Arsenate removal using a combination treatment of precipitation and nanofiltration

F. F. Chang and W. J. Liu

ABSTRACT

A combination treatment of Ca-precipitation and nanofiltration membrane was studied to remove arsenate from water. The selected nanofiltration membrane was an amphoteric charged membrane, proved by the results of ATR-FTIR spectra and zeta potential. The arsenate and calcium removal efficiencies had the lowest values at the isoelectric point of the nanofiltration membrane, attributed to the loosest steric hindrance and the weakest electrostatic repulsion. Above the isoelectric point, arsenate precipitated with calcium ion to form the low solubility compound calcium arsenate, while steric hindrance was the main mechanism of arsenate removal. In contrast, below the isoelectric point, the nanofiltration membrane with positive charges rejected calcium ion by electrostatic repulsion. The high electrostatic shielding of calcium ion prevented arsenate from coming close to the NF membrane. Either high feed arsenate concentration or high calcium oxide dose improved the removal amount of arsenate during the nanofiltration membrane separation process. In addition, the arsenate removal efficiency approached the highest value at 200 μg/L of feed arsenate concentration. The optimal transmembrane pressure was in a range of 0.5–0.7 MPa to restrict the formation of fouling cake on the nanofiltration membrane surface.

Key words | arsenate, calcium, nanofiltration, precipitation

INTRODUCTION

As one of the world’s most hazardous elements, arsenic can accumulate in rivers, lakes, groundwaters, and soils under the right geological conditions. Generally, the common valence states of arsenic in water are arsenate (As(V)) and arsenite (As(III)), depending on the surrounding oxidation-reduction conditions. In shallow groundwater and surface water, As(V) in the form of H₂AsO₄⁻ and HAsO₄²⁻ is the dominant arsenic species (pKₐ₁, pKₐ₂, and pKₐ₃ of H₂AsO₄ are 2.2, 7.08, and 11.53, respectively) (Kartinen & Martin 1995).

Because chronic ingestion of low concentration arsenic will cause possible health risks to humans, source water containing arsenic must go through advanced treatment before being used as drinking water (Saha et al. 1999). A large number of advanced treatment processes have been evaluated for arsenic removal from water, and can be classified on the basis of the principles involved: (a) precipitation; (b) adsorption; and (c) membrane technology (Shih 2005; Song et al. 2006; Mohan & Pittman 2007). In many underdeveloped locations, a low cost, simple, and appropriate method is required.

Calcium oxide (CaO) addition to arsenic contaminated water has been proved to be useful in stabilizing the mobility of dissolved arsenic, presumably through the formation of calcium arsenates (Ca₃(AsO₄)₂) (Bothe & Brown 1999; Camacho et al. 2009). Compared with common flocculants and coagulants (e.g. polymeric aluminium and ferric sulfate), calcium oxide is economically attractive to be used for arsenic removal. So far, only a few studies have been conducted to evaluate arsenic removal by calcium addition in drinking water. Bench scale and pilot scale studies by Sorg & Logsdon (1978) exhibited arsenic removal of 75–100% using calcium precipitation at pH greater than 10.5, although the removal efficiency was low at pH less than 10. McNeill & Edwards (1997) employed the co-precipitation of Mn(OH)₂ and CaO to remove 90% of As(V) at pH 11. Fields et al. (2000) reported about 45% removal of arsenic in lime softening treatment for drinking water.
water at a pH of 9.6. Apparently, arsenic removal during calcium precipitation process is pH dependent.

In order to control the water quality, membrane filtration usually follows the precipitation process (Leiknes 2009). A method of coagulation with ferric ions following microfiltration membrane was tested by Wickramasinghe et al. (2004) to remove arsenic from groundwater. The arsenic concentration was reduced from 68 μg/L to below 10 μg/L under the effects of 15 mg/L ferric ion and microfiltration, while the turbidity of permeate water increased significantly. Kettunen & Keskitalo (2006) proved that drinking water quality could be improved by the combination of limestone and reverse osmosis (RO)/NF filtration. However, the application of calcium precipitation with membrane filtration for arsenic removal from drinking water has not been reported.

In this study, a potential application of Ca-precipitation combined with nanofiltration (NF) membrane was tested for As(V) removal from water. The effects of original water quality, operational conditions, and membrane property were also investigated based on the cross-flow NF membrane experiments.

## EXPERIMENTS

### Materials

The stock solutions of As(V) were prepared by dissolving appropriate quantity of Na₃AsO₄·12H₂O (analytical grade, Beijing Chemical Reagents Co., China) into tap water. The original tap water quality is shown in Table 1. Either HCl or NaOH was used to adjust the pH of feed water.

