HPWD Annual Progress Report

Tarleton State University

(Grant Period October 2018 – September 2019)

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Progress report till June 2019

Title of the project: Plant based polymers as effective treatment agents in removal of dissolved solids and ions and reuse the treated water in plant irrigation

1) **Progress made to date with the project:**

Following objectives were proposed

Part I: Optimization of the polymer dose for maximum contaminant removal. This will be carried out in Dr, Rajani Srinivasan's Lab in the department of Chemistry Geosciences and Physics

Part II: Study the effect of irrigating the plants using treated and untreated water: This will be carried out by Dr. Narayanan Kannan from Texas Institute for Applied Environmental Research (TAIER) co-located in the same campus as Tarleton State University.

Part 1: Optimization of the polymer dose for maximum contaminant removal. This was carried out in Dr, Rajani Srinivasan's Lab in the department of Chemistry Geosciences and Physics located in Tarleton State University. Following tasks were performed to achieve the above objective

1. Synthesis and characterization of polysaccharides derived from the plants: Polysaccharides were extracted from husks of the psyllium, seeds of fenugreek and fruits of okra. Tamarind polysaccharide is available commercially. It was bought and used as it is. Polysaccharides from fenugreek/okra and psyllium were extracted by soaking their seeds / fruits /husks respectively in cold /hot water overnight. Mucilage was extracted using a muslin cloth. Polymers were precipitated by treating the mucilage with ethanol in 1:3 ratio. The crude polymer was further purified by treatment with acetone and the final product was dried at 40-50 °C.

   Characterization: The prepared materials were characterized using Fourier transform Infra-Red (FTIR) spectrophotometer.

2. Collection of water from the Dockum Aquifer: Water samples collected from the Dockum aquifer was brought back to the lab for experimentation. Water samples were collected from five different wells. The number corresponding to the wells are as follows: 30159, 85324, 91347, 18693 and 18698

3. Characterization of the collected water sample: Collected water samples were characterized for water quality parameters like suspended solids (SS), Total dissolved solids (TDS), Total Solids (TS), Cations and Anions. Solids were characterized using gravimetric analysis. Anions and Cations were analyzed using Thermo fisher Scientific Dionex Aquion Ion chromatograph. Tables below show the cation and anions present in the individual well water samples

Cations (Each well water sample)

Well sample	Potassium (mg/L)	Sodium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Ammonium (mg/L)
18698	3.8	1184	21	29	ND
18693	3.8	1173	20	28	ND
30159	4.3	1599	7	13	ND
85324	12.5	939	141	314	ND
91347	3.1	1485	2	6	ND

Anions (Each well sample)

Well sample	Fluoride(mg/L)	Chloride (mg/L)	Nitrate (mg/L)		Bromide (mg/L)	Phosphate(mg/L)	Sulfate (mg/L)
30159	1.6	2443	ND		2.3	ND	1559
85324	4.3	922	ND		1.2	ND	616
91347	0.6	4110	ND		1.3	ND	195
18693	1.3	2358	0.8		1.2	ND	989
18698	2.5	2964	ND		1.2	ND	756

4. Lab scale adsorption experiments were performed to study the removal efficiency of the polymers individually and in combination in removal of TDS, sodium, chloride, sulfate, magnesium and fluoride. This was done by series of batch adsorption experiments using Jar test.

Stock polymer solutions of Fenugreek, Psyllium and Tamarind polysaccharides were made by dissolving 0.5 g of the polymer in 100 mL of the DI water. The concentrations of the polymers were varied by adding different volume of the polymer solutions. The Polymer dose was varied from 0.5g/L to 1.5g/L. The contact time of the polymers with water were varied from immediately to 60 minutes to determine the optimum contact time for maximum removal of contaminants using different polymer doses.

The contaminants concentrations were measured before and after the treatment to determine the efficiency of the polysaccharides as treatment agents. Ion chromatograph was used to detect anions and cations. Standard gravimetric method was used to determine the solids in the water samples. The flocs were dried. FTIR of the dried flocs, well water and the polymer were taken and compared to determine the mechanism.

