NM WRRI Student Water Research Grant Report

1. **Student Researcher:** Muchu Zhou
   Faculty Advisor: Reza Foudazi

2. **Project title:** Design of Optimized Produced Water Treatment Units for the Agricultural Irrigation

3. Description of research problem and research objectives.

New Mexico (NM) is the fifth driest state in the nation; hence, water scarcity is a big issue in the state. Over 80% of water is consumed in agriculture sector.[1] The crude oil production of 246 million barrels in NM in 2018 ranked third in the United States, which is almost three times the 86 million barrels produced in 2012.[2,3] The growing oil output is due to the advanced horizontal drilling and hydraulic fracturing technology. However, hydraulic fracturing generates a large amount of wastewater known as "produced water" (PW). Four to five barrels of PW are generated per barrel of oil.[2] 900 million barrels of PW were generated in NM in 2017.[2] The composition of PW is complex including various toxic organic and inorganic chemicals. Conventionally, the PW is considered as the wastewater. However, State Regulatory Framework and the advanced wastewater treatment make the reuse (e.g. irrigation) of the PW possible.[2]

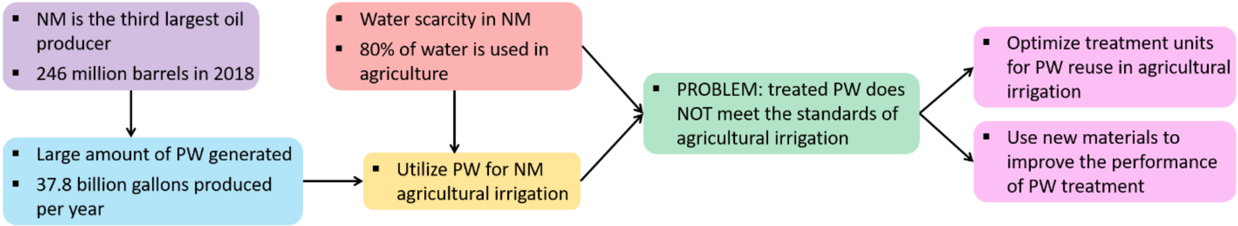


Figure 1. Problem and objectives in the present work

Currently, the process to treat the PW includes cyclones, phase separators, and decanters.[4] Nevertheless, these operation units do not meet the requirements of the PW reuse for agricultural irrigation. Therefore, the goal of the present work is to design and optimize a PW treatment unit for the agricultural irrigation, by considering high efficiency, low energy consumption, and low cost as three key factors. We believe that the current treatment technologies are mature enough to be utilized for PW treatment. However, the missing part is how to design an optimum unit operation by considering these key factors. Therefore, in this work, different treatment technologies will be compared and combined depending on the constituents present in the PW. Furthermore, commercial materials and the polyHIPEs porous materials synthesized in our lab[5] will be tested and compared as well.

4. Description of methodology employed.

The composition of PW strongly depends on the geographic location. We considered four units for designing PW treatment: (1) pretreatment, (2) organic matter removal, (3) reduction of salinity, and (4) heavy metal ions removal. For each unit, two or three methods were compared for the optimization. We chose microfiltration (MF)[5] or sedimentation for the pretreatment to remove total suspended solid (TSS). The Reusable Petroleum Adsorbent media (RPA®) (polyurethane-based materials),[4] MF, or activated carbon were chosen to separate the oil droplets. Step 1 and step 2 might be combined because the oil droplet usually can be removed in the pretreatment. We compared the ion-exchange resin, electrodialysis, nanofiltration (NF), or reverse osmosis (RO) to decrease salinity. The hazardous metal ions can be treated by using chitosan-based adsorbents or activated carbon. Step 3 and step 4 might be combined since heavy metal ions can also be removed in the step 3. The concentration of contaminants in the original PW and treated samples will be tested. The energy and cost of the treatment were studied for each step.

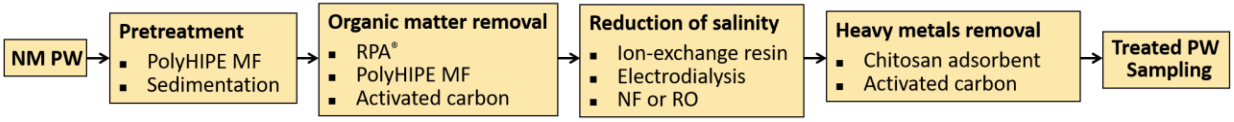


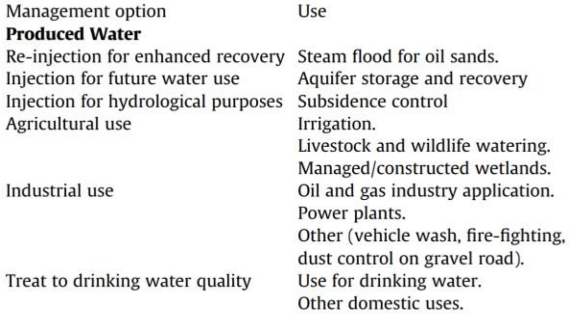
Figure 2. Proposed process for the treatment of PW in NM

