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Effect of dissolved organic matter on arsenic removal by nanofiltration

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ABSTRACT

Arsenic is known as a carcinogen that causes skin cancer and various internal cancers. The arsenic contamination in water forced the water and health authorities to introduce stringent standards for arsenic control level in drinking water. Nanofiltration presents a promising method to remove arsenic, by the effect of both size exclusion and electric repulse, which is reliable, easy to produce, obtain, operate, and maintain. In this work, the influences of dissolved organic matter (DOM) on arsenic removal by nanofiltration process were investigated through a series of laboratory bench-level experiments. The existing of humic acid (HA), which was used as substitute of DOM, increased the arsenic removal due to the formation of humic/arsenic complexes. With the presence of high concentration of HA (10 mg total organic carbon [TOC]/L), the removal efficiency of arsenic was almost 100%, which was higher compared with the result (80%) obtained at low concentration of HA (2 mg TOC/L). The membrane flux for the membrane separation of the various concentration of DOM decreased to 80% of the initial flux after 400 min with the same cross-flow velocity (3.5 cm/s). The mechanism of arsenic removal by nanofiltration was further presented article.

Keywords: Arsenic; DOM; Nanofiltration; Membrane fouling

1. Introduction

Arsenic, atomic number 33, is located in group VA of the periodic table directly below phosphorus. The ingestion of inorganic arsenic could cause either cancerous or non-cancerous health issues. It could cause liver, lung, kidney, and bladder cancers. Furthermore, arsenic has acute and chronic effects on dermal and nervous system. Chronic exposure to low levels of arsenic (less than 50 μg/L) has relationships with health complications, including cancer, skin diseases, and neurological and cardiovascular system conditions.

Main causes of artificial contamination of arsenic are industrial effluent and mining, and it also occurs naturally in groundwater and hot spring water. There are millions of people subject to arsenic-contaminated drinking water all over the world. Increasing high concentration levels of arsenic in commonly found in groundwater in countries such as India, Bangladesh, China, Chile, Argentina, Mexico, Hungary, Taiwan, Vietnam, Japan, New Zealand, Germany, and the USA, where arsenic naturally occurred in the aquifer

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sediment [1] with a large proportion from 100 to 2,000 μg/L in groundwater. Arsenic is a toxic semimetallic element that could be fatal to human. Consequently, in recent years, authorities have taken a more stringent approach to arsenic in public environment. In particular, World Health Organization and US Environmental Protection Agency have published guidelines proposing the new standard limit for arsenic in drinking water to be less than 10 μg/L.

In natural environment, arsenic as the free element could rarely be found. It is most commonly in four oxidation states ($-3, 0, +3, +5$), and the two predominated oxidation states commonly found in drinking water are oxyanions of trivalent arsenic and pentavalent arsenic [2]. Pentavalent arsenic is the thermodynamically stable form of inorganic arsenic in oxic water and generally predominates in surface water, whereas well water is more reducing due to less aeration, thus arsenic would take As (III) form under this condition [3]. Arsenate and arsenite are part of the arsenic (H_3AsO_4) and arsenous (H_3AsO_3) acid systems, respectively. Hence, the pH of the system will control the degree of protonation of the acids. Within a pH range of 5.0–8.0, which is typical of natural waters, As (V) exists as an anion, while As (III) remains fully protonated and is present as a neutral species; thus, As (V) is better adsorbed on most media than As (III) [4–6].

Arsenic cannot be destroyed; it can only be transformed into different forms or combined with other elements to be converted into insoluble compounds. There is a tremendous demand for developing cost-efficient methods for arsenic removal from drinking water. Various technologies such as coagulation, filtration, lime softening, activated alumina, anion exchange, and reverse osmosis have been studied to determine efficacy of arsenic removal [7,8]. Appropriate treatment depends on many factors, such as concentration of arsenic, water composition, pH, and cost-effectiveness [9]. The main disadvantages of chemical coagulation followed by settling and/or filtration of the treated water are primarily related to the need for the direct addition of the coagulant to the water, thus leading to increased residual levels of iron or aluminum, which is undesirable.

Nanofiltration is considered as one of the methods that can be used to meet regulations for lowered arsenic concentrations in drinking water [10–12]. Low-pressure operation of the nanofiltration process has advantage on energy efficiency. The efficiency of the system can vary, depending on the membrane module properties and the feed water composition.

