DETERMINATION OF NANOFILTRATION EFFICENCY IN ARSENIC REMOVAL FROM DRINKING WATER

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ABSTRACT

Nowadays nanofiltration has been considered for the treatment of organic and inorganic pollutants in surface and groundwater resources. In this study, rejection characteristics of arsenic compounds such as As(III) to form As_2O_3 and As(V) to form $Na_2HAsO_4.7H_2O$ by a commercial nanofilter NF90 (DOW-FilmTec) was investigated. Arsenic rejection experiments included variations of feed arsenic concentration, transmembrane pressure and pH. In these experiments, as increasing initial concentration As(V) from 120 μg/L to 1026 μg/L in feed water, the percentage of rejection of As(V) decreased from 98.35% to 96.59% (permeate water concentration was 2 μg/L to 35 μg/L) ,while as increasing initial concentration As(III) from 118 μg/L to 985 μg/L in feed water ,the percentage of rejection of As(III) decreased from 94.07% to 87.51% (permeate water concentration was 7 μg/L to 123 μg/L). Due to increase of pressure from 4 bar to 7 bar, the percentage of rejection of As(V) in finished water increased from 95.68% to 99.02% (permeate water concentration decreased from 21 μg/L to 5 μg/L),while the percentage of rejection of As(III) decreased from 80.99% to 95.11% (permeate water concentration decreased from 96 μg/L to 25μg/L). Also due to increasing pH from 3 to 11, the percentage of rejection of As(V) in finished water increased from 95.45% to 99.00% (permeate water concentration decreased from 22 μg/L to 5 μg/L), while the percentage of rejection of As(III) decreased from 86.6% to 94.81% (permeate water concentration decreased from 65 μg/L to 25 μg/L). Finally, nanofiltration application for arsenic removal from drinking water was recognized suitable regarding its proper efficiency and convenience operation and was recommended for point-of-use applications.

Key words: Nanofilteration; Arsenic; Nernst Planck equation; Donnan equilibrium; Drinking water

INTRODUCTION

In general, there are two causes for arsenic contamination of drinking water: natural geological formation and human activity (Meng *et al*., 2001). Since long time ago, arsenic has been recognized as a toxic and fatal factor, as nowadays, toxic of arsenic has became a very hazard agent for the environment which can endanger the lives of millions of human (Mandal and Suzuki, 2002). At typical pH values for drinking water (between 6 and 9), arsenic may often be found as inorganic, As(III) or arsenite and As(V) or arsenate (As(III) is the most toxic). In the pH of natural water, As(III) species are found as neutral (H_3AsO_3) and As(V) species are found in anionic form as $HAsO_4^{-2}$ and $H_2AsO_4^{4-}$; The charge of arsenic is controlled by pH and arsenic charge becomes more negative as pH increases (Gomez *et al*., 2001). According to the Iran drinking water standard, the maximum contaminated level (MCL) of arsenic is 50ppb (μg/L). In the United States Environmental Protection Agency (USEPA), this value is 10μg/L (EPA, 2001; ISIR,

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1997). In Iran, arsenic contamination has been reported in groundwater sources in vast areas of western and north-western provinces especially in Kurdistan province and it has been caused serious problems. (Mosaferi *et al*., 2005). Technologies of arsenic removal include absorption, ion exchange, precipitation and membrane filtration. In the membrane filtration, that this study is trying to introduce one of the kinds, arsenic removal is made through physical filtration using membranes with selective penetrability (Wagner, 2001). nanofiltration has been noticed considerably in recent years due to high efficiency in removing multivalent ions, lower pressure than to reverse osmosis membrane, consumption of less energy, application to form point-of-use (P.O.U). This technology is considered as a new method for arsenic removal in this study. More accurate predictions can be made using models. Generally there are models that have been used to describe filtration by a membrane. In each case, the performance of the membrane is predicted in two separate components: the pure water flux and the solute flux that their relationships are independent from each other , in each of the models the pure water flux is related primarily to the pressure (ΔP). The pure water flux can be related to pressure using the Hagen-Poiseuille equation, as shown in equation 1 (Bandini and Vezzani., 2003).

$$J_w = \frac{r_p^2 \cdot \Delta p}{8\mu\delta} \qquad (1)$$

Where:
J_W = the pure water permeability;
rp = pore radius;
Δp = the difference in applied pressure across the membrane;
δ = the thickness of the membrane;
μ = viscosity of fluid;

According to equation 1, increasing the pressure will increase the pure water flux, while the solute flux is proportionally related to the solute concentration gradient across the membrane. Solute flux is defined using in the Extended Nernst-Planck equation as shown in equation 2.