We tested the new materials such as polyHIPEs, which have the potential to reduce the cost and energy of PW treatment. The polyHIPEs have been widely explored due to their highly interconnected porous structures. Our lab has successfully synthesized polyHIPEs that have shown better MF performance and good ability for removal of hazardous ions.[5,6] We also considered using chitosan-related materials since the chitosan is a biodegradable polymer from the shellfish. It has been used in the literature since it is biodegradable and relatively cheap.

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

This section starts with a literature review in order to better address the problem in this project. Different technologies for each treatment unit will be reviewed to obtain a general comparison of them, and thus the optimization can be obtained.

The PW comes from the underground, and it is usually generated and brought onto the surface during the hydraulic fracturing processes. Different geographic locations of the PW make its composition more complicated, but the PW usually contains the following matters which are total suspended solids (TSS), total dissolved solids (TDS), dissolved and undissolved organic compounds, and even the heavy metal ions and radionuclides.[7,8] Those toxic chemicals are very hard to be removed limiting the PW reuse, which has been the most considerable amount of byproducts in oil and gas production. Another issue with the PW is the high costs of PW management. It has been estimated that a trillion dollars will be used for the oil extraction, and a large amount of them will be used for the PW management.[7] Injecting the PW into the saltwater disposal (SWD) wells or reinjecting the PW into the reservoirs for enhanced oil recovery is the most common ways to deal with the PW.[9] However, they all have their limitations, such as environmental pollution and corrosion due to toxic chemicals. Therefore, the reuse of PW is still changing. Moreover, there are limited reports systematically investigating the PW treatment unit optimization for its reuse in NM.



Management option	Use
Produced Water	
Re-injection for enhanced recovery	Steam flood for oil sands.
Injection for future water use	Aquifer storage and recovery
Injection for hydrological purposes	Subsidence control
Agricultural use	Irrigation. Livestock and wildlife watering. Managed/constructed wetlands.
Industrial use	Oil and gas industry application. Power plants. Other (vehicle wash, fire-fighting, dust control on gravel road).
Treat to drinking water quality	Use for drinking water. Other domestic uses.

Figure 3. Water Re-Use and recycle management options[4]

Although there are many conventional methods available to treat the PW, PW's pretreatment is still necessary for the enhanced treatment efficiency. Moreover, the TSS will influence the membrane performance through the fouling and scaling.[10] Typically, the primary and simple method used in the PW pretreatment is the sedimentation, which is a gravity-dominated separation process to separate solids/liquids from the liquids due to different density. The sedimentation is a relatively slow process, and flotation is usually used with the sedimentation. In order to accelerate the sedimentation-flotation process, coagulation-flocculation will be used to increase the particle size, and thus, the separation efficiency. AZ. Rodriguez et al.[9] also mentioned that the process of coagulation-flocculation-sedimentation-filtration is sufficient to remove the TSS from the water. For the coagulation, it includes chemical coagulation and physical coagulation. The most commonly used chemicals for the chemical coagulation are calcium hydroxide ($25.25/L), aluminum sulfate ($57.76/kg), iron sulfate ($212/L), and ferric chloride ($82.5/L). S. Jimenez et al.[11] used the ferric chloride as the coagulant in the sedimentation process. They found that the optimal process conditions are 86 mg/L of ferric chloride concentration and 83 min of settling time, which results in a 69% chemical oxygen demand (COD) removal percentage and 90% turbidity removal. AZ. Rodriguez et al.[9] reported that aluminum sulfate exhibited higher turbidity removal than ferric chloride at the same molar concentration, leading to lower chemical demand and cost. 36mg/L of aluminum sulfate will be needed to reach 60% turbidity removal, whereas 134 mg/L of ferric chloride will be used to obtain the same level of turbidity removal. However, the disadvantages of using the chemical coagulation include producing a large amount of residual sludge and the relatively low level of the coagulating agent in the chemical coagulants.