Results

Optimization experiment using Jar test

The tables 1-5 below gives the results of adsorption experiments performed on the water collected from individual well sites. Several experiments were performed to optimize the best polymer, polymer concentration and contact time. From the experiments it was found that the optimum polymer dose, contact time and polymer used varied from site to site based upon the concentration of the anions, cations and solids. From the results it was found that the optimum polymer dose was 2g/L and contact time was 30 minutes. Experiments are still in progress to find the best polymer/ dose mixture. It was found that the maximum TDS removal increased from 25% to 61% as the polymer concentrations were increased from 1g/L to 2g/L using Fenugreek polymer. Removal of Chlorides ranged from 30% to 90% ; Sulfates 14% to 90%; Sodium 22% to 90 % ; Magnesium 18% to79%; calcium 5%- 83% and potassium 40-80% using different polymers and polymer mix at varying contact time

Before treatment

After treatment

Water for irrigation:

Based on the results above irrigation experiments were performed by mixing water from all the five wells in equal ratios and flocculation experiment was performed to remove the contaminants using the following.

1) Water was treated using 1g /L and 2g/L of fenugreek polymer
2) Water was treated using 1g of Fenugreek and 1g of tamarind in 1:1 ratio
3) Contact time used was 30 minutes.

After the 30 minutes of treatment the water was filtered using muslin cloth and was sent to Dr. Narayanan Kannan at TIAER for irrigation of the plants in the green house. During the experiment 50 mL water was collected before and after water treatment. The collected water sample was analyzed for TDS, anions and cations. Tables 6 and 9 shows the results of the water treatment. The results show approximately 63% of TDS removal in the treated water.

FTIR results

Figures 1 and 2 shows the comparative FTIR of well water, Polymer and the flocs. From the figure it can be seen that the polymer was capable of adsorbing the pollutants using flocculation process.

