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Comparison of nanofiltration and adsorption techniques to remove arsenic from drinking water

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ABSTRACT

Arsenic occurs naturally in the ground and surface water and is not desired in the drinking water due to carcinogenic effect on human body. The common types of arsenic are arsenate (As V) and arsenite (As III). Although arsenate removal has been achieved by membranes, adsorption, ion exchange and coagulation, arsenite removal is difficult to decrease the concentration up to the standard level (below to 10 µg/L). In this study, nanofiltration (NF) and adsorption techniques have been compared to remove arsenite from drinking water. In nanofiltration study, different NF membranes and arsenite feed concentrations have been studied. Feed water was prepared synthetically and laboratory scale cross-flow mode filtration apparatus with a flat-sheet membrane cell was used for NF experiments. In the adsorption experiments with granular iron hydroxide (GIH), all studies were performed in the free water flow and at the normal pH of tap water. It was concluded that arsenite concentration was lowered to below 10 µg/L with adsorption. These results showed that GIH adsorption can be used to remove arsenite concentration of 0.1 and 0.5 g/L from water supplies.

Keywords: Arsenite removal, Nanofiltration membranes, Granular iron hydroxide, Drinking water

1. Introduction

Arsenic is natural element found in the earth's crust. It is introduced into water through the dissolution of minerals and ores, erosion from local rocks as well as anthropogenic sources. Arsenic is toxic, carcinogenic and detrimental to human health. Long-term intake of arsenic with water leads to liver, lung, kidney, bladder, skin and nerve tissue injuries [1–2]. Therefore, arsenic removal is urgent and important. Recently, arsenic concentration in drinking water is promulgated and maximum contaminant level (MCL) of 10 µg/L arsenic in drinking water is recommended by WHO, European Union (EU), U.S. Environmental Protection Agency (EPA) and Turkish Regulation Concerning Water Intended for Human Consumption.

The most common arsenic species in the natural water include arsenate and arsenite [3]. These are inorganic and more toxic than the organic arsenic species. Arsenite removal is more difficult than the arsenate because of its high solubility. Titanium oxide, potassium permanganate, ozone, hydrogen peroxide, chlorine or other oxidants can be utilized to oxidize the arsenite to arsenate [4].

A number of treatment technologies have been used to remove arsenate and arsenite from waters and USEPA [5] has recommended seven best available technologies for arsenic removal. These technologies and maximum removal rates for arsenate are given in Table 1.

A number of studies have been performed to examine the removal of arsenic. Different methods including ion

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Table 1
Best available technologies and their arsenate removal efficiencies [5].

Treatment technologies	Maximum removal ratio, (%)
Ion exchange ((sulfate ≤ 50 mg/L)	95
Activated alumina	95
Reverse osmosis	>95
Modified coagulation/filtration	90
Electrodialysis reversal	85
Oxidation/filtration (iron to arsenic = 20/L	80

exchange, membrane filtration, iron and aluminum coagulation, and adsorption for arsenic removal have been carried out. Granular Iron Hydroxide (GIH) material showed good performance in filtration both arsenate and arsenite removal [1].

Reverse osmosis, nanofiltration, ultrafiltration and microfiltration membrane processes have been also used to remove arsenate and arsenite. Amy and coworkers [6] used RO membrane for arsenic removal. Results from this study indicated that the removal efficiency of arsenate can reach to 96%. However, low removal efficiencies of arsenite around 5% was obtained. Kang et al. [7] also studied the RO membranes. They found that arsenate removal was around 95% whereas arsenite removal varied from 20 to 80%. Polyamide thin-film composite nanofiltration membrane was studied and 45 to 90% arsenate and 10 to 20% arsenite removal efficiencies were obtained [8]. Aromatic polyamide NF membrane was also studied to remove arsenite and 50 and 89% of removal efficiencies were obtained at the pH of 3 and 10, respectively [9]. UF and MF membranes are not suitable to remove arsenic without adding coagulant [10]. Iron and manganese ions were used to remove arsenic by microfiltration [10]. Results of this study showed that Fe/As ratio of 60 is sufficient to reduce the arsenic concentrations from 25–250 μg/L to below 10 μg/L (primary MCL for arsenic) with aeration and microfiltration at the pH of 7.0.

There is no detailed analysis on the effect of arsenic concentrations on the treatment performances. In this study, nanofiltration (NF) membranes and granular iron hydroxide adsorption (GIH) were used to investigate the removal efficiency of arsenite. Different NF membranes and arsenic concentrations were used during membrane treatment study. Additionally, different GIH heights in the column, hydraulic loading rates and arsenic concentrations were studied in the adsorption study. Comparison of the two methods has also been done.

