Frontiers in Advanced Materials Research

# Degradation of telmisartan (TELMA-H) compounds in aqueous solution using non-thermal atmospheric pressure plasma jet

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**ABSTRACT:** In this study we investigate the degradation of telmisartan (Telma-H) in simulated aqueous solution using non-thermal atmospheric pressure plasma jet (APPJ). Aqueous solution containing Telma-H was treated with APPJ as a function of applied potential and reaction time. The degradation of Telma-H was investigated by means of UV-Visible spectroscopy. Optical emission spectra (OES) of the plasma jet was used to identify the reactive species that contributed to degrade Telma H compounds. The variation of pH and conductivity of the plasma treated Telma H aqueous solution was also measured.

**Keywords:** T-H wastewater, degradation, OES, APPJ, EC.

## 1. Introduction

Pollution of water resources and aquatic environments like river, pond, and ground water by organic compounds and pharmaceuticals is a serious environmental problem in recent years. The presence of pharmaceutical and medical wastes in the green environment is a matter of serious concern as it affects living organisms and ecosystems [1]. The pharmaceutical compounds pollute water sources via animal and human medical waste containing drug, large amount emission from pharmaceutical production sites, direct disposal of unused medicine by hospitals and human beings. Furthermore, the use of these pharmaceutical related products cannot be reduced or eliminated due to the increasing population growth. Most of the pharmaceutical compounds are non-biodegradable and stable in aquatic environment. Concurrently, many pharmaceutical compounds are harmful even in very low concentration [2-3] and therefore, it is necessary to develop efficient water treatment process for reducing or eliminating pharmaceutical wastes in aquatic environments. Conventional methods like filtration, sedimentation, biodegradation are ineffective to remove pharmaceutical compounds and organic compounds. Advanced oxidation process (AOPs) can be used to for degradation and elimination of pharmaceutical wastes efficiently. AOPs such as non-thermal atmospheric pressure plasma jet (APPJ) process are very effective and efficient alternative to conventional methods. Since last decade, the APPJ treatment process has received considerable attention for removal of pharmaceuticals and toxic organic compounds from water.

Furthermore, in APPJ-assisted AOP high energetic nitrogen, oxygen species, and OH radicals are generated, which destroy and oxidize the organic molecules. The APPJ assisted process is eco-friendly and ensures complete destruction and removal of organic compounds [4-5]. The pharmaceutical compound T-H tablet (medicinal compound containing Telmisartan and Hydrochlorothiazide) is widely used for treatment of high blood pressure, kidney failure, and liver failure [6]. The aim of the present work is to study the degradation of commercially available T-H tablet using non-thermal APPJ. The degradation of the T-H tablet was investigated with respect to various plasma parameters such as applied potential and treatment times. Degradation of the T-H tablet in aqueous solution was carried out and the degradation products were characterized using various analytical techniques.

## 2. Experimental Procedure

Commercially available pharmaceutical drug Telma-H tablet was used for the studies. A stock solution of T-H drug in deionized water containing $10^{-4}$ mole concentration of the drug was prepared and samples from this stock solution were used for experiments. Samples of the aqueous solution of the drug were treated by APPJ at different applied potentials (29, 31 and 33 kV) and treatment time (05, 10, 15, 20 and 25 min).

