Evaluation of Conventional Treated and UV-Ozone Treatment Water Processes for Organic Pollutants from Shendam Dam in Plateau State, Nigeria

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Abstract

The use of contaminated water makes human populations to suffer from water borne diseases. The potential application of ultraviolet-ozone synergy for the removal of organic pollutants in raw water source from Shendam in Plateau state, Nigeria was undertaken. The conventional and uv-ozone treated water samples were extracted with dichloromethane and screened with GC-MS for organic pollutants. GC-MS chromatogram for the conventional treated water yielded 18 different organic pollutants while the uv-ozone treated water yielded 8 different organic compounds. GC-MS of the solvent blank (dichloromethane) used as the control showed similar profile of organic compounds detected as those of uv-ozone treated water. The profile obtained indicated reduction in the number of the organic pollutants because most of the organic compounds detected in the conventional treated water were not detected in the uv-ozone treated water. The results obtained during the evaluation period indicated that the conventional treatment system is highly vulnerable to passing on contaminated treated water to the end user. Uv-ozone treatment system, therefore, can represent an alternative drinking water treatment option. The use of the uv-ozone treatment process could be integrated in a drinking water flow sheet to replace the conventional disinfection processes because it is effective and environmentally friendly.

Keywords: *Conventional treatment, Uv-ozone synergy, Hydroxyl radical, Shendam*

Introduction

Water is an indispensable resource and crucial to sustaining life. However, many poisonous substances including dangerous organic material from different sources find their ways into the water bodies, pollutes the water and causes considerable harm to humans and other species that use such water for drinking. The treatment of such water, therefore, becomes basic before they are used.

Shendam dam has been used to provide a store of water for agriculture, industrial uses, and treated using the conventional process for household uses including drinking.

Water treatment is the process of removing all those substances whether biological, physical or chemical that are potentially harmful to the water supply for human and domestic use.

Conventional water treatment plants use a combination of screening, coagulation/flocculation, sedimentation, filtration and disinfection to provide clean, safe drinking water to the public (Sani *et al*., 2021). The water treatment method may eliminate potential or certain harmful substances in the water to prevent the consumption of contaminated water sources that can cause potential health problems.

The conventional treatment uses chlorine which is effective at sanitizing drinking water (Sathasivam *et al*., 2016) but it can be difficult to handle without expertise and experience. It has the disadvantage of producing toxic disinfection by-products (Diana *et al*., 2019). Studies have found that chlorine itself is not the main problem; rather it has to do with what happens when the chlorine mix with any type of organic matter in the water. It is accepted only because of its low price (Mazhar *et al*., 2020) and not because it is the safest or most effective way to disinfect water.

The presence of hazardous micro pollutants in water is one of the main concerns in water management systems. These micro pollutants exists in low concentrations (Tijani *et al*., 2016) but these are possible hazards to humans and organisms using the water. There recalcitrant to microbiological degradation makes it difficult to deal with during conventional treatment process (Grandclément *et al*., 2017).

The synergistic effect of ozone and ultraviolet radiation can realize the efficient and stable degradation of these organic pollutants in complex water bodies, and the treatment capacity can be greatly improved (Lu *et al*., 2022).

The main principle mechanism of uv/ozone based treatment process is the use of uv light to initiate generation of hydroxyl radicals used to destroy persistent organic pollutants.

The combined use of UV and ozone promotes the formation of hydroxyl radicals by photolysis of ozone through a hydrogen peroxide pathway. Aqueous ozone absorbs UV radiation at wavelengths of 200 to 310 nm, and, in turn, decomposes to form hydrogen peroxide. Hydrogen peroxide then further reacts with UV to produce hydroxyl radicals. The formation process of·OH in O_3/UV system is as follows (Shao *et al*., 2019).

$$O3 + hv \rightarrow O_2 + O\cdot \qquad (1)$$

$$O\cdot + H_2O \rightarrow H_2O_2 \qquad (2)$$

$$H_2O_2 + hv \rightarrow 2\cdot OH \qquad (3)$$

Introducing the research progress of the UV- O_3 process in the treatment of trace organic pollutants and drinking water provides theoretical support for the practical application and prospects for applying the green advanced oxidation process in water treatment (Lu *et al*., 2022). The research is aimed at Screening the water samples, conventional and uv-ozone treated, for organic pollutants, and evaluating the treatment systems.

Materials and Methods

Sampling area

The sampling area considered for this research is a dam in Shendam LGA (8°43'N latitudes and 9°30' E longitude) in southern Plateau, Nigeria. The dam supplies water to a treatment plant which treats the water conventionally and distribute same for use by the public.