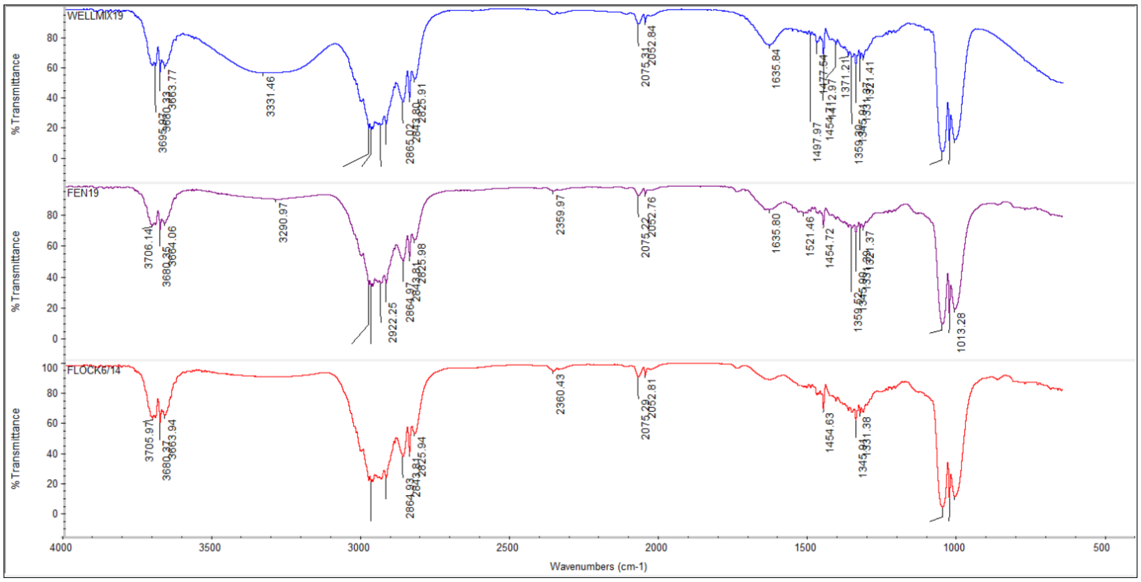

Figure 1: Well water mix, Fenugreek Polymer and Floc

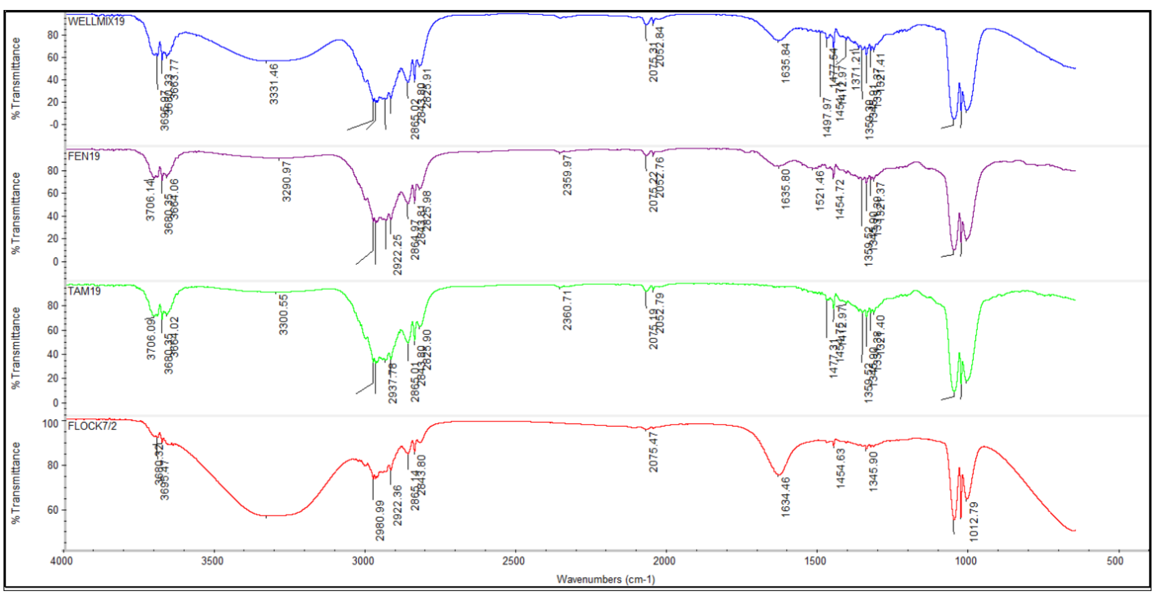

Figure 2: Well water mix, Fenugreek, Tamarind Polymer and Floc

Summary of the results as tables

Table1: Anion and cation removal using varying doses and mixture of polymers in individual well water samples

% Removal (contact time in minutes)									
Polymer	Well site	Chloride	Sulfate	phosphate	Sodium	Magnesium	calcium	potassium	TDS
Psy 1	1(91347)	49.74%(30)	58.09% (30)						
Psy2		58.11%(30)	62.46%(30)						
Psy3									
F1		34.43% (5)	30.51%(15)						
F2		35.62%(5)							
T1									
O1									23.23%(30)
O2									17.71%(30)
T2									
Mix 1					30.23%(30)	63.46%(i)	15.89%(5)		
Mix 2					41.73%(30)	79.51%(5)	83.76% (5)		
Mix 3									
Mix 4									

Table 2: Anion and cation removal using varying doses and mixture of polymers in individual well water samplesYOu need to explain

% Removal (contact time in minutes)									
Polymer	Well site	Chloride	Sulfate	Phosphate	Sodium	Magnesium	Calcium	Potassium	TDS
Psy 1	2(30159)	47(60)	85%(5)		22% (15)	18(60)			
Psy 2		45(60)	85%(5)		33% (5)	28(15)			
Psy 3		77.78 %(15)	55.27%(60)		82 (5), 30(60)	64(5)	25%(5)		
F1		59%(60)	53%(60)		81%(im)); 37%(5)	22%(5)			
F2		56%(60)	35%(60)		30% (30);				
T1					25.03%(15)	21.61%(i)	17.20%(15)		
T2					31.06 %(15)	21.12%(30)	17.90(15)		
									20.89%(15)
									23.32%(15)
Mix 1					81.7 %(30)	58.02%(30)	27.11%(30)	48.39 % (0)	
Mix 2					90% (30)	65.63% (03)	31.29 (30)	67.4%(0)	
Mix 3					78%(30)	55.63%(30)	47%(5)	69.35% (0)	
Mix 4					88%(15)	68.36 %(15)	54%	80.65%(0)	

the abbreviations shown in column 1

Psy: Psylllium

Table 3: Anion and cation removal using varying doses and mixture of polymers in individual well water samples

