

NM WRRRI Student Water Research Grant Progress Report Form

Final Report

1. **Student Researcher:** Alireza Bandegi
Faculty Advisor: Dr. Reza Foudazi
2. **Project title:** Electrochemical-assisted ultrafiltration membranes for simultaneous removal of As, Cd and Cr
3. **Description of research problem and research objectives.**

Heavy metals have been used in variety of industrial applications. Because of poor wastewater management practices and natural geological formations, the heavy metals level has increased significantly in many communities' drinking water resources.¹ Toxic heavy metals of concern in treatment of industrial wastewaters include cadmium (Cd), arsenic (As), and specially chromium (Cr). Exceeding any of these metals above their critical level can cause eminent health problems. The main removal mechanisms of the investigated Cd, As, and Cr ions through electrochemical filtration is hydrolyzation of ions and co-precipitation as hydroxides. However, the Cr (VI) will first be reduced to Cr (III) at the cathode before precipitating as hydroxides. In the environment, chromium is usually in one of the two stable redox states: hexavalent chromium, Cr (VI), and trivalent chromium, Cr (III)). Cr (VI) is highly soluble and mobile at neutral pH, and Cr (III) is considered a trace element needed in the human diet. 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 and the New Mexico State ground water standard is 50 ppb. However, recently high levels of chromium have been found in one of the Los Alamos well (250 ppb, five time more than state groundwater standard).² The most commonly used technologies in industry to remove heavy metals are adsorption and chemical reduction followed by precipitation. However, these processes produce large volumes of waste sludge that requires expensive disposal. Due to the low pressure demands and wide range of chemical stability, ultrafiltration (UF) membranes are widely used in water treatment processes. However, Cr (VI) removal by typical UF membranes is very limited, due to the maximum rejection of 20%. Decreasing the pore size of the membrane and incorporating a charged surface can increase the heavy metal ions rejection by UF membranes. In this work, we produce new type of electro-responsive membranes (ERMs) to remove heavy metals simultaneously from contaminated water.

The objectives of this research are as follows:

- a) Synthesize electroconductive UF membranes.
- b) Study the effect of membrane composition on the final performance of the membrane.
- c) Study the effect of electrochemical potential on the removal efficiency of heavy metals.
- d) Characterize the membranes by different techniques, such as filtration test, conductivity measurement, antifouling properties and rejection performance.

4. Description of methodology employed.

Materials

Poly [(ethylene oxide)100-block-(propylene oxide)65-block-(ethylene oxide)100] known as Pluronic F127 (Mw=12600 g/mol) was kindly provided by BASF. Bovine serum albumin (BSA), from Sigma-Aldrich, was used as a solute for rejection tests. The polyethylene oxide (Mw=1000 g/mol) and *N, N*-Dimethyl formamide (DMF) was purchased from Sigma-Aldrich. Polyethersulfone (PES), 92 type Ultrason E6020 was supplied from BASF. Potassium dichromate stock solution was prepared by dissolving potassium dichromate (purchased from Sigma-Aldrich, ≥99.5%) in deionized water. Deionized water was purified through an EMD Millipore water purification system.

Preparation of Membranes

PES membranes were prepared by phase inversion method.^{3,4} The composition of membrane casting solution is given in Table 1. At first, desire amount of carbon nanotubes (CNT) were sonicated for 15 minutes in DMF solvent. Then the PES, PEG 1000, and Pluronic polymers were dissolved in DMF solution and stirred at 60 °C for about 8 h to ensure the complete dissolution of the polymer. After released bubbles completely, the solutions were cast on glass plates with a doctor blade coater at a wet thickness of 200 μm forming nascent membranes, and then nascent membranes on glass plates and the glass plates were both immersed in a coagulation bath of deionized water. Subsequently, the formed membranes were peeled off and washed thoroughly with deionized water to remove residual solvent and pore-forming agent, and then kept in deionized water before use (the experimental procedure is shown in Figure 1).

Table 1. Composition of the different PES membranes prepared with NIPS process.