$$J_i = \left(-D_i \frac{dc_i}{dx}\right) - \left(D_i \cdot z_i \cdot c_i \cdot \frac{F}{RT} \cdot \frac{d\psi}{dx}\right) + (K_i \cdot c_i \cdot J_v) \qquad (2)$$

Where:
Ji = solute flux i ;
D_i = diffusivity of solute i ;
c_i = the concentration of solute i at the surface of the membrane*;*
x = mole fraction for solute i ;
z_i = the valance of solute i ;
F = Faraday's constant ;
R = the gas constant;
T = temperature ;
ψ = the electric potential ;
K_i = the distribution coefficient of solute i ;
J_v = the volume flux and can be estimated based on the membrane area;

Each of the terms of the Nernst-Planck equation describes a different component of the solute flux. The first term describes (as a function of concentration gradient across the membrane), the second term quantifies the flux due to electrostatic forces (as a function of the charge gradient) and the last represents the convection of the solute (as a function of volume flux). In all three terms of the Extended Nernst-Plank equation is found the term c_i, the concentration of solute i at the surface of the membrane. The concentration at the surface of the membrane can be estimated using the Donnan equilibrium as shown in equation 3.

$$\psi_D = \psi_m - \psi_s = c_i = C_i \exp\left(-z_i \cdot \frac{F}{RT} \cdot \Delta\psi_D\right) \qquad (3)$$

Where :
Ci = the bulk (or feed) concentration of solute i ;
Donnan potential (ψ_D) is the difference between the electrical potential of the solution (ψ_s) and the electrical potential of the membrane (ψ_m).
The Nernst-Plank equation coupled with the Donnan Equilibrium have been shown to accurately predict the rejection of various salts by nanofiltration and reverse osmosis membrane (Afonso *et al*., 2001; Bandini and Vezzani, 2003). Equation 2 and 3 shows that the solute

concentration at the surface of the membrane determines the solute passage. If the charge (or electrical potential) of the membrane increases, the concentration of co-ions (ions with a similar charge) at the membrane surface decreases, while the concentration of counter ions (ions with the opposite charge) increases. If the ion is neutrally charged, then the concentration at the membrane surface is unaffected by the charge of the membrane. (Afonso *et al.,* 2001; Bandini and Vezzani, 2003).

MATERIALS AND METHODS

In this study, in all cases raw water was used as the feed liquid and arsenit or As(III) and arsenate or As(V) was added to it.The standard solutions of trivalent arsenic and pentavalent arsenic were prepared from 1000 mg/L of arsenic standard solution (As_2O_3 and NaOH in water pH=5.0 with HCl, Wako Pure Chemical Industries, Ltd., Japan) and sodium arsenate dibasic heptahydrate ($Na_2HAsO_4,7H_2O$, Wako Pure Chemical Industries, Ltd., Japan), respectively. Membrane module used was spiral wound thin film composite and aromatic polyamide, model NF90-2540, manufactured by Dow-Film TecCo. Equipments for experiments and specifications of the membrane in the pilot scale system are described in Table 1.

Table1: Specifications of NF 90-2540 membrane

Membrane Type	Polyamide thin film composite
Maximum operating temperature	113ºF (45ºC)
Maximum operating pressure	600 psig (31 bar)
Continuous operating pH range	3-10
pH range in cleaning (30 min)	1-12
Maximum influent discharge	70 gpm (15.9 m3/h)
Membrane area	2.6 m^2

In all experiments, the feed water discharge was 15L/min (900 L/h) and temperature was 27 ºC. pH measurement was carried out by HACH digital pH meter and temperature was measured by a digital thermometer. Experiments were carried out based on Standard Methods (AWWA and WPCF, 2002).The pilot unit used in this study included feed tank to which stream from

module to permeate and retentate streams were returned. The measurements were performed with an ICP-OES (inductively coupled plasma optical emission spectrometry); the minimum detection limit for arsenic measurements by ICP-OES is of 5 µg/L.

In this section study on initial concentration of As, pH and pressure were considered. In experiments on the effect of initial concentration, arsenic concentration was changed from 120 µg/L to 1000 µg/L in feed water, pH was 8 and pressure was 6 bar. In experiments on the effect of pressure, pressure was changed from 4 bar to 7 bar, pH was 8 and initial concentration was 500 µg/L and in experiments on the effect of pH, it was changed from 3 to 11, pressure was 6 bar and initial concentration was 500 µg/L.

