soil structure degradation during artificial groundwater recharge. In addition, NF90 can reduce the concentrations of heavy metals in the reclaimed water to far below the national standards for groundwater.

Key words | desalination, groundwater recharge, nanofiltration, reclaimed water

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INTRODUCTION

Water scarcity is likely to become more problematic in the near future because of rapid population growth, increasing per capita water consumption and geographical disparities between centres of population growth and availability of water. Groundwater, as an important source of fresh water, has been overexploited in many parts of the world. Artificial groundwater recharge with reclaimed water is gaining acceptance as a method for supplementing aquifers, with additional advantages as follows: seasonal and long-term water storage; emergency water storage; help to reuse municipal wastewater; help to control saltwater intrusion; aquifer recharge and conveyance; and help to reduce costs of water management and facilities expansion (Miller 2006).

Soil aquifer treatment (SAT), as the main process in the recharge system, provides significant removal of municipal effluent organic matter (EfOM), viruses and pathogens in order to guarantee groundwater safety (Kopchynski *et al.* 1996; Quanrud *et al.* 2003; Lee *et al.* 2004; Fox *et al.* 2005). However, many inorganic chemicals in the reclaimed water also have public health and environmental risks: for example, making the groundwater unsuitable for drinking by continuously penetrating into the soil layers and eventually reaching the aquifer (Johnson *et al.* 1999), or altering the soil permeability by changing soil composition. In addition, over-extraction of groundwater has resulted in seawater intrusion in some coastal areas. The recharged water must be extensively desalinized to dilute the high level of salinity in the original groundwater (Durham *et al.* 2002; Rebhun 2004).

Membrane technologies–reverse osmosis (RO) and nanofiltration (NF)–are not only an important barrier for organic matter but also an effective desalinization process in

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groundwater recharge activities (Asano 1998; Wintgens *et al.* 2005). Compared with RO, NF has lower energy demands; in addition, it could be effective for the removal of viruses, total dissolved solids (TDS), organic compounds and trace contaminants (Monthon *et al.* 2002; Kimura *et al.* 2003; Rubia *et al.* 2008). The integration system of NF and traditional SAT has been studied with respect to organic matter removal for indirect potable reuse (Jarusutthirak *et al.* 2003). In this paper the combination of NF and the enhanced direct injection-well recharge (EnDir) system will be studied with respect to desalination. EnDir was put forward by Tsinghua University based on a 10-year study of an appropriate recharge approach in Beijing, and has the advantages of less land use and less dependence on local soil permeability. As shown in Figure 1, reclaimed water first percolates the so-called short-term vadose soil, an artificial 1.5–2.0 m deep sand layer. Via the collection pipe system at the layer bottom, water is pumped to NF module. The polished water is transferred to the injection well and then to the aquifer directly for long-term aquifer treatment. The hydraulic retention time of reclaimed water in the long-term aquifer must not be less than 20 days. The operation cycle of the short-term vadose soil normally comprises 2–3 days flooding and 1 day drying, which helps to complement oxygen content in soil and accelerate the biodegradation progress in the short-term area. Percolation velocity of reclaimed water in the artificial short-term vadose layer ranges from $0.05\,m\,h^{-1}$ to $0.5\,m\,h^{-1}$, which is several times higher than that of natural soil in Beijing and therefore dramatically reduces land use compared with a surface spreading basin. In addition, the set up of the short-term vadose soil can, to a large extent, preserve the favourable purification properties of a natural spreading basin, since dissolved organic carbon (DOC) removal mainly occurs in the upper soil within the depth of 1.0–1.5 m (Quanrud *et al.* 2003; Fox *et al.* 2005) and biodegradable organic carbon (BOC) is primarily removed within 30 cm soil depth (Rauch-Williams & Drewes 2006). NF, embedded into the EnDir system, forms an important barrier for inorganic salts and minimizes any negative effect of reclaimed water on the local groundwater quality. The additional advantage of the EnDir-NF system is that the short-term vadose soil can remove the compounds that cause membrane fouling. By the EnDir-NF system, the problems related to distinct