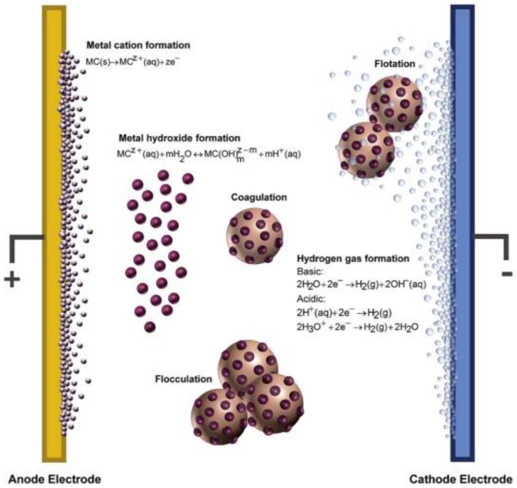


Figure 4. Schematic view of an electrochemical (EC) unit[12]

S. Zhao et al.[10] used the electrocoagulation as the pretreatment to treat the PW from the Saskatchewan oil field in Canada. They achieved the removal efficiencies of 66.64 and 93.80% to remove COD and turbidity, respectively, and 85.81% for the hardness removal. AZ. Rodriguez et al.[9] also tested electrocoagulation's efficiency, which removed 70% of turbidity and 63% of total organic compounds (TOC) from the PW.

Another alternative method for the pretreatment of PW is the MF membranes. In this project, we also considered using a porous polymer, which is also known as polyHIPE to produce the MF membranes. The polyHIPEs are produced through the emulsion templating. Emulsions are mixtures of two immiscible liquids stabilized by the surfactants. An emulsion is a colloidal dispersion in which a liquid is dispersed (dispersed phase) in another immiscible liquid (continuous phase). High internal phase emulsions (HIPEs) are classified by Lissant[13], in which the volume of internal phase occupies more than 74% of the whole volume, even up to 99%.

HIPEs can be prepared using oil-in-water (O/W) emulsions or water-in-oil (W/O) emulsions. The typical procedure used to prepare the polyHIPEs is showing below.

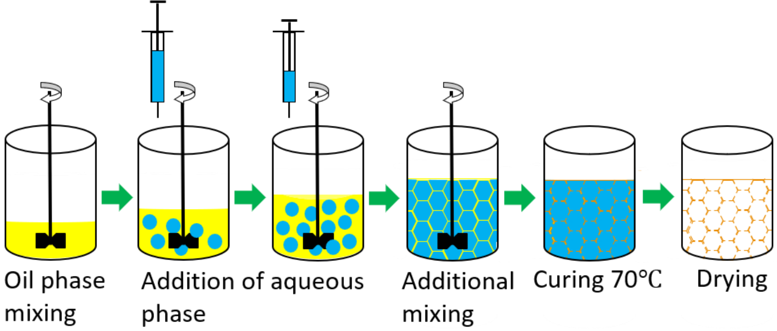


Figure 5. Schematic process of polyHIPE synthesis[5]

The continuous phase, including the organic monomers of the HIPEs, is polymerized, followed by the removal of the internal phase droplets by washing and drying to obtain the polyHIPEs. Removal of the internal phase generates the voids in the polyHIPEs and highly interconnected open-pore structures obtained from the emulsion-templated methods. PolyHIPEs have attracted much interest due to their potential applications, such as scaffolds for tissue engineering, supports for chemical reactions, and separation media. Figure 6 shows the typical porous structure of polyHIPEs.

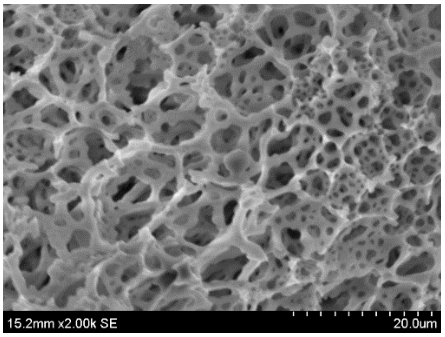


Figure 6. SEM image showing the porous structure of polyHIPEs

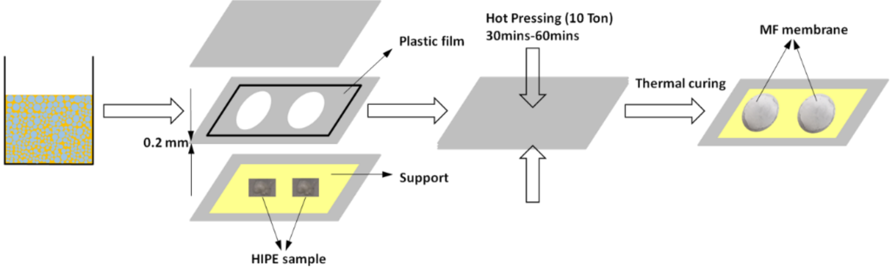


Figure 7. Casting a thin layer of an HIPE on a support for polyHIPE MF membrane production[5]

