Removal of arsenic and humic substances (HSs) by electro-ultrafiltration (EUF)

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Abstract

A laboratory scale electro-ultrafiltration (EUF) system was developed and used to explore the removal of arsenic and humic substances (HSs) from water. As a negatively charged species, arsenate(V) was readily removed after applying voltage to the EUF cell. Arsenite(III) was removed via EUF after the pH of the water had been adjusted. Meanwhile, the rejection of HSs increased due to the presence of an electric field. This study also showed that the removal of arsenite(III) from water relies primarily on electrostatic and non-electrostatic mechanisms. In the presence of HSs, arsenate(V) complexed with the HSs and was then able to be removed by EUF. This study demonstrates that EUF is a highly promising means of removing arsenic from water.
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1. Introduction

Arsenic-contaminated groundwater has caused serious health problems in numerous countries, such as Bangladesh, India, and Taiwan [1,2]. Drinking water that contains arsenic is both chronically carcinogenic and toxic to humans. Recent studies suggest that the current maximum contaminant level (MCL) of 50 µg/L needs to be revised in order to minimize the risk of cancer [3]. Thus, the U.S. Environmental Protection Agency has recently announced that the amount of arsenic allowed to be present in drinking water will be reduced from 50 to 10 µg/L as of January 23, 2006 [4]. In Taiwan, a new limit of 10 µg/L was also introduced in 2003 [5]. Therefore, it is essential to develop technologies that can effectively remove arsenic from water.

The task of removing arsenic from water has received extensive attention. Major approaches include coagulation [6], adsorption [7–10], electrochemical methods [11,12], and membrane separation [13–19]. Of these processes, membrane technology, due to the stringent environmental regulations that must be considered, shows the greatest potential for application in the treatment of drinking water [20,21]. It is generally easier to remove arsenate(V) with the use of membranes than it is to remove arsenite(III), due to the differing charge characteristics of these two species [13,14,16–18]. Brandhuber and Amy [14] have reported that As(V) can be removed from spiked groundwater with an 8 kDa ultrafiltration (UF) membrane. Interestingly, Donnan exclusion also plays a crucial role during UF of water-containing As(V). In other words, when using membranes to remove arsenic from water, the differing charge characteristics of As(V) and As(III) is an important factor to be taken into consideration.

At neutral pH, the predominant As(V) is negatively charged, whereas that of As(III) is neutral. This explains why even the most promising membrane process – reverse osmosis (RO) – is considerably less efficient at removing As(III) from water than it is at removing As(V) [13,16]. Nevertheless, there are still two strategies that can be used to tackle this problem—elevating the pH of water-containing As(III) or oxidizing As(III) to As(V) [16,20,22].

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Ubiquitous in groundwater and surface water, humic substances (HSs) are the precursors of carcinogenic disinfection by-products (DBPs) during chlorination of finished water. The production of DBPs, such as trihalomethanes (THMs) and halo acetic acids (HAAs), is a public health concern. The membrane process has shown the potential to control the amount of HSs in drinking water [21].

Both arsenic and HSs are negatively charged at neutral pH and it is important to note that HSs cannot be removed from water by electrochemical methods. Therefore, there is an interest in improving the performance of UF through the application of an electrical force, in order to attract these charged species. Applying an electric field through the membrane during membrane filtration is known as 'electrofiltration' [23]. In this process, the imposed electric field is parallel to the pressure gradient applied to the membrane. Although it has been reported that the removal of HSs was more successful after voltages were applied through UF [24], it is still not known whether it is possible to remove arsenic and HSs simultaneously by electro-ultrafiltration (EUF).

In this study, a laboratory-sized EUF unit was employed to remove arsenic and HSs from water. Total arsenic concentration and dissolved organic matter (DOC) were used as water quality indicators. In addition to evaluating the performance of EUF during treatment of water-containing arsenic and HSs, this study focused on understanding the removal mechanisms more thoroughly.