Humic acid (HA), which represents the major fraction of dissolved natural organic matter (NOM) in aquatic environments, has been the focus of much research. It is responsible for natural water color and for initiating photochemical transformations of both organic compounds and trace metals [13]. HA is highly negatively charged, in which the oxygen-containing functional groups representing a quarter of the total molecular weight [14]. HA combines with free radicals, including As and other metal groups, fatty acids, phthalate esters, and other unspecified compounds. Arsenic can bind directly to NOM in inner-sphere complexes via organic functional groups such as hydroxyl groups [15], but it was also suggested that metal cations act as bridges between As and OM forming ternary complexes [16]. The objective of this paper is to investigate the effect of organic matter on the arsenic removal efficiency by nanofiltration process.

2. Materials and methods

2.1. Feed solution

In this study, HA, which has been well characterized and widely taken as model foulant, was used as a substitute of dissolved organic matter (DOM). The stock solution was purified following the procedure described by Hong and Elimelech [17] with HA solution adjusted to 10 g/L and stored in a sterilized bottle at 4℃. Arsenic oxide ($As_2O_3 \cdot XH_2O$) and HAs were supplied by Sinopharm Chemical Reagent Co., Ltd. The powdered arsenic was dissolved in Mill-Q water (1 g/L) and diluted prior to use.

2.2. Analytical methods

Arsenic analysis was performed using an (atomic fluorescence spectrometry, Haiguang 230E) with samples acidified by adding hydrochloric acid (trace metal grade). Measurement of the commercial humic content was carried out with a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan). HAs were also measured by the fluorescence method (Cary Eclipse, Varian) where a spectrum of emitted light was recorded in the function of the wave length of the generating light. This three-dimensional figure gives information from the intensity values for qualitative and quantitative determination of organic materials in the solution. Data were analyzed using Matlab (MathWorks Inc., Natick, MA, USA). The arsenic or DOM removal of the membrane was defined as below:

$$R_j(\%) = \left(1 - \frac{C_j}{C_0}\right) \times 100$$

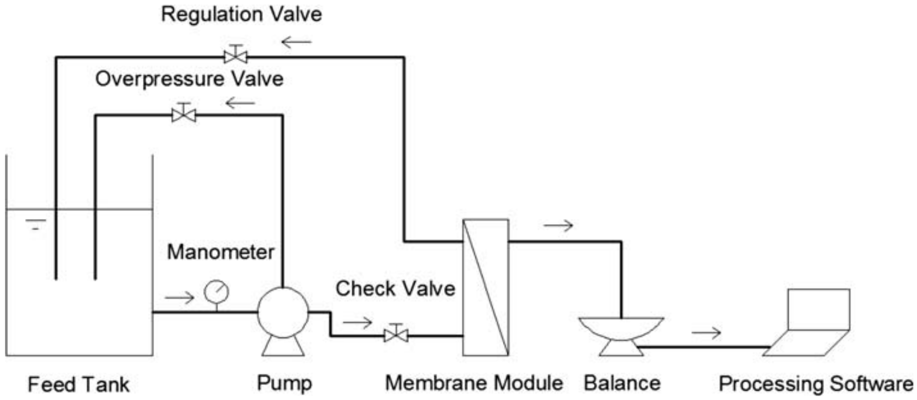


Fig. 1. Schematic experimental unit for nanofiltration.

in which R_j represents the arsenic or DOM removal, while C_j stands for the permeate concentration and C_0 symbolizes the feed concentration.

2.3. Membrane test unit

A laboratory-scale plate-and-frame cross-flow membrane separation test unit was constructed for the nanofiltration (NF) studies, as shown in Fig. 1. The water was synthetic and was pumped to a flat sheet membrane module with an effective membrane area of 60 cm^2 (NF90, DOW). NF90 is a thin film composite polyamide membrane. Table 1 summarizes the typical characteristics of NF90 membrane. The operating pressure and cross-flow velocity were controlled at 500 kPa and 3.5 cm/s by means of by-pass and regulating valves. The initial volume of water in the feed tank was 10 L. The concentration of the feed water was almost unchanged during each experiment due to the low permeate flux of nearly 200 mL/h while the concentrate flux was approximate 19,000 mL/h. In addition, the permeate water that balanced was put back manually to the feed tank at regular intervals. New membranes were used in each experiment to avoid the effect of residual arsenic or humic organic matter on membrane separation and to compare the results obtained under different membrane operating conditions.

