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Study of arsenic removal by nanofiltration and its application in China

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Abstract

Arsenic contamination of groundwater and associated health risks have been reported in many parts of China. Nanofiltration (NF) is a promising technology for arsenic removal since it requires less energy than traditional reverse osmosis membranes. In this study, the removal of arsenic from synthetic waters by nanofiltration (NF) membranes was investigated. Arsenic rejection experiments included variation of arsenic feed concentration, pH, and existence of other ionic compounds. The possible influence of natural organic matter on As (V) rejection by nanofiltration membranes was also explored. The study shows the nanofiltration point-of-use (POU) systems were particularly suitable to treat arsenic-rich groundwater in suburban China.

Keywords: Drinking water; Nanofiltration; Arsenic; Groundwater; Water treatment

1. Introduction

Arsenic, atomic number 33, is located in group VA of the periodic table directly below phosphorus. Arsenic is listed as a hazardous material

and is a suspect carcinogen, reportedly responsible for lung and skin cancer [1]. The level of arsenic allowed in drinking water has been set at 0.01 mg/l by the World Health Organization (WHO). However, the current maximum permissible limit of arsenic in drinking water of China is 0.05 mg/l. In order to improve drinking water quality, the

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National Construction Ministry of China promulgated new Water Quality Standards for Urban Water Supply, in which arsenic is regulated below 0.01 mg/L in 2006. The lower permitted concentration will affect a significant number of water suppliers and users in many regions of China.

There are currently many methods for removing arsenic from drinking water. Widespread variations in the projected costs of arsenic removal are partially attributable to the large number of possible arsenic removal technologies. All of the following methods are intended to remove As(V). As(III) can be oxidized to As(V) by using ferric chloride, potassium permanganate, or chlorine. A number of arsenic removal technologies, namely, activated alumina sorption, polymeric anion exchange, sorption by iron oxide coated sand (IOCS) particles, enhanced coagulation with alum or ferric chloride dosage, ferric chloride coagulation followed by microfiltration, pressurized granulated iron particles, iron oxide doped alginate, manganese dioxide coated sand, polymeric ligand exchange and zero-valent iron have been tried in the laboratory and/or field-scale testing for removals of trace arsenic. Of the available technologies for the treatment of arsenic in drinking water, membrane treatment is the technically superior method to obtain the low level of arsenic concentration in finished water stipulated by the EPA [2].

Reverse osmosis has been identified as the best available technology for arsenic removal, but economic studies have shown it to be the most costly. Because charged NF membranes primarily reject As(V) by electrostatic repulsion, membranes with a more open pore structure can be utilized and higher productivity compared to RO can be realized. Considering the developing countries' (as China) situation, with low annual income and low electric popularization, traditional RO technology seems difficult to apply due to its high energy consumption. In addition, because arsenic is typically present in natural waters as a divalent oxidation (HAsO_4^{2-}), there has been much interest in the use

of NF membranes which are known to be quite effective at removing divalent ions [3].

In this paper we report the results of NF experiments fed with synthetic water spiked with arsenic. The purpose of this study was to evaluate the factors which influence the rejection of arsenic, such as arsenic feed concentration, pH, organic matter and background salt concentration.

2. Materials and methods

2.1. Reagents and arsenic analysis

All salts were prepared fresh using reagent grade chemicals dissolved in deionized water. The sodium chloride and calcium chloride were prepared from NaCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salts. To separate arsenic species such as arsenite and arsenate, samples were preserved by adding hydrochloric acid. Arsenic analysis was performed using an AFS (atomic fluorescence spectrometry, Haiguang 230E). Ca^{2+} and Na^+ ions were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Measurement of the commercial humic matter content was carried out with an ultraviolet spectrophotometer.

2.2. Nanofiltration membrane and nanofiltration unit

The pilot consisted of a feed tank, a pump and a spiral module containing a 0.5 m² membrane. The membrane material used had an active polyamide layer and was obtained from Toray (Japan). The experimental setup is shown in Fig. 1. The feed solution was pumped to the membrane by the raw water pump. The filtration in the module occurred in cross-flow.