2. Materials and methods

2.1. Feed solution

Sodium arsenite (NaAsO$_2$) and arsenate oxide (As$_2$O$_5 \cdot X$H$_2$O) (supplied by Sigma–Aldrich) were used in preparing As(III) and As(V) solutions. These two arsenic oxidation states are common in natural water. The powdered arsenic was dissolved in Mill-Q water and diluted to 20–40 µg/L prior to use.

The HSs solution was prepared by dissolving powdered humic acid (Aldrich), which was then filtered through a 0.45 µm filter, in order to represent dissolved organic matters in water. The concentration of dissolved organic carbon in the feed water was approximately 4 mg/L. For most of the experiments, the pH was not adjusted (~6). Sodium hydroxide was only used to adjust the pH of the solution in particular circumstances.

2.2. Membranes and module

Osmonic 100 kDa UF membranes were used in this study. These membranes are made of polyacrylonitrile (PAN) and are hydrophilic on the surface. Table 1 lists the typical characteristics of these membranes. A new membrane was used for each experiment. Fig. 1 shows the schematic drawing of the EUF module. The filtration module comprises of plastic

Table 1
Characteristics of UF membrane[a]

Characteristics	Value
Size (kDa)	100
Contact angle	4°
Operating pH range	2–10
Typical operating pressure (kPa)	98–400
Maximum temperature (°C)	50
Filtration area (m^2)	14.7
Material	Polyacrylonitrile (PAN)

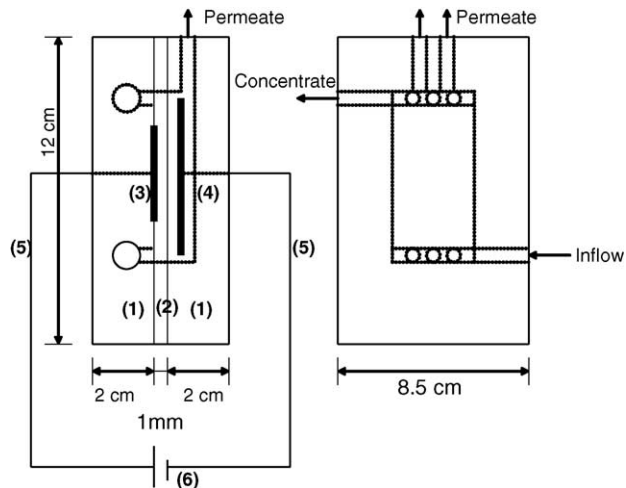[a] Data were obtained from catalog of the manufacturer.

Fig. 1. Electro-ultrafiltration (EUF) module. (1) Plastic plate, (2) silicon lining, (3) anode: (+), (4) cathode: (−), (5) wire, and (6) power supply.

plates, silicon lining, and electrodes, and the module measures 8.5 cm in length, 2.3 cm in width, and 12 cm in height. The silicon lining between the plates creates a filtration channel 1 mm wide. Since the HSs are negatively charged, the anode (positively charged) is placed on the feed side (concentrate side) to attract the pollutants. The anode is platinum and the cathode is titanium. The distance between the electrodes is about 4 mm.

2.3. Filtration experiment

Fig. 2 demonstrates the operational mode of the experiments. Five litres of arsenic solutions, with and without HSs, were prepared as the feed water for each experiment. A power
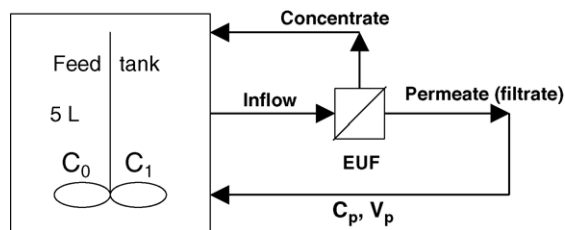