### 2.1 Non-Thermal Atmospheric Pressure Plasma Jet (APPJ)

The atmospheric pressure plasma jet (APPJ) device consists of a copper rod and copper ring, which act as the live electrode(cathode) and ground electrode respectively.
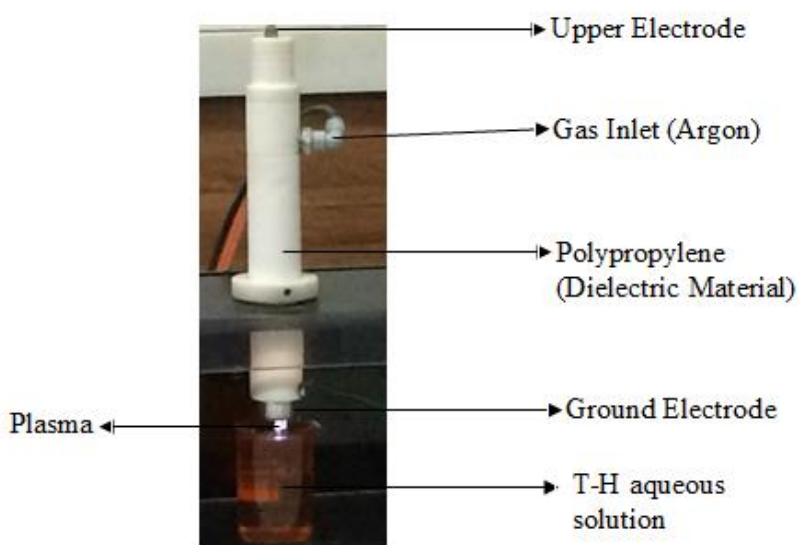
Fig 1. Photographic image of Non-thermal APPJ

Table 1. typical parameter of plasma treatment of aqueous solution of T-H drug

| Applied Potential | 29, 31 and 33 kV |
|---|---|
| Treatment time | 05, 10, 15, 20 and 25 minutes |
| Distance between live electrode and ground | 2.5 cm |
| Distance between the plasma torch and water surface | 5 mm |
| Plasma forming gas | Argon |
| Ar gas flow rate | 9000 sccm |

The electrodes are isolated by a dielectric material such as polypropylene (**Fig.1**) [7]. A high-voltage (40 kV) and high-frequency (30 kHz/ MHz) power supply was used as the power source to generate the plasma. Furthermore, argon gas was used as the plasma-generating gas and carrier gas. The plasma treatment experiments were carried out at various applied potentials with constant gas flow rate to generate the non-thermal plasma jet. The experimental parameters used for APPJ- assisted T-H drug degradation are listed in Table.1.

## 2.2 Analysis of the plasma treated samples

Aqueous samples of T-H pharmaceutical solution were analysed by various analytical tools after exposure to APPJ. The concentration of the T-H drug was measured spectrophotometric ally (Ocean Optics HR 4000) after plasma exposure. The electrical conductivity of the samples was measured using an Elico digital electrical conductivity meter-611 (Eloco Ltd, India) and pH of the water samples was measured using HANNA pH meter.

## 3. Results and Discussion

### 3.1 Optical Emission spectra analysis of RONS and Argon emission.

Fig 2a and 2b show the optical emission spectra of the APPJ (without the sample) and the plasma jet during plasma treatment respectively. The Ar-plasma jet was generated at 29 kV and it exhibits well-defined argon emission peaks in the wavelength range of 650-900 nm. Spectral peak of weaker intensity, attributed to OH-radicals

Was also observed at 309 nm. The OH radicals are produced as a consequence of the plasma jet interacting with water molecules and oxygen in the surrounding atmospheric. The intensities of the spectral peaks of OH radicals and argon emission lines were found to increase with increasing applied potential and this may be caused by higher energy electrons and excited atoms produced at higher potential.