3. Results and methods

3.1. Effects of applied pressure on membrane flux

Before the experiments, we measured the membrane permeability to water at 20°C. As

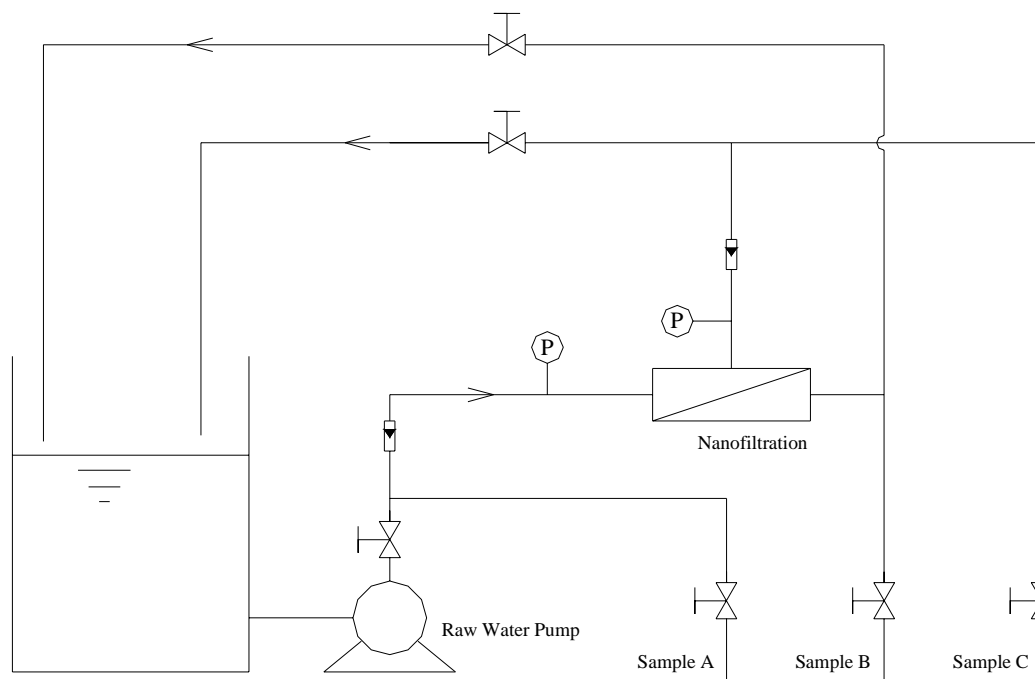


Fig. 1. Schematic of the experimental unit for NF.

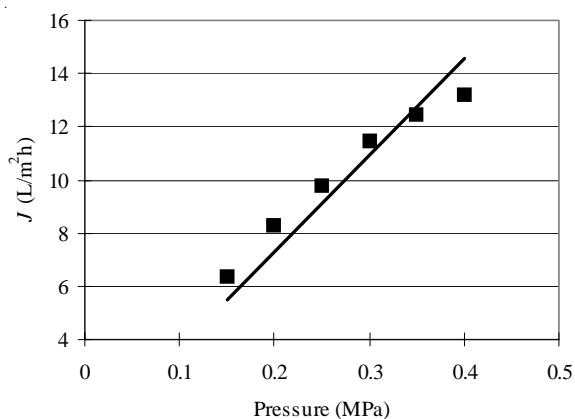


Fig. 2. Effect of applied pressure on membrane flux.

shown in Fig. 2, the membrane obeys the Darcy law and the mean value of permeability was 365 L/hm²MPa. This is a typical value for nanofiltration membranes. The permeability measured

was considered as reference to evaluate the cleaning procedure, concentration polarizations and fouling.