Fig. 2. Operational mode of a laboratory scale EUF system. C_0: initial concentration, C_1: concentration after experiment, C_p: concentration in permeate stream, and V_p: amount of permeate passing cathode.

supply (Chroma, Model 6210K-600) was utilized to provide electrical voltage through the membrane. Before each experiment, the membrane was soaked for 1 h in, and then flushed for 1 h with, deionized water, in order to remove any impurities and preservatives. A peristaltic pump conveyed solutions into the EUF cell with an averaged crossflow velocity of 0.1 m/s. Pressure was kept at 98 kPa with a back regulator. The amount of permeate passing through the membrane was determined with an electric balance (Satorius). Data were then transferred to a personal computer via RS232. Both concentrate and permeate streams were recycled back into the tank and samples were taken before and after each experiment for the analysis of total arsenic and organic concentrations.

2.4. Chemical analysis

DOC was analyzed with an OI Analytical 1010 and measurement of pH was carried out with a Consort C831 pH meter. Conductivity was measured with a Suntex SC-120 conductivity meter.

Total arsenic concentration was analyzed with a Perkin-Elmer Analyst 800. The experiment procedures followed standard methods [25]. As(V) was reduced to As(III) by adding concentrated trace metal HCl and KI (20%, w/v). After 1 h of reaction time, arsine gas was generated by continuous addition of $NaBH_4$. Absorbance of arsine at 193.7 nm was recorded as peak high.

3. Results and discussion

3.1. As(III) and As(V) removal efficiency

The rejection of arsenic (R_f), with and without HSs, was calculated using Eq. (1).

$$R_f = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \tag{1}$$

In this equation, C_p is the arsenic concentration in the permeate and C_0 is the initial arsenic concentration. The total arsenic measurement follows the method described in Section 2.4.

The results of the experiment proved that applying voltages through the membrane enhanced the removal of As(V) (Fig. 3a). Arsenic rejection increased from 30% to more than 90% after applying voltages. At neutral pH, As(V) exists in water as the negative ion $HAsO_4^-$. The surface charge of the PAN membrane is also negative at neutral pH. Thus, it was possible to repel the negatively charged As(V) ions by Donnan exclusion. However, since the pores on the membrane are much larger than the As(V) ions, Donnan exclusion was not as pronounced as that in nanofiltration, in which more than 90% of As(V) was removed [13]. During traditional UF, the differing As(V) rejection rates in water with and without HSs may be due to the formation of an As–HSs complex, which is retained easier than As(V) alone. The improvements in As(V)
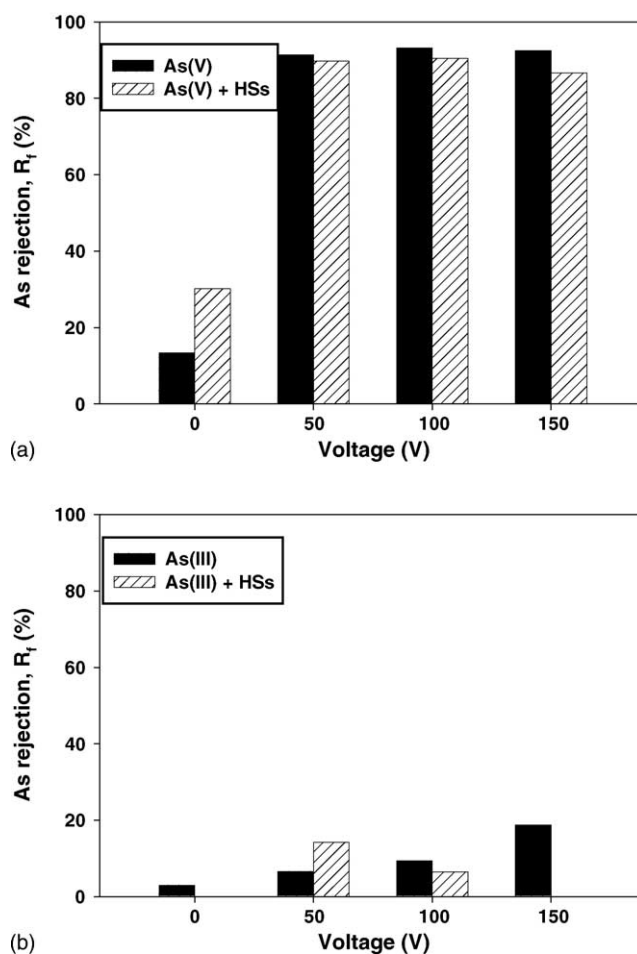

