



# Electrochemical removal of hexavalent chromium using electrically conducting carbon nanotube/polymer composite ultrafiltration membranes



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## ABSTRACT

Hexavalent chromium (Cr(VI)) contamination in drinking water resources remains a challenge in many parts of the United States, as well as in regions affected by industrial pollution. In this study, we demonstrated how electrically conducting carbon nanotube (CNT) – polyvinyl alcohol (PVA) composite ultrafiltration (UF) membranes can be used to remove Cr(VI) from water through a combined process of electrostatic repulsion, electrochemical reduction, and precipitation. The impact of different operational (flux, contact time, applied electrical potential) and environmental (pH and salinity) conditions on Cr(VI) removal were evaluated. Due to the native electrical potential of the CNT/PVA UF membrane material, approximately 45% removal of 1 ppm Cr(VI) solution was detected under neutral pH conditions in deionized water. Increased Cr(VI) removal was observed with increasing membrane surface charge density, which was accomplished through the application of an external potential (3 V, 5 V and 7 V, membrane as cathode) to the electrically conductive membrane surface. The solution ionic strength showed a significant impact on Cr(VI) removal. By increasing the ionic strength without applying external potential on the membrane, the electrostatic repulsive force between the charged membrane surface and the  $\text{CrO}_4^{2-}$  ion was eliminated, and Cr(VI) removal dropped to zero. The highest removal (95%) was achieved when 7 V was applied to the membrane/counter electrode with a 6  $\mu\text{m}$ -thick membrane. Here, Cr(VI) was electrochemically reduced to Cr(III) on the membrane surface, followed by Cr(III) precipitation as chromium hydroxide  $\text{Cr}(\text{OH})_3(\text{s})$ , which occurred by Cr(III) reacting with hydroxide ions generated via water splitting on the CNT network. Precipitated  $\text{Cr}(\text{OH})_3$  was then removed by the UF membrane. In addition, CNT-PVA UF membranes were used to treat tap water spiked with Cr(VI); under these conditions, 99% Cr(VI) removal was observed when 7 V were applied to the membrane/counter electrode. Furthermore, we demonstrate that other trace inorganic contaminants, such as uranium, were effectively removed as well.

## 1. Introduction

Chromium is a common element that is both naturally ubiquitous and widely used in a variety of industrial applications, such as electroplating, textile processing, oil refining, corrosion protection, and pigment manufacturing [1]. A combination of poor wastewater management practices and natural geological formations have led to its wide occurrence in many communities' drinking water resources [2–6]. In the environment, chromium is generally found in one of two stable redox states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) [7,8]. Cr(VI) is highly soluble and mobile at neutral pH, and Cr(III) is considered a trace element needed in the human diet [7].

The redox state and speciation of chromium depends on water chemistry, including the pH, and chromium concentration [9]. Due to the high toxicity of Cr(VI), the US EPA set the maximum concentration level (MCL) for total chromium in drinking water at 100 ppb [10]. The state of California set the MCL for Cr(VI) (the toxic form,) at 10 ppb [11]; the US EPA does not currently have a specific MCL for Cr(VI). However, a recent study reported that the safe drinking water concentration of Cr(VI) may be as low as 0.02 ppb, which means that approximately 75% of American households may be exposed to harmful Cr(VI) concentrations in their water [11–13].

Several technologies have been developed to remove Cr(VI) from water. Conventional Cr(VI) treatment technologies include physical

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adsorption [14,15], ion exchange [16–18], nanofiltration (NF) and reverse osmosis (RO) [19–21], chemical reduction followed by precipitation [22], photo-catalytic reduction [23,24], bio-mitigation [22] and electrochemical reduction [22,25,26]. The most commonly used technology in industry to treat Cr(VI) is chemical reduction (e.g. using ferrous iron) followed by precipitation [4,22]. Unfortunately, this process produces large volumes of waste sludge that requires expensive disposal [27,28]. Ion exchange, NF, and RO have shown great potential to efficiently remove different heavy metals [20,29], but they all result in the production of toxic brine and are expensive to operate [30]. Ultrafiltration (UF) membranes are widely used in water treatment processes due to their low pressure demands and wide range of chemical stability [31]. Several studies have demonstrated the use of UF membrane for Cr(VI) removal, however, Cr(VI) removal for typical polysulfone (10 kDa) UF membranes is very limited, with the maximum rejection of 20% [32–34]. Typical approaches attempted to increase Cr(VI) rejection by UF membranes include reducing the UF membrane's pore size [32] and increasing the membrane surface charge [33,34]. To the best of our knowledge, very few UF membrane has been demonstrated to efficiently and reliably reduce Cr(VI) concentrations to acceptable limits.