% Removal (contact time in minutes)									
Polymer	Well site	Chloride	Sulfate	Phosphate	Sodium	Magnesium	Calcium	Potassium	TDS
Psy 1	3 (85324								
Psy2									
Psy 3									
O1		71.52% (5)	86.71%(15)		16.75%(15)		22.92%(15)	69.57% (15)	18.4(30)
O2		91.2%(60)	95.74%(60)		23.35%(30)		31.26%(30)	76.09%(15)	9.74 (30)
F1									
F2									
Mix 1		72%(5)	97.52%(5)						
Mix 2		74%(15)	63% (30)						
Mix 3		44.43%(5)	39%(0)						
Mix 4		57%(5)	31.75% (5)						

Table 4: Anion and cation removal using varying doses and mixture of polymers in individual well water samples

% Removal (contact time in minutes)									
Polymer	Well site	Chloride	Sulfate	Phosphate	Sodium	Magnesium	Calcium	Potassium	TDS
Psy 1	4 (18698)	49.74% (30)	58.09% (30)						
Psy2		58.11%(30)	62.46% (30)						
Psy3									
F1		29.24% (15)	50.51%(15)						
F2		35.62%(0)							
T1		7.94%(30)			39.25%(30)		10.53%(30)		12.90%(30)
T2		38.04%(0)			44.10%(30)		5.26%(30)		
Mix 1		38.68%(0)			44.97%(30)				17.56%(60)
Mix 2		42.42%(0)			76.78%(60)				11.55%(60)
Mix 3			14.38%(60)						
Mix 4									

T1: 0.50g Tamarind Gum
T2: 1.00g Tamarind Gum
M1: 0.25g Tamarind Gum/ 0.25g Psyllium = 0.50g Mixture
M2: 0.50g Tamarind Gum/ 0.50g Psyllium = 1.00g Mixture

Jartest was done with Tam, and Psy:Fen:Tam mixtures at 0.5g and 1.0g concentrations 11/9/18 Water samples from Lubbock Site 4		
SS 40ml	T1 = Tam 0.5g	M2= 1:1:1 Psy:Fen:Tam 1.0g
TDS 20 ml	T2 = Tam 1.0g	
TS 20 ml	M1= 1:1:1 Psy:Fen:Tam .5g	

Table 5: Anion and cation removal using varying doses and mixture of polymers in individual well water samples

% removal (Contact time in minutes)									
Polymer	Well site	Chloride	Sulfate	Phosphate	Sodium	Magnesium	Calcium	Potassium	TDS
Psy 1	5 (18373)	47.30%(60)	34.38%(60)		27.31%(60)	18.42%(60)			
Psy2		44.79% (60)	84.73% (5)		33.98%(5)	27.52 (15)			
Psy3		48.48960)	55.27% (60)		30.56% (60)	64.79% (5)	24.91(30)		
F1		58.68%(60)	53.04% (60)		37.0%(5)	21.83% (5)	24.91(0)		
F2		55.65(30)	34.66% (60)		29.8% (30)		13.87(5)		
T1									
T2									
Mix 1		71.77% (5)	92.61% (30)		81.72%(30)	58.02%(30)	27.06%(30)	50.00%(30)	
Mix 2		74.43% (15)	62.84%(30)		90.78%(30)	65.53%(30)	31.29%(30)	48.32%(i)	
Mix 3		44.43%(5)	38.97%(0)		78.15%(30)	55.63%(30)	47.01%(5)	69.35%(i)	
Mix 4		56.98%(5)	31.75% (5)		88.29%(15)	68.36%(15)	53.91%(5)	80.65%(i)	

Site 5

M1: 0.25g Psyllium and 0.25g Fenugreek = 1.00g Mixture
M2: 0.50g Psyllium and 0.50g Fenugreek = 1.00g Mixture
M3: 0.1667g Psyllium/0.1667g Fenugreek/0.1667g Tamarind Gum = 0.50g Mixture
M4: 0.3333g Psyllium/0.3333g Fenugreek/0.3333g Tamarind Gum = 1.00g Mixture

Psy1: 0.50g Psyllium
Psy2: 1.00g Psyllium
Psy3: 1.50g Psyllium
F1: 0.50g Fenugreek
F2: 1.00g Fenugreek
T1: 0.50g Tamarind Gum
T2: 1.00g Tamarind Gum
M1: 0.25g Tamarind Gum/ 0.25g Psyllium = 0.50g Mixture
M2: 0.50g Tamarind Gum/ 0.50g Psyllium = 1.00g Mixture

