NM WRRI Student Water Research Grant Report

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2. Project title: Assessment of Disinfection Byproducts (DBPs) formation in algae-treated wastewater for safer reuse in restricted applications

3. Research problem and research objectives:

Wastewater utilities in water-stressed regions are now considering the reuse of treated urban wastewaters as an option to manage their water portfolio in the face of freshwater shortages and droughts. Towards this end, a novel algal wastewater treatment system (A-WWTS) developed at New Mexico State University (NMSU) is being demonstrated at the Las Cruces Wastewater Treatment Plant. Previous studies have documented that this A-WWTS can remove organic carbon, nutrients, and pathogens in urban wastewater to below discharge permits. Under WRRI funding, we intend to assess the feasibility of this A-WWTS in recovering water for safer reuse in restricted applications. Possible reuse applications of the effluent of A-WWTS are non-food irrigation, landscaping, and recreational activities where human exposure is restricted [1]. It is proposed to compare the water quality of the effluent of A-WWTS against the guidelines for reuse of water to assure microbially-safe water by inhibiting bacterial regrowth at a low cost.

Traditionally, wastewater utilities have been using chlorine for disinfecting the effluent to ensure microbial safety and prevent bacterial regrowth. However, a serious concern about chlorination is the production of disinfection byproducts (DBPs) which are now recognized as human health hazards. Based on our previous work on the A-WWTS, it is hypothesized that its inherent disinfection capability can be beneficial in reducing the final disinfectant demand and the potential for DBPs formation. As such, the specific goal of this research is to evaluate DBP levels in the effluent of the A-WWTS in comparison to the water reuse guidelines.

Under WRRI funding, the goal of this research is to track nitrosamines (NA), a highly carcinogenic category of DBPs [2], in the chlorinated algal effluent. Specific tasks of this study are to:

1) Assess the variation of water quality parameters in chlorinated algal effluent (AE)
2) Determine the pH level and minimum chlorine dosage to maintain 0.5 mg/L chlorine residual after 30 minutes
3) Track NA concentrations as a function of operating conditions
4) Compare the effluent of A-WWTS with the guidelines for restricted reuse

4. Methodology employed

This study consisted of the following two experiments: Experiment 1) analyzing the variations of water quality parameters with excess chlorination of the algal effluent; and, Experiment 2) determining suitable operating conditions for chlorination of the algal effluent. Samples of the AE were collected at the end of 4 days of fed-batch processing and filtered through 1.5 μm filter papers to remove algae and other large particles. Following water quality parameters were measured in the AE; dissolved organic carbon (DOC) in terms of non-purgeable organic carbon (NPOC); UV absorbance at 254 nm; total nitrogen (T-N); inorganic nitrogen (Inorg-N); and pH. Organic nitrogen (Org-N) content and specific UV absorbance (SUVA) were calculated.

In Experiment 1, the Standard Method 5710 B was followed to assess the variation of water quality parameters after chlorination. Briefly, pH of the AE was increased to 7 and chlorinated with excess chlorine such that the residual chlorine level after 24 hours was 3-5 mg/L. In Experiment 2, algal effluent was chlorinated with three different initial chlorine concentrations at both pH 4 and 6. Residual chlorine level was measured after 30 minutes and dechlorinated with 10 mg of sodium sulphite to 100 mL sample. After dechlorination, samples were analyzed again for the above water quality parameters. These samples were further extracted by solid phase extraction to concentrate any formed NAs and analyzed via high-resolution nanoflow liquid chromatography/mass spectrometer (LC/MS). All experimental conditions were duplicated and repeated for 2 or 3 batches of the algal effluent. The experimental plan is summarized in Figure 1.