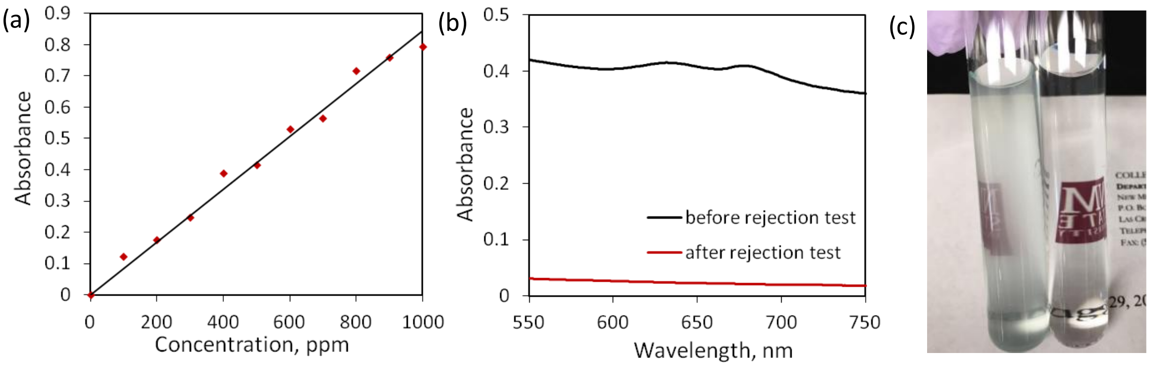


Figure 8. Rejection test results of the polyHIPE MF membrane[5]

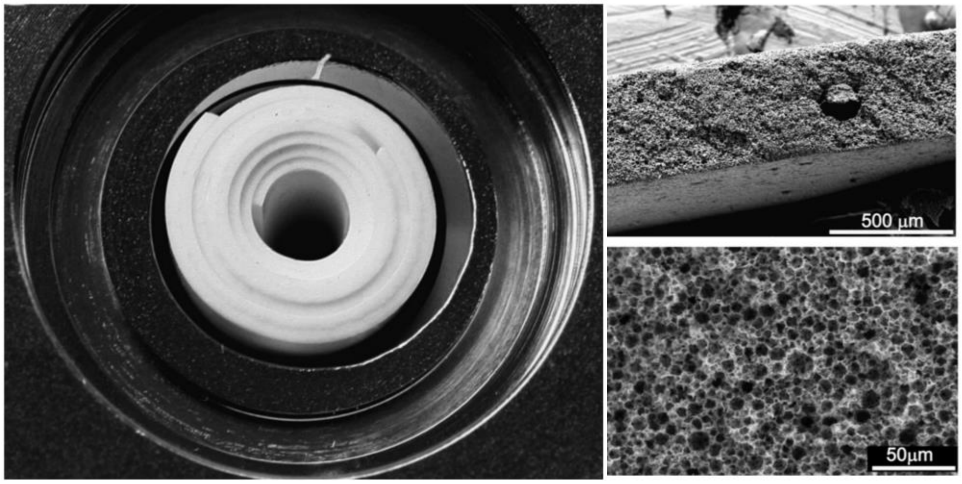


Figure 9. PolyHIPE membranes for the protein purification[14]

M. Zhou et al.[5] prepared the polyHIPE MF membranes (Figure 7 shows the preparation of the polyHIPE MF membranes) and tested the membrane performance. The permeability was calculated by the Darcy's law. Galdieria sulphuraria (G. sulphuraria) is a unicellular extremophilic red microalgae. It was used to test the polyHIPE MF membranes' rejection performance, and the average rejection rate is 95%.[5] Additionally, the polyHIPE membranes show nitrite ion removal capability as the ion-exchange membranes,[15] and protein purification.[14] The windows of the polyHIPEs are the pores of the polyHIPE MF membranes, and they are typically ranging from 0.5 μm to 5 μm. Furthermore, the polyHIPE materials are made of organic monomers, and thus, they have a hydrophobic structure. Therefore, the polyHIPE MF membranes are a good candidate for PW's pretreatment to reduce the turbidity and remove the TSS and oil droplets.