The removal efficiency was calculated by following equation:

$$R(\%)= (1-(C_p-C_o))\times 100 \qquad (4)$$

Where:
R = dye removal efficiency (%);
C_p = dye concentration in permeate water;
C_o =dye concentration in input water;

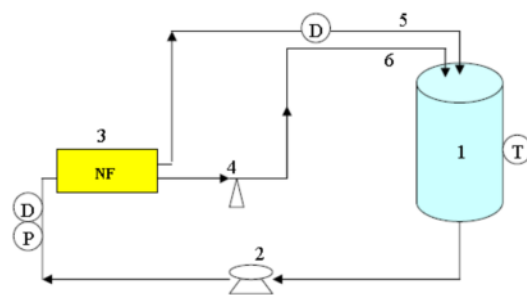The schematic layout of the NF process used in this work is shown in Fig. 1.

Fig.1: Schematic layout of the nanofiltration pilot

1: feed Tank, 2: pump, 3: membrane module, 4: valve,
5: permeate stream, 6: retentate stream, P: pressure gage,
D: flow meter, T: temperature controller

RESULTS

Effect of initial concentration

Fig. 2 shows the effect of initial concentration on arsenic rejection efficiency. Overally, the percentage of rejection of As(III) and As(V) decreased in the finished water. With increasing initial concentration of As(V) from 120 μg/L to 1026 μg/L in the feed water, the percentage of rejection of As(V) decreased from 98.35% to 96.59% (permeate water concentration = 2 μg/L to 35 μg/L), while with increasing initial concentration As(III) from 118 μg/L to 985 μg/L in the feed water, the percentage of rejection of As(III) decreased from 94.07% to 87.51% (permeate water concentration = 7 μg/L to 123 μg/L).

Fig. 3: Effect of pressure (4-7 bar) on As(V) and As(III) removal efficiency using NF90;
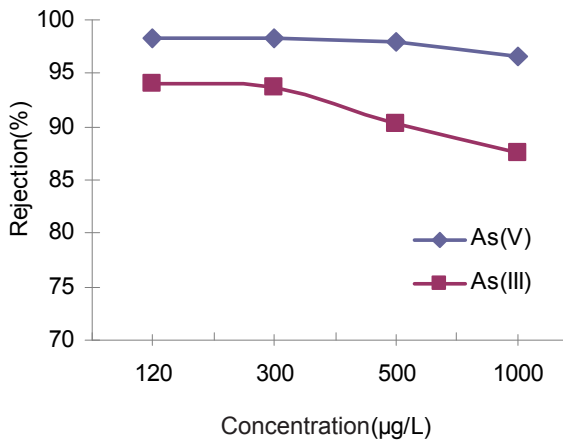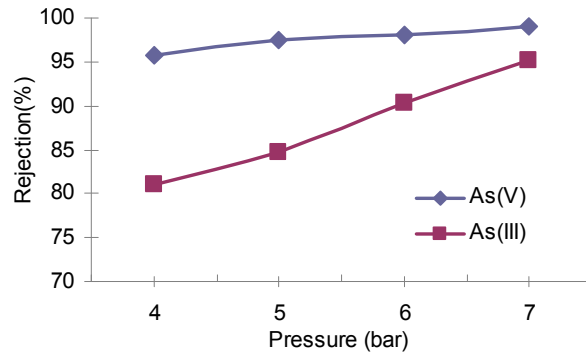concentration = 500 μg/L; temperature = 27°C; pH = 8; recovery = 30%

Fig. 2: Effect of initial concentration (120-1000 μg/L) on As(V) and As(III) removal efficiency;
pressure = 6 bar; temperature = 27°C; pH = 8; recovery = 30%

Effect of pressure

Effect of pressure on rejection efficiency of arsenic is shown in Fig. 3. Increase of pressure from 4 bar to 7 bar in the feed water, resulted to the percentage of rejection of As(V) in finished water increase from 95.68% to 99.02% (permeate water concentration decreased from 21 μg/L to 5 μg/L) ; the percentage of rejection of As(III) decreased from 80.99% to 95.11% (permeate water concentration decreased from 96 μg/L to 25μg/L).

Effect of pH

As shown in Fig. 4, due to increasing pH from 3 to 11 in the feed water, the percentage of rejection of As(V) in the finished water increased from 95.45% to 99.00% (permeate water concentration decreased from 22 μg/L to 5 μg/L), while the percentage of rejection of As(III) decreased from 86.6% to 94.81% (permeate water concentration decreased from 65 μg/L to 25 μg/L).
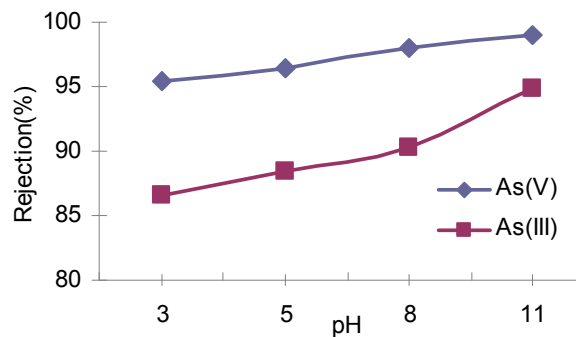