Sample collection and treatment

Water samples of about 4litres each were collected from Shendam dam and the conventional treated water from the treatment plant in dry season in clean plastic containers and stored in an ice bag at a low temperature of about 4°C. During the sampling, the plastic containers were rinsed with the sample water three times before collection.

The water samples from the dam (raw water) was subjected to a uv-ozone synergy treatment process. After effectively subjecting the raw water from the dam to the uv-ozone treatment processes, the water sample was then screened for the presence of organic pollutants. The conventional treated water was also sampled and screened for organic pollutants and comparison was made between the two treatment methods.

Extraction of Organic Pollutants from Water Samples

The extraction procedure described by Nuro *et al.* (2017) was used for the extraction of organic pollutants from the water samples. The Water samples each of 100 mL was poured into a separating funnel and 100 mL of organic solvent of dichloromethane was added and the mixture separated for about 15 minutes by thorough shaking, afterwards the extract was poured into a beaker and left for few minutes to evaporate, then to the remaining extract anhydrous sodium tetraoxosulphate (VI) (Na_2SO_4) in excess was added to absorb any remaining water in the sample and this was totaled into a vial bottle up to 2 mL ready for Gas Chromatography analysis.

Chromatographic Analysis

Gas Chromatography analyses were performed with a gas chromatograph equipped with Mass Spectrometer detector (GC/MS (Agilent 7890BGC /Agilent 5977A MSD) on extracts of the water samples.

Results and Discussion

The GC-MS results of the screened water samples, conventional and uv- ozone (AOP) treated water and reagent blank are presented in tables below alongside the chromatograms respectively. The interpretation of the mass spectrum GC-MS was conducted using the data based on National Institute for Standards and Technology (NIST) having more than 62,000 patterns. The spectra of the unknown compounds were compared with the spectrum of the known compounds stored in the NIST library. The name, molecular weight and structure of the components of the tested water samples were ascertained.

The peak area percent was used to estimate the amount of the various components detected in the samples. The method used the area of a component peak as a proportion of the total area of all the detected peaks to analyze quantity. The area of the component is proportional to the amount of the component reaching the detector.