Jar test was done with Psyllium, and Fenugreek mixtures at 0.5g, 1.0g, and 1.5g concentrations water samples came from Lubbock Site 5 #2		
SS 40ml TDS 20 ml TS 20 ml	Psy1= Psyllium 0.5g Psy2= Psyllium 1.0g Psy3= Psyllium 1.5g	F1= Fenugreek 0.5g F2= Fenugreek 1.0g

Table 6: Total Dissolved solid and total solid removal from the mixed well samples used for Irrigation

Treatments / dose/date	TDS removal	TS removal
Fen 1g/L (4/24)		17.5%
Fen (5/1)	25%	5%
Fen 5/3)	37%	18%
Fen 5/17	27.2%	23%
Fen 5/28	23.3%	18.2%
Fen 5/31		5%
Fen (2g/L)6/3	61%	53%
Fen 6/7	60%	53%
Fen 6/18	59%	63%

Table 7

Cations (Each well water sample)

Well sample	Potassium (mg/L)	Sodium (mg/L)	Magnesium(mg/L)	Calcium (mg/L)	Ammonium (mg/L)
18698	3.8	1184	21	29	ND
18693	3.8	1173	20	28	ND
30159	4.3	1599	7	13	ND
85324	12.5	939	141	314	ND
91347	3.1	1485	2	6	ND

Table 8

Anions (Each well sample)

Well sample	Fluoride(mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Bromide (mg/L)	Phosphate(mg/L)	Sulfate (mg/L)
30159 (Hale)	1.6	2443	ND	2.3	ND	1559
85324 (Swisher)	4.3	922	ND	1.2	ND	616
91347 (Lubbock)	0.6	4110	ND	1.3	ND	195
18693 (Deaf Smith)	1.3	2358	0.8	1.2	ND	989
18698 (Deaf Smith)	2.5	2964	ND	1.2	ND	756

Table 9: Average values for the Anions and Cations removed from the mixed well water samples used for irrigation

% Removal						
Polymer / dose	Fluoride	Chloride	Sulfate	Sodium	Magnesium	Calcium
Fenugreek/ 1g/L		12%	12%	12.15%	17%	14%
Fenugreek / 2g/L	22.2%	35%	51.49%	-	-	-

Part II: Study the effect of irrigating the plants using treated and untreated water: This was carried out by Dr. Narayanan Kannan from Texas Institute for Applied Environmental Research (TIAER) Lab co-located in the same campus as Tarleton State University.

Progress of the Irrigation Experiment

Experimental Setup in the Greenhouse

We started the irrigation experiment on May 23, using 15-inch Grossfillex lightweight planters (bought from Walmart located in Stephenville, TX [local Walmart hereafter]). The planters did not have holes to drain excess water. Therefore, we made four large size holes in each pot for adequate drainage if more water is applied than what the pot can hold. Then, about 2/3rd of the pot was filled with potting mix (Expert Gardner or MiracleGro brand from local Walmart). After that, the rosemary seedlings (bought from local Walmart) were transferred to the pot, some more potting mix was added, and the potting soil surface was leveled. The final level of the potting soil occupied about 3/4th of the total pot volume. The remaining space was

Figure 1 Experimental setup in the greenhouse for rosemary (okra plants on the back)

Figure 2 Experimental setup in the greenhouse for Okra and Rose

allowed for the expansion of the soil when the plant grows its roots and stem. The space between the potting soil level and the edge of the planter also helps to apply water efficiently without spilling outside. Potting mix was chosen rather than the real soil because container plants can thrive better in potting mix than the real soil. Figures 1 shows the experimental setup in the greenhouse for rosemary. A similar experimental setup was made for okra (Figure 2). The only difference in the experimental setup for okra is the planter size and shape. The planter used for okra is Grosfillex 15.79-in W x 21.17-in H Rust Resin Shell Planter, slightly taller than that used for rosemary. This is because okra is a relatively tall growing and deep-rooted plant than rosemary. The experiment with rose plants has just started (Figure 2). We could not start the irrigation experiment with bluebonnet because greenhouse space was not available until the beginning of May 2019. The irrigation experiment is conducted in a greenhouse using a randomized complete block design with three water treatments- tap water (control), well water (without treatment), and treated well water, using three replications for each plant type (Table 1).