Electrochemical reduction is a process that relies on the transfer of electrons from a charged cathode to the Cr(VI) species, which reduces the Cr(VI) to Cr(III) and can lead to the formation of a solid precipitate [35]. Cr(VI) speciation at environmentally-relevant concentrations is pH dependent, with  $\text{HCrO}_4^-$  being the dominant species at  $\text{pH} < 6.45$ , and  $\text{CrO}_4^{2-}$  the dominant species at  $\text{pH} > 6.45$  [9]. This process has been considered an environmentally “clean” technology for Cr(VI) treatment [36], because the precipitate it produces is pure  $\text{Cr}(\text{OH})_{3(s)}$  [27]. Electrochemical reduction processes are highly dependent on the pH, electrolyte species, electrode material, and mass transfer rates [4,25,27,37]. Typical electrodes used for the electrochemical reduction of Cr(VI) are made of metals [38] or carbon [32,39,40]. As carbon electrodes are cheap and can be fabricated into structures with high surface-area-to-volume ratios, many groups have adopted their use. However, electrochemical treatment of Cr(VI) is typically conducted in a mass-transport limited batch process that requires long contact times, making the process difficult to scale up [26]. To reduce these mass transfer limitations, flow-through electrochemical processes (also known as electrochemical filtration), where the contaminated water is forced through a porous electrode, have been demonstrated for a wide range of electrochemical redox processes [41,42].

Electrically conducting carbon nanotube (CNT)/polymer composite and other conductive membranes have been demonstrated to be effective at multiple membrane separation processes, including UF, NF, and RO [43–51]. In these membranes, the CNT provides the electrical conductivity, while a crosslinking polymer (e.g. polyaniline (PANI) or polyvinyl alcohol (PVA)) is used to control the pore-size between the CNT strands [41]. These membranes have been demonstrated to be capable of supporting electrochemical reactions, such as water splitting, oxygen reduction, and chloride oxidation [41,47,48,52,53]. In this work, we used CNT/PVA composite UF membranes to electrochemically and reductively remove Cr(VI) from contaminated water, with removal efficiencies exceeding 95%. We demonstrate that the removal mechanism is highly dependent on solution conductivity, with higher solution conductivity leading to electrochemical reduction and precipitation of Cr(III) on the membrane surface, while very low conductivity leads to electrostatic repulsion being responsible for Cr(VI) rejection from the permeate. In addition, we evaluated the impact of electrical potential and membrane residence time on Cr(VI) removal and transformation, and characterized the precipitates that form on the membrane surface in response to the potential application. Finally, we evaluated the membrane performance while treating tap water spiked with Cr(VI). Under these realistic conditions, less than 20 ppb chromium was able to be detected in the UF permeate, and we determined that the membrane

was capable of removing other hazardous metal anions, such as uranium.

## 2. Materials and methods

### 2.1. Chemical and materials

PS-35 polysulfone UF membranes were purchased from Nanostone (Nanostone Inc., Oceanside, CA). Multi-walled carboxylic group functionalized CNTs were purchased from CheapTubes (Cheaptubes Inc., Brattleboro, VT), with the reported parameters: outer diameter of 13–18 nm, length of 3–30  $\mu\text{m}$ , and functional group content  $\geq 7.0$  w/w %. Analytic grade dodecylbenzenesulfonic acid (DDBS), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) glutaraldehyde, hydrochloric acid and 150 kDa PVA were purchased from Fisher Scientific (Pittsburg, PA), and used as received. Deionized water ( $18 \text{ m}\Omega \text{ cm}^{-1}$ ) was obtained from a Millipore Milli-Q system. Grade 2 titanium sheet (1/8" thick) was used as a counter electrode (McMaster, Santa Fe Springs, CA).

### 2.2. PVA-CNT membrane fabrication

The PVA-CNT membrane fabrication method has been previously developed by Dudchenko et al. [43]. In short, 0.01 wt% CNT powder and 0.1 wt% DDBS in DI water were well-suspended using a horn sonicator. 1 wt% of 150 kDa PVA was dissolved in DI water. 1:3 ratio of PVA:CNT solution was pressure deposited onto a PS-35 UF membrane support and cross-linked in glutaraldehyde and hydrochloric acid solution for 1 h at 90 °C, then dried at same temperature for 5 min and stored at room temperature.

### 2.3. Membrane characterization

The Membrane's surface morphology and cross-section were imaged by scanning electron microscopy (SEM, FEI XL 30 SEM-FEG, Hillsboro, RO). New membrane samples were sputter-coated with a Pt/Pb target for 40 s (Sputter coater 108 Auto, Cressington, UK) and examined at 10 keV using SEM. For cross-sectional images, membranes were frozen in liquid nitrogen and fractured, then affixed onto SEM stubs with copper tape. Post-experiment membrane samples were gently washed with DI water, dried at room temperature and examined using SEM without any additional coating and by energy dispersive X-ray spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) provided information on elemental composition and oxidation state of all the compounds. A Kratos AXIS ULTRA<sup>DL</sup> XPS system equipped with an Al K $\alpha$  monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer was used to acquire the data. The conditions for Cr analysis were 0.1 eV step, 200 ms of dwell time and 20 eV of pass energy. Vacuum pressure was kept below  $3 \times 10^{-9}$  Torr during the acquisition. Zeta potentials of suspended surfactant-free CNTs were measured in both pH and ionic strength controlled solutions using a ZetaPals instrument (Brookhaven Instruments Corp., Holtsville, NY).

### 2.4. Synthetic Cr(VI) solution

1 g/L Cr(VI) stock solutions were prepared by dissolving 5.65 g potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) in DI water without pH adjustment. The experimental solutions were diluted to 1 ppm from the stock solution using DI water, except in tap water experiments, which used City of Riverside tap water for dilution.  $\text{Na}_2\text{SO}_4$  salt was used to adjust the ionic strength (background electrolyte) of the Cr(VI) because of its relative electrochemical stability [54].

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