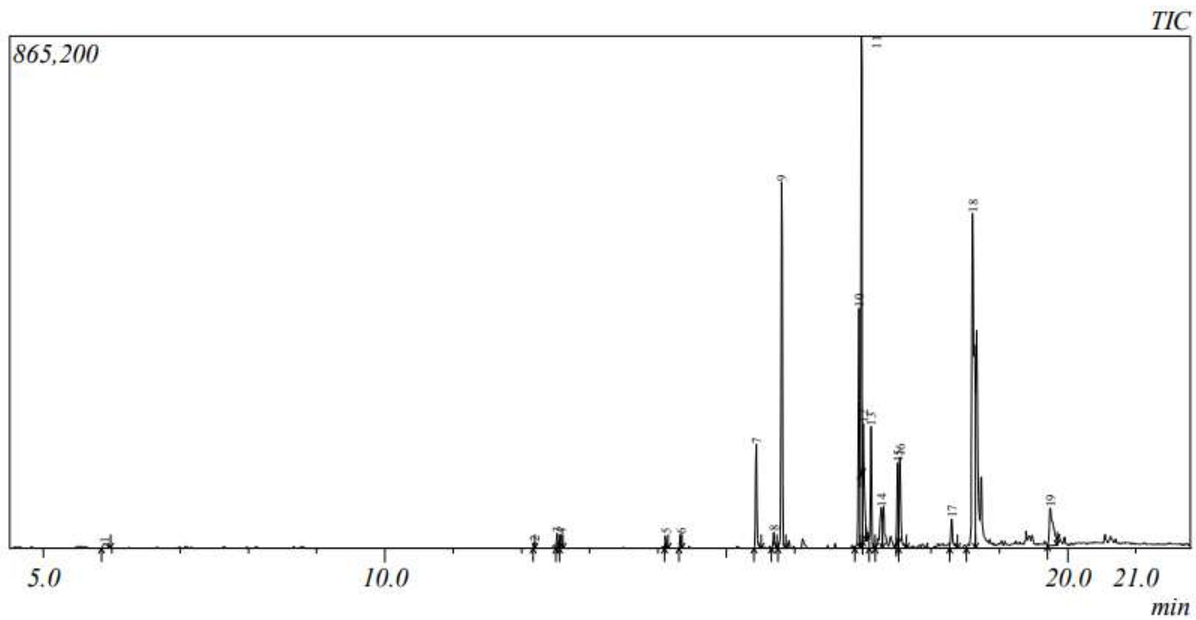

Figure 1: GC-MS Chromatogram for Conventional Treated Water from Shendam Dam

Table1: GC-MS Results for Conventional Treated Water from Shendam Dam

S/N	Name of compound	Retention time	% Area concentration
	Aliphatic compounds		
1	2,2-dimethyl, butane	12.187	0.19
	Carboxylic Acid		
2	Pentanoic acid, 2-methyl	12.577	0.58
	Esters		
3	Pentanoic acid, 5-hydroxy-2,4-di-t-butylphenyl ester	12.525	0.60
4	Tetradecanoic acid, 10,13-dimethyl-, methyl ester	14.328	0.52
5	Hexadecanoic acid, methyl ester	15.811	14.28
6	9,12-Octadecadienoic acid, methyl ester	16.941	9.53
7	(E)-9-Octadecenoic acid, methyl ester	16.978	16.92
8	(Z)- 9-Octadecenoic acid, methyl ester	17.008	4.48
9	Methyl stearate	17.117	4.40
10	Methyl-10-trans-12-cis-octadecadienoate	17.512	3.33
11	Eicosanoic acid, methyl ester	18.303	1.59
	Phthalates		
12	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	15.440	4.02
	Alcohols		

13	cis-9-Tetradecen-1-ol	17.268	3.23
	Amides		
14	Octadecanamide	17.543	4.11
15	(Z)-9-Octadecenamide	18.610	25.99
	Ketones		
16	Acetophenone	5.893	0.66
17	3,5-Dimethyl-4-octanone	14.109	0.52
	Halogenated Aliphatics		
18	1-iodo-Nonane	15.692	0.86

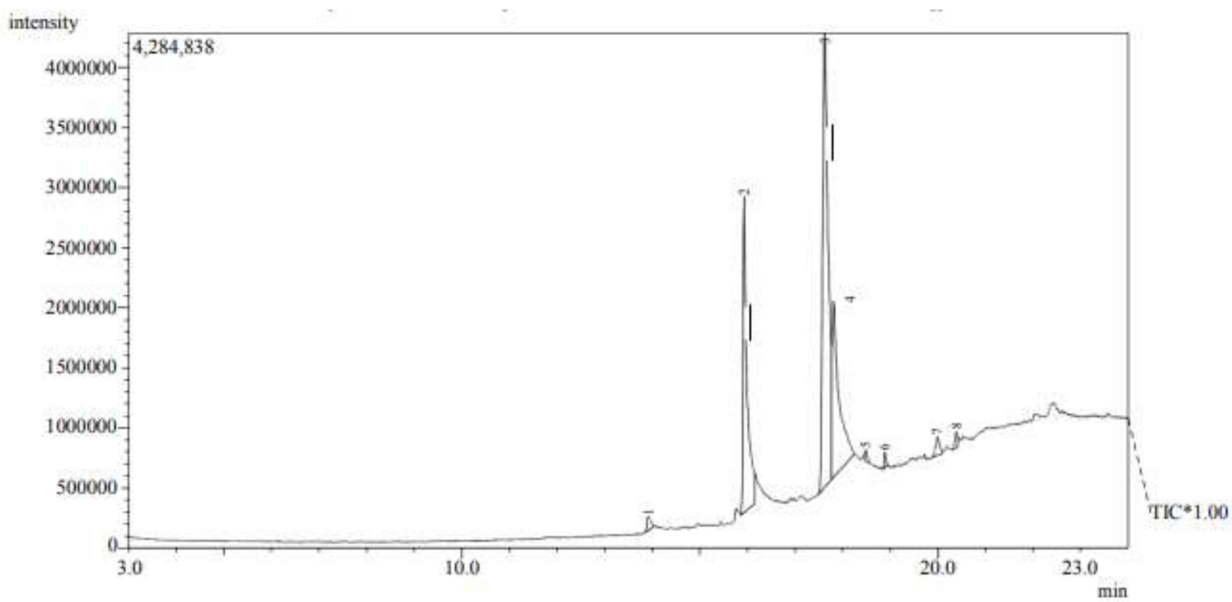

Figure 2: **GC-MS chromatogram for Uv-Ozone Treated Water from Shendam Dam**

Table 2: GC-MS Results for Uv-Ozone (AOP) Treated Water from Shendam Dam

S/N	Name of compound	Retention time	% Area concentration
	Carboxylic Acid		
1	tetradecanoic acid	13.916	1.04
2	hexadecanoic acid	15.933	23.90
3	oleic acid	17.625	48.52
4	stearic acid	17.810	23.23
	Ester		
5	hexadecanoic acid-2,3-dihydroxy propyl ester	18.461	0.47
	Alcohol		
6	2-butyl-1-octanol	18.889	0.57
7	dodeca-1,6-dien-12-ol	20.385	0.75
	Aldehyde		
8	9-tetradecenal	19.994	1.52