Sample	PES (g)	PEG (g)	Pluronic (g)	CNT (wt%) *	DMF (g)
1	3.6	-	-	-	13.6
2	3.6	3.0	-	0.5	13.6
3	3.6	-	-	0.5	13.6
4	3.6	-	0.26	0.5	13.6
5	3.6	3.0	0.26	0.5	13.6
6	3.6	-	0.26	-	13.6
7	3.6	3.0	0.26	-	13.6
8	3.6	3.0	-	-	13.6
9	3.6	3.0	-	1	13.6
10	3.6	-	-	1	13.6
11	3.6	-	0.26	1	13.6
12	3.6	3.0	0.26	1	13.6

*weight percent of CNT relative to PES.

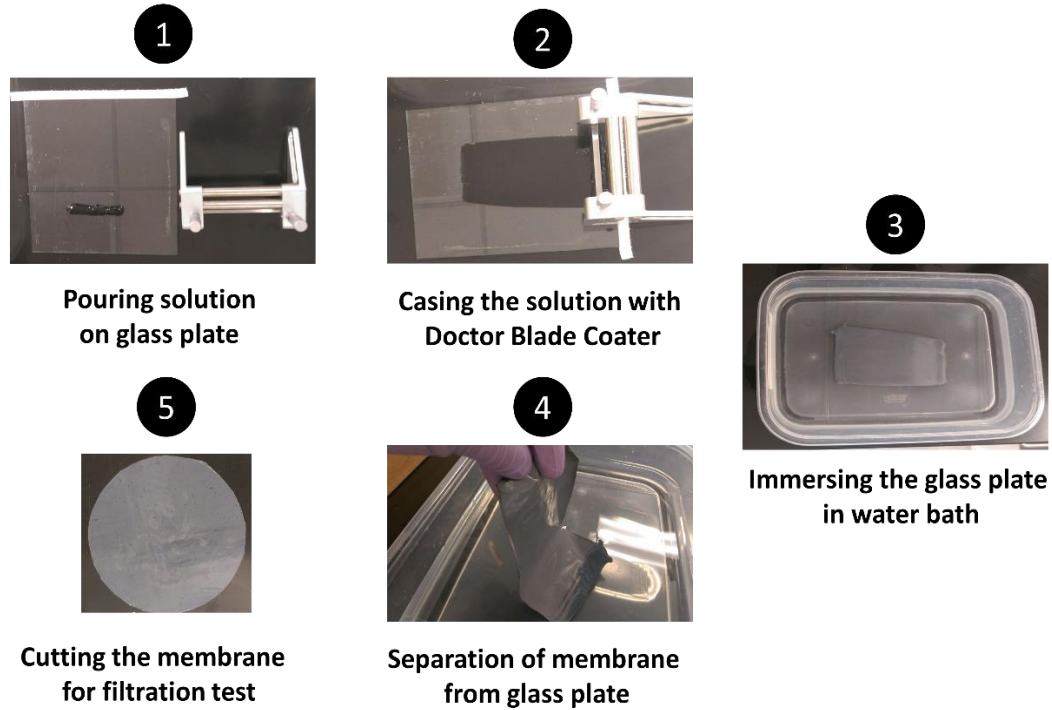


Figure 1. The procedure for preparing PES membranes through NIPS process.

Ultrafiltration Experiments

A dead-end stirred cell filtration system connected with a nitrogen gas cylinder and solution reservoir was designed to characterize the separation performance of blend membranes. The system consisted of a filtration cell (Sterlitech Corporation) with membrane effective area of 14.6 cm^2 . The feed side of the system was pressed by nitrogen gas. All the ultrafiltration experiments were carried out at a stirring speed of 350 rpm and a temperature of $25 \pm 1 \text{ }^\circ\text{C}$. After membrane was fixed, the stirred cell and solution reservoir were filled with deionized water. The permeate was measured at fixed time under the operating pressure of 100 kPa. The water flux (J_{w1}) was calculated by the following equation:

$$J_{w1} = \frac{V}{A \cdot \Delta t} \quad (1)$$

where V was the volume of permeated water, A the membrane area and Δt was the permeation time.