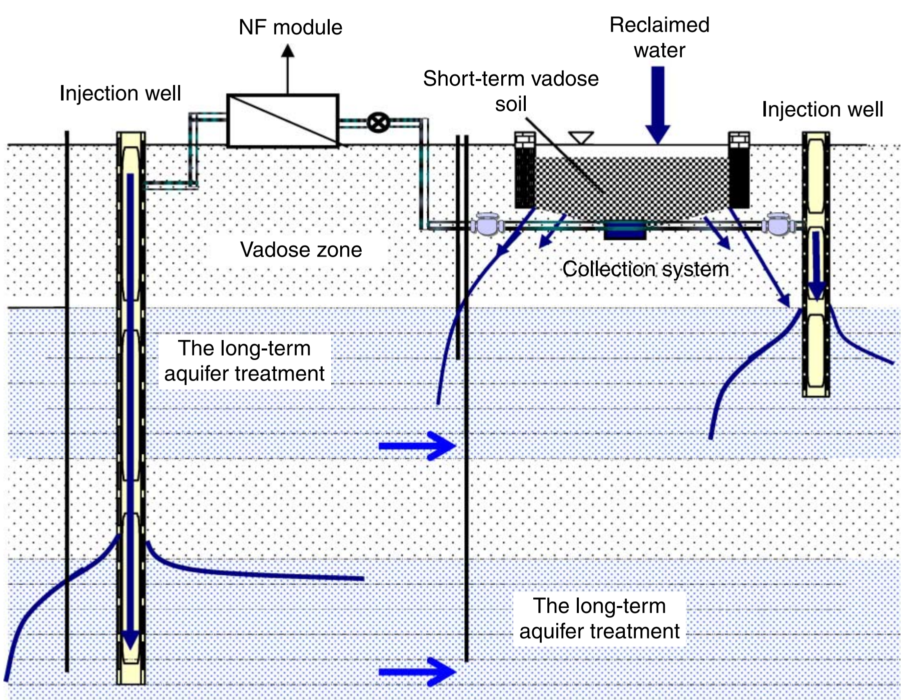

Figure 1 | NF combined with the enhanced direct injection-well recharge.

impermeable soil layers between the unsaturated and saturated zone, which is rather common in Beijing, may be solved without great loss of reclaimed water purification.

In this study, four NF membranes were examined related to their desalination efficiencies and flux performance based on the lab-scale EnDir-NF system.

EXPERIMENTAL

Membrane, raw water

The membranes studied in this paper are commercially available. Table 1 summarizes their respective properties. For the experiments, membrane material was first treated with demineralized water to remove impurities from their synthesis. At the beginning of experiments, NF membranes were pre-compacted with demineralized water under the pressure of 0.6 MPa to obtain stable membrane structure.

The raw water for the lab-scale experiment was transported from secondary effluent from the traditional activated sludge process in Gaobeidian wastewater treatment plant (WWTP). All the raw water for experiments was stored at 4°C prior to their use after they had been prefiltered by 0.45 μm filtration. The water composition is summarized in Table 2.

Lab-scale experiment

The soil column is 0.25 m in diameter and 2 m in height with a packed bed height of 1.7 m, which was used to simulate the short-term vadose process. The porosity of the soil column is 0.39, and the sand size is between 0.4 and 0.8 mm.

Table 1 | Tested membranes and their characteristics

Membrane	NF	NF90	NF270	DK
Manufacturer	Filmtec	Filmtec	Filmtec	Osmosis
Material	PPZ	PA	PA	PPZ
pH	3–10	3–10	3–10	2–11
MWCO (Da)	200	150–300	150–300	150–300
Pressure, max. (bar)	41	41	41	40
Temperature, max. (°C)	45	45	45	50
Surface charge	Negative	Negative	Negative	Negative

Table 2 | Inorganic salts removal by short-term vadose soil column

	Secondary effluent	Short-term soil effluent
DOC, $mg\,l^{-1}$	5.53 ± 0.54	
UVA, cm^{-1}	0.132 ± 0.01	
TDS, $mg\,l^{-1}$	510 ± 32	508 ± 20
Ca^{2+}, $mg\,l^{-1}$	72.6 ± 1.4	72.2 ± 2.4
Mg^{2+}, $mg\,l^{-1}$	24.7 ± 5.5	25.4 ± 4.1
Na^{+}, $mg\,l^{-1}$	63.2 ± 7.4	64.2 ± 7.0
K^{+}, $mg\,l^{-1}$	14.3 ± 4.2	14.5 ± 7.4
Cl^{-}, $mg\,l^{-1}$	104.4 ± 3.2	110.3 ± 2.0
SO_4^{2-}, $mg\,l^{-1}$	72.8 ± 5.6	76.2 ± 2.1
Nitrate-N, $mg\,l^{-1}$	20.5 ± 4.3	21.5 ± 3.5

The column was operated under unsaturated conditions at room temperature of 20 ± 2°C in the dark by continuously pumping secondary effluent to the top of the column. The operation cycle comprised 3 days flooding and 1 day drying. After an acclimatization of more than one year, the soil column was biologically adapted and the effluent was pumped into an intermediate buffer vessel from which it was conducted across the NF installation. The NF set has an effective membrane area of 36 cm^2 and was operated in cross-flow mode. The operating pressure and cross-flow velocities were controlled by means of by-passage and regulating valves at 0.4 MPa and 0.44 $m\,s^{-1}$, respectively. The concentrate was recirculated during experiments. Feed water and permeate samples were regularly sampled to monitor water quality. The membrane flux (J) is defined as the permeate volume per square metre of membrane area and per hour.