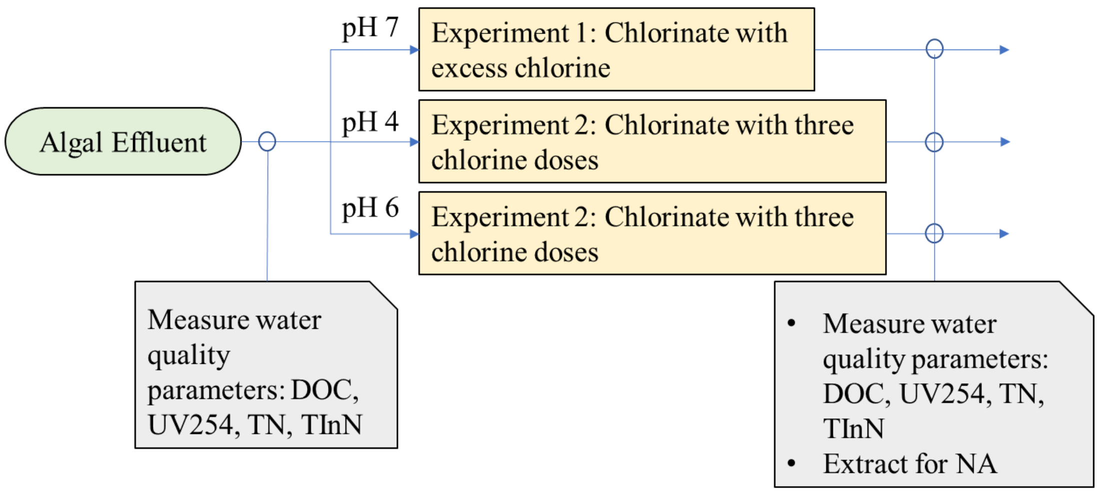

Figure 1: Schematic diagram of the experimental plan

5. Results

Even though the fecal coliform concentration in the algal effluent was well below the discharge standard (126 CFU/100mL), which was also below the detectable limits, a final disinfection process has to be included to ensure microbial safety and prevention of bacterial regrowth. If this treated water is to be reused, guidelines suggest at least 30 minutes of chlorination to a residual level of 0.5-1 mg/L [3], which provided the baseline for the study.

Figure 2 shows the results of Experiment 1, where the algal effluent was chlorinated with excess chlorine. As shown in Figure 2, dissolved organic carbon, organic nitrogen, and inorganic nitrogen concentrations decreased after 24 hrs of chlorination. The maximum average percentage reductions of DOC, organic-N, and inorganic-N due to chlorination are only 24, 35, and 16% respectively. These reductions suggest possible reactions of carbon and nitrogen with free chlorine and forming disinfection byproducts that need to be analyzed further. But the specific UV absorbance values of all raw algal effluents are below 2 L/mg-m indicating the presence of non-humic organics and thus indicate a low potential for DBP formation [4]. These findings could be merged to expect that chlorination of the algal effluent is less receptive to form carbonaceous DBPs but, might have a tendency to form nitrogenous DBPs such as nitrosamines.