Table 1 Experimental Setup

	Tap Water (control)	**Well water**	**Treated well water**
Okra	Experiment ongoing	Experiment ongoing	Experiment ongoing
Bluebonnet#	Could not start	Could not start	Could not start
Rosemary	Experiment ongoing	Experiment ongoing	Experiment ongoing
Rose	Experiment started	Experiment started	Experiment started

Bluebonnet experiment should have started in the fall. We couldn't start the experiment because greenhouse space was not available for a long time.

The irrigation water was applied to rosemary and okra plants under three treatments, as outlined in Table 1. We made sure that the plants are not water stressed. Because of the high heat in Stephenville and aggravation of heat in the greenhouse environment, water from the pots gets evaporated quickly. Also, the potting mix used in the experiment does not hold water for too long like how soil will hold water in field conditions. Therefore, we are irrigating the plants two times a week. The complete schedule used to irrigate the plants are outlined in Table 2. As of July 5, 2019, the plants are growing well in the greenhouse (Figure 3 and figure 4). The height of the plants and their physical appearance are monitored regularly to observe their growth in response to the application of water in different qualities (Figure 5).

Table 2 Irrigation Schedule for the experimental crops

Rosemary	**Okra**	**Rose**
05/17/2019		
05/23/2019		
05/28/2019		
05/31/2019		
06/03/2019		
06/07/2019		
06/11/2019	06/11/2019	
06/14/2019	06/14/2019	
06/18/2019	06/18/2019	
06/21/2019	06/21/2019	
06/25/2019	06/25/2019	
06/28/2019	06/28/2019	06/28/2019
07/03/2019	07/02/2019	07/02/2019