Fig. 3. Removal of synthetic (a) As(V) and (b) As(III) from water by EUF at different voltages (pH ∼ 6).

removal efficiency after voltages had been applied may result from the external electrical field which may have kept As(V) in the concentrate side, or led to a reduction reaction occurring at the cathode.

In contrast, As(III) rejection was quite low, even with the addition of electrical voltages (Fig. 3b). Applying an electrical charge through a membrane did not increase the As(III) removal efficiency either in the presence or absence of HSs as, since As(III) is nonionic at a neutral pH, it was not influenced by the electrical field. On the other hand, it was easier to remove As(V) due to its negativity. Electrochemical reduction studies on arsenic reduction have showed that it is easier to reduce As(III) than As(V) [12,26]. Thus, it was not anticipated that electrochemical reduction would play an important role in the EUF of arsenic, due to its low conductivity (∼7 μS/cm), low current (∼4 mA) and various cathode materials.

Nonetheless, there are two methods of increasing the removal of As(III) that look promising [16,20,22]. The first involves the oxidation of As(III) to As(V), whilst the second method raises the pH of water, causing protons to dissociate, and thus leaving As(III) negatively charged. Since it is pos-
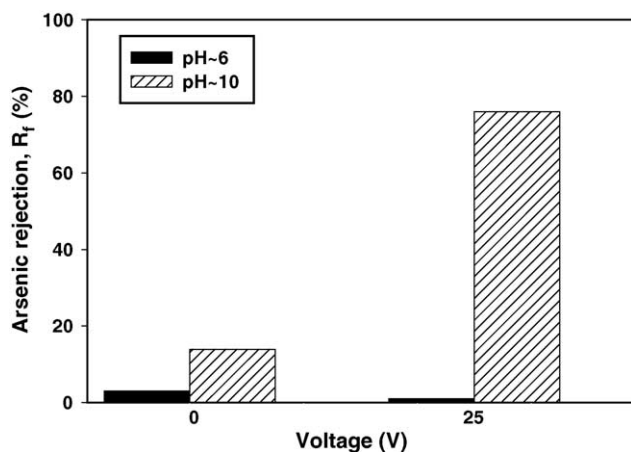
Fig. 4. Removal of As(III) by EUF via pH adjustment (pH ∼ 10).

sible to remove As(V) with EUF as previously indicated, the second option of increasing pH value was explored.

Fig. 4 shows the removal of As(III), with and without electrical voltage, and before and after pH adjustment. It is obvious that, without pH adjustment or electrical voltage, the UF membrane would only be able to remove a minimal amount of As(III). However, after adjusting the pH of the water to ∼10 and applying a 25 V charge through the membrane, As(III) removal efficiency increased from 14 to 76%. After pH adjustment, the solution conductivity increased, thus signifying a decrease of resistance. It should be noted that, at high solution conductivity, the current increased dramatically as voltage was increased. Therefore, in order to reduce the joule heating and the hydrolysis rate of the water, voltage was only raised to 25 V. The removal mechanisms for As(III) after pH adjustment might be similar to that for As(V), with the exception of the oxidation of As(III) at the anode. Oxidization of As(III) to As(V) could facilitate the removal of As(III) by EUF. The increment of arsenic rejection after pH adjustment in traditional UF has also been reported in various studies [14,16–18].