Next, the stirred cell and solution reservoir were emptied and refilled rapidly with 1.0 mg/ml BSA solution and flux (J_p) was obtained by the method described previously. The BSA rejection ratio was calculated by the following equation:

$$\text{Rejection ratio (\%)} = \left(\frac{1 - C_p}{C_f} \right) \quad (2)$$

where C_p and C_f (mg/ml) were the protein concentrations of permeate and feed solutions, respectively; and they were measured by UV-Vis spectroscopy. After 30 min of ultrafiltration, the

membranes were backwashed with deionized water for 20 min and the water flux of cleaned membranes was measured (J_{w2}). In order to evaluate the fouling-resistant ability of blend membranes, flux recovery ratio (FRR) was introduced and calculated using the following expression:

$$FRR (\%) = \left(\frac{J_{w2}}{J_{w1}} \right) * 100 \quad (3)$$

Conductivity Measurement

The conductivity was measured via electrochemical impedance spectroscopy (EIS, Figure 2). The membrane was sandwiched between two stainless steel blocking electrodes. The measurement was performed at room temperature (25 °C). The AC amplitude was 50 mV and the frequency were scanned from 1 MHz to 1 Hz. The conductivity of the samples was calculated from the complex impedance ($Z^* = Z' - iZ''$). The high-frequency plateau in the real impedance (Z') was taken as the bulk resistance (R) of the sample, and the conductivity was calculated as follows:

$$\sigma = \frac{L}{RA} \quad (4)$$

where L is the sample thickness and A is the electrode contact area (1 cm²).

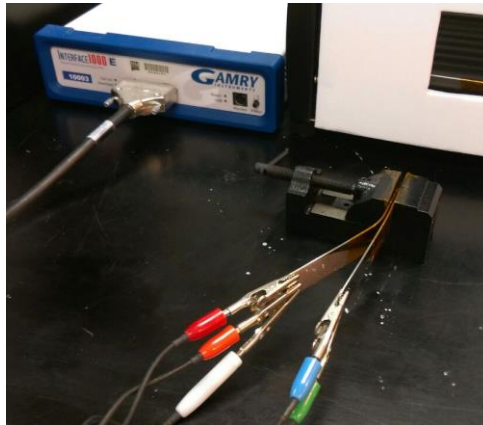


Figure 2. Picture of impedance spectroscopy device for measuring the conductivity of the membrane.

5. Description of results; include findings, conclusions, and recommendations for further research.

In figure 3, the picture of typical PES membranes which were prepared with NIPS process are shown. As it can be observed, the CNT is homogeneously dispersed in the membrane.

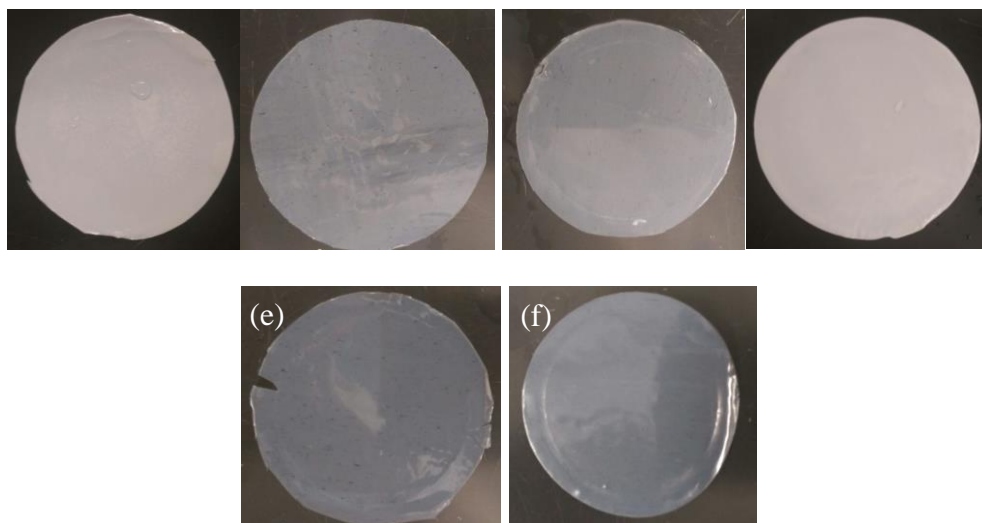


Figure 3. Image of the membranes (a) sample 1, (b) sample 2, (c) sample 4, (d) sample 8, (e) sample 9, (f) sample 12 prepared with NIPS process.