2. Material and methods

2.1. Experimental setups

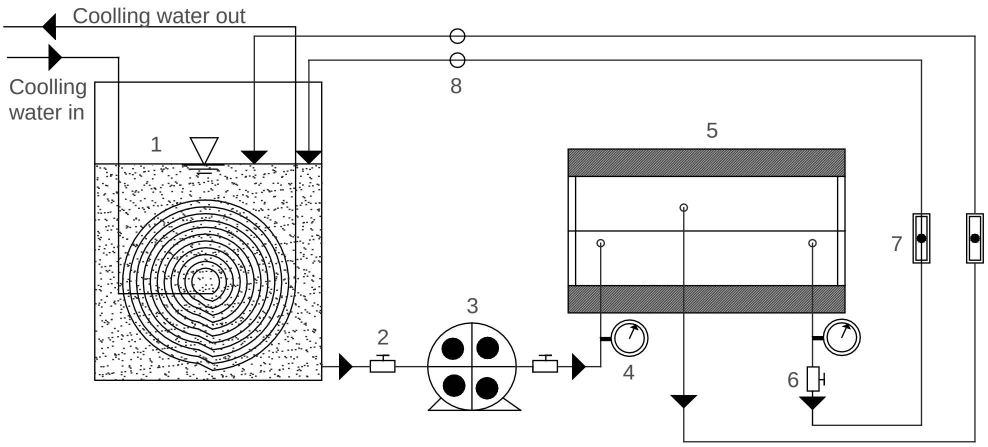
Laboratory scale cross-flow mode filtration apparatus with a flat-sheet membrane cell produced by OSMONICS was used (Fig. 1). NF200 membrane produced by Dow-FilmTec and DS5 membrane produced by Osmonics were used in this study. The characteristics of these membranes are summarized in Table 2. The effective membrane area was 155 cm^2. All experiments were carried out at constant temperature of 25 ± 1°C. Heat exchanger which tap water was flowed into thin spiral cooper pipe was used as cooling system. Fresh membranes were pre-compacted at the pressure of 20 bar with deionized water before the experiments. During the experiments, the transmembrane pressure was 10 bar.

In the column experiments, all studies were performed with free water flow and at the normal pH of tap water. Column experiments were performed at a laboratory scale. The column used in this study was prepared by Plexiglas (30 mm diameter and 1000 mm long) (Fig. 2.). The arsenite solutions were pumped by peristaltic pump to column. Granular Iron (III) Hydroxide (GIH) produced by Evers e.K. Co. was used as filter materials. The characteristics of GIH are summarized in Table 3. The height of GIH and hydraulic loading rates in the column were changed in order to observe effects of the contact time on arsenite removal. After each study, the column was backwashed by tap water for 10 min with 50% expansion.

Empty-bed contact time (EBCT) was calculated by following formula:

Table 2
Characteristics of membranes used in this study.

Parameters	NF200	DS5
Membrane Type	Thin-Film Polyamide	Thin-Film Polysulfone
Maximum operation temperature, (°C)	45	50
Maximum operating pressure, bar	40	40
pH range	3–10	2–11
MWCO, Da	200–300	150–300
Rejection	97 % (2000 mg $MgSO_4$/L)	80 % (2000 mg Na_2SO_4/L)



1. Feed reservoir 2. Control valve 3. Feed pump 4. Pressure gauge
5. Membrane cell 6. Crossflow control valve 7. Flowmeter 8. Sampling port

Fig. 1. Schematic diagram of laboratory scale membrane unit.