3.2. Removal mechanism

The increased arsenic removal efficiency that occurred after applying voltages could be a result of external field separation (electrophoresis), cathodic reduction and/or adsorption on membrane pores. Since both the concentration and permeate were recycled back to the feed tank (Fig. 2), the total arsenic concentration before and after the experiment would only be the same as that at the beginning of the experiment if the electrical separation had occurred. Table 2 summarizes the changes in the total arsenic concentrations before and after the experiments under three test conditions, i.e., As(III) at pH ∼ 10, As(V) at pH ∼ 6, and As(V) with HSs at pH ∼ 6. The overall arsenic removal efficiency ranges from 71 to 100%. Surprisingly, as is shown in column 3 of Table 2, the concentration of both As(III) and As(V) was less at the end of the experiment than at the start. A simple calculation,

Eq. (2), was used in order to account for this loss of arsenic.

$$C_1 \times V_0 = C_0 \times (V_0 - V_p) + C_{ave} \times V_p \qquad (2)$$

In Eq. (2), the water after the experiments is treated as consisting of two separate volumes. First, there is the volume of water $(V_0 - V_p)$ containing the original arsenic concentration (C_0). And second, there is the volume of water passing through the cathodic chamber (V_p), which has an averaged arsenic concentration (C_{ave}). The volume of permeate passing through the cathode (V_p) can be obtained by integrating a flux curve with time.

Notably, C_{ave} could be regarded as the part of the arsenic compound that can be recovered with EUF. If C_{ave} were equal to C_0, i.e., if C_1 were equal to C_0, then EUF would not lose arsenic ions and thus physical separation would occur. Conversely, if C_{ave} were markedly different from C_0, then EUF would lose arsenic ions as a result of either adsorption or deposition on the cathode. Therefore, the difference between C_0 and C_{ave} was adopted as the amount of arsenic lost due to non-electrostatic interaction, whereas the difference between C_{ave} and C_p came from electrostatic interaction. It should be noted that, if arsenic is removed either by electrostatic or non-electrostatic reactions, C_p will always be lower than C_{ave}. Moreover, the unknown C_{ave} can be obtained by using Eq. (2).

For condition (I), as displayed in Table 2, the initial As(III) concentration of 40.2 μg/L (C_0) reduced to a final value of 11.5 μg/L (C_p). The averaged arsenic concentration of permeate (C_{ave}) of 25.3 μg/L can be computed from Eq. (2). The experiment data in Table 2 also indicate that both external electrical separation and cathodic reduction could be the key mechanisms during EUF of As(III) water under high pH. Different mechanisms must be used for the removal of As(V), depending on whether HSs are present or not. For test condition (II), the averaged arsenic concentration (C_{ave}) of 3.7 μg/L was slightly greater than the arsenic concentration in permeate (C_p) (2.4 μg/L) at the end of experiment. A possible reason for this might be that As(V) was reduced and deposited on the cathode during the experiment. Another explanation might be that As(V) was adsorbed on the membrane, thus resulting in the loss of As(V) after the experiment. In contrast, there was little arsenic loss in condition (III), with a C_0 of 19.5 μg/L and a C_{ave} of 18 μg/L, as shown in Table 2. The C_{ave} was higher in condition (III) than in condition (II) because in condition (II) As(V) complexed with HSs, thus eliminating the potential of an As(V) reduction reaction in the cathode.