Fig. 4: Effect of pH (3-11) on As(V) and As(III) removal efficiency using NF90;
concentration = 500 μg/L; temperature = 27°C; pressure = 6bar; recovery = 30%

DISCUSSION

Results of the study showed that the rejection of As(III) and As(V) decreased due to increasing concentration. Based on presented models, the solution flux is related to concentration gradient

at the membrane surface. Thus as the initial concentration is increased, the concentration at the membrane surface increases which leads to increasing of concentration polarization for which the membrane must filter a solution with a higher solute concentration than the feed (or bulk) solution. Therefore more groups of salts are passed through the membrane and the removal increases. For As(V), based on Nernst Plank model (equation 2) and Donnan equilibrium (equation 3), with increasing of the solution concentration, Donnan potential becomes weaker and concentration at the membrane surface increases therefore rejection decreases. Also, As(V) rejection is higher than As(III) due to stronger repellent force.

Some researches have found increasing the concentration of As(III) in feed water would result in the decrease of rejection (Seidel *et al*., 2001). They considered that since As(III) is neutrally charged, the diffusion of As(III) is proportional to the bulk concentration resulting in a reduced solute flux. Some researches have found that increase in the concentration of As(V) has increased the passage of As(V) (Brandhuber and Amy , 2001), while others have found the opposite (Seidel *et al.* 2001; Vrijenhoek and Waypa , 2000). Brandhuber and Amy have pointed out that this observation is consistent with the Nernst-Plank equation and Donnan theory. Seidel *et al.*(2001)*,* and Vrijenhoek and Waypa (2000) have stated that their observations are due to the presence of the more permeable and more mobile bicarbonate ion that are therefore more likely to permeate in comparison to As(V).

The increase of pressure from 4 to 7 bar increased As(V) and As(III) rejection. The reason for the increase of removal can be explained as follows: in the models presented for nanofiltration membranes, pure water flux is related to pressure (equation 1). Thus by increasing pressure, pure water flux will increase, while the solute flux is constant and due to the "dilution" of the solutes, the overall solute passage decreases. This is true for both As(V) and As(III). Yuko Sato *et al*., (2002) reported that arsenic removal efficiency increased slightly with the increase in applied pressure and this was attributed to the increase in permeate flux resulted from increasing the applied pressure. (Yuko Sato *et al.,* 2002).

Increasing pH from 3 to 11 increased both As(III) and As(V) removal. The reason for the removal increase can be related to two factors:-Charge of arsenic is controlled by pH and arsenic charge becomes more negative as pH increases.

By increasing pH, the zeta potential of the membrane will also increase. Nanofiltration membranes are, in general, negatively charged. The zeta potential (or charge) of the membrane is influenced by pH. Hence by increasing pH, the zeta potential of membranes has been shown to become more negative (Kang *et al*., 2001; Oh *et al*., 2004). In higher pH, the electrostatic repellent force becomes strong and rejection will increase. The reason for higher As(V) removal is that As(III) neutral (H3AsO3) up to pH=9.1 and thereafter they act as anionic species, while As(V) is mono-valent oxyanion up to pH=6.9 and thereafter it changes to divalent oxyanion. This causes As(V) to have stronger repellent force and higher removal than As(III). Some researcher have found increasing the charge of arsenic resulting in increase of the rejection of arsenic (Vrijenhoek and Waypa , 2000; Brandhuber and Amy , 2001; Kang *et al*., 2001; Seidel *et al*., 2001; Oh *et al*., 2004). Some of the researchers have reported a decrease of rejection of both As(III) and As(V) at higher pH. However, these observations are not clearly addressed (Vrijenhoek and Waypa, 2000).

In all experiments, the As(V) removal was higher than for As(III) due to more repellent forces.

Based on this study and the dominant conditions, arsenic removal efficiency by nanofiltration membrane process may be considered to be highly efficient; (the maximum rejection efficiency in this study was 99.02%). Arsenic concentration in the permeate solution for As(V) salts in all experiments were less than the maximum contaminated level (MCL) specified by Iranian Standard, whereas this was not the case for As(III). Arsenic concentration in permeate solution for As(V) salts were less than the maximum contaminated level (MCL) specified by the United States Environmental Protection Agency (USEPA) in low concentration and high pressure.

Considering results of this study, the nanofiltration membrane process has shown high efficiency

in arsenic removal and this is possible in lower pressures and can be used as (POU) systems. Applying this method in problematic areas within Iran is recommended to be considered for fast set up and implementation and simple operation.

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