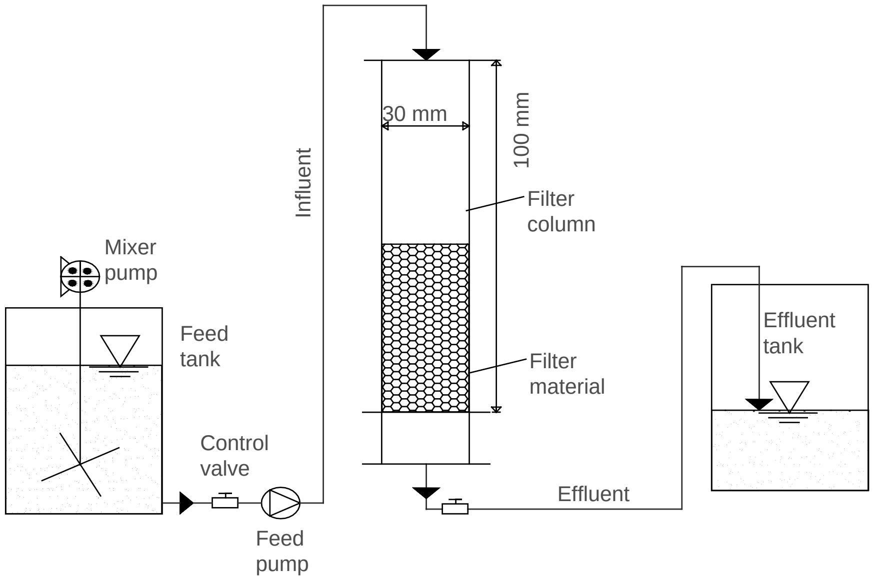


Fig. 2. Schematic diagram of laboratory scale filter column unit.

$$EBCT = \frac{V}{Q} \quad (1)$$

where V is the volume occupied by the GIH and Q is the flow rate.

2.2. Chemicals

Arsenite chemical used was of analytical reagent grade. The feed arsenite solution was prepared by 0.1 N stock arsenic (III) solution (Merck, Germany; 99% purity; CAS number 7784-46-5) immediately before utilization. The tap water was used in this study. The characteristics of tap water were given in Table 4. All glassware was cleaned by soaking in 10 % HNO_3 and rinsed three times with de-ionised water.

2.3. Analytical method and instruments

All samples were acidified (pH < 2) with HNO_3 for metal analyses. Arsenic analyses were carried out by using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) (Varian Inc.) at 188.980 nm.

2.4. Experimental procedures

NF200 and DS5 membranes were used for arsenite removal. The same temperature, pressure and arsenite

Table 3
Technical characteristics of granular iron hydroxide [11].

Formula	$Fe(OH)_3$
Iron hydroxide content min.	70 %
Color	reddish brown
Bulk density approx	625 kg/m^3
Grain size	0.5–2.0 mm
Density	1,91 g/cm^3
Special surface (BET) min.	300 m^2/g
Total Porosity min.	70 %

concentration were applied to both membranes. Arsenite solution was added into 30 L tap water. The feed water was passed from cartridge filter and then pumped by high pressure pump to membrane unit. Fluxes were obtained by collecting permeate in a beaker. Pressure on the membrane was arranged as constant at 10 bar pressure. Feed arsenite concentrations of 0.5, 1.0, 2.0 and 5.0 mg/L were applied.

Arsenite solution for column study was added into 100 L tap water. The water was mixed and then pumped by peristaltic pump though the inlet of gravity filter column. Arsenite concentrations of 0.1 and 0.5 mg/L, hydraulic loading rates of 0.93, 2.80 and 4.70 m^3/m^2/h and filter media heights of 15, 30, 45 and 55 cm were applied during experiments.

3. Results and discussions

3.1. Nanofiltration studies

Arsenite removal efficiencies for both NF200 and DS5 membranes and all applied arsenite concentrations were shown in Fig. 3. As shown in this figure, arsenite removal by NF200 membrane was better at the low arsenic concentrations (0.5 and 1.0 mg/L) than DS5 membrane. However, DS5 membrane showed better performance at high concentrations (2.0 and 5.0 mg/L). It was seen that DS5 and NF200 membranes cannot decrease the arsenic concentration below 10 μg/L at these feed concentrations. So, further treatment is necessary to meet the standards.

Arsenite removal rates in this study showed differences from the literature. Many researchers used feed arsenite concentrations below 0.5 mg/L [12–14]. In this study we used feed arsenic concentrations higher than 0.5 mg/L. As shown in Fig. 3, arsenite removal rates were decreased by the elevated feed arsenite concentrations for both the nanofiltration membranes. However, Uddin et al. [12] reported that arsenite removal rates by NF200 were increased by the elevated feed arsenite concentration. Additionally, it has been reported that the removal ratios of arsenite by NF200 membranes were 23% and 25% at 10 bar pressure for the feed arsenite concentrations of 0.05 and 0.25 mg/L [12]. This was obtained in this study as nearly 90% for the concentrations of 0.5 and 1.0 mg/L. The reason of high removal efficiencies can be due to the tap water characteristics used to prepare synthetic feed water and can have been adsorbed to iron in tap water which can cause high arsenic removal efficiencies.