Analytical methods

Dissolved organic carbon (DOC) was analysed by Shimadzu TOC-VWP (Shimadzu Corporation, Japan). UV absorbance (UVA) was measured by Shimadzu UV-3100 (manufactured by Shimadzu Corporation of Japan) at a wavelength of 254 nm. TDS was measured by TDScan 1 meter (Eutech corporation, Singapore). Cations were measured by IRIS Intrepid II XSP ICP-OES (Thermo Electron Corporation, Massachusetts) and anions were measured by DIONEX ICS-3000 ion chromatogram (DIONEX Corporation, California).

RESULTS AND DISCUSSION

The short-term vadose soil column had been acclimatized for more than one year with raw water, which was ozonated prior to the soil treatment with the ozone dosage of $10\,mg\,l^{-1}$. The lab-scale experiment demonstrates that the short-term vadose treatment can remove 47% to 60% of DOC from the ozonated effluent (Zhao *et al.* 2009). However, the vadose soil column did not exhibit positive performance with respect to salts removal, as shown in Table 2. A slight negative influence can even be observed. In addition, no obvious denitrification can be observed owing to the lack of a carbon source.

In this study, NF is placed between the short-term soil layer and injection well, which is different from the normal artificial groundwater recharge practice (Ernst & Jekel 1999; Kazner *et al.* 2008). The possible advantages are that: (a) the purification properties of the upper soil can be utilized; (b) the short-term vadose layer can remove compounds causing membrane fouling; (c) NF forms an effective barrier for organic contaminants (Weber *et al.* 2004; Yoon *et al.* 2006); and (d) desalination can be expected.

The removal efficiencies of DOC, UVA, TDS and alkalinity by different NF membranes are presented in Figure 2. The four membranes can remove more than 80% of organic matter. Compared with the other three membranes, NF90 shows the most significant removal of TDS and alkalinity, with a corresponding efficiency of 89% and 96%.

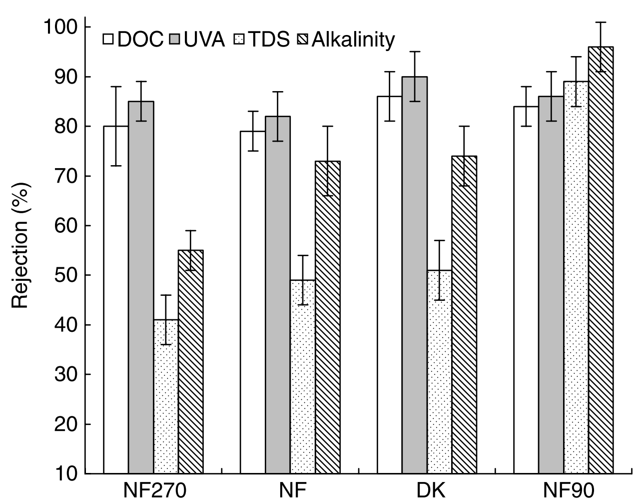

Figure 2 | Removal of DOC, UVA, TDS and alkalinity with the NF membranes.

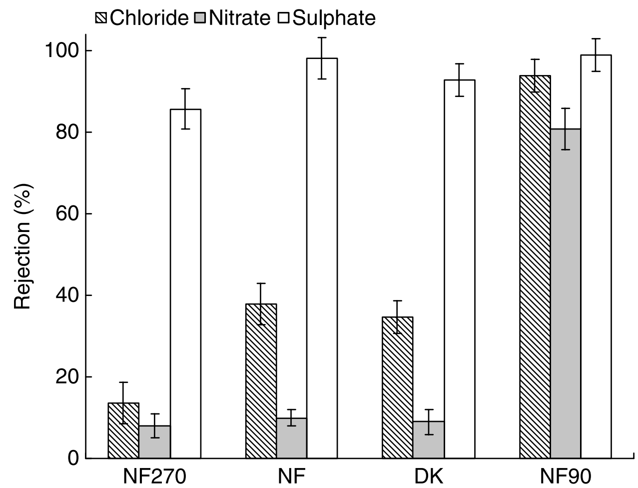

Figure 3 | Removal of anions with the NF membranes.