Flux Measurements

The performance of the membranes is measured in terms of BSA rejection, antifouling properties, conductivity, water flux and flux recovery ratio. At first experiment, the flux of membranes have been measured and as it can be observed in Figure 4, membrane 9 has the highest water flux and then the membranes 12 and 4. The lowest flux is belong to membranes 8 and 5.

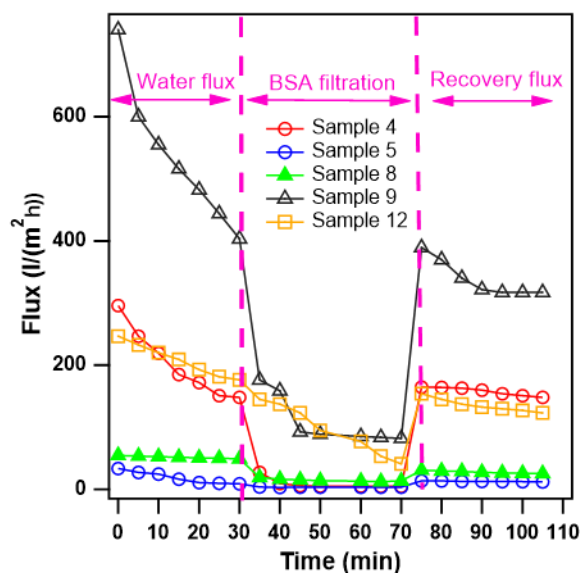


Figure 4. Time-dependent flux of membranes during ultrafiltration process for PES-F68 blend membranes. The ultrafiltration process includes four steps: pure water flux measurement, BSA solution ultrafiltration, water washing (not shown) and pure water flux measurement of cleaned membranes. Ultrafiltration was carried out at temperature of 25 °C and pressure of 100 kPa. The BSA concentration is 1.0 mg/ml.

After performing the filtration test, the flux recovery ratio (FRR) was obtained using equation (3). As shown in Figure 5, all the membranes have good FRR specially membranes 5 and 4 with FRR more than 80 percent.

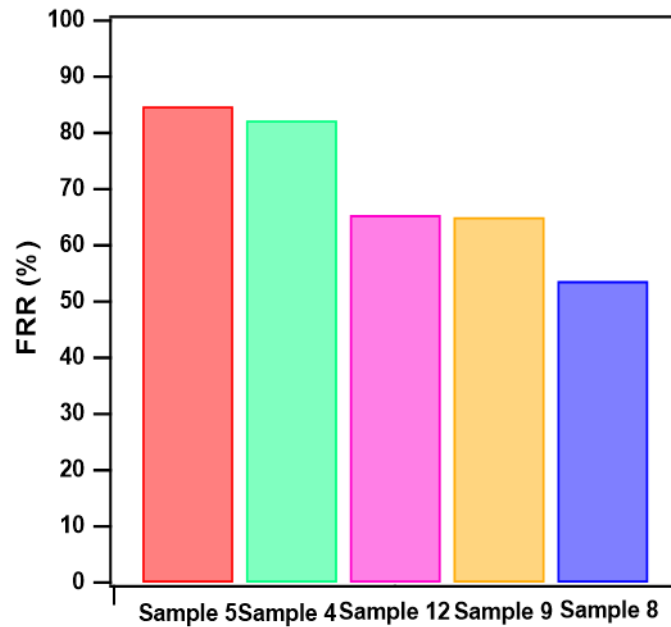


Figure 5. Flux recovery ratios of PES–Pluronic blend membranes at different.

BSA Rejection

To evaluate the performance of the membrane in terms of rejection, the UV-Vis is used for measuring the concentration of BSA in the permeate and feed solution. As shown in Figure 6, membranes 5 and 8 have highest BSA rejection more than 90 percent and membranes 12 and 4 have low rejection less than 70 percent.

