

NM WRRRI Student Water Research Grant Progress Report Form
Progress Report due October 1, 2018
Draft Final Report due July 15, 2019
Final Report due August 31, 2019

1. Student Researcher: Zahra Abbasian
Faculty Advisor: Reza Foudazi

2. Project title: Recyclable monolithic aerogels as efficient adsorbents for chromium VI removal from rural ground-water resources

3. Description of research problem and research objectives.

In July 2017, the Los Alamos National Laboratory (LANL) detected chromium, Cr, contamination in the sole source regional groundwater aquifer, five times greater than the New Mexico groundwater standard of 50 micrograms per liter.¹ Chromium VI is a highly toxic cancer-causing chemical targeting eyes, skin, kidneys and liver² and usually appears in groundwater due to the industrial wastewater failing to apply an appropriate method of waste disposal. Environmental Protection Agency calls a water source as a sole source aquifer when it supplies at least 50% of regional drinking water and there is no available alternative drinking water source in case of contamination. Therefore, there is a need for a prompt action and developing an affordable efficient water treatment system to remove Cr (VI). According to the literature,³⁻⁴ technologies such as reverse osmosis, ion exchange, filtration and solvent extraction. The limitation of the conventional methods are incomplete metal removal or low selectivity, energy utilization, and generation of wastes that usually are difficult to dispose and result in application restriction for efficient Cr (VI) removal.⁵ The objective of the present work is to produce an efficient adsorbent for Cr (VI) removal in water treatment systems. The adsorbent is a composite porous polymer based on acrylic acid (AA) and a conductive polymer, polypyrrole (PPy). AA is crosslinked with N,N'-methylenbisacrylamide, MBA, which has shown the high adsorption capacity of heavy metal ions. In addition, recently PPy has captured researchers' attraction due to its relatively environmental stability and its potential characteristic in separation and filtration applications. Using methyl orange as a soft template in the polymerization of pyrrole results in PPy formation of tubular structure. Emulsion templating method is used to produce PPy@poly(AA-co-MBA) composites with increased surface area through inducing porous structure in resulting materials. The combination of PPy and MBA-crosslinked acrylic acid results in stability of porous monoliths in adsorption/desorption cycles and a suitable adsorbent for efficient Cr(VI) removal. This method provides stable monoliths that are easy to separate from the effluent.

4. Description of methodology employed.

Materials: Acrylic acid, N,N'-methylenbisacrylamide, toluene, Triton X-405, ammonium persulfate (APS), Tetramethylethylenediamine (TEMED), methyl orange (MO) and potassium dichromate are purchased from Sigma-Aldrich and used as received, except pyrrole which is distilled before use.

Experimental: A high internal phase emulsion (HIPE) with 80% oil phase volume fraction was prepared. High internal phase emulsions are emulsions with a dispersed phase volume fraction greater than 74% of the total emulsion volume, which results to deformation of dispersed phase droplets into the polyhedral.⁶ These droplets are separated with a very thin film of a continuous

phase. PolyHIPEs can easily be prepared by having a monomer in the continuous phase (or both phases) of a HIPE. Fig. 1 exhibits a schematic of polyHIPE synthesis process.⁷

