



## Ultrafiltration membranes modified by PSS deposition and plasma treatment for Cr(VI) removal



Ivette G. Sandoval-Olvera<sup>a</sup>, Pilar González-Muñoz<sup>a</sup>, Laura Palacio<sup>b</sup>, Antonio Hernández<sup>b</sup>, Mario Ávila-Rodríguez<sup>a</sup>, Pedro Prádanos<sup>b,\*</sup>

<sup>a</sup> Departamento de Química, Universidad de Guanajuato, Cerro de la Venada s/n, 36040 Guanajuato Gto., Mexico

<sup>b</sup> Grupo de Superficies y Materiales Porosos, Dpto. Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

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### ABSTRACT

Ultrafiltration, UF, membranes positively-charged on a substrate of polyvinylidene fluoride, PVDF, have been modified by the deposition of a layer of poly(styrenesulfonate), PSS, which is negatively charged. These membranes have been treated by radiofrequency plasma at different powers and with different gases (argon, air and carbon dioxide). The membrane treated at 10.2 W with argon gave the best chromate retentions with good stability in water, alkaline and acid media.

Surface zeta potential measurements confirmed a positive surface charge on the PVDF-substrate membranes, whereas those modified with PSS and argon-plasma treatment had a negative charge in the pH range 3–10. FTIR-ATR showed a true grafting of PSS on PVDF for the medium-power argon-treated membrane. SEM pictures of transversal sections confirmed continuity between the PVDF substrate, modified by the manufacturer, and the PSS layer. The chromium found on the modified membranes confirmed an electrostatically-determined retention. Pore-size distribution, as obtained by image analysis of SEM pictures of the surface, gave a slight reduction of pores but still within the ultrafiltration range in accordance with a non-size exclusion mechanism for retention.

The modifications studied led to UF membranes provided with enough negative charges to boost retention of anionic species quite similar to those of nanofiltration membranes but with much lower applied pressures.

### 1. Introduction

The increase in industrial and technological activity has brought with it high levels of water contamination. This water contamination has become one of the main global health problems, causing various infections and mortality in all living organisms.

One water contaminant that has attracted a great deal of attention due to its high toxicity in living beings is Cr(VI). In humans it can cause skin irritation and even cancer [1–3]. The main sources of Cr(VI) contamination are derived from anthropogenic activities such as mining, electroplating, pigment production and leather tanning [4,5]. The wastes from these industries are discharged directly into wastewater or, illegally, into rivers, lakes and seas in less-developed countries. Due to the high mobility of Cr(VI) in neutral and alkaline soils, it is often easily incorporated into aquifers [6,7].

The removal and elimination of water contaminants and specifically Cr(VI) is a global priority challenge for the protection of the environment and living beings. That is why the scientific community is making

great efforts to find new water treatment methods and technologies for the removal and elimination of Cr(VI). Among the various technologies that have been used in treating water with Cr(VI) we can include precipitation [8], adsorption [9], biodegradation [10], photodegradation [11], reduction [12], ionic exchange [13] and photocatalytic reduction [14].

Gong et al. [15] used iron sulfide-iron coated magnetic nanoparticles (Fe/FeS) for Cr(VI) removal in simulated groundwater. Nanoparticles reduced Cr(VI) to Cr(III). The authors reported that the process had the highest efficiency at pH 3.5 and Cr(VI) solutions at concentrations of 10 mg/L; however, by increasing pH or the Cr(VI) concentration of the solution, its removal decreases by up to 60%.

In the study reported by Yu et al. [16], the removal of Cr(VI) was done by adsorption in microspheres of cellulose functionalized with amino groups. The functionalization was carried out with Gamma radiation. According to their results, the microspheres reached a removal of 129 mg Cr(VI)/g microspheres at pH 3.08. These microspheres had a removal of 91% Cr(VI) in solutions and showed good stability.

\* Corresponding author.

E-mail address: [pradanos@termo.uva.es](mailto:pradanos@termo.uva.es) (P. Prádanos).

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Sinha et al. [17] removed Cr(VI) through phytoremediation with the plant *Tradescantia pallida*. The removal was carried out continuously by accumulation of chromium in the roots of the plant. Scale laboratory contaminated water was used in concentrations of 20 and 30 mg/L. The pH effect for each dissolution was studied. The best result for maximum total chromium removal efficiency was 86–88.2% achieved at pH 7.

Chen et al. [18] designed a Cr-methanol fuel cell that produces electrical energy from Cr(VI) removal. According to their study, from an initial concentration of Cr(VI) of 3500 mg/L, the concentration decreased more than 91% in a cycle of 400 min. The cell can produce up to 903 W/m<sup>2</sup> and can work in a temperature range of –14 °C to 45 °C.

However, the currently available technologies are usually expensive, produce new toxic by-products and even prove to be inefficient at low concentrations of Cr(VI).

Another option for treating water contaminated with Cr(VI) is separation with membrane technology. Membranes have been widely used in water treatment as they have the ability to concentrate contaminants in a small volume, can be re-used and do not generate toxic by-products.

Membrane technology has also been used in hybrid processes, combining the advantages of membranes with compounds such as clays [19], nanoparticles [20] or microorganisms [21]. In this way, the adsorption and/or reduction advantages of membranes are exploited to design ad hoc technologies for the removal of Cr(VI).

The membrane processes typically used in removal of Cr(VI) are Nanofiltration (NF) and Reverse Osmosis (RO). Since they require small pores (below 1 nm), they are usually quite effective in the removal not only of Cr(VI) but of any ionic species. Their main drawback is that they are the processes that require the highest pressures of membrane processes used in water treatment.