Untreated well water	Control (tap water)	Treated well water

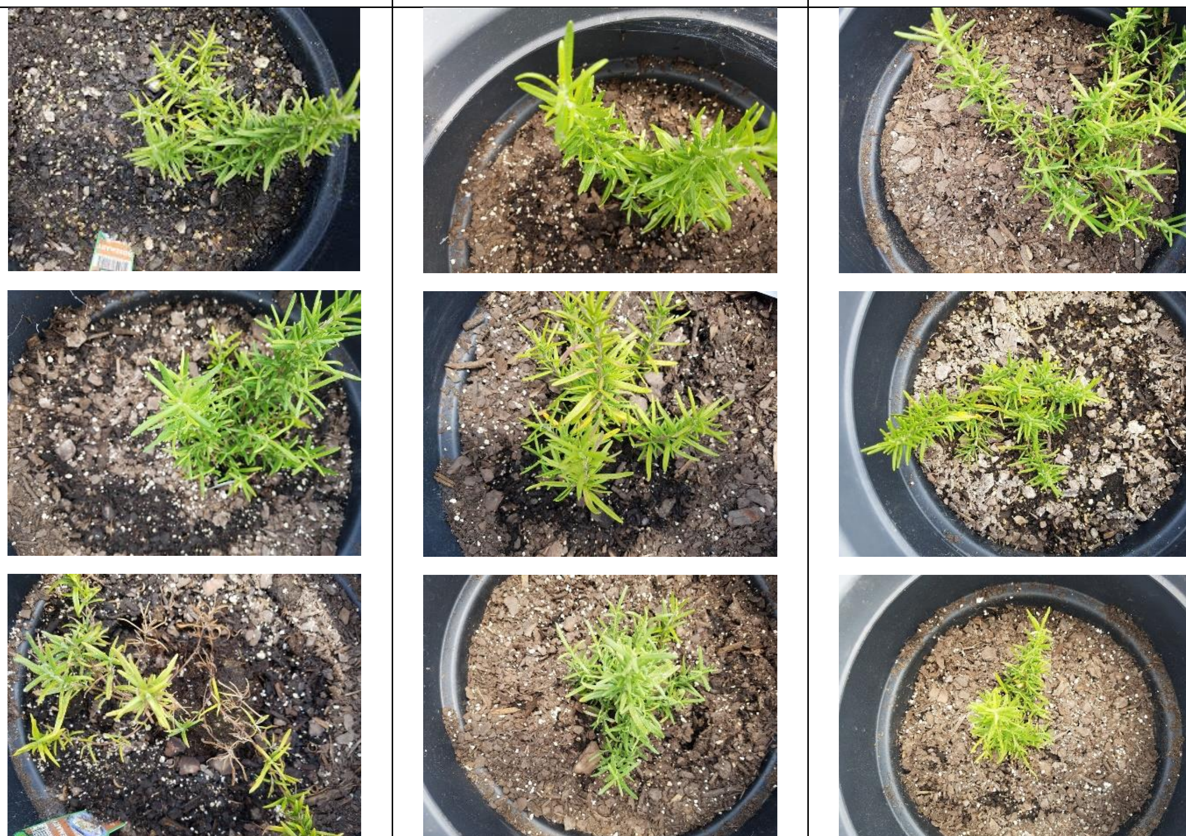

Figure 3 Status of the rosemary plants as of June 19, 2019

As of now, we can make the following preliminary conclusions:

1. One plant under “untreated” (Panel 3, bottom left in Figure 2) scenario, was not growing well. As of July 5, 2019, the plant is dead completely.
2. In general, rosemary is salinity tolerant. However, the well water from Dockum aquifer has high salinity . More than six weeks of continuous irrigation with well water from Dockum aquifer with high salinity appears to have caused the plant death. The other two plants in the untreated scenario have started showing yellowing of leaves. Also, there appears to be white salt deposits on the surface of the potting mix in all the untreated scenario.
3. The growth rate of rosemary plants in control treatment appears better than both treated and untreated scenarios (Figure 5). The growth of rosemary in treated scenario is better than the growth in untreated scenario (untreated scenario shows the least growth).
4. Okra needs a few more weeks of irrigation before analyzing anything on the plant response to irrigation.