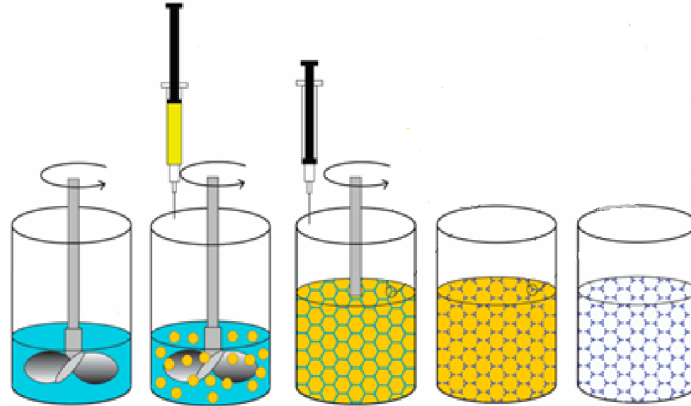


Fig. 1: PolyHIPE preparation schematic⁷

To prepare a HIPE, 2.78gr of a surfactant (Triton X-405) was dissolved in the water. AA and MBA were dissolved in the surfactant solution with 90:10 volume/volume ratio while stirring. Subsequently, 40 ml oil phase was added to the solution dropwise under stirring. The mixing was continued for 20 min after the oil phase addition was completed. APS as the initiator was then added and after 3 min of additional stirring the reaction accelerator, TEMED, was added to the emulsion. The emulsion was transferred to containers and cured at 50 °C for 20 h. The resulting monolith was purified with the methanol through soxhlet extraction for 24 h to remove the oil phase. To grow the tubular structure of PPy, the resulting highly porous poly(AA-co-MBA) was subsequently placed in pyrrole and then APS/MO solution. The PPy@poly(AA-co-MBA) composite was studied by scanning electron microscopy (SEM) and fourier-transform infrared spectroscopy (FTIR) to confirm the presence of PPy incorporated into the polyHIPE template. The prepared composite was tested for Cr (VI) removal from potassium dichromate water solution. PPy homopolymer and poly(AA-co-MBA) were also tested for comparison at the same experimental condition.

For Cr(VI) removal tests, potassium dichromate was dissolved in the deionized water at the desired concentration at pH=2. The prepared adsorbent was added to 80 ml of Cr(VI) solution. The concentration of Cr (VI) in the solution was measured by using inductively coupled plasma mass spectrometry (ICP-MS) at different time intervals. The adsorption capacity of adsorbents was calculated using the following equation⁸:

$$q_t = (C_0 - C_t)V/m$$

Where q_t (mg/g) is the adsorption capacity at a certain time t , C_0 and C_t (mg/L) are the Cr (VI) initial concentration and concentration at a certain time t , respectively. V (L) is the solution volume and m (g) is the mass of adsorbent.

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

To begin with this project, literature was reviewed to obtain a complete overview of water contaminated with heavy metal ions particularly Cr, different Cr removal techniques, and the latest advancement in adsorption process. A brief review of literature is presented in following paragraphs.

Chromium exists in 2+, 3+ and 6+ oxidation states.⁹ Cr²⁺ is unstable and very little is known about its hydrolysis. Cr(III) hydrolysis produces species such as CrOH²⁺, Cr(OH)₂⁺ and Cr₃(OH)₄⁵⁺, while the hydrolysis of Cr⁶⁺ produces mostly CrO₄²⁻, HCrO₄²⁻, Cr₂O₇²⁻. In Fig. 2, the speciation diagram of Cr(VI), concentration versus pH, has been shown.⁹

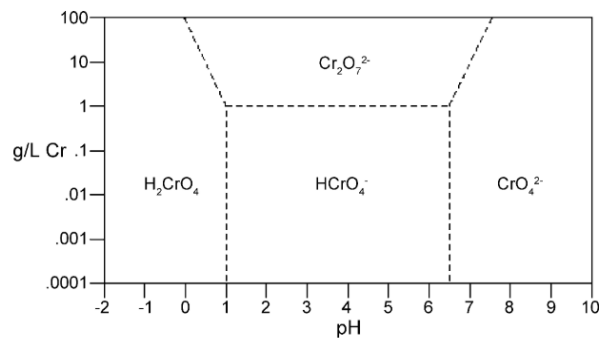


Fig. 2: Cr (VI) speciation diagram⁹

Higher water solubility and mobility of Cr (VI) compounds makes them more toxic than Cr(III). Leather tanning, painting, cement, and power plant industries are some of the major industrial source of Cr(VI) contamination in groundwater due to inappropriate waste disposal.⁵