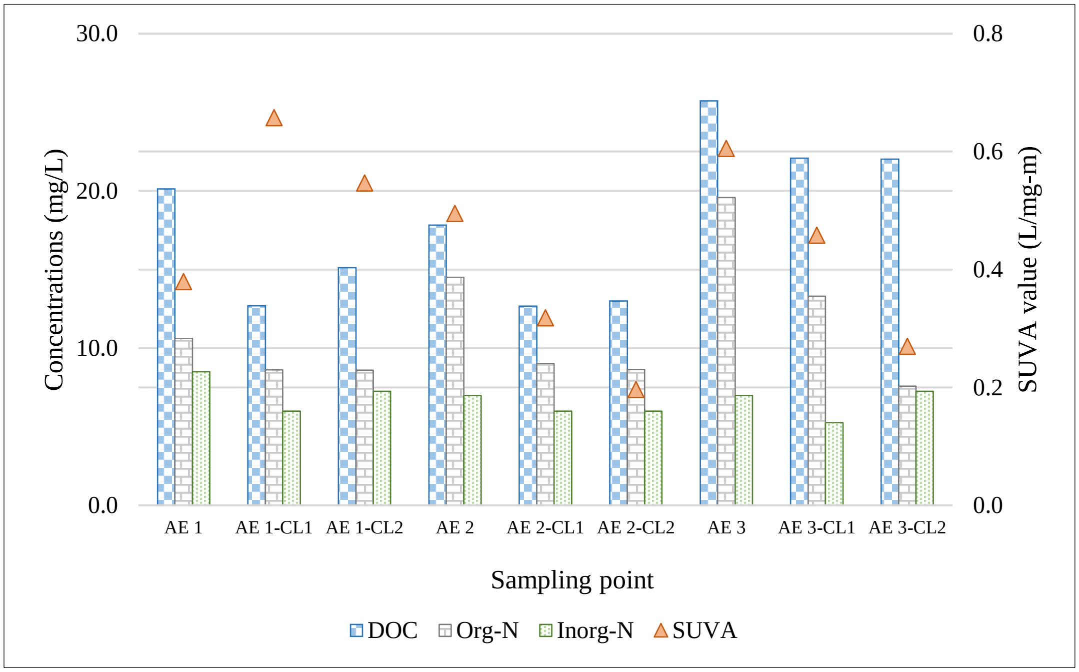

Figure 2: DOC, organic N, inorganic N, and SUVA variations of raw algal effluent and chlorinated (excess) effluent after 24 hrs; AE 1-3: raw AE from batches 1-3; AE CL1-2: duplicates of the chlorinated reactors

Experiment 2 was aimed at determining 1) suitable pH value for chlorination and 2) minimum required initial chlorine dose. Variations of residual free chlorine after 30 minutes of contact time for different initial chlorine concentrations at pH 4 and 6 are shown in Table 1. It is evident that to meet the regulation of 0.5-1 mg Cl_2/L after 30 minutes, chlorinating at pH 6 is suitable because it requires less chlorine dose (12 mg Cl_2/L of initial concentration). But, if the AE is chlorinated without pH adjustment, it will need more dosing of disinfectant. Hence, as a preliminary result, chlorinating after pH adjusting to 6 is considered favorable in reducing the disinfectant demand. To ensure that the chlorinated AE is safe for reuse, other water quality parameters and the presence of NAs are also analyzed.

Table 1: Residual free chlorine concentrations for different initial chlorine concentrations

Initial free chlorine concentration ($mg\ Cl_2/L$)	**Residual free chlorine after 30 minutes of contact time ($mg\ Cl_2/L$)**			
	pH 4		**pH 6**	
	AE 1	**AE 2**	**AE 1**	**AE 2**
15.7	0.16	0.11		
16.0	0.41	0.38		
18.0	0.61	0.65		
12.0			0.70	0.52
13.0			0.62	0.72
16.0			3.10	1.64

For further analysis, the lowest initial chlorine doses at both pH levels were selected. Figure 3 illustrates the variations of DOC, nitrogen, and SUVA after chlorinating with the lowest initial doses at pH 4 (15.7 mg Cl_2/L) and 6 (12 mg Cl_2/L). DOC concentrations at pH 6 are less than at pH 4. This implies that the organic carbon substances in the algal effluent react with more chlorine when pH was increased to 6 yielding more carbonaceous DBPs. But since the SUVA value of unchlorinated AE is below 2 L/mg-m, it could be expected that the organic carbon is transformed into other products. In contrast, the organic nitrogen compounds present in algal effluent tend to react with free chlorine at pH 4 than at pH 6. Hence, there is a risk of formation of nitrogen related DBPs (NAs) if chlorinated at pH 4.