Table 1
Characteristics of NF90 membrane used in this study

Surface material	Polyamide
Support material	Polysulfone
Average pore diameter (nm)	0.68 [18]
Molecular weight cut-off (Da)	100 [19]
Contact angle (°)	63.2 [20]
Maximum pressure (MPa)	4.1
Recommended pH range	3–10
Mean roughness (nm)	63.86
Surface zeta potential (mV)	
pH 3	3.7
pH 12	−19.4

3. Results and discussion

3.1. Effect of DOM concentrations on arsenic removal

In this study, synthetic water was used. To investigate the effect of DOM concentration on the arsenic removal in nanofiltration process, the As(V) concentration of raw water was set at 0.05 mg/L by adding arsenic stock solution (1 g/L) in deionized water to be filtered by nanofiltration membrane, while the DOM was spiked with 2, 4, 8 and 10 mg/L, respectively. The contact time was 10 s while the mixing time was 60 s. The arsenic removal efficiency and membrane flux were shown in Figs. 2 and 3, respectively. It was shown in Fig. 2 that the existing of DOM has positive effect on the arsenic removal, when the DOM concentration of feed water was higher (TOC = 10 mg/L), the average removal efficiency of arsenic is higher, comparing to lower feed concentration of 2 mg/L DOM. The obtained results were in agreement with the results in Lin et al. [22], whereby arsenic removal by UF alone is only 10%, while at the presence of humic compounds, the arsenic removal of 22% is obtained. Although the UF membrane does not have a totally identical function mechanism with NF membrane, the role of physical-barrier they played in the separation process could still provide references for rejecting. This may be caused by the presence of DOM as it enhances arsenic removal by two ways: (i) formation of DOM gel layer on membrane surface, which

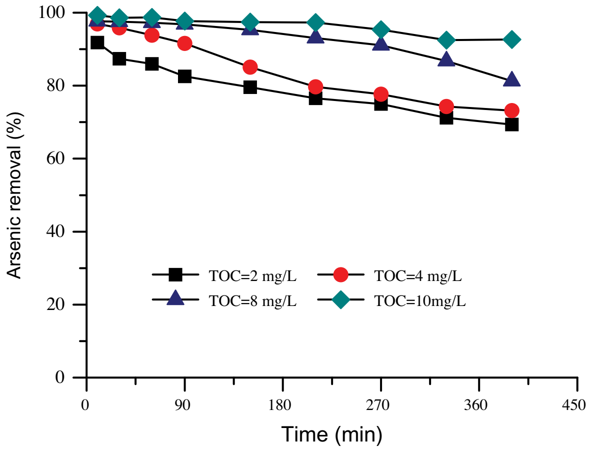


Fig. 2. Effect of DOM concentration on arsenic removal.

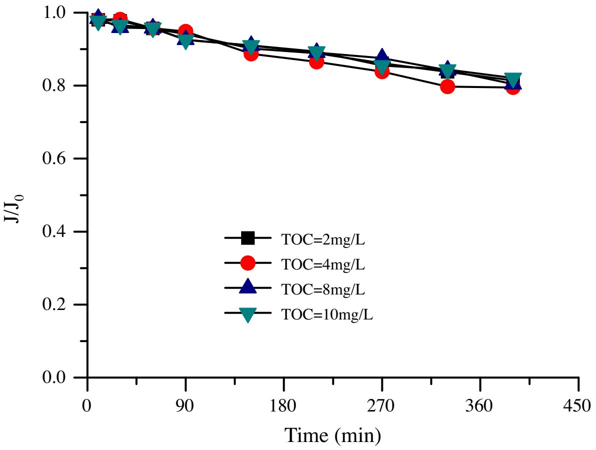


Fig. 3. Effect of DOM on membrane flux.

enhance arsenic separation and (ii) formation of humic/arsenic complexes, which is rejected by membrane. Regarding to the arsenic removal efficiency decreased after 400 min, this behavior may be attributed to concentration polarization effects, which was also found in Prabhu et al. [21] on dye retention using an organic NF membrane with MWCO 400. They explained that the decrease in dye retention after a certain period of study to the build-up of concentration polarization of solute particles over the membrane surface, thus enhancing the solute permeation by convection through the membrane. It is well known that membrane fouling is a major obstacle to the efficient application of membrane technology in applications involving water treatment. Fig. 3 showed the membrane flux decline with different humic matter concentration, in which *J* stands for real-time flux while J_0 represents initial flux of nanofitration. The membrane flux for the separation of the DOM decreased to 80% of the initial flux after 400 min due to the fouling of organic matter on membrane surface. It is interesting to note that the membrane flux decline kept almost the same regardless of the feed concentration of the humic matter, which may be explained that the cross-flow velocity was maintained the same; thus, the morphological and hydraulic properties of the fouling layer formed on the membrane are expected to have little difference.

3.2. Effect of fouling layer on arsenic removal

Francis R. Livens et al. [23] pointed out that organic matter could react with arsenic, producing large particle complexes. In order to study the effect of dissolved NOM on arsenic removal in nanofiltration, three sets of experiments were carried out for comparison: (1) DOM and arsenic were mixed in a container for 30 min, then the mixture was filtered by NF90 membrane; (2) the DOM solution was firstly filtered by NF90 membrane for 180 min, then alternative water that only had arsenic was filtered by the membrane; (3) the DOM solution was firstly filtered by NF90 membrane for 180 min, then alternative water that had DOM and arsenic was filtered by this membrane. In the three sets of experiments, the DOM concentration was kept at TOC = 10 mg/L and the arsenic concentration was kept at 0.05 mg/L. The test results were shown in Fig. 4, which clearly demonstrates that the arsenic removal can reach a higher rate (all over 92%) in test 1 where DOM and arsenic mixed before filtration; while in test 3, at the beginning of arsenic addition, the removal rate of arsenic declined, then after arsenic contacted with DOM for a while (about 200 min), the removal rate of arsenic began to increase.

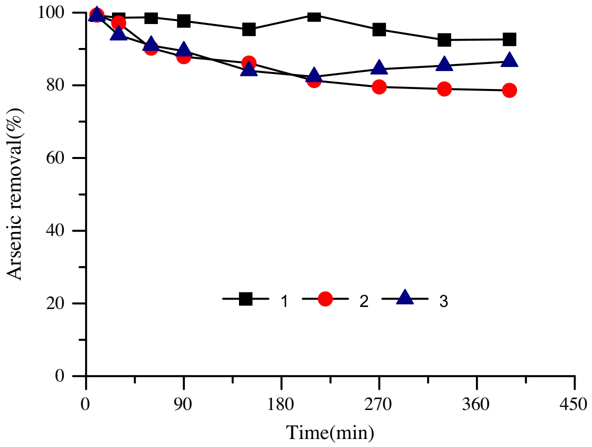


Fig. 4. Comparison of arsenic removal of three experiments.

It is suggested that due to arsenic reacts with DOM and produces large particle complex compound, the arsenic is intercepted and removed by NF membrane. The comparison between test 2 and test 3 indicates that the formation of fouling layer on membrane surface could not improve the removal rate of arsenic, which demonstrates that the effect of DOM on arsenic removal in nanofiltration is mainly based on the associated reaction of arsenic and DOM, and finally the arsenic is removed by interception.

At the normal range of pH, because of the dissociation of carboxyl group (or phenolic aldehyde), the NOM carries negative charges. Generally, the long-chain organic molecular is strongly hydrophobic. This kind of molecular could be accumulated on membrane surface by means of hydrophobic reaction with membrane surface. Large molecular organic matter is accumulated on the surface of NF membrane, at the same time it could shield the negative charges repulsion. That is why the removal rate of arsenic decreases in low DOM concentration (not more than 10 mg/L) as shown in Figs. 2 and 4. In addition, because the negative charges on NF membrane surface are shielded at the low DOM concentration, the repulsion between arsenic and NF membrane decreases, which causes the arsenic removal rate declined at the beginning of test 2 and test 3.

3.3. Removal efficiency of DOM by nanofiltration

In this study, the HA was used as a substitute of dissolved natural organic matter (DOM) in raw water. The removal efficiency of DOM by NF membrane is shown in Figs. 5 and 6. It could be found in Fig. 5 that NF90 membrane could reach a high HA removal rate and that the higher the HA concentration, the higher HA removal obtained. Fig. 6 is the fluorescence spectra of DOM, in which the color scale represents the fluorescence intensity that stands for a relative value rather than the absolute one. Therefore, unit of fluorescence intensity is a.u. (Arbitrary Unit). The emission wavelength was used as the X-axis, while the excitation wavelength was used as the Y-axis. When exited by ultraviolet and visible light, NOM fluoresces and the characteristics and intensity of the fluorescence would vary depending on the fluorophores present [24]. The composition of NOM can be visualized as a pattern of fluorescence peaks, within excitation-emission matrices (EEM). Fluorescence peaks can be attributed to both humic-like fluorescence and protein-like fluorescence, which defined as peaks C located in the region of 300–360 nm excitation and 400–480 nm emission wavelength, and peaks T located in the region around 280 nm excitation and 350 nm emission [25], respectively. The feed was HA

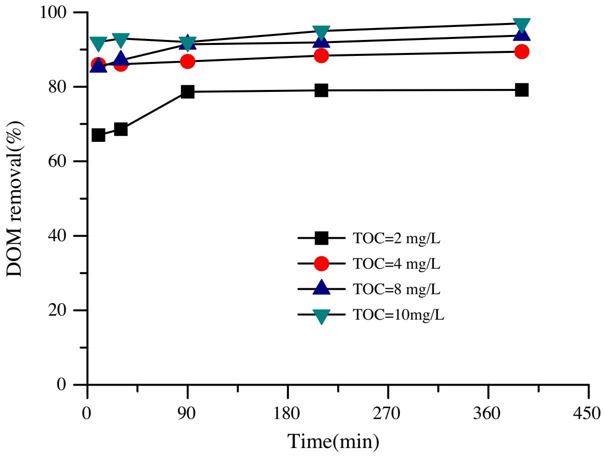
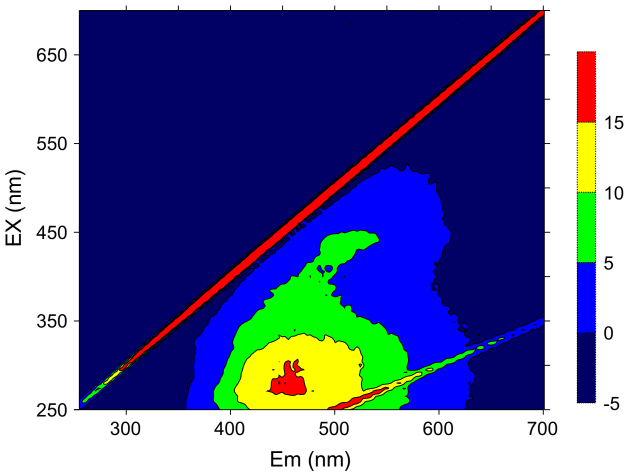
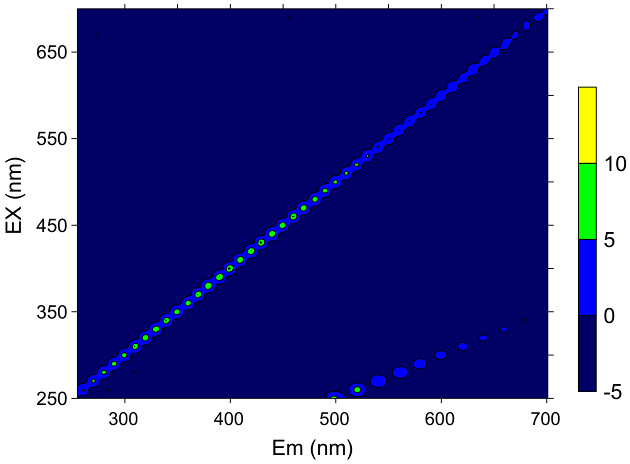


Fig. 5. DOM removal by nanofiltration membrane.



(a) Feed water



(b) Permeated water

Fig. 6. Fluorescence spectra of DOM.

in this filtration test. And discussion will focus on peaks C as shown in Fig. 4 that peaks C dominated over all the other areas of the EEM, which indicated that the DOM used in the test is mainly HA analogues (Ex is about 350∼440 nm and Em is about 430∼510 nm) and fulvic acid analogous (Ex is about 240∼270 nm and Em is about 370∼440 nm). When NF90 membrane is used in the treatment of DOM in raw water in which TOC = 10 mg/L, DOM could almost be removed completely.

4. Conclusions

Membrane processes have been known to successfully remove the target contaminants in the clean-up methods for drinking water of the available and applicable technologies. This study focused on the effect of DOM on arsenic removal by nanofiltration. It was found that the existence of DOM increased the arsenic removal efficiency due to the formation of humic/arsenic complexes. Furthermore, when the DOM concentration of feed water was higher (TOC = 10 mg/L), the removal efficiency of arsenic was almost 100%, which was higher comparing to 80% at lower feed concentration of 2 mg/L DOM. In addition, it was also found that the higher HA concentration, the higher HA removal obtained with the same arsenic concentration. The membrane flux for the separation of the varied concentration of DOM decreased to 80% of the initial flux after 400 min with the same cross-flow velocity.

Acknowledgments

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