Reduction of Cr(VI) to Cr(III) at pH 2.0 and precipitation of Cr (OH)₃ with lime at pH 9–10 is the most common conventional method for Cr(VI) removal.² The disadvantage of precipitation is producing high amount of sludge making the disposal process cost intensive. There is no significant adsorption of Cr(VI) at pH values higher than 6.0 due to competition of the anions HCrO₄⁻, Cr₂O₇²⁻ and OH⁻ for the adsorption sites.⁸ Adsorption includes uncomplicated and mostly eco-friendly operations offering significant advantages like being cost effective and technically feasible in comparison with conventional methods (such as membrane filtration or ion exchange). Different natural and synthetic materials have been used as Cr(VI) sorbents, including activated carbons, biological materials, zeolites, chitosan, and industrial wastes.¹⁰

PPy is one of the most attractive conducting polymers that can be formed by using an oxidant agent such as FeCl₃ or ammonium persulfate (APS) and methyl orange as a dopant.¹¹⁻¹² PPy produced can be doped with -SO₃²⁻ which is supplied with methyl orange. The oxidant/pyrrole ratio, reactant concentration and dopant affect the conductivity of PPy.¹³ The replacement of methyl orange with ethyl orange leads to the globular morphology of PPy. Methyl orange produces a solid template for the nanotubular growth of polypyrrole under acidic conditions after addition of the oxidant agent, while ethyl orange acts just like surfactants. Ethyl orange also enhances the conductivity of PPy but not as much as the methyl orange does. According to Huang et al.,¹⁴ the formation of a stable PPy/CS hydrogel depends on the materials concentration and the

order of adding them to the solution. They studied samples with different feeding orders, and observed some of them were unstable during purification in distilled water and lost their shapes. In the present research work, poly(AA-co-MBA) monoliths and PPy@poly(AA-co-MBA) composites were synthesized according to the procedure in the previous section. Chemical structure and morphology of PPy@poly(AA-co-MBA) monoliths were analyzed by FTIR and SEM. Optical microscope images from the concentrated emulsions have been shown in Fig.3. Fig. 4 exhibits the images from the PPy@poly(AA-co-MBA) monoliths at different preparation steps after emulsification. Fig. 5 shows the SEM images from PPy homopolymer and PPy@poly(AA-co-MBA) monoliths.

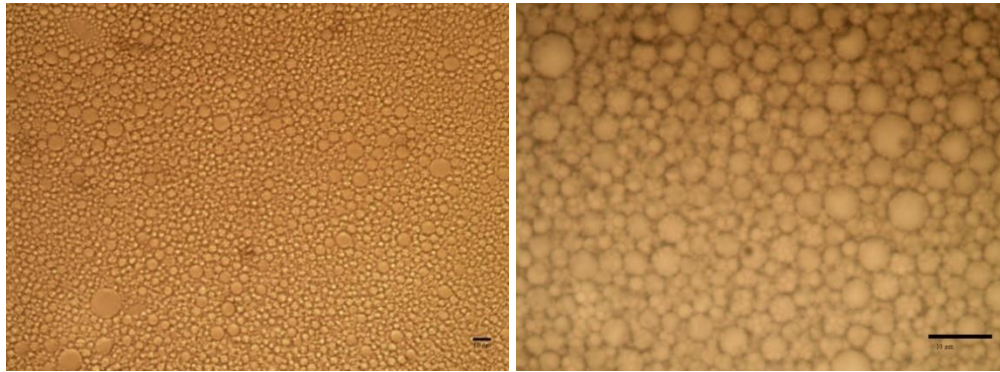


Fig. 3: Concentrated emulsions under microscope at two magnifications of 40 and 100 (scale bar: 10 μm).