The variation between reaction rates of chlorine with inorganic nitrogen at pH 4 and 6 is negligible. When comparing the final inorganic nitrogen concentrations from experiment 1 (5-8.5 mg N/L) and experiment 2 (7-9 mg N/L), it could be concluded that the reaction of inorganic N with chlorine is not pH-dependent and the reaction is faster within the first 30 minutes after chlorination. The results suggest and verify that the optimum condition to chlorinate the AE is to first adjust pH to 6 and then chlorinating with at least 12 mg Cl_2 per L of AE. Hence, the disinfectant demand for a 1 MGD plant would be 100 lb Cl_2/d.

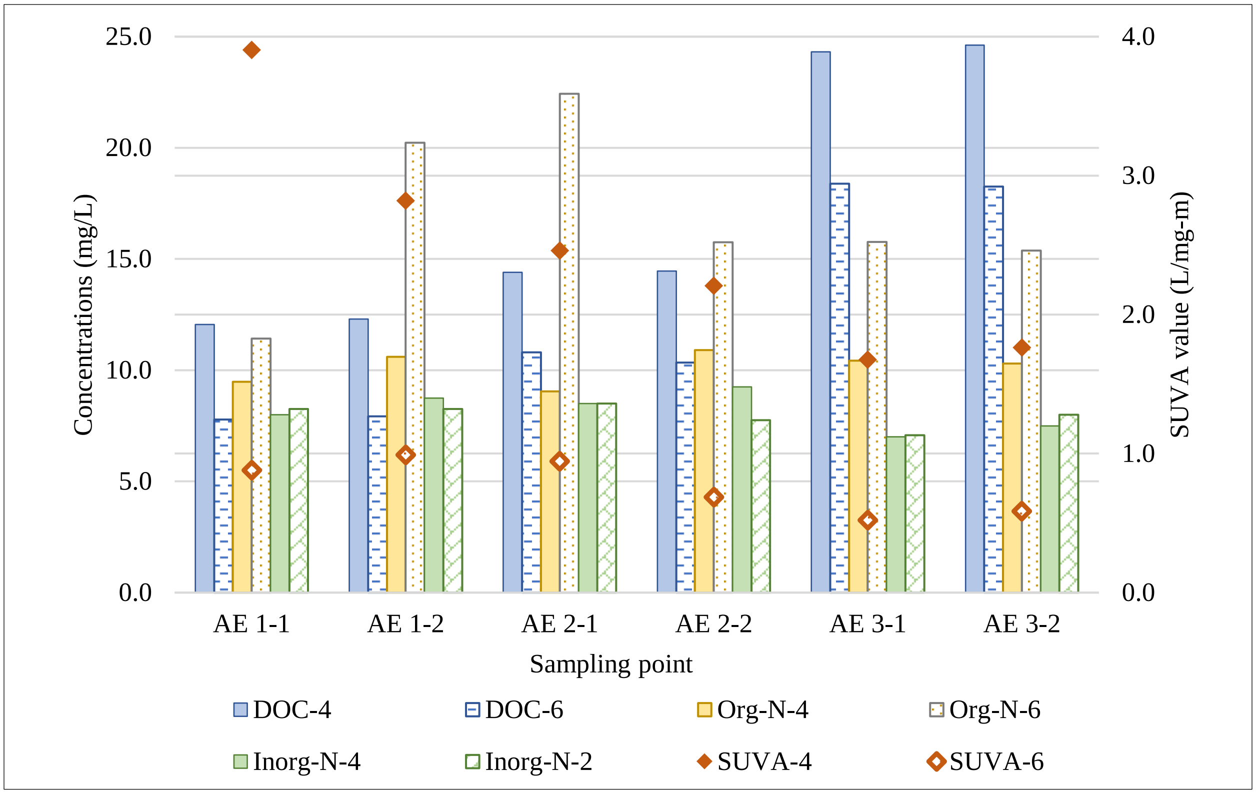

Figure 3: DOC, organic N, inorganic N, and SUVA variations of chlorinated algal effluent at the lowest initial chlorine dose at pH 4 and 6; AE 1-3: effluent from batches 1-3; AE1-1,1-2: duplicates of the chlorinated reactors; solid columns/points represent results at pH 4 and hatched columns/points represent results at pH 6