Fluxes for both NF200 and DS5 membranes and all applied arsenite concentrations were shown in Fig. 4. As shown on Fig. 4, DS5 membrane fluxes for all arsenite concentrations were higher than the NF200 membrane. These results suggest that NF200 membrane has a smaller pore size than DS5 since all feed conditions

Table 4
Tap water characteristics.

Parameters	Values	Parameters	Values
Sodium (mg/L)	22.02	Nitrate (mg/L)	2.47
Amonium (mg/L)	0.38	Sulfate (mg/L)	62.3
Iron (mg/L)	<0.2	pH	7.3–7.6
Magnesium (mg/L)	7.97	TOC (mg/L)	3–3.5
Calcium (mg/L)	54.15	DO (mg/L)	10–10.5
Fluoride (mg/L)	0.07	Temperature (°C)	14–15
Chloride (mg/L)	29.12	Alkalinity (mg $CaCO_3$/L)	80–110

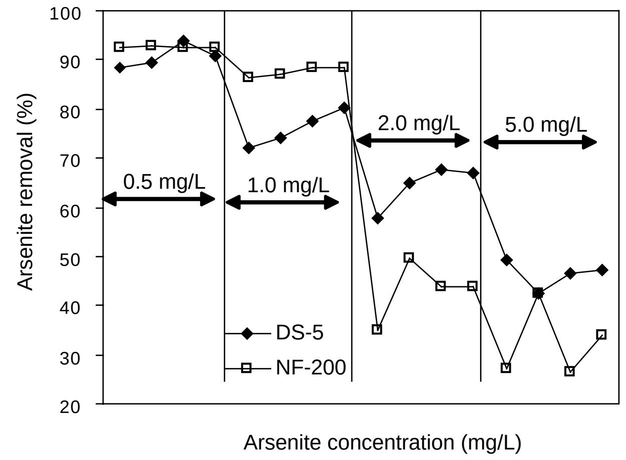


Fig. 3. Influence of the arsenite concentration on the arsenite removal by NF200 and DS5 nanofiltration membranes.

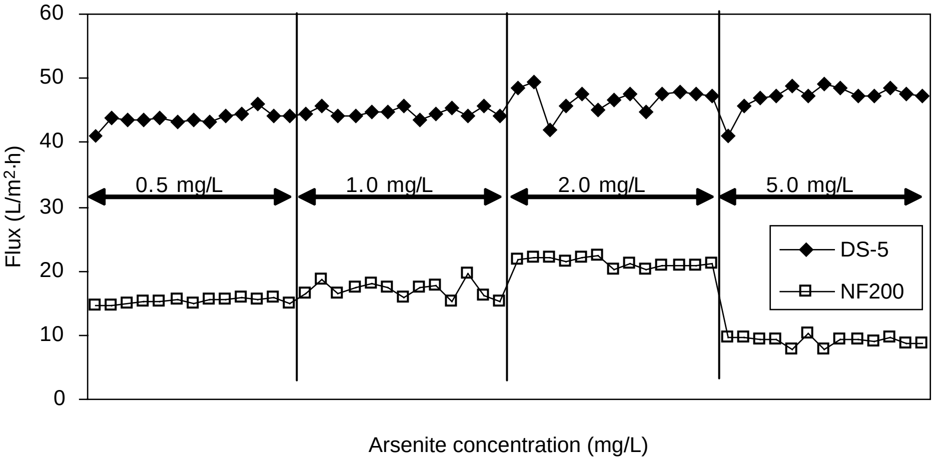


Fig. 4. Influence of the arsenite concentration on permeate flux.

were the same for both membranes. Although there were no important flux fluctuations for DS5 membrane with arsenite concentrations, the flux of NF200 membrane showed fluctuations with arsenite concentrations. The reason of the fluctuation can be due to the changes on operating parameters during operation such as temperature.

3.2. Granular iron hydroxide (GIH) study

Column studies with tap water using GIH were carried out for initial feed arsenite concentrations of 0.1 and 0.5 mg/L. Three hydraulic loading rates were applied and all studies were performed for 8 h. The effects of hydraulic loading rates were shown on Fig. 5. The contact times for 0.93, 2.80 and 4.67 $m^3/m^2/h$ hydraulic loading rates were 28.90, 9.63 and 5.78 min, respectively. As seen in Fig. 5a the first 240 min for the initial arsenite concentration of 0.1 mg/L, arsenite removal rates showed a fluctuations and then the removal rates for all there loading rates were approximately the same. The removal rates were reached over the 90% and MLC was already supplied by all hydraulic loading rates. Arsenite removal rates for the arsenite concentration of 0.5 mg/L were over 94% for three hydraulic loading rates (Fig. 5b). GIH arsenite removal efficiency increased with increasing initial arsenite concentration. While all measured samples supplied the standards for feed arsenic concentration of 0.1 mg/L, effluent of 0.5 mg/L of feed arsenic concentration did not reach the 10 µg/L standard and remained around 50 µg/L.