3.2. Arsenic removal with different feed concentrations

The removal of arsenic with feed concentration is shown in Fig. 3. There is a large difference in the removal of As(V) and As(III). The rejection of As(V) by the NF membrane was found to be between 90 and 100% for arsenic concentration in feed in the range of 20 and 90 ug/L, while the As(III) removal was below 10%. Compared to As(V), the rejection of As(III) is significantly lower (Fig. 3). An almost linear relationship was found to relate the feed concentration to As(III) rejection. The rejection of As(III) decreases from 9.8 to 2.0%, as opposed to about 99% for As(V), when the arsenic concentration in feed increases

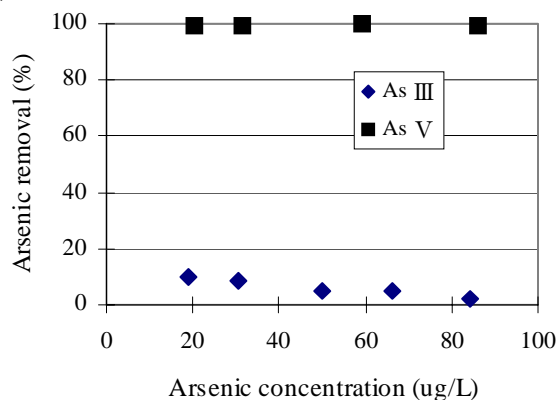


Fig. 3. Arsenic removal with different feed concentrations V.

from 20 to 90 ug/L. When arsenic concentration in feed increases, both diffusion and convection of the uncharged As(III) species increase, resulting in an additional decrease of its rejection [4]. As(V) removal efficiency is higher than that of As(III). It is because As(III) exists in a neutral molecular form, while As(V) exists as a negatively charged ion. Because As(V) in natural waters is found as monovalent (H_2AsO_4^-) and divalent (HAsO_4^{2-}) oxyanions, while As(III) is in the form of the uncharged species H_3AsO_3 , it is expected that arsenic removal by the NF membrane will be quite different for the various arsenic species since the NF separation may be due to charge exclusion. In this sense, pre-oxidation of arsenite to arsenate must be considered to obtain safe drinking water in view of the total arsenic rejection.

3.3. Effect of organic matter on arsenic removal

Fig. 4 shows the arsenic removal with different organic matter concentrations in the synthetic water. Arsenic was spiked to deionizer water to 60 ug/L and the commercial humic acids was spiked to a range concentration. The removal of As(V) was higher than that As(III) with different humic acids. As(III) in the high UV_{254} water was consistently rejected at a higher ratio than in the low UV_{254} water. It may be due to co-rejection of ar-

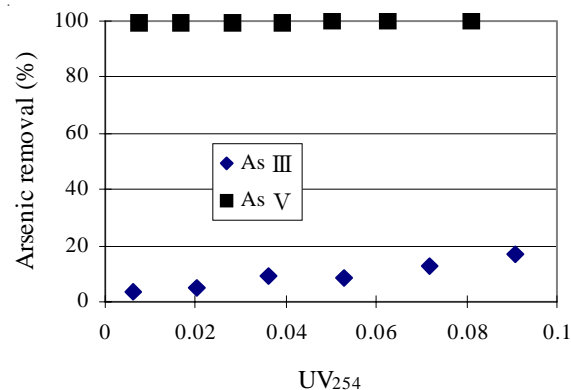


Fig. 4. Effect of organic matter on arsenic removal.

senic with humic materials in the high DOC water improving As(III) rejection. DOC, comprised largely of humic substances, plays a major role in the behavior and mobility of metals in the aquatic environment. NOM is comprised of a range of organic materials, with average molecular weights of 1000–10,000 Dalton [2]. Several studies have indicated possible association between humic substances and arsenic [5]. The higher the concentration of humic acids, the more As(III) complexes produced. The size of the complexes may be larger than the NF membrane hole. So the removal of As(III) was increased.