The above results on DBP formation are further verified by analyzing for seven nitrosamines in algal effluent chlorinated at the selected optimum conditions (pH 6 and 12 mg Cl_2/L initial concentration). The analyzed NAs are; N-nitrosodimethylamine, N-nitrosomethylethylamine, N-nitrosopyrrolidine, N-nitrosodiethylamine, N-nitrosopiperidine, N-Nitrosodi-n-propylamine, and N-nitrosodibutylamine. For comparison purposes, Figure 4 illustrates the expected peaks for each component when spiked with a standard at 0.05 ng/L. Figure 5 shows the observed peaks for the seven NAs in chlorinated AE. In comparison, it clearly demonstrates that none of the peaks in Figure 4 are observed in the mass spectrometric chromatograms of the AE in Figure 5, meaning, the NAs concentrations are below 0.05 ng/L level. This is well below the reuse guideline for nitrosamines at 10 ng/L set by California Department of Public Health. Hence, it is concluded that chlorination of the treated water under the selected conditions is safe for restricted reuse as the NAs concentrations are well below the guidelines.

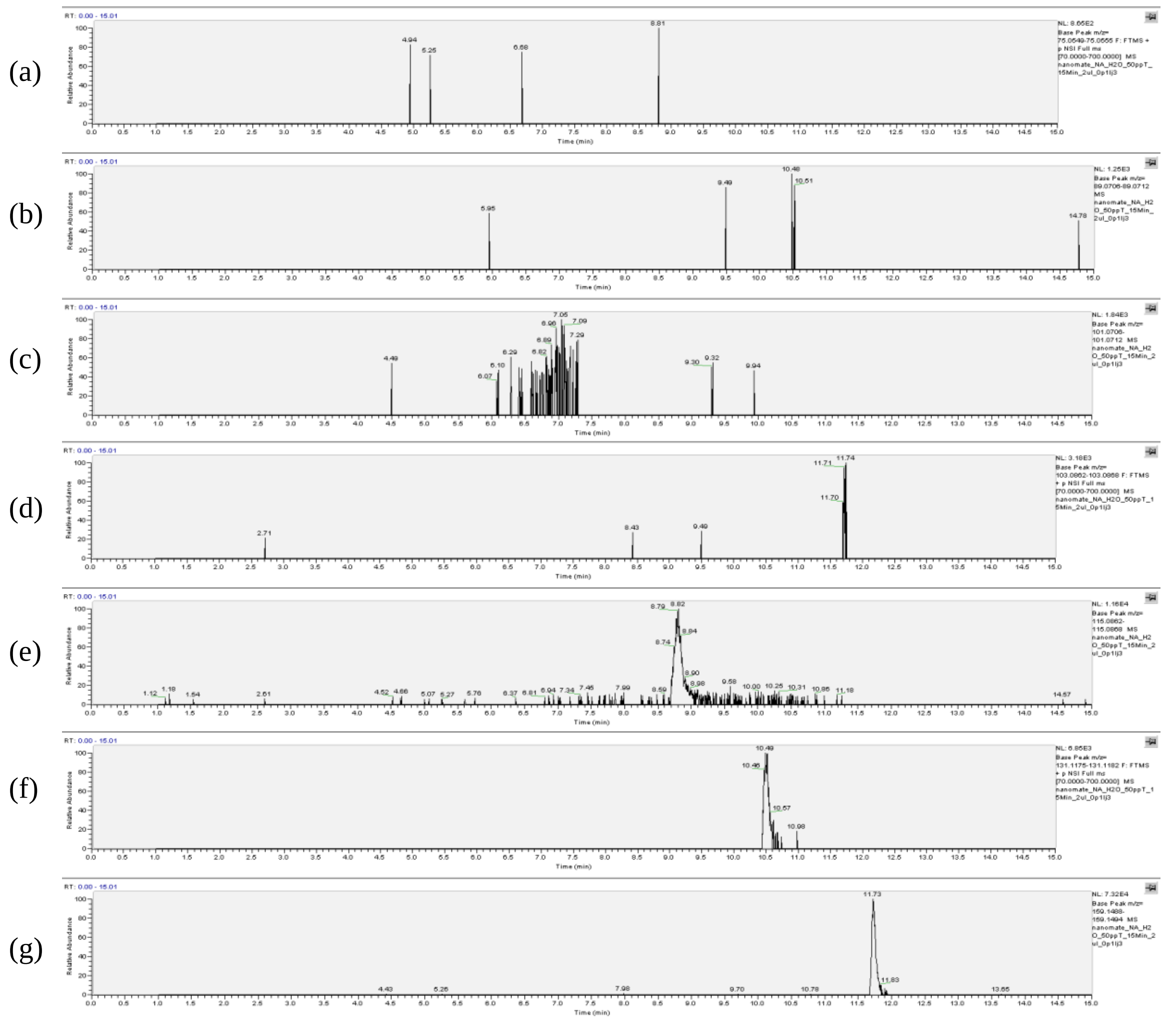

Figure 4: Standard peaks for seven nitrosamines at 0.05 ng/L concentration: (a) N-nitrosodimethylamine, (b) N-nitrosomethylethylamine, (c) N-nitrosopyrrolidine, (d) N-nitrosodiethylamine, (e) N-nitrosopiperidine, (f) N-Nitrosodi-n-propylamine, and (g) N-nitrosodibutylamine