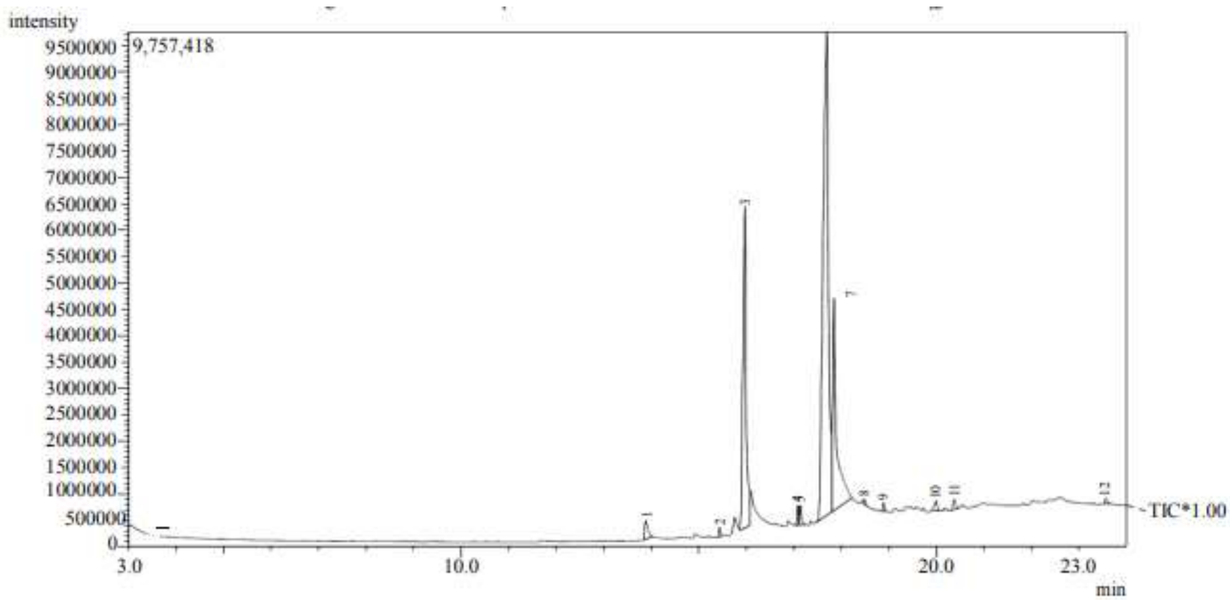

Figure 3: GC-MS Chromatogram for Reagent Blank

Table 3: GC-MS Results for Reagent Blank

S/N	Name of compound	Retention time	% Area concentration
	Carboxylic Acid		
1	tetradecanoic acid	13.885	1.29
2	hexadecanoic acid	13.885	22.18
3	oleic acid	17.693	55.54
4	stearic acid	17.846	17.42
	Ester		
5	hexadecanoic acid methyl ester	15.435	0.34
6	9, 12-octadecanoic acid, methyl ester	17.086	0.64
7	11-octadecenoic acid, methyl ester	17.135	0.78
8	hexadecanoic acid-2, 3-dihydroxy propyl ester	18.488	0.16
	Alcohol		
9	2-butyl-1-octanol	18.887	0.30
10	E, E-2, 13-octadecadien-1-ol	20.376	0.57
	Aldehyde		
11	9-tetradecenal	19.989	0.53
12	Squalene	23.571	0.24

The greatest threat to the water systems are contaminants that are water soluble, environmentally stable, highly toxic or infectious, available in large quantities, tasteless and odorless, and not affected by treatment processes. According to Shumbula *et al.* (2021), the conventional method of water treatment does not always allow the removal of all undesired substances. The method may just transfer impurities from one medium to another. A study conducted by Waterhoff *et al.* (2005) concluded that conventional water treatment processes can achieve some chemical removal, but specific chemical constituents are difficult to target and removal is sporadic.