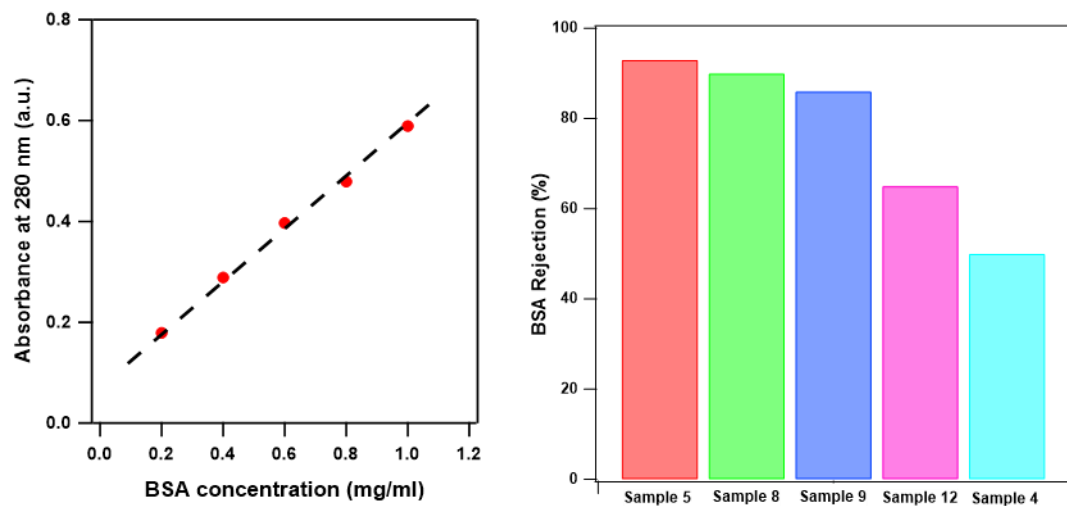


Figure 6. (Right) UV–Vis calibration curve of BSA (Left) BSA rejection of PES membranes with different composition.

Conductivity Measurement

One of the most important characteristics of the membrane for electrochemical removal of heavy metals from the wastewater is the conductivity of the membrane. In this Measurements the conductivity of the membranes which had the best performance in terms of flux and BSA rejection have been measured (Figure 7). It has been shown that the sample 2 have the highest conductivity which is probably due to the very small thickness of the membrane. However, this membrane is not stable under filtration condition due to the defects in the membrane. The conductivity of the other samples with CNT are in the same range and approximately close to each other.