3.4. Effect of background salt concentration on arsenic removal

The influence on As(III) and As(V) rejection exerted by the presence of background ions is summarized in Fig. 5. The cations (Na^+ , Ca^{2+}) in the presence of a common co-ion (Cl^-) were added in separate experiments to As(III) and As(V) spiked deionizer water solution. The presence of additional salts has been shown to have an impact on the rejection of As(V). Some reports show that increasing the concentration of anions or cations increased the passage of As(V). In this research, the results were also founded. The reduction in

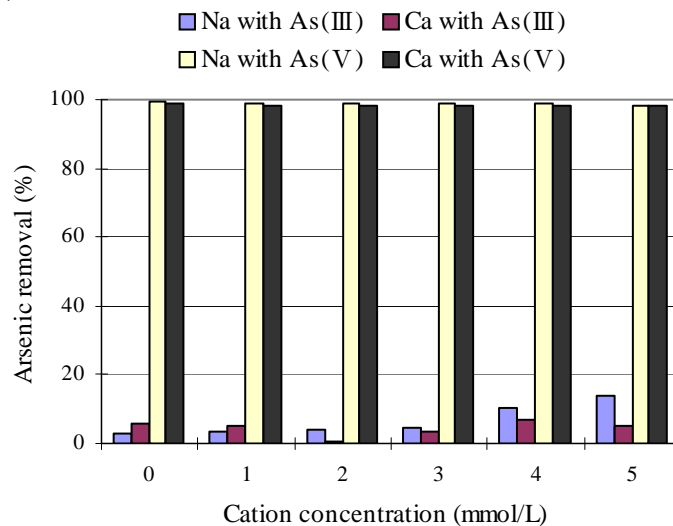


Fig. 5. Effect of cation concentration on arsenic removal.

As(V) rejection in the presence of divalent Ca^{2+} was greater than for monovalent Na^+ by about 1%. But there was no obvious trend in the removal of As(III) with different additional salts added.

3.5. Effect of pH on arsenic removal

Based on the idea that negatively charged membranes generally have higher rejection for charged solutes than for non-charged solutes, the effect of pH on arsenic removal was studied. Fig. 6 summarizes the effect of pH on the rejection of As(V) and As(III). Incremental additions of hydrochloric acid were used to adjust the test solution pH in studies on the effect of pH on separation of the arsenic species. The arsenic rejection by the membrane increased with increasing pH. The removal of arsenate was higher than that of arsenite over the pH range of 3–10 investigated in this study. Most arsenite existed in neutral solute at a pH range from 3 to 7, while most of arsenite was in the monovalent anion at pH 10, because pK_{al} of arsenite is 9.1 at 25°C. So As(III) was characterized by a higher removal because the species changed from H_3AsO_3 to H_2AsO_3^- .

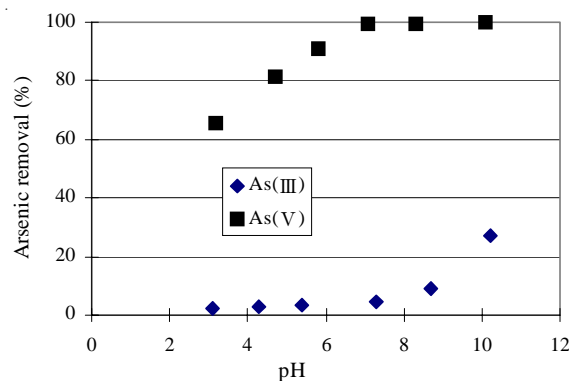


Fig. 6. Effect of pH on arsenic removal.

4. Conclusion

In China, some groundwater is rich in arsenic. Nanofiltration membranes were used to investigate arsenic removal with synthetic water. The results show that there is a large difference in the removal of As(V) and As(III). As(V) was almost fully removed, while As(III) was removed about 5%. The removal of As(V) was higher than that

of As(III) with different humic acid concentrations. The presence of additional salts has been shown to have an impact on the rejection of As(V). The arsenic rejection by the membrane increased with increasing pH.

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