Table 1. Chemical composition of the PW in NM

Parameter	Value[9]	Unit	Value[16]	Unit
Total organic carbon (TOC)	83.1±30.8	mg/L	21.9±1.2	mg/L
Total dissolved solids (TDS)	129.3±8.5	g/L	129.3±8.5	g/L
Total phosphorus	<0.1	mg/L		
pH value	7.30±0.21		7.35±0.10	
Alkalinity	2345±329	mg/L as CaCO3		
Elctrical conductivity	201.2±13.3	mS/cm		
Turbidity	53.4±5.0	NTU		
Ammonium	655±77	mg/L	598.6±10.2	mg/L
Arsenic	1.1±0.0	mg/L	0.88±0.09	mg/L
Barium	1.0±0.0	mg/L		
Bromide	591±16	mg/L	591.1±15.8	mg/L
Calcium	4247±752	mg/L	4779.4±105.4	mg/L
Chloride	65800±1600	mg/L	65800±1600	mg/L
Iron	11±9	mg/L	1.66±0.03	mg/L
Lithium	18.8±0.3	mg/L	18.8±0.3	mg/L
Magnesium	727±54	mg/L	763.9±25.4	mg/L
Manganese	0.66±0.02	mg/L	0.66±0.02	mg/L
Nickel	0.02±0.004	mg/L	0.02±0.004	mg/L
Potassium	805±230	mg/L	968.5±30.5	mg/L
Silica	32±2	mg/L	16.3±1.4	mg/L
Sodium	42720±2093	mg/L	44200±2500	mg/L
Strontium	257±20	mg/L	256.8±19.7	mg/L
Sulfate	1010±9	mg/L		

It was proposed that the second unit for the PW treatment is organic matter removal. However, the suspended oil droplets are not the main chemicals in the PW from NM (the chemical compositions are shown in Table 1, which are from two different sources). Hence, the second unit will be combined with the first unit. The main purposes to pretreat the PW are: 1) reducing the turbidity/removing the TSS; 2) removing the suspended oil/removing the organic matter. The pretreatment will increase the following treatments' efficiency and decrease the membrane fouling in the following treatment units. Conventional physical pretreatments can easily remove the TSS. Therefore, the key is removing the organic matter. The activated carbon is another choice to remove the organic matter from the PW. S. Riley et al.[17] compared three types of granular activated carbon (GAC), which are Norit GAC 816, Aurora Binney Water Purification Facility, Colorado, Norit GAC 400 and Darco 12 × 40, Cabot Norit Activated Carbon, Boston, MA, with the biologically active filtration (BAF) regarding the performance of the organic matter removal. They reported that the Norit GAC 816 with the biofilm system is the most efficient system to remove the organic matter, 92% dissolved organic carbon (DOC) is removed, and the concentration of DOC and COD are 18 mg/L and 154 mg/L, respectively.

After the first unit, the next treatment is for the reduction of salinity of PW. It can be seen that the high salinity is the main concern with the PW in the NW, especially for the Chloride and Sodium. Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been evaluated and employed to reduce the salinity of wastewater or seawater. The main difference between these filtration types is the pore size of the membrane and the operating pressure. Figure 10 illustrates the level of filtration that each membrane can achieve. The MF membrane has the largest pore size in the range of 0.1-1.0 μm, but the lowest operating pressure.[18] The driving force in the membrane process is the pressure difference across the membrane. For the MF membrane, the operating pressure is 0.1-2 bar, while the reverse osmosis membrane's operating pressure is up to 120 bar.[19] MF, UF, and NF membranes are pressure-driven. The NF membrane has properties between those of UF and RO membranes. The advantages of the NF process include relatively low energy consumption and high efficiency of removing the contaminants. Polyethersulfone (PES) and polyamide (PA) are the basic materials for making the UF, NF, and RO membranes.[20,21] K. Walha et al. tested the UF and NF membranes as the pretreatment of the seawater's salinity reduction. The RO membranes were used as the following treatment to reduce the salinity further. They reported the NF works more efficiently compared with the UF, and the salinity can be reduced to around 3.7% of the raw seawater via the combination of NF and RO processes.[20]