The generation of reactive oxygen and nitrogen (RONS) species was investigated by OES (Fig 2b) during plasma treatment. The most intense argon emission lines can be found in the wavelength region of 680-850 nm. The plasma jet also produced a significant amount of OH radicals, first and second positive species of $N_2$ and atomic $O_2$ at 309 nm, 320-400 nm ,774 nm, and 842 nm respectively [8-9].  These emission spectral lines result by interaction of the plasma jet with the drug sample solution and water vapour and air in the surrounding atmosphere and consequent formation of OH radicals and reactive nitrogen species. It was also observed that the concentration of RONS species and hence the spectral intensity increased with increasing applied potential. Subsequently, these reactive species interact with water molecules to ionize and oxidize the pharmaceutical drug molecules to nontoxic simpler species. Therefore, the RONS species play an important role in the degradation of T-H molecules.
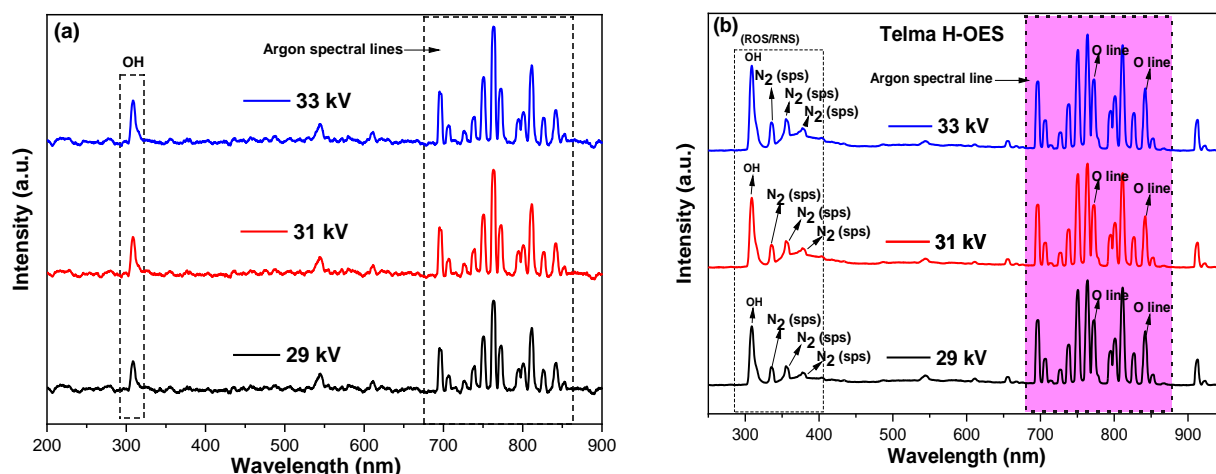
**Fig 2.** The optical emission spectrum of argon spectral lines with and without T-H aqueous solution.
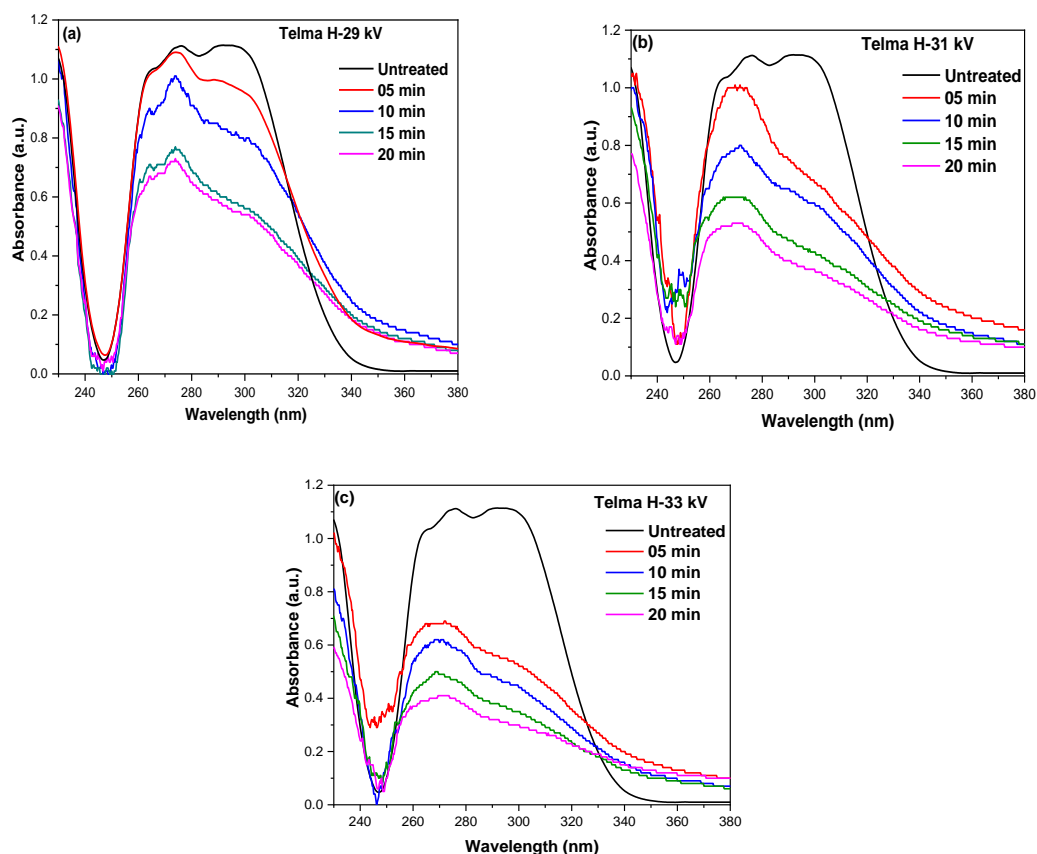