Contact time of adsorbent and water is very important. Different heights of adsorbent were performed to obtain optimum contact time for arsenite removal by GIH. The effects of contact time on the arsenite removal for 0.1 mg/L feed arsenite concentration were obviously seen on Fig. 6a. The removal rates increased for the first 120 min of operation for the contact time of 1.93 min and then decreased. The removal efficiencies were approximately over 90% for all contact times except 1.93 min. The contact time for arsenite concentration of 0.1 mg/L was required as 3.85 min to obtain MLC standard. As seen on Fig. 6b, arsenite removal for 0.5 mg/L were higher than 90%, but it is not enough to meet Turkish and EU MLC. The same fluctuation was observed on removal efficiencies for contact time of 1.93 min for arsenite concentration of 0.5 mg/L. In the first 60 min, removal rates increased and then decreased.

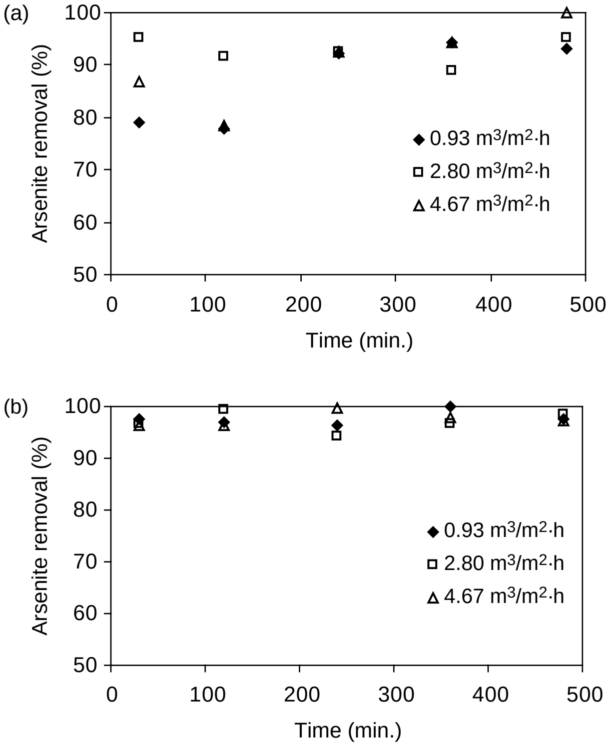


Fig. 5. Arsenite removal with the hight of the filter media 45 cm (a) 0.1 mg/L and (b) 0.5 mg/L initial arsenite concentrations.

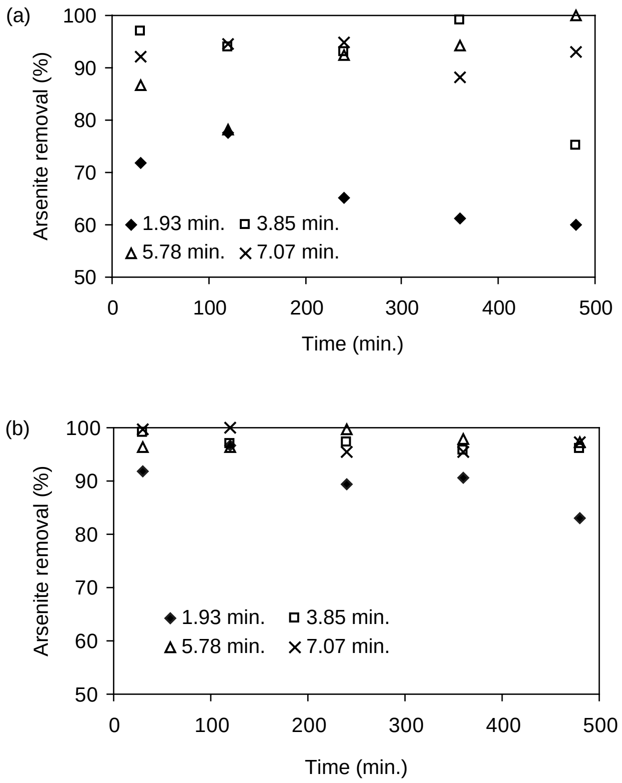


Fig. 6. Contact time effects on arsenite removal with the hydraulic loading rate of 4.67 $m^3/m^2/ha$ (a) 0.1 mg/L and (b) 0.5 mg/L initial arsenite concentrations.