A wide range of organic compounds were detected in the conventional treated water sample. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in the conventional treatment systems due to their resistance to degradation and toxic effect. The conventional treatment plant in operation was not designed with the purpose of eliminating organic pollutants. The treatment process is not generally targeted at removing chemicals: rather, it is aimed to remove sediments, pollutants associated with sediments and microorganisms through use of chlorine as disinfectant. Degradation of these organic pollutants become so difficult, therefore their continuous introduction in the drinking water. This allows the discharge of the pollutants into drinking water and presents a challenge that calls for modification of the conventional treatment protocol.

Ultraviolet (uv) radiation and ozone are clearly established as viable secondary disinfection methods (Puspita *et al*., 2015). It is logical to combine the two for better potency. This research work utilized the synergistic effect of ultraviolet (uv) radiation and ozone in combination for disinfection and oxidation purposes. This synergistic action as observed by many researchers has been attributed to the formation of hydroxyl ($^{\bullet}OH$) radicals when UV interacts with ozone in the water medium. According Denkewicz (2015), the potent nature of hydroxyl radicals results in what is effectively a one-two-three punch when uv and ozone are used together. Magbanua *et al*. (2006) attributed the synergy associated with uv/ozone water treatment to the presence of supplementary hydroxyl radicals. While ultraviolet has virtually no oxidizing ability, the resulting hydroxyl radical has (Gligorovski *et al*., 2015). The hydroxyl radical is a powerful oxidant species that can oxidize and mineralize almost any chemical compound yielding environmentally benign CO_2 and inorganic ions (Wols and Hofman-Caris, 2012). The free radical can also damage microbial cells by attacking cell wall, cytoplasmic membrane and intracellular structure (Aprioku, 2013).

Typical gas chromatogram obtained for the uv-ozone treatment of the water samples indicated reduction in the number of prominent peaks of the organic pollutants consequently the number of organic pollutants.

The conventional treated water samples indicated 18 prominent peaks (Figure 1 and Table 1) of various organic pollutants. The uv-ozone treatment process had 8 prominent peaks (Figure 2 and Table 2) of various organic pollutants as observed from the chromatogram for the water sample which include; long chain carboxylic acid, esters, alcohols, and aldehydes. These compounds are identified as contaminants emanating from the reagent (DCM) used for the extraction and not essentially from treated water sample.
In the work of Cheema *et al.* (2018), it was found that various DBP from swimming pool water were eliminated by continuous combined UV and ozone system. The reagent blank which served as control allows to identify and provided a background interference and contaminants from the

dichloromethane (DCM) used for the extraction. Few of the organic compounds were identified as contaminants as shown in Figure 3 and Table 3.

Peyton *et al.* (1982) demonstrated the efficiency of uv-ozone system for organic compounds especially to eliminate tetra chloromethane from water compared to ozonation and photolysis only. In the work of Charles *et al.* (2014), using the uv-ozone system, complete mineralization of organic compounds was achieved. Ding *et al.* (2014) also demonstrated degradation of trichloronitromethane in drinking water. These treatments were facilitated through the production of highly reactive hydroxyl radicals (•OH) which rapidly and with high unselectivity react with the majority of organic compounds leading to their mineralization or transformation to less toxic products.

Uv-ozone treatment process in this study showed significant improvement in the quality of the resulting water.

Conclusion

Screening of the water samples collected for the conventional treated water from Shendam using GC-MS indicated that the conventional treated water sample was highly contaminated with organic pollutants including several hydrocarbons, long chain carboxylic acids, esters, several aromatic compounds, ketones, aldehydes, alcohols and many others which compromised the quality of drinking water for population who largely depend on the water. The uv/ozone treatment showed far less of the organic pollutants.

The results obtained during the evaluation period indicated that the conventional treatment system is highly vulnerable to passing on contaminated treated water to the end user.

Both the plant operators and the communities confirmed that the conventional treatment plant do not operate at optimal level and often passed on sub-standard water.

According to Magbanua *et al.* (2006), the synergy associated with uv-ozone water treatment is attributed to the presence of supplementary hydroxyl radicals.

Uv-ozone treatment system, therefore, represent an alternative drinking water treatment option.