Kazemi et al. [22] modified polyamide nanofiltration membranes with chitosan and iron and titanium dioxide (nZVI@TiO<sub>2</sub>) photocatalytic nanoparticles. The modifications were made with the technique known as layer by layer (LBL) and were tested in the removal of Cr(VI). They found that, in the first stage, Cr(VI) was adsorbed on chitosan while, in the second stage, UV light-activated nanoparticles accomplished photodegradation. They obtained chromium removal percentages higher than 95% at pH 2 in Cr(VI) solutions of 10 mg/L.

Gaikwad and Balomajumder [23] studied the simultaneous rejection of fluoride and Cr(VI) with reverse osmosis membranes. Solutions of 5 mg/L and pH 8 were used, while the pressure was 16 bar. They reported that membranes reached rejections of 94.99% for fluoride and 99.97% for Cr(VI) under those conditions.

On the other hand, Ultrafiltration (UF) is among the membrane processes that require the lowest pressures. The main application of UF is to separate high-molecular-weight contaminants such as peptides and polysaccharides. Due to their pore size, UF membranes are not able to carry out the separation of ionic species. However, they can be modified by acquiring characteristics of NF membranes, for example, the ability to separate small ionic species. At the same time, they retain the need of only relatively low pressures during separation, which is a characteristic of UF. Therefore, modified UF membranes are a new alternative in the treatment of water contaminated with Cr(VI) or ionic species.

Yao et al. [24] modified polyvinylidene fluoride (PVDF) ultrafiltration membranes with polymers with tertiary amino and quaternary ammonium groups for Cr(VI) removal. The membranes acquired a positive charge after modification, so the key separation mechanism was adsorption. The membranes had a Cr(VI) uptake of 63.17 mg/g at pH 7. The concentration of the solutions was 10 mg K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/L and the pressure, 1 bar. The authors concluded that these membranes can be applied for low concentrations of Cr(VI).

Gebru and Das [25] made cellulose acetate UF membranes modified by impregnation of different polymers with amino groups and nanoparticles of titanium dioxide within the membrane structure. The membranes were used in Cr(VI) removal and, according to their results, the separation mechanism was through electrostatic interactions of

attraction between the positive amino groups and the negative Cr(VI) at pH 3.5, whereas, at pH 7 the separation was by electrostatic repulsions between the negatively-charged titanium dioxide nanoparticles and negative Cr(VI). The membranes showed the best performances at pH 3.5 and a Cr(VI) concentration of 10 mg/L.

As can be seen, there are many membrane modification techniques. With surface coating, a new layer is deposited on the active layer of the original membrane [26]. This new layer usually consists of nanoparticles or some monomer or polymer that causes a change in the surface charge density or the wettability of the membrane surface. This produces a reduction of fouling and/or an increase in retention. The main drawback of surface coating techniques is that, if there is not a grafting process, the duration of the modification is far too short [27] for most relevant applications.

For its part, plasma treatment can consolidate previously adsorbed or deposited layers “in situ.” This technique works with gaseous or vapor phase reactives; it is easy to use and especially suitable for creating new layers on a membrane. Therefore, plasma treatment can cause uniform and permanent grafting of the modifying agent [28,29]. When a polymer is used, the built layer keeps its chain mobility and functional groups [30]. In our case, we will focus on plasma generated by inorganic gases. It is known that this way of using plasma can induce crosslinking or chain disruption and, in some cases, even the appearance of new functional groups [31].

This paper proposes Cr(VI) removal from synthetic solutions through modified ultrafiltration membranes. Positively-charged membranes with a PVDF substrate will be coated with negatively-charged sodium polystyrenesulfonate (PSS); subsequently, they will be treated separately with the plasma of several inorganic gases. After the modification, the negatively-charged membranes will be shown to have achieved good removal of Cr(VI), and to have good stability after 5 weeks. In addition, they will be tested for the removal of other anions. They will be shown to retain nitrates and acid chromates with acceptable results, as well as to have a good separation rate of phosphate mixtures. Therefore, these membranes will be proved to have good potential for the removal of contaminant anions.

## 2. Experiment

### 2.1. Materials and chemicals

Ultrafiltration PVDF (polyvinylidene difluoride) membranes (HFM-183, Koch Membrane Systems, Wilmington, MA, USA) were used. These membranes are claimed to have a 100 kDa MWCO (molecular weight cut off). Manufacturers also say that this membrane is positively charged, what can only be accomplished by an appropriate modification of their PVDF surfaces. Hereafter, they will be called HFM-183 membranes.

Their water permeability, as measured by us, was  $(8.09 \pm 1.57) \cdot 10^{-10}$  m/Pa·s, as obtained from 15 experiments. PSS (poly(styrenesulfonate)) of a molecular weight Mw = 70,000 Da, which was tested to modify the virgin PVDF-substrate membranes, was bought in a 30% w/w water solution from Sigma Aldrich (Sigma-Aldrich, St. Louis, Missouri, USA).

The other chemicals (potassium dichromate, sodium nitrate, monosodium phosphate (anhydrous), potassium chloride, hydrochloric acid, sodium hydroxide, glycerol, sulfuric acid, antimony potassium tartrate, ammonium molybdate and ascorbic acid) were acquired at analytical grade from Sigma-Aldrich as well. Ultrapure (ASTM Type I) water was always used.

All filtration tests and experiments were performed on a flat membrane dead-end device (HP4750, Sterlitech Co., WA, USA). Each membrane sample was used as a 14.6 cm<sup>2</sup> disc. Nitrogen was used to pressurize.

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