### Experimental set-up

Laboratory scale experiments were conducted by using a cross-flow filtration setup equipped with a flat-sheet membrane cell (Sepa II, osmonics, General Electric Co., USA), a high-pressure pump (DP-60, Shanghai Qiquan Co., China), a feed and permeate container, and other accessories (Figure 1). The effective membrane surface area and the cross-sectional flow area were 139 and 0.9 cm², respectively. The feed water flow rate was kept at 100–200 mL/min, equalling a superficial cross-flow velocity of approximately 0.019–0.038 m/s. Desal HL Membrane (General Electric Co., USA) was used in this study.

### Analytical methods

The pH of feed water was determined by using a pH meter (pB-21, Sartorius Co., Germany). Conductivity, total dissolved solids (TDS), and salinity were measured by a handheld meter (Senion156, Hach Co., USA). Turbidity was determined using a turbidimeter (2100P, Hach Co., USA). Total organic carbon (TOC) was measured in a model TOC-V CPH instrument (Shimadzu, Japan). Permeate water samples were also assayed for anion concentrations by ion chromatography (ICS-2000, Dionex Co., USA).

Inductive coupling plasma-mass spectrometry (ICP-MS) (7500, Agilent Co., USA) was used for arsenic detection. The limit of arsenic determination on ICP-MS was 0.5 μg/L with a calibration curve from 0 to 100 μg/L. Precision of the parallel measurements was ±5% RSD (relative standard deviation). Calcium concentrations of solution samples were measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP, Thermo Co., USA).

### Table 1

<table>
<thead>
<tr>
<th>Quality parameters of the original tap water</th>
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<tbody>
<tr>
<td>Arsenic (μg/L)</td>
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<tr>
<td>Not detected</td>
</tr>
<tr>
<td>Total organic carbon (mg/L)</td>
</tr>
<tr>
<td>0.79</td>
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scanning electron microscope (ESEM) (Quanta 200, FEI Co., Czech Republic).

RESULTS AND DISCUSSION

Membrane property

The selected NF membrane was a thin film composite membrane with aromatic polyamide top layer. When polyamide membrane gets in contact with an electrolyte solution, the functional groups of the membrane can cause the variation of membrane charge density, depending on the feed pH (Tang et al. 2006). According to the study of Tang et al. (2009b), the protonation of amides (Equation (1)) and deprotonation of carboxylic acids (Equation (2)) play important roles in the charge property of polyamide membrane.

\[
\text{R-NH}_2 + \text{H}^+ \rightarrow \text{R-NH}_3^+ \quad (1)
\]

\[
\text{R-COOH} \rightarrow \text{R-COO}^- + \text{H}^+ \quad (2)
\]

Generally, membrane zeta potential is used to correlate with the membrane charge density. The zeta potential of the selected NF membrane was evaluated in 10 mmol/L KCl solution. As shown in Figure 3, the isoelectric point of the virgin NF membrane was around pH 5.8. Below the critical pH, the zeta potentials were positive, e.g. 10 mV at pH 4. In contrast, above the critical pH, the zeta potential was negative, e.g. –15 mV at pH 8. The membrane rejection performance would be affected by the amphoteric behaviour of the selected NF membrane, especially in anion removal.

Effect of feed pH on As(V) removal

As noted before, both As(V) species forms and the NF membrane charge property depend on the feed pH. Therefore, the effect of feed pH on As(V) removal by the NF membrane was investigated as shown in Figure 4. With an increase of feed pH from 4 to 10, As(V) removal efficiencies exhibited...
as V-shaped curves. The lowest efficiency was obtained at pH 7.5–8.0. Above this critical pH, the As(V) removal efficiency had a sharp rise of 20%. When calcium oxide dose was 0.25 mmol/L, the highest As(V) efficiency approached 40% at feed pH 10. Every 5–10% of As(V) rejection rate was improved by an additional 0.1 mmol/L calcium oxide.

The feed water contained about 20.21 mg/L of calcium, which played an important role in As(V) removal. In addition, feed calcium concentration increased 4 and 10 mg/L × 0.1 mmol/L and 0.25 mmol/L of CaO addition, respectively. The calcium removal efficiencies are shown in Figure 5. The calcium species percentages without the presence of As(V) in feed water were also exhibited. Above feed pH 8, the co-precipitation of CaAsO$_4^-$, CaCO$_3$ and CaSO$_4$ formed the concentration polarization on the NF membrane surface, restricting the membrane pore size. Due to the steric hindrance, As(V) and Ca removal efficiencies increased significantly with an increase of feed pH in alkaline feed water. About 40% of As(V) and 90% of Ca were rejected by the NF membrane at feed pH 10.