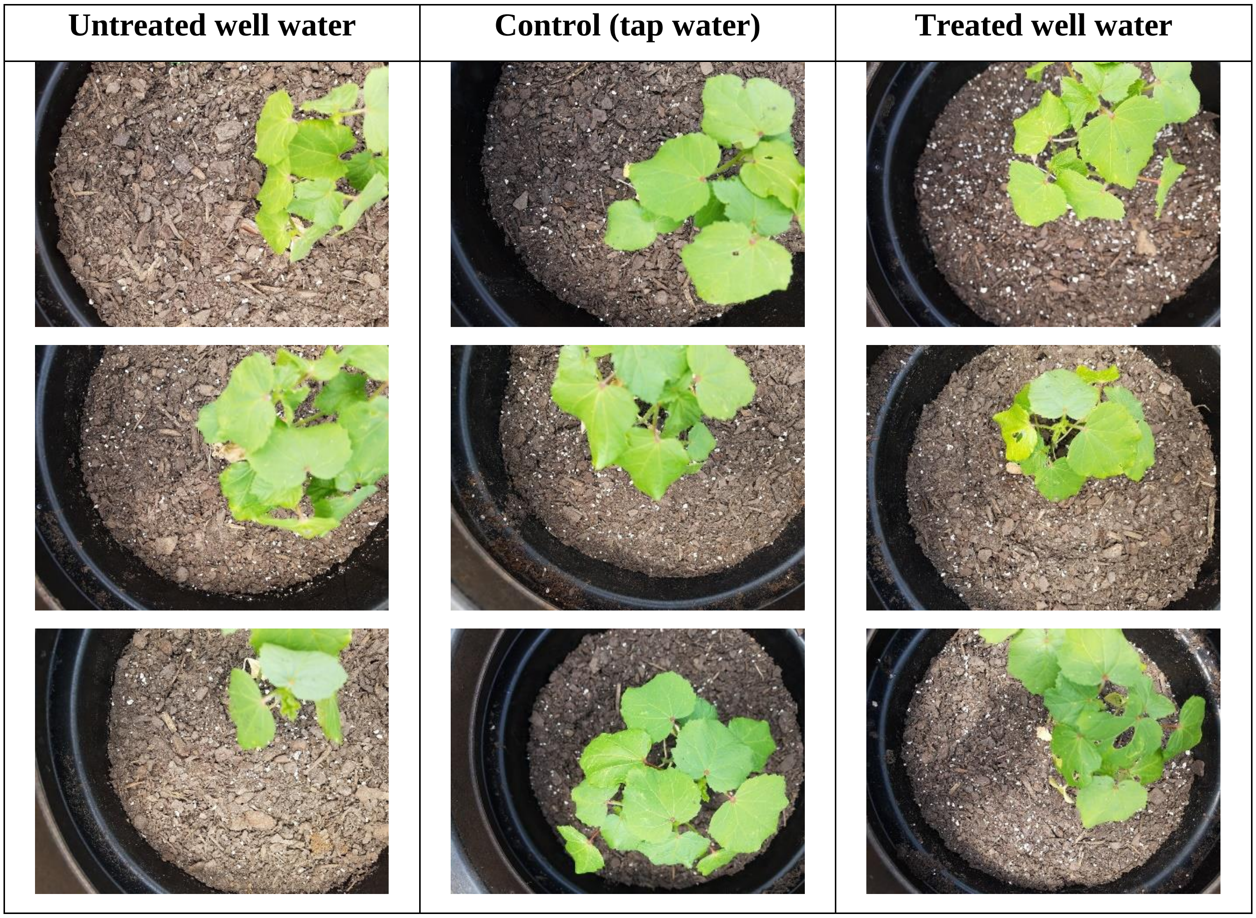

Figure 4 Status of the okra plants as of June 19, 2019

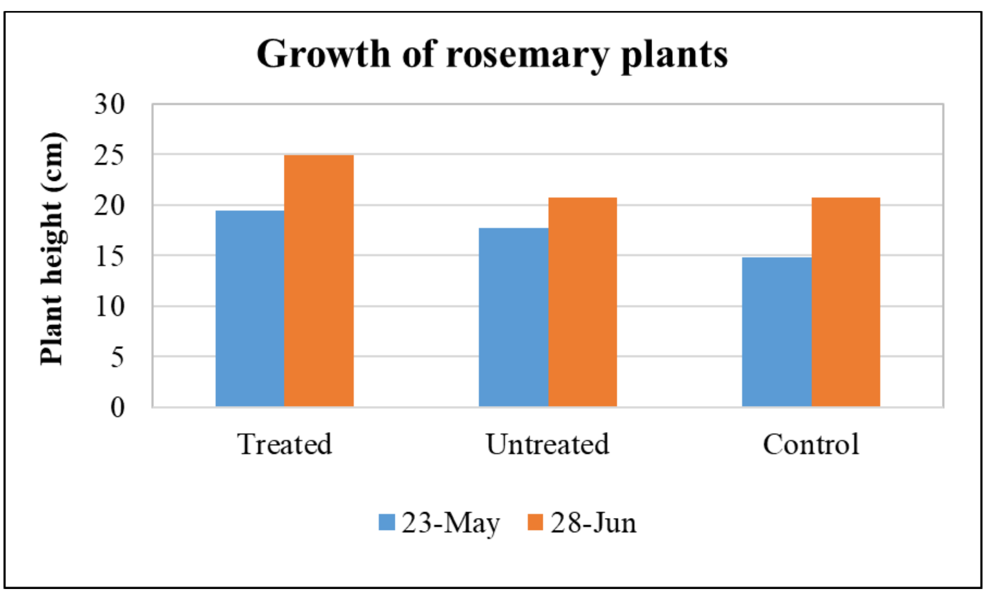

Figure 5 Growth of rosemary plants in three weeks from May 23

2) **Successes and setbacks observed with the project:**

Successes: From the series of experiments we were able to confirm that the plant based polysaccharides are capable of removing appreciable amounts of TDS, Anions and cations. The irrigation experiment shows the effects of treated and untreated water on plant growth. More experiments are performed to get additional data.

Setbacks:

1) Due to variable concentration of the pollutants in the water samples it was difficult to arrive at an optimum polymer dose and contact time.
2) Due to new building constructions in the campus, greenhouse was not available in time and the start of the irrigation experiment got delayed.

3) **Conservation impact to the district**

With the preliminary results that we got so far we are confident enough to say that these materials work in the type contaminants present in Dockum aquifer and will be an efficient alternative green materials for water treatment in the groundwater district. These materials being food grade will not have any adverse effect to the ecosystem. These new materials and methods will help in reducing the dissolved solids present in the water and help in reusing the contaminated water in the district.

4) **Budget Expense Report and remaining grant fund balance.**

	Cost ($)	Spent ($)	Balance
Travel to collect samples	$3000	$1180.34	1819.66
Student wages/salaries	$12,000	$9179.11	2820.89
Materials and Supplies	$ 12088.62	$12,355.08	-266.46
Total	$ 27088.62	$22,714.19	4374.43