Fig. 5 summarizes the results of the laboratory work. For condition (I), both electrostatic and non-electrostatic removals were important. For condition (II), non-electrostatic removal, such as arsenic reduction at the cathode and adsorption on the membrane, dominated the reaction. On the other hand, electrostatic removal, i.e., electrophoresis, was the major removal mechanism in condition (III). The results of this study demonstrated that non-electrostatic separation

Table 2
Experimental data and calculation of averaged As concentration (C_{ave}) passing through membrane

Test condition[*]	Initial As concentration (µg/L) C_0	As concentration after filtration (µg/L) C_1	Volume of water in feed tank (mL) V_0	Amount of permeate passing cathode (mL) V_p	As concentration in permeate at end of experiments (µg/L) C_p	As removal efficiency R_f (%)	Averaged As concentration in permeate (µg/L) C_{ave}[**]
(I)	40.2	37.2	4950	991	11.5	71	25.3
(II)	24.8	20.5	4950	1004	2.4	90	3.7
(III)	19.5	19.2	4950	1096	N.D.	100	18.0

[*] (I) As(III) with an initial pH $\sim$ 10 at 25 V; (II) As(V) with an initial pH $\sim$ 6 at 150 V; (III) As(V) + HSs with an initial pH $\sim$ 6 at 150 V.

[**] C_{ave} was obtained from Eq. (2).

for As(V) might be more significant than that for As(III). In the past, it has generally been considered that electrochemical reduction of As(III) has been more active than that of As(V) [12]. The major differences between this study and previous studies lie in the use of different cathode materials and ionic strength of the solution. Notably, cathode material influences the deposition rate of arsenic [26].

3.3. Flux and HSs removal efficiency

Fig. 6a shows the final flux versus voltages plot. The incremental flux during EUF is similar to that in results obtained from studies on the electrofiltration of proteins, bacteria, and colloids [24,27–29]. The incremental flux during EUF was attributed to electrophoresis, which carried foulants away from the membrane, and to electroosmosis phenomenon—the complement of electrophoresis [30]. Flux declination was not significant during the traditional UF ex-

periment. Electrophoresis, which refers to the motion of particles influenced by an electrical field, could not thoroughly explain the flux incremental. Therefore, it was anticipated that electroosmosis, in combination with electrophoresis, resulted in an incremental flux.

The HSs removal efficiency increased after applying electricity through the membrane (Fig. 6b). The enhanced removal rate occurred due to the fact that the applied external electrical field counterbalanced the convective movement of negatively charged HSs toward the membrane [23]. More than 98% of HSs removal from water was
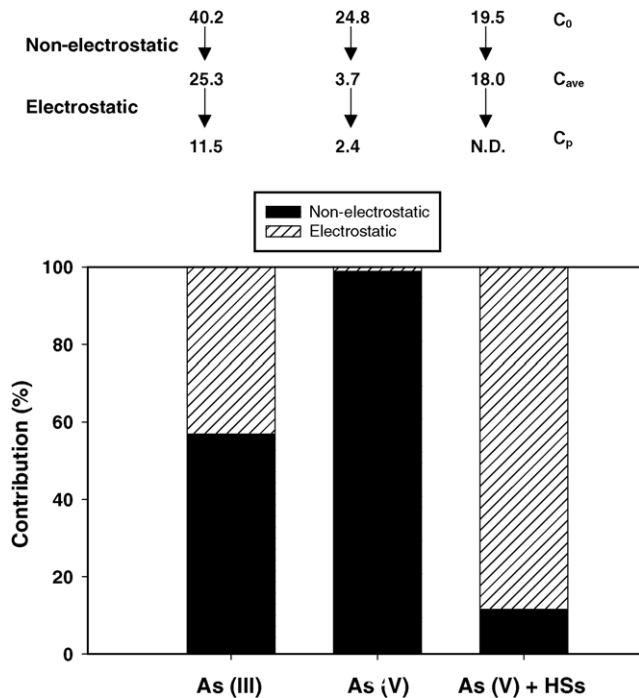