Below feed pH 8, the As(V) species existed as the forms of H$_2$AsO$_4^-$ and HAsO$_4^{2-}$, while Ca$^{2+}$ was the main form of calcium species. During the separation process of NF membrane, electrostatic interaction is responsible for ion rejection (Abitoye et al. 2005). In acid feed water, the selected NF membrane had positive membrane charges, and could reject most of the Ca$^{2+}$. High calcium concentration formed an electrostatic shielding on the NF membrane surface, enhancing the rejection of arsenic. With the decrease of positive zeta potential, the removal efficiencies of As(V) and Ca declined. Obviously, the lowest removal efficiency was obtained at the isoelectric point of the NF membrane. The similar result was reported by Qin et al. (2004), who studied the membrane performances of HL NF membrane in NaNO$_3$ solution. It is believed that zeta potential of NF membrane was affected by both feed pH and ion strength, while the isoelectric point of NF membrane depended on solutes in the feed water (Childress & Elimelech 2000). Below feed pH 6.5, calcium removal efficiency decreased significantly, attributed to the competition with H$^+$ which was abundant in acid feed water. Compared with the rejection of Ca$^{2+}$, H$^+$ had priority to be rejected by the positive NF membrane.

Effect of feed concentration on As(V) removal

In order to determine the maximum treatment capacity of the NF membrane with CaO precipitation, the feed As(V) concentration was investigated from 100 to 400 μg/L with a CaO dose range of 0–0.25 mmol/L. As shown in Figure 6(a), either higher feed As(V) concentration or higher CaO dose enhanced the removal amount of As(V) in the NF membrane separation process at feed pH 9.0. Meanwhile, the removal amount of Ca increased significantly with the increase of feed As(V) and CaO concentrations (Figure 6(b)). When feed As(V) concentration was higher than 200 μg/L, the slopes of As(V) and calcium removal curves descended slowly. Although the accumulated removal amount of As(V) continuously increased in the whole investigated range of feed concentration, the highest As(V) removal efficiency was obtained at 200 μg/L of feed As(V) concentration.
Fouling cake formed on the NF membrane surface

When feed As(V) concentration (100 μg/L) and CaO dose (0.25 mmol/L) were constant, As(V) and Ca removal efficiencies were enhanced slightly with increased transmembrane pressure, shown in Figures 7(a) and (b), respectively. Under very low or very high transmembrane pressure, membrane fouling cake would be formed on the surface of the NF membrane. Because low transmembrane pressure caused flux decline, particles were easily deposited on the membrane surface. In contrast, caused by high transmembrane pressure, high flow velocity would retain particles of sizes similar to membrane pore diameter on the membrane pores. The results of this study indicated

![Figure 6](https://iwaponline.com/wst/article-pdf/65/2/296/442280/296.pdf)

**Figure 6** | Effect of feed concentration on As(V) (a) and Ca (b) removal by the NF membrane (transmembrane pressure 0.69 MPa, feed water pH 9.0).

![Figure 7](https://iwaponline.com/wst/article-pdf/65/2/296/442280/296.pdf)

**Figure 7** | Effect of transmembrane pressure on As(V) (a) and Ca (b) removal by the NF membrane (feed arsenic concentration 100 μg/L, CaO dose 0.25 mmol/L).
that the optimized transmembrane pressure range was from 0.5 to 0.7 MPa.

The ESEM image of the fouled NF membrane shows a fouling cake layer on the membrane surface in Figure 8. The average thickness of the fouling cake layer was about 23.1 μm. As discussed before, CaAsO₄, CaCO₃ and CaSO₄ formed a high concentration of precipitates close to the NF membrane surface, and deposited as a nonporous and loose layer on the membrane surface after the experiment.

CONCLUSIONS

The application of Ca-precipitation combined with NF membrane was proved to be practicable for As(V) removal in this study. The selected NF membrane was an amphoteric charged membrane, and its membrane charge depended on the feed pH. As(V) removal efficiency exhibited a V-shaped curve, and the lowest value was obtained at the isoelectric point of the NF membrane. Steric hindrance played an important role in the As(V) removal process, due to the formation of calcium arsenate. With an increase of calcium oxide dose, the As(V) removal efficiency was enhanced significantly. The NF membrane exhibited the highest effective removal for As(V) with CaO addition when the feed As(V) concentration was 200 μg/L. Because CaAsO₄, CaCO₃ and CaSO₄ were the major compositions of the fouling cake, acid washing method could be used to effectively clean the fouled NF membrane surface.

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