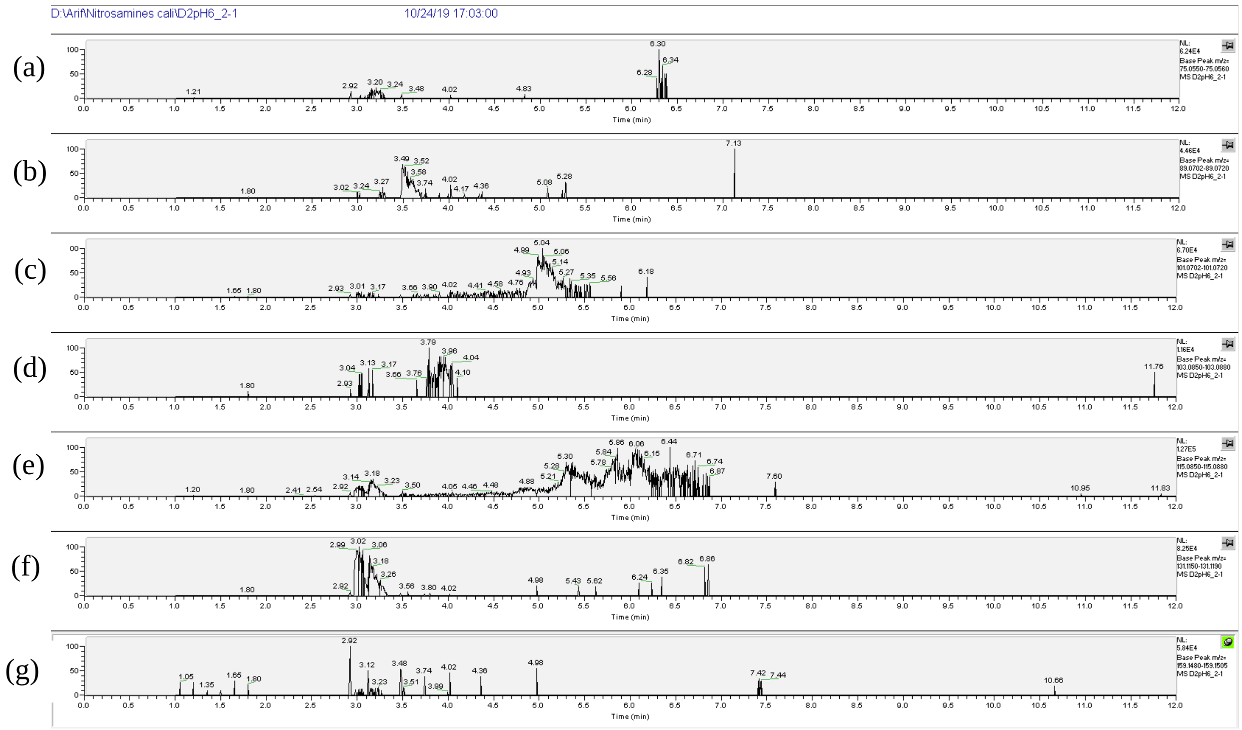

Figure 5: Observed peaks for seven nitrosamines analyzed after chlorinating the AE at pH 6 and 12 mg Cl_2/L initial concentration: (a) N-nitrosodimethylamine, (b) N-nitrosomethylethylamine, (c) N-nitrosopyrrolidine, (d) N-nitrosodiethylamine, (e) N-nitrosopiperidine, (f) N-Nitrosodi-n-propylamine, and (g) N-nitrosodibutylamine

6. Who will benefit from the results

The algae-based wastewater treatment system developed at NMSU has been demonstrated to be a sustainable alternative for the current energy intensive multi-step wastewater treatment systems. The inherent bacterial inactivation ability of the A-WWTS adds significant value to the system. Yet, the treated effluent cannot be discharged or diverted to reuse applications without post-disinfection process to ensure microbiologically safe water. Hence, chlorine is employed as the disinfectant in this study to demonstrate a cost-effective and environmentally friendly treatment option for safer reuse.

The findings of this study suggest that chlorinating at pH 6 would demand low chlorine dose and 12 mg Cl_2/L is identified as the minimum required dose to meet reuse regulation of residual free chlorine (0.5-1.0 mg Cl_2/L). It is further validated that chlorinating under these conditions form very low levels or zero nitrosamines indicating the potential for reuse of treated water. Hence, the chlorinated algal effluent is both biologically and chemically safe.

These results can be beneficial to wastewater utilities in providing sustainable utility services. Based on the preliminary findings, the algal effluent can be seen to have the potential to yield low-cost, high quality reclaimed water for safe reuse in restricted applications reducing the demand for the limited freshwater supplies.