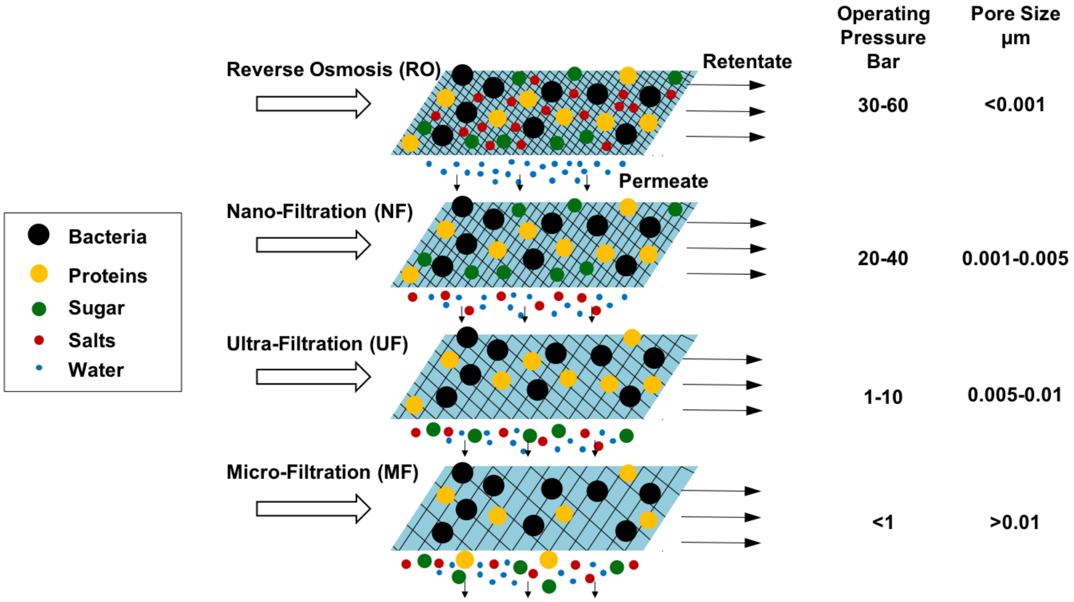


Figure 10. Membrane pore size and operating pressure

Styrene (ST)-co-divinylbenzene (DVB) polymers are a type of promising material for producing the ion-exchange resin. Poly (ST-co-DVB) polyHIPE ion-exchange resin shows promising results of removing nitrate ions.[15] However, the PW in NM does not have that much nitrate ions. RO and electrodialysis (ED), effective for wastewater treatment, are parts of membrane desalination. However, the ED is only suitable for treating the PW with a lower concentration of chemicals. Otherwise it will be an expensive treatment method for PW treatment.[22]

Chitosan is a biodegradable polymer from shellfish. It has been used in the research since it is biodegradable and relatively cheap. S. Pu et al.[23] synthesized a porous magnetic chitosan hydrogel (PMCH) to remove Pb(II) ions. Magnetic Fe_3O_4 nanoparticles are used in order to make the magnetic chitosan beads. The maximum adsorption capacity is 84.02 mg of Pb(II)/g. They also reviewed the capacity for removing the heavy metal ions of the other different chitosan-based adsorbents, see Table 2 below. S. Popuri et al.[24] also showed that the chitosan-coated PVC beads have the ability to remove the Cu(II) ions and Ni(II) ions. The table showing the adsorption capacity of the Cu(II) ions and Ni(II) ions for different chitosan-based adsorbents is shown in Figure 14.

Table 2. Adsorption capacity of the chitosan-related adsorbents

Heavy metal ion	Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Arsenic (III)	Magnetic chitosan beads	35.3	25
Arsenic (V)	Magnetic chitosan beads	35.7	25
Cadmium (II)	Magnetic chitosan/cellulose microspheres	61.12	26
Chromium (VI)	Ethylenediamine-magnetic chitosan resin	51.813	27
Cobalt (II)	PVA/chitosan magnetic composite	14.39	28
Copper (II)	Epichlorohydrin-crosslinked chitosan particle	35.46	29
	Chitosan-bound Fe3O4 nanoparticles	21.5	30
	Poly(methacrylic acid)-chitosan microspheres	83.2	31
	Chitosan	71.2	32
		16.8	33
		59	34
		33.4	35
	Chitosan coated perlite	196.1	36
	Chitosan/PVA	47.9	35
	Non-crosslinked chitosan	80	37
	Chitosan acetate crown ether	23.9	38
	Chitosan diacetate crown ether	31.3	38
	Epichlorohydrin cross-linked chitosan	16.8	38
	Chitosan coated PVC	87.9	24
Lead (II)	Epichlorohydrin-crosslinked chitosan particle	34.13	29
	Magnetic chitosan/cellulose microspheres	45.86	26
	Magnetic chitosan beads	84.02	23
Ni (II)	Chitosan	2.4	33

	Chitosan coated perlite	114.9	36
	EDTA-Chitosan	123.3	39
	DTPA-Chitosan	117.4	40
	Chitosan acetate crown ether	0.7	38
	Chitosan diacetate crown ether	4.1	38
	Epichlorohydrin cross-linked chitosan	6.4	38
	Chitosan coated PVC	120.5	24
Zinc (II)	Epichlorohydrin-crosslinked chitosan particle	10.21	29

However, according to Table 1, it seems that the toxic ions in the PW of NM is the Arsenic. R. Zowada and R. Foudazi synthesized a porous hydrogel incorporated with Fe_3O_4 nanoparticles via the HIPE templating to remove the Arsenic from the water. Their results show that the synthesized functionalized polyHIPE hydrogel can remove about 50% of the As(V) ions, having the adsorption capacity of 2.25 mg of As(V)/g.[6]