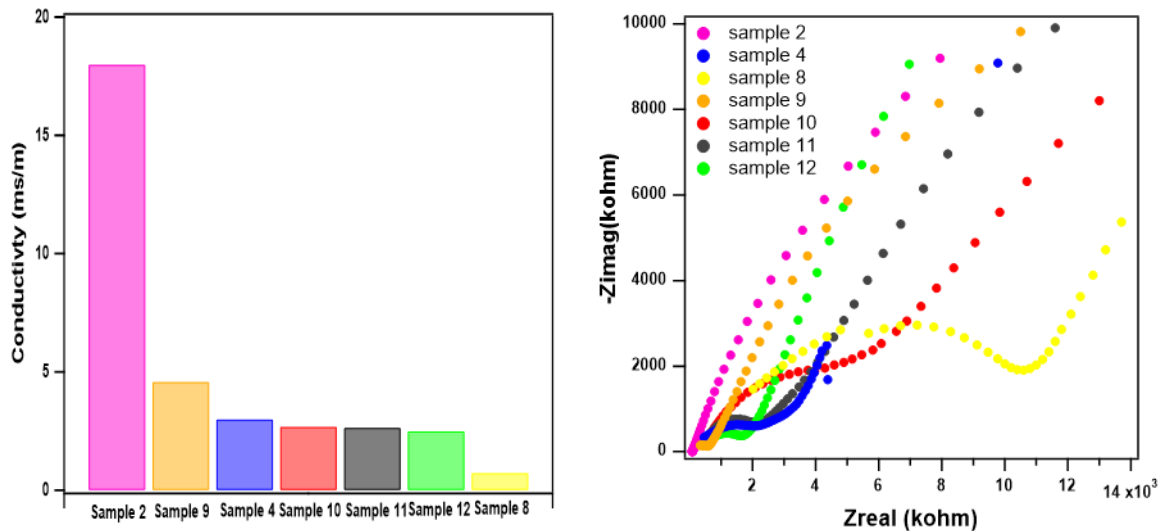


Figure 7. (Right) Conductivity and (Left) Nyquist plot of the PES membranes with different compositions.

Electrochemical Removal of Chromium

The Cr (VI) solution of 1 mg/L was prepared through dissolving $K_2Cr_2O_7$ in DI water. The sodium sulfate with concentration of 100 mM used as supporting electrolyte to adjust the solution conductivity.⁵ Dead-end vacuum filtration was applied to evaluate the electrochemical removal of Cr (VI) in the electrochemical filtration setup as shown in Figure 8.

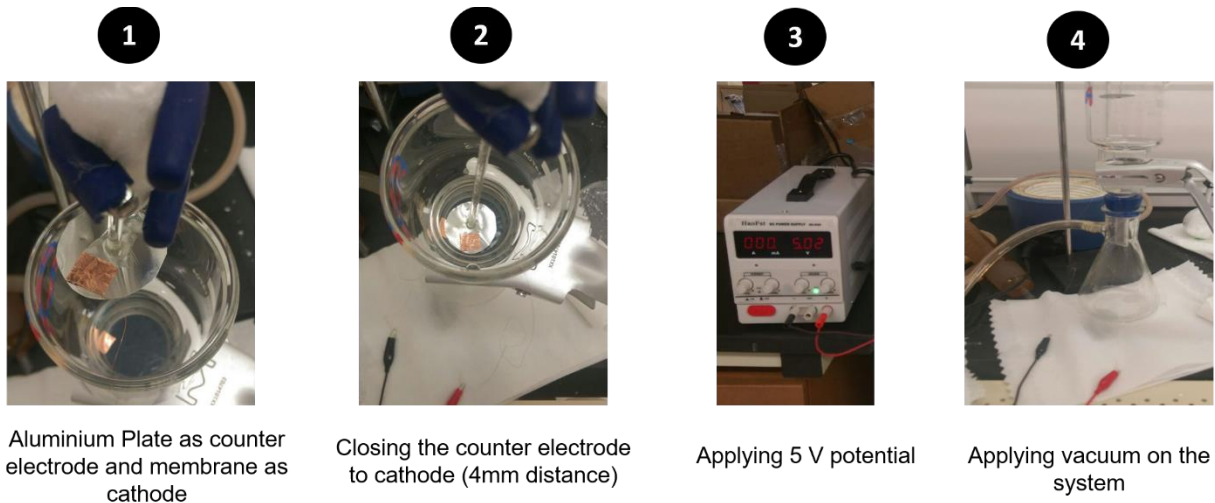


Figure 8. Electrochemical membrane system.

The cell potential was supplied by a DC power source. Conductive membrane and aluminum plate were served as cathode and counter electrode, respectively. The membrane surface was located 4 mm above the aluminium plate and the effective area of both membranes and aluminium plate was 14 cm^2 . The concentration of chromium was measured by inductively coupled plasma mass spectroscopy (ICP-MS). Sample 9 is used for measuring the electrochemical removal of chromium because of good conductivity, high flux and antifouling properties. As it is shown in Figure 9, after performing the filtration test the chromium removal efficiency was approximately 60%.