7. Expenditure of the grant funds

Funds were utilized (100%) to provide summer-stipend to complete the research.

8. Presentations related to the project

Part of the results was presented at the 64th Annual New Mexico Water Conference held at Santa Fe, New Mexico.

9. Publications

It is expected to submit a paper on "Applicability of Algae-treated Chlorinated Wastewater for Restricted Reuse: Analysis of Disinfection Byproducts Formation" based on the results of this study.

10. Other students/faculties assisted with the project

Dr. T. Schaub: Director/Research Professor

Dr. A. Ahmed: Postdoctoral researcher

Miss K. Sparks: MS student

11. Special awards/achievements

12. Career plans

I am reading for a PhD in Environmental Engineering at New Mexico State University and planning to graduate by Fall 2020. As an Environmental Engineer, I am interested in water conservation and reuse. I am planning on a career related to the water/wastewater sector to contribute to the betterment of humans while preserving the environment.

References

[1] L. Wu, W. Chen, C. French, A. Chang, Safe application of reclaimed water reuse in the southwestern United States, UCANR Publ. 8357 (2009).

[2] W.A. Mitch, D.L. Sedlak, Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination, Environ. Sci. Technol. 36 (2002) 588–595. doi:10.1021/es010684q.

[3] US Environmental Protection Agency, Guidelines for Water Reuse (EPA/625/R-04/108), 2004.

[4] H.L. Tang, Y.-C. Chen, J.M. Regan, Y.F. Xie, Disinfection by-product formation potentials in wastewater effluents and their reductions in a wastewater treatment plant, J. Environ. Monit. 14 (2012) 1515–1522. doi:10.1039/c2em00015f.