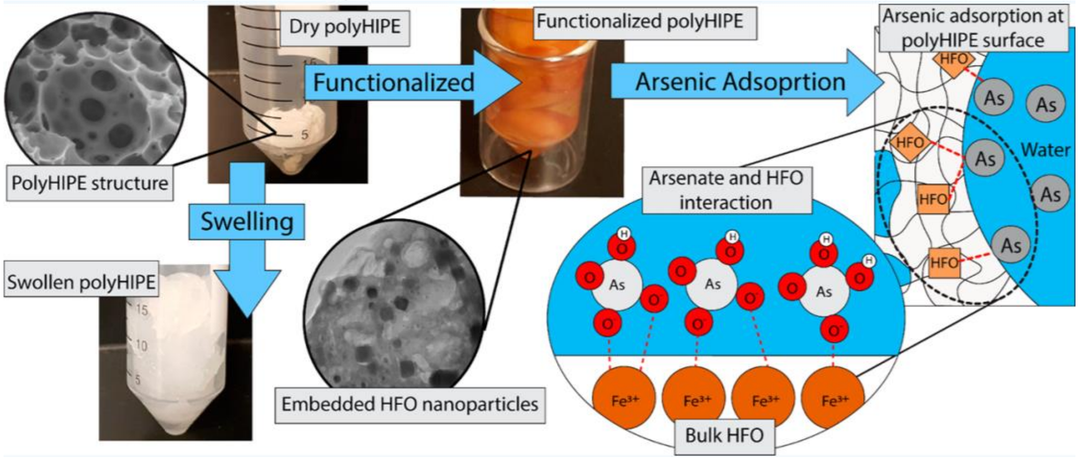


Figure 11. Schematic process showing the adsorption of As(V) by using the polyHIPE hydrogels[6]