Fig.4: Sample images from poly(AA-co-MBA) and poly(AA-co-MBA)/PPy formation: after curing, washing, soaking in pyrrole solution, and PPy formation (from left to right)

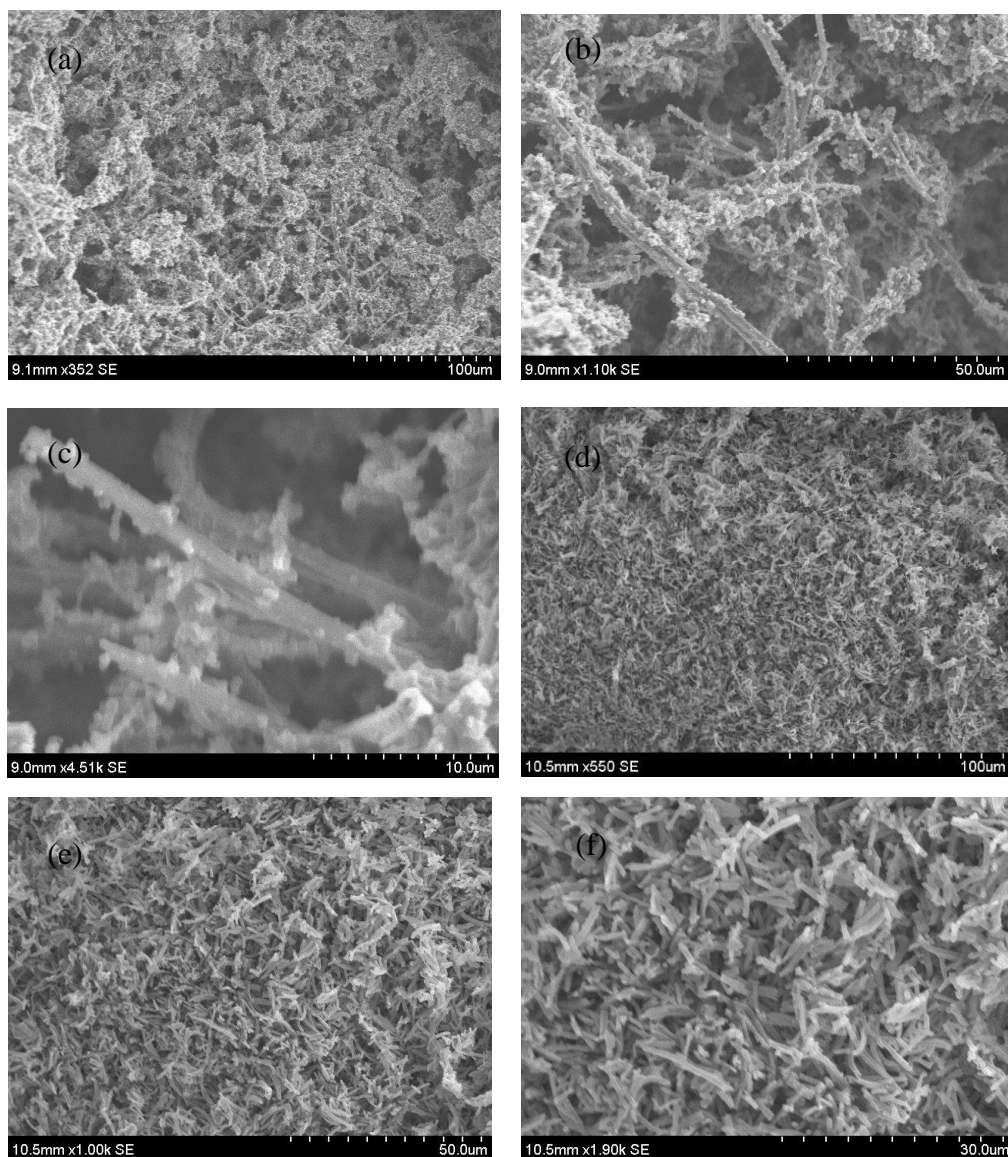


Fig.5: SEM images from PPy homopolymer (a-c) and PPy@poly (AA-co-MBA) monolith (d-f)

As shown in SEM images, polypyrrole has been grown in poly(AA-co-MBA) bulk. Using MO as a soft template in PPy formation led to growing PPy of tubular structure, which is more beneficial to the stability of monoliths and Cr removal efficiency due to increased surface area. Fig.6 shows the FTIR spectra of PPy, poly(AA-co-MBA) and PPy@poly(AA-co-MBA) monoliths. The peaks at 1549 and 1427 cm^{-1} , as the characteristic PPy peaks, are attributed to pyrrole ring stretching and C-N conjugated stretching mode, respectively.¹¹ The peaks located at 1165 and 860 cm^{-1} corresponds to C-N stretching mode of doping state of PPy. The presence of these peaks at poly(AA-co-MBA)/PPy monoliths confirms the PPy grown on the surface of poly(AA-co-MBA).