References

Aprioku, J.S. (2013). Pharmacology of free radicals and the impact of reactive oxygen species on the testis. *Journal of reproduction & infertility*, *14*(4), p.158

Charles, J., Crini, G., Morin-Crini, N., Badot, P.M., Trunfio, G., Sancey, B., De Carvalho, M., Bradu, C., Avramescu, S., Winterton, P. and Gavoille, S. (2014). Advanced oxidation (UV-ozone) and cyclodextrin sorption: effects of individual and combined action on the chemical abatement of organic pollutants in industrial effluents. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(2), 603-608

Cheema, W. A., Andersen, H. R., Kaarsholm, K.M.S. (2018). Improved DBP elimination from swimming pool water by continuous combined UV and ozone treatment, Water Research
doi: https://doi.org/10.1016/j.watres.2018.09.030

Denkewicz, R. (2015). Combining UV & ozone for increased disinfection and oxidation efficacy; Water Quality Products, 16-19. Retrieved from www.wqpmag.com

Diana, M., Felipe-Sotelo, M. and Bond, T. (2019). Review-Disinfection by-products potentially responsible for the association between chlorinated drinking water and bladder cancer: a review. Water Resources, 162, 492-504

Ding, S., Deng, Y., Bond, T., Fang, C., Cao, Z., and Chu, W. (2019). Disinfection byproduct formation during drinking water treatment and distribution: A review of unintended effects of engineering agents and materials. *Water research*, *160*, 313-329

Gligorovski, S., Strekowski, R., Barbati, S. and Vione, D. (2015). Environmental implications of hydroxyl radicals (•OH). *Chemical reviews*, *115*(24), 13051-13092

Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., Roche, N. and Doumenq, P. (2017). From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review. *Water research*, *111*, 297-317

Lu, H., Li, Q. and Feng, W. (2022). Application progress of O_3/UV advanced oxidation technology in the treatment of organic pollutants in water. *Sustainability*, *14*(3), p.1556

Magbanua, B.S., Sauvant, G. and Truax, D.D. (2006). "Combined Ozone and Ultraviolet Inactivation of Escherichia coli," Journal of Environmental Science and Health, Part A, 41 (6): 1043-1055

Mazhar, M.A., Khan, N.A., Ahmed, S., Khan, A.H.,Hussaini, A., Rahisuddin Changani,F., Yousefi, M., Ahmadi, S. and Vambol, S. (2020). Chlorination disinfection by-products in municipal drinking water-A review. Journal of clean water production 123159. https//doi.org/10.1016/j.jclepro.2020.123159

Nuro, A., Marku, E., Murtaj, B. and Plaku, V. (2017). Organic pollutants in water samples of Vjosa River–Albania. Zastita Materijala 58(3):385–393; doi: 10.5937/ZasMat1703385N

Peyton, G.R., Huang, F.Y., Burleson, J.L. and Glaze, W.H. (1982). Destruction of pollutants in water with ozone in combination with ultraviolet radiation.1. General principles and oxidation of tetrachloroethylene. *Environmental Science & Technology*, *16*(8), 448-453

Puspita, P., Roddick, F. and Porter, N. (2015). Efficiency of sequential ozone and UV-based treatments for the treatment of secondary effluent. *Chemical Engineering Journal*, *268*, 337-347

Sani, G.M., Alyasa'u, J. and Bello, M. (2021). Design and Construction of a Simple Portable Water Treatment Plant for Use in Rural Areas.

Sathasivam, R., Ebenezer, V., Guo, R. and Ki, J.S. (2016). Physiological and biochemical responses of the freshwater green algae Closterium ehrenbergii to the common disinfectant chlorine. *Ecotoxicology and Environmental Safety*, *133*, 501-508.

Shao, Q., Wang, Y., Li, J., Li, M.K., Li, J. and Qiang, Z.M. (2019). Technical principle and research progress of UV/O3 process in water treatment. China Water Wastewater, 35, 16–23.

Shumbula, P., Maswanganyi, C. and Shumbula, N. (2021). Type, Sources, Methods and Treatment of Organic Pollutants in Wastewater. In *Persistent Organic Pollutants (POPs)-Monitoring, Impact and Treatment*. IntechOpen

Tijani, J.O., Fatoba, O.O., Babajide, O.O. and Petrik, L.F. (2016). Pharmaceuticals, endocrine disruptors, personal care products, nanomaterials and perfluorinated pollutants: a review. *Environmental chemistry letters*, *14*, 27-49

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005). Fate of endocrine-disruptor, pharmaceutical, and personal care products chemicals during simulated drinking water treatment processes. *Environmental Science Technology*, 39(17):6649-6663

Wols, B. and Hofman-Caris, C. (2012). Review of photochemical radiation constants of organic micro pollutants required for UV advanced oxidation processes in water. *Water Resources*, 46: 2815 - 2827