Elevated concentrations of nitrate, chloride and sulphate have been considered as indicators of groundwater pollution. Due to the aerobiotic operating conditions, there is no obvious denitrification in the soil processes. Therefore, effective removal of nitrate by NF membrane would be very important. As the 'tight' nanofiltration membrane, NF90 performs well in removing nitrate with an efficiency of 80% and parallel rejection of chloride with an efficiency of 94% (Figure 3). The removal efficiencies for nitrate and chloride by the other three membranes range from 8 to 10% and 14 to 35%, respectively. It is also shown that all four NF membranes have higher removal efficiency for chloride than for nitrate, which can be explained by hydration differences (Choi *et al.* 2001; Paugam *et al.* 2004) and different affinity with membrane materials (Ratanatamskul *et al.* 1998). Generally, all four membranes exhibit marked rejection of sulphate, with an efficiency range of 85–99%.

Figure 4 presents the removal of several cations by NF membranes. From Figures 3 and 4, the removal efficiencies of divalent ions are generally higher than those of monovalent ions with the four NF membranes because of the higher electrostatic repulsion effect. Compared with the other three materials, the NF90 membrane exhibits the most favourable rejection of K^{+}, Na^{+}, Ca^{2+} and Mg^{2+}, with efficiency ranges of 85–98%. Artificial groundwater recharge with reclaimed water commonly presents high

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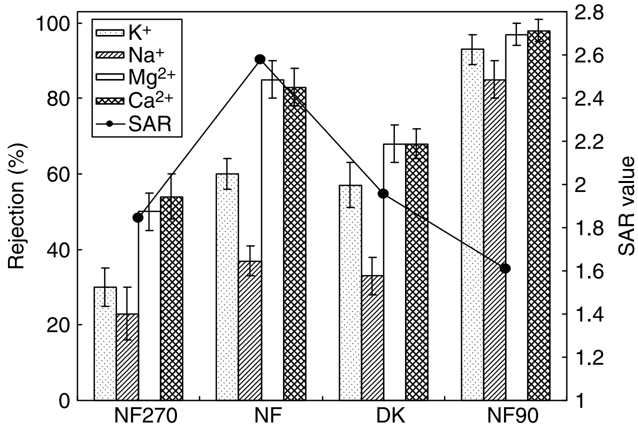

Figure 4 | Removal of cations with the NF membranes and average SAR values of the NF permeate.

concentrations of sodium relative to other cations, which is quantified by sodium adsorption ratio (SAR) (Leal *et al.* 2009). A widely used relationship for SAR is shown in Equation (1).

$$SAR = \frac{(Na^+)}{\sqrt{(Mg^{2+}) + (Ca^{2+})}} \quad (1)$$

where (Na^+) is sodium concentration, (Ca^{2+}) is calcium concentration and (Mg^{2+}) is magnesium concentration, in $mol\,l^{-1}$.

High SAR is expected to cause an increase in the percentage of soil exchangeable sodium, enhancing the risk of sodification associated with soil structure degradation. This may result in waterlogging and decreased water infiltration (Leal *et al.* 2009) while the time scale for artificial groundwater recharge may be on the order of years. In the soil system, the irrigation water has a SAR

Table 3 | Permeate heavy metal content compared with national standards for groundwater

	Short-term soil effluent	NF270	NF	DK	NF90	National standards for groundwater
Fe, $\mu g\,l^{-1}$	8.4	6.7	4.8	5.9	5.6	300
Cr, $\mu g\,l^{-1}$	0.8	ND	ND	ND	ND	50
Cd, $\mu g\,l^{-1}$	0.3	0.2	0.3	0.3	0.2	10
Pb, $\mu g\,l^{-1}$	23.4	15.5	17.5	20.1	8.4	50
Ni, $\mu g\,l^{-1}$	34.7	13.3	12.3	7.6	ND	50
Co, $\mu g\,l^{-1}$	9.2	4.0	ND	5.6	4.6	50