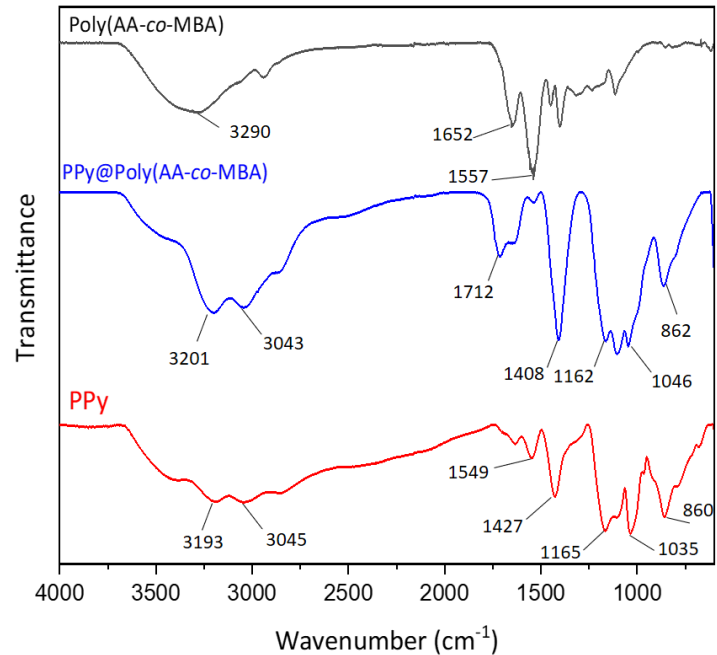


Fig.6: FTIR spectrum of PPy, poly(AA-co-MBA), and PPy@poly(AA-co-MBA) monoliths

The prepared composites, PPy homopolymer and poly(AA-co-MBA) were used for Cr (VI) adsorption experiments. Cr concentration in the solution was measured by using ICP-MS at different intervals. The adsorption experiments were performed at low pH value of 2, due to the lower adsorption free energy of HCrO_4^- than other Cr (VI) species in the water which is favorable for adsorption process. According to the Fig. 1, HCrO_4^- exists in the acidic pH range. There also could be a competitive interaction between $-\text{OH}$ and $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ at alkaline pH for the same adsorption site which results to the decreased Cr (VI) removal efficiency. Therefore, the lower pH is more beneficial for Cr (VI) removal.

Adsorption capacity of PPy adsorbent vs time has been shown in Fig.7. The color changing of the initial Cr(VI) solution after 24 hr from yellow to totally transparent reveals a highly efficient adsorption process.

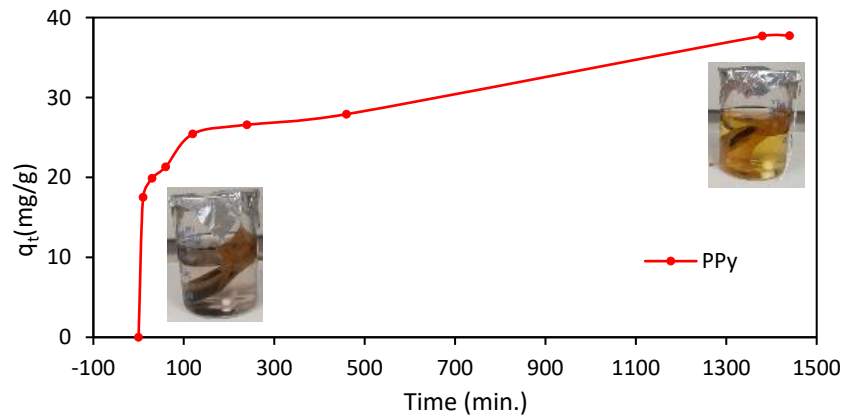


Fig.7: Adsorption capacity of PPy homopolymer at pH=2 and initial Cr (VI) solution of 77 ppm

Fig.8 represents the adsorption capacity of poly(AA-co-MBA) and PPy@poly(AA-co-MBA) composite. The prepared composite exhibits higher adsorption capacity than the porous poly(AA-co-MBA) sample due to the PPy presence as an efficient adsorbent for Cr removal.