In this study it was concluded that arsenite concentration in the effluent was lowered to 50 µg/L with GIH and some times to 10 µg/L. The effluent arsenite concentrations were less than 10 µg/L with granular ferric hydroxide for EBCT of 2.0 min and flow rate of 5.0 m/h in the literature [1]. The only difference between these two studies was granular iron (III) hydroxide. Different commercial granular iron (III) hydroxides were used in these two studies. These results showed that the content of granular iron hydroxide was very important to achieve of Turkish MLC.

4. Conclusions

Nanofiltration and GIH are the technologies that have potential for arsenite removal and drinking water treatment. The conclusions that can be drawn from the results of this study are as follows:

- DS5 membrane was showed higher arsenite removal rate and flux than the NF200 membrane at 10 bar pressure under all feed concentrations. Arsenic rejections decreased with increasing feed arsenic concentration. Effluent arsenite concentrations except for 0.1 mg/L of feed concentration were exceeded for Turkish regulation. If arsenite concentration is 0.5 mg/L and higher, nanofiltration is not enough to meet the Turkish regulation.
- All effluent arsenite concentrations were supplied the 50 µg/L, but not Turkish standard with GIH. However, some of the effluents were lower than the 10 µg/L. The most important parameters for arsenite removal with GIH were the type of GIH and contact time. It can be concluded that the optimum contact time for the studied GIH is 3.85 min. There was no importance of hydraulic loading rate over this optimum contact time.

References

[1] O.S. Thirunavukkarasu, T. Viraraghavan, K.S. Subramanian, Arsenic removal from drinking water using granular ferric hydroxide. *Water Sa*, 29(2) (2003) 161–170.

[2] L.C. Roberts, S.J. Hug, T. Ruettimann, M.M. Billah, A.W. Khan, and M.T. Rahman, Arsenic removal with iron(II) and iron(III) waters with high silicate and phosphate concentrations. *Envi ron. Sci. Technol.*, 38(1) (2004) 307–315.

[3] Z.M.Gu, J. Fang, B.L. Deng, Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environ. Sci. Technol.*, 39(10) (2005) 3833–3843.

[4] D. Mohan, C.U. Pittman, Arsenic removal from water/wastewater using adsorbents–A critical review. *J. Hazard. Mat.*, 142(1–2) (2007) 1–53.

[5] USEPA. Technologies and Costs for Removal of Arsenic from Drinking Water, *EPA/815/R-00/028*, Washington, 2000.

[6] G.L. Amy, M. Edwards, M. Benjamin, K. Carlson, J. Chwirka, P. Brandhuber, L. McNeill, and F. Vagliasindi, Technologies and costs for removal of arsenic from drinking Water Draft Report, *AWWARF*, 1998.

[7] M. Kang, M. Kawasaki, S. Tamada, T. Kamei, Y. Magara, Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination*, 131(1–3) (2000) 293–298.

[8] A. Seidel, J.J. Waypa, M. Elimelech, . Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane. *Environ. Eng. Sci.*, 18(2)(2001) 105–113.

[9] T. Urase,; J. Oh, K. Yamamoto, Effect of pH on rejection of different species of arsenic by nanofiltration. *Desalination*, 117(1–3) (1998) 11–18.

[10] S. Caniyılmaz, Arsenic removal from groundwater by Fe-Mn oxidation and microfiltration. University of Pittsburgh, *MS thesis*, 2005.

[11] Evers e.K. Co, Granular iron-hydroxide for effective removal of arsenic from water. *EVERS e.K. Water Technology and Filter Materials*, Germany, 2005.

[12] M.T. Uddin, M.S.I. Mozumder, M.A.S. Islam, A. Deowan, J. Hoinkis, Nanofiltration membrane process for the removal of arsenic from drinking water. *Chem. Eng. Technol.*, 30 (2007) 1248–1254.

[13] S.J. Xia, B.Z. Dong, Q.L. Zhang, B. Xu, N. Gao, and C. Causseranda, Study of arsenic removal by nanofiltration and its application in China. *Desalination*, 204(1–3) (2007) 374–379.

[14] H. Saitua, M. Campderros, S. Cerutti, P.A Perez, Effect of operating conditions in removal of arsenic from water by nanofiltration membrane. *Desalination*, 172(2) (2005) 173–180.