**Fig .3.** the UV-visible absorption spectrum of Telma-H

### 3.2 UV-Visible absorption analysis

The T-H drug concentration in the aqueous solution was measured by UV-Visible absorption spectroscopy after plasma exposure at different discharge potentials and reaction time. The results are depicted in Fig 3, which clearly shows that the T-H concentration decreases after exposure to plasma. It is further found that the decrease in drug concentration   is more as the exposure time increases and also as the discharge potential is increased. The degradation of the T-H drug by plasma treatment into simpler organic species is evident from the above results. The highest peak intensity of T-H was observed at 274 and 293 nm [6]. The intensity of these peaks decreased with increasing plasma exposure time at 29 kV of discharge potential due to degradation of the drug molecules; the intensity of absorbance peak is a direct indicator of the presence of T-H molecules in the aqueous solution.
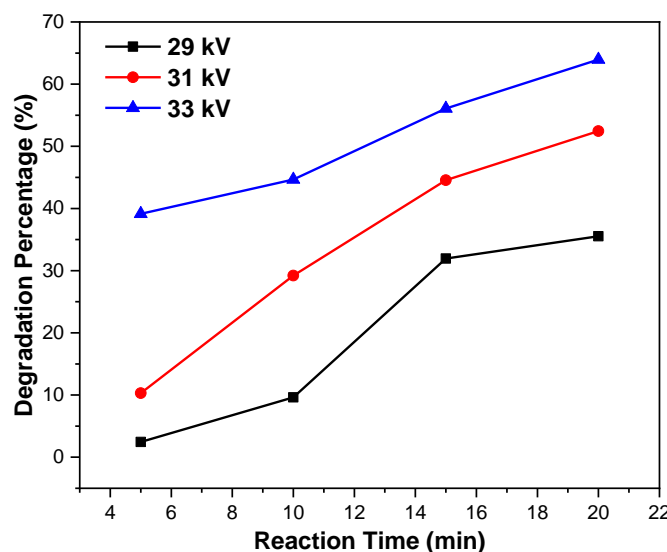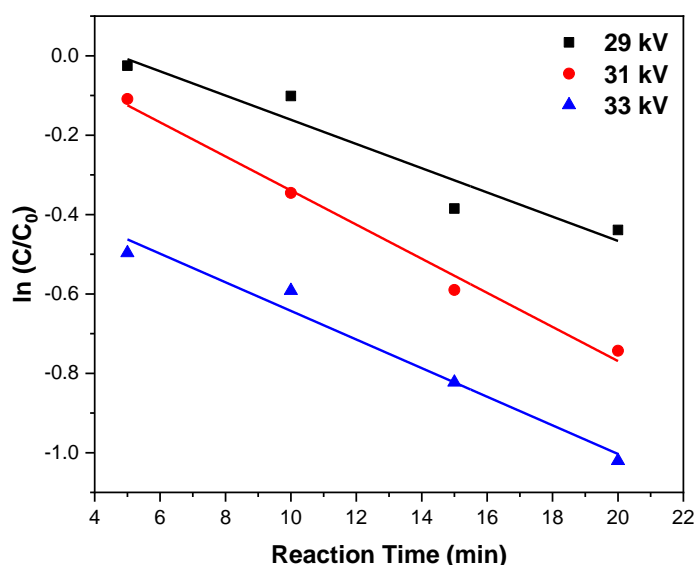
**Fig 4** T-H drug degradation efficiency spectrum



**Fig.5** First order kinetic