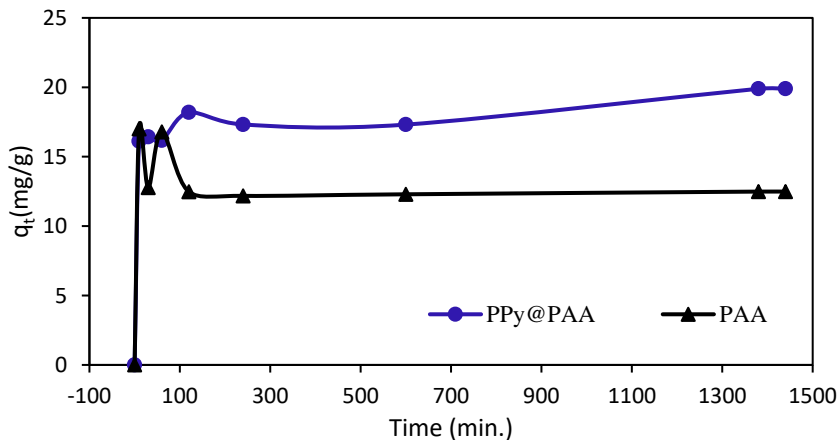


Fig. 8: Adsorption capacity of poly(AA-co-MBA) and PPy@poly(AA-co-MBA) composite at pH=2 and initial Cr(VI) solution of 77 ppm

The results obtained from this research presents poly(AA-co-MBA) polyHIPE as an appropriate template for PPy growth, as the SEM and FTIR analysis confirm the PPy incorporation into the polyHIPE template. Furthermore, PPy and its composite prepared by the present technique exhibits Cr(VI) removal of ~38 mg/g and ~20 mg/g; respectively, from the aqueous solution. Although PPy@poly(AA-co-MBA) composite shows lower adsorption capacity than PPy homopolymer resulting from a lower amount of PPy at the same amount of adsorbent, it is a monolithic adsorbent which is strong enough to be used in several adsorption/desorption cycles. The main problem associated with the most PPy-based adsorbents is that they are in powder form so that the adsorbents cannot be separated easily from the effluent. Therefore, the monolithic PPy composite prepared in the present work by using polyHIPE templates are addressing this common problem.

For future works, we suggest the studies on competitive effect of co-existing ions in the water/wastewater resources such as CO_3^{2-} and SO_4^{2-} on the Cr(VI) removal.

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

Compared to the existing adsorbents, the present work produces high capacity adsorbents with recyclable properties and without generating difficult-handling wastes. The fact that the monoliths prepared in this work are reusable compared to the most adsorbents in powder form contributes to their use in continuous operation and then the scale-up of process. Therefore, 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 15, 2019, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)

Budget balance:

- Printing poster for WRRRI conference (~ \$70)
- Student' tuition fee (~ \$2900)
- Supplying the materials and characterization (~ \$1000)
- Attending the ACS conference to present the research (~ \$2000)

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

- Poster presentation in 63th Annual New Mexico Water Conference, October 17-18, 2018, Las Cruces Convention Center.
- Oral presentation in ACS Fall 2019 National Meeting, August 2019, San Diego.

9. List publications or reports, if any, that you are preparing. Remember to acknowledge the NM WRRRI funding in any presentation or report that you prepare.

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

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.

This project is a part of a PhD research project.

Because of a growing demand for drinking water with increasing population, permanent industries challenges in their wastewaters disposal, and also student's interest and background, it seems likely to get involved in water-related areas after degree completion.

You are encouraged to include graphics and/or photos in your draft and final report.

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