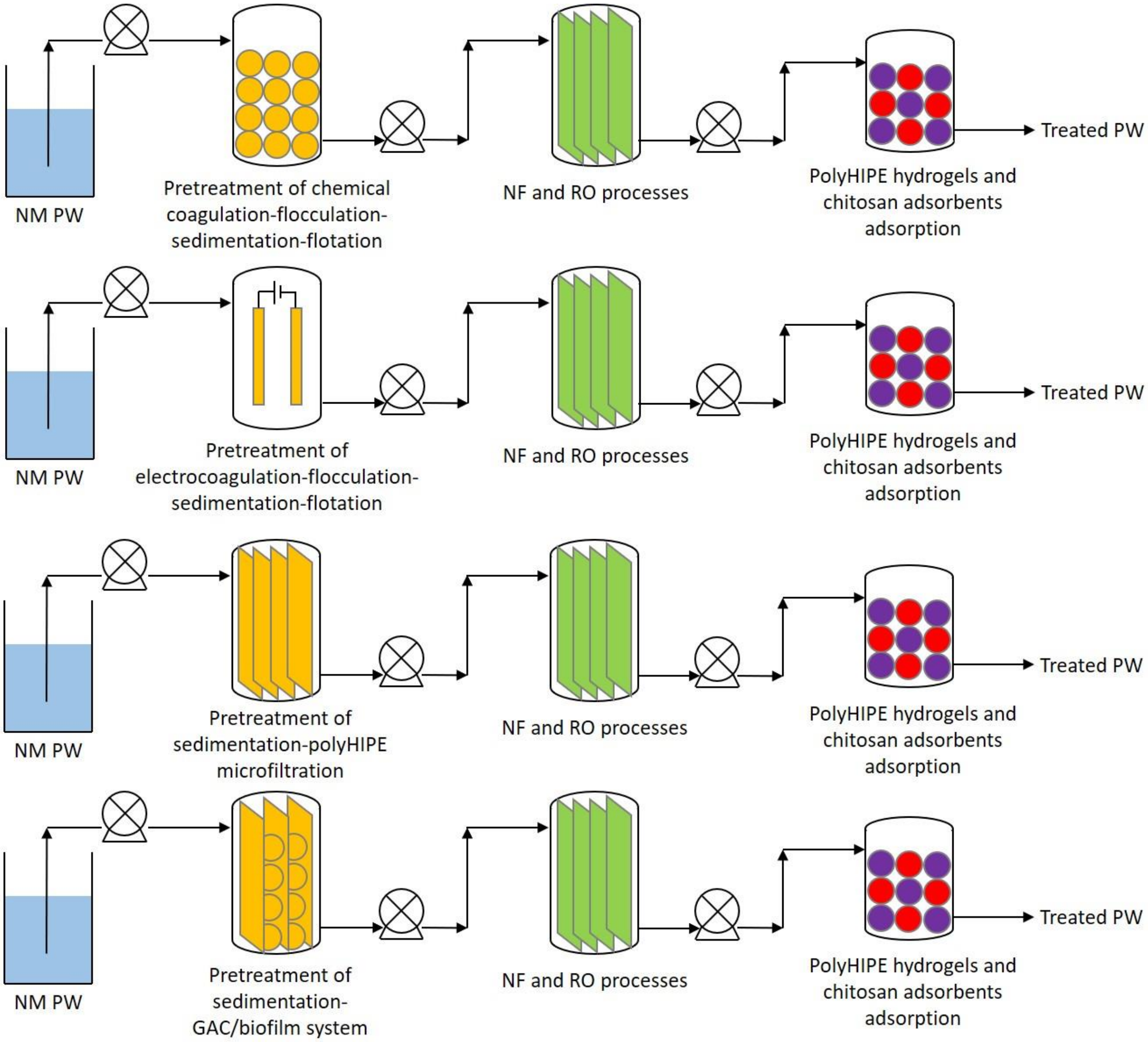


Figure 12. Schematic process of the proposed PW treatment units

Table 3. Chemical composition estimation after treatment (Original concentration is the average value from Table 1, and the efficiency is taken the maximum based on the efficiency mentioned in the content)

	Original concentration	Chemical coagulation-flocculation-sedimentation-flotation	Electrocoagulation-flocculation-sedimentation-flotation	PolyHIPE MF membranes	GAC along with biofilm system	NF and RO processes	PolyHIPE hydrogel adsorption
Turbidity	53.4 NTU	5.34 NTU	3.31 NTU	2.67 NTU	-		
Total organic carbon	52.5 mg/L	16.28 mg/L	17.51 mg/L	2.63 mg/L	4.2 mg/L		
Ammonium	626.8 mg/L					-	
Arsenic	0.99 mg/L						0.5 mg/L
Bromide	591.05 mg/L					-	
Calcium	4513.2 mg/L					27.08 mg/L	
Chloride	65800 mg/L					394.8 mg/L	
Magnesium	745.45 mg/L					2.24 mg/L	
Potassium	886.75 mg/L					-	
Sodium	43460 mg/L					173.84 mg/L	
Sulfate	1010 mg/L					20.2 mg/L	

Table 4. Energy consumption and *cost estimation*

Chemical coagulation (Al)	Chemical coagulation (Fe)	Electrocoagulation	NF	RO	Reference
$\$0.222/m^3$ $0.4\ kWh/m^3$	$\$0.325/m^3$ $0.4\ kWh/m^3$	$\$0.44/m^3$ $0.36\ kWh/m^3$	-	-	[9]
$\$0.768/m^3$	$\$0.497/m^3$	-	-	-	[41]
$\$0.12/m^3$	-	$\$1.19/m^3$	-	-	[42]
-	-	-	$\$0.30\text{-}0.40/m^3$	-	[43]
-	-	-	$\$0.09\text{-}0.13/m^3$ $0.22\text{-}0.63\ kWh/m^3$	-	[44]
			-	$\$0.85/m^3$ $0.81\text{-}1.09\ kWh/m^3$	[45,46]

Table 5. Cost estimation for the proposed treatment train

	Unit 1	Unit 2	Unit 3	Total
Train 1	$\$0.12/m^3$	$\$0.98/m^3$	$\$0.5/m^3$	$\$1.6/m^3$
Train 2	$\$0.44/m^3$	$\$0.98/m^3$	$\$0.5/m^3$	$\$1.92/m^3$
Train 3	$\$4.28/m^2$ of membrane	$\$0.98/m^3$	$\$0.5/m^3$	$\$5.76/m^3$
Train 4	$0.04/g of GAC	$\$0.98/m^3$	$\$0.5/m^3$	$\$41.48/m^3$

Four PW treatment trains are designed as shown in Figure 12. Four different pretreatments are used which including the chemical coagulation-flocculation-sedimentation-flotation, Electrocoagulation-flocculation-sedimentation-flotation, polyHIPE MF membrane filtration, and GAC along with biofilm system. The chemical composition after each treatment unit is showing in the Table 3. It reveals that each treatment is effective for reducing the chemical level of PW in the New Mexico. Table 4 shows the energy consumption and cost estimation of each treatment unit. Based on the Table 5, the treatment train including the chemical coagulation will be the cheapest one.

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

This research provides some ideas about how to systematically purify the PW, for using it again, for the Department of Agriculture and inspires the companies who are dealing with the PW.

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:
-Student graduate assistant ($5718.70)
-Fringe rate students ($56.05)
-Supplies ($25.00)
-Printing reproduction ($100.00)
-Lab analysis ($600.25)
-Indirectly costs ($1553.50)

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

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.**

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 WRRI project is a part of my Ph.D. research work. Because of the large amount of PW in the New Mexico state, it is crucial to investigate and find the optimized treatment units for the PW reuse. Porous polymer is one of my research interests, and I would like to use my porous polymer to do the PW treatment as the potential membranes or the adsorbents. Therefore, a water-related field matches my research field, and I would be likely to get involved in the water-related areas after completing the Ph.D. degree.

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

Reference:

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