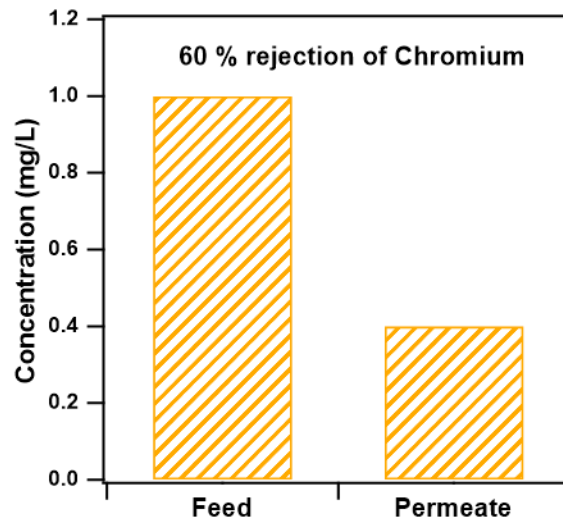


Figure 9. The concentration of chromium in feed and permeate solution of the electrochemical filtration system under the condition of $100 \text{ mM Na}_2\text{SO}_4$, and $\text{pH}=7$.

Conclusion

In conclusion, membrane with the composition of the PES/PEG/CNT/DMF (3.6 g/3g/1g/13.6g) had a good performance with conductivity of 4.8 mS/m, water flux of 400 LMH, FRR of 65% with BSA rejection of more than 80%, and 60 % chromium rejection through the electrochemical filtration system. This membrane is promising for application in electrochemical removal of heavy metals from wastewater due to the high conductivity, water flux and antifouling properties.

- 6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results.**

All water and wastewater treatment plants particularly those industries with Cr (VI) in their effluents such as painting, and leather tanning industries will benefit from the present research results. Furthermore, from a more general point of view, communities with potential Cr (IV) contamination in their water resources will benefit from the results.

- 7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after May 31, 2020, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)**

Budget balance:

- Salary (~ \$2962)
- Supplying the materials and characterization (~ \$3538)

- 8. List presentations you have made related to the project.**

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- 9. List publications or reports, if any, that you are preparing. For all publications/reports and posters resulting from this award, please attribute the funding to NM WRRI and the New Mexico State Legislature by including the account number: NMWRRI-SG-2019.**

- 10. List any other students or faculty members who have assisted you with your project.**

Mark Chidester (Lab Manager)

- 11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.**

- 12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.**

I passed my PhD comprehensive exam and I am planning to graduate next year.

Reference

- (1) Duan, W.; Chen, G.; Chen, C.; Sanghvi, R.; Iddya, A.; Walker, S.; Liu, H.; Ronen, A.; Jassby, D. Electrochemical Removal of Hexavalent Chromium Using Electrically Conducting Carbon Nanotube/Polymer Composite Ultrafiltration Membranes. *J. Memb. Sci.* **2017**, *531*, 160–171. <https://doi.org/https://doi.org/10.1016/j.memsci.2017.02.050>.
- (2) Albuquerque Journal <https://www.abqjournal.com/1065665/high-chromium-readings-found-beyond-los-alamos-plume-boundary.html>.
- (3) Mosqueda-Jimenez, D. B.; Narbaitz, R. M.; Matsuura, T.; Chowdhury, G.; Pleizier, G.; Santerre, J. P. Influence of Processing Conditions on the Properties of Ultrafiltration Membranes. *J. Memb. Sci.* **2004**, *231* (1), 209–224. <https://doi.org/https://doi.org/10.1016/j.memsci.2003.11.026>.
- (4) Machado, P. S. T.; Habert, A. C.; Borges, C. P. Membrane Formation Mechanism Based on Precipitation Kinetics and Membrane Morphology: Flat and Hollow Fiber Polysulfone Membranes. *J. Memb. Sci.* **1999**, *155* (2), 171–183. [https://doi.org/https://doi.org/10.1016/S0376-7388\(98\)00266-X](https://doi.org/https://doi.org/10.1016/S0376-7388(98)00266-X).
- (5) Liu, L.; Xu, Y.; Wang, K.; Li, K.; Xu, L.; Wang, J.; Wang, J. Fabrication of a Novel Conductive Ultrafiltration Membrane and Its Application for Electrochemical Removal of Hexavalent Chromium. *J. Memb. Sci.* **2019**, *584*, 191–201. <https://doi.org/https://doi.org/10.1016/j.memsci.2019.05.018>.