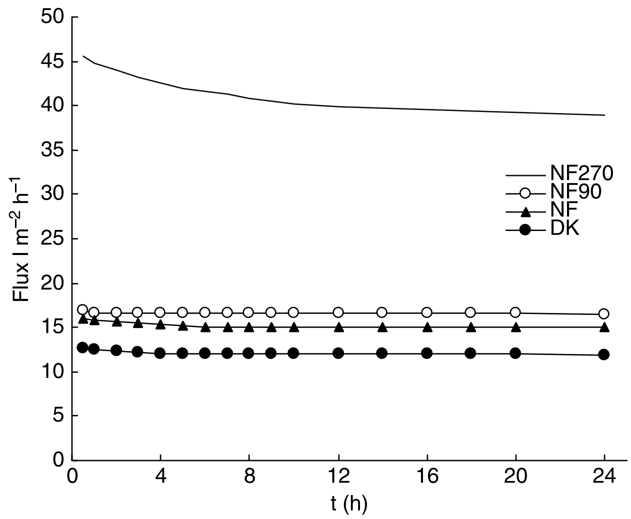

Figure 5 | Flux variations of the NF membranes.

value of less than 3.0, which is acceptable for soil permeability (Chang *et al.* 2005). From the data in Table 2, the average SAR value of the secondary effluent is 1.62, and it is 1.65 after the short-term soil treatment. However, average SAR values of NF270, NF, DK and NF90 permeate amount to 1.95, 2.58, 1.84 and 1.61, respectively, since the membranes have different separation capability for mono- and divalent cations. Although the SAR value of the NF permeate was within the safe range, this increased SAR value will affect the permeability of the soil. Therefore, compared with the other three NF membranes, NF90 is preferable in order to minimize the effect of the elevated SAR value on the permeability of the soil.

In general, as a compensatory process of soil adsorption, NF can form a barrier for trace heavy metal contaminants, as summarized in Table 3. After the treatment by NF, concentrations of heavy metals are far below the national standards for groundwater. In particular, the NF90 membrane exhibits relatively high removal efficiencies for both Pb and Ni. The concentration of Pb is only $8.4\,\mu g\,l^{-1}$ (the national standard is $50\,\mu g\,l^{-1}$), and concentration of Ni is below the limit of determination.

The variations of membrane flux during the 24-h operation at the transmembrane pressure of 0.4 MPa are shown in Figure 5. The initial fluxes of the four membranes are $47.32\,l\,m^{-2}\,h$ (NF270), $18.59\,l\,m^{-2}\,h$ (NF90), $16.91\,m^{-2}\,h$ (NF) and $13.52\,l\,m^{-2}\,h$ (DK), respectively. The normalized flux of NF270 is higher than the other three membranes because of its relatively higher pore size and porosity (Hilal *et al.* 2005). From Figure 5, the flux decline of NF270, NF90, NF and DK is 18%, 12%, 11% and 12%, respectively, after 24-h operation. A good correlation between the initial flux decline rate and membrane pore size has been observed (Nghiem & Hawkes 2009). To identify the membrane fouling control effect of short-term soil treatment, the flux decline of NF270 was also examined with secondary effluent as feed water instead of short-term soil column effluent. With the same filtration procedure, the flux decline of NF270 is about 30% after 24-h operation. The removal of organic matter in the effluent (EfOM) may be the major mechanism for membrane fouling control by the short-term soil treatment.

CONCLUSION

NF is embedded in the enhanced direct injection well system to prevent salinization of soil and groundwater during the recharge process with reclaimed water. The characteristics of four NF membranes have been examined in respect of both the desalinization efficiency and flux performance. The following conclusions can be drawn from the results of the study:

- The NF membrane can perform as an important barrier for contaminants in artificial groundwater recharge, especially for inorganic salts that normally cannot be removed effectively by the soil aquifer.
- The NF membrane shows significant removal of TDS and alkalinity. The most favourable removal can be achieved with the membrane material NF90, with corresponding efficiencies of 89% and 96%.
- Compared with the other three membranes, NF90 shows particularly high nitrate removal efficiency of 80% and chloride removal efficiency of 94%. All four membranes exhibit marked rejection of sulphate, with an efficiency range of 85–99%.
- SAR values of the NF permeate are within the range 1.61–2.57. NF90 permeate has the lowest SAR value of 1.61, which can minimize the risk of sodification associated with soil structure degradation in artificial groundwater recharge.
- NF can remove heavy metals as a compensatory process of soil adsorption. Concentrations of heavy metals in the permeate are far below the national standards for groundwater.
- NF90 exhibits a marked superiority over the other types of nanofiltration membrane, with respect to the desalinization of reclaimed water for artificial groundwater recharge. NF270 provides the advantage of high normalized flux.

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