Fig. 5. Preliminary removal mechanisms. (I) As(III) with initial pH of $\sim$10, at 25 V and 71% total As removal after experiment. (II) As(V) with initial pH of $\sim$6, at 150 V and 90% total As removal after experiment. (III) As(V) + HSs with initial pH of $\sim$6, at 150 V and 100% total As removal after experiment.
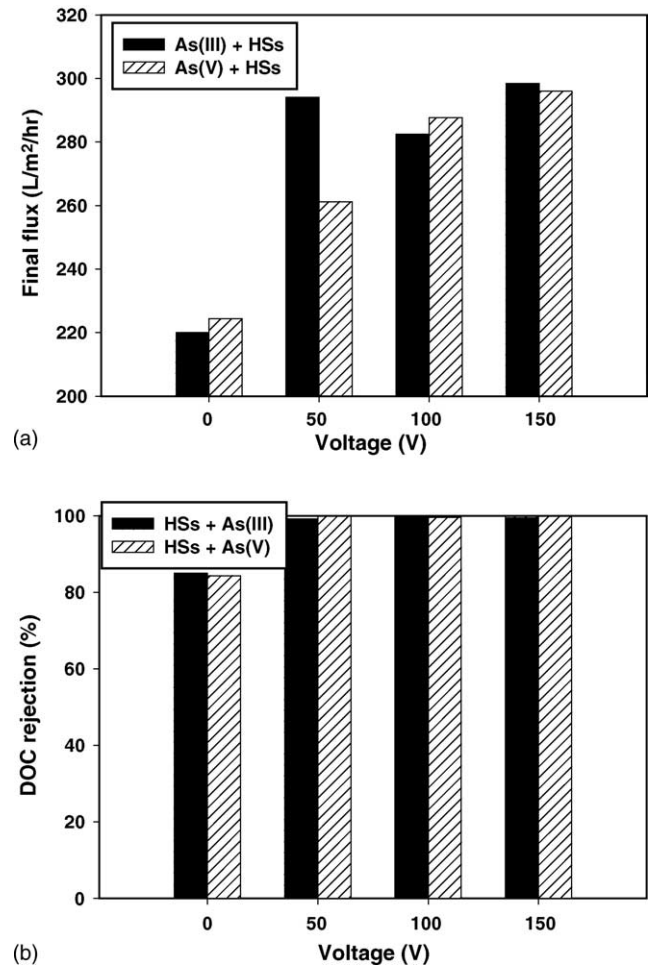

Fig. 6. Flux and DOC results: (a) final permeate flux and (b) water quality analysis of synthetic water at different voltage.

achieved by applying 25 V, which corresponds to an electrical field of 41 V/cm ($I = 0.004$ A, area $= 14.7$ cm^2, conductivity $= 6.7 \times 10^{-6}$ S/cm). A theoretical field strength ($E_{critical}$) that could retain all charged particles was calculated at 24 V/cm by using Eq. (3), where J (cm/s) is the filtration flux and u_p (cm^2/(V s)) is the electophoretic mobility of charged species.

$$E_{critical} = \frac{J}{u_p} \tag{3}$$

The averaged filtration flux in this study was approximately 7.2×10^{-3} cm/s. HSs have an electrophoretic mobility of 3.0×10^{-4} cm^2/(V s) [24]. When the applied electrical field approaches the theoretical $E_{critical}$ value of 24 V/cm, the removal of HSs from water can be expected. Other studies have also reported similar improvements when the solute size was smaller than the pores on the membrane [24,28].

4. Conclusion

Based on the authors' knowledge, this study is the first in which EUF was used to treat water-containing arsenic. The traditional 100 kDa UF membrane is unable to remove As(III) or As(V) from water, regardless of whether HSs are present or not. After applying electricity to UF, As(V) rejection increased dramatically. The removal mechanisms adopted for As(V) were electrophoretic force and electrochemical reduction, depending on whether As(V) had complexed with HSs. Additionally, the removal of As(III) with EUF was achieved via pH adjustment. In short, both non-electrostatic and electrostatic separation of arsenic are important steps during EUF treatment of water-containing arsenic. The results of these experiments showed that there is significant potential in applying EUF to treat water, which contains arsenic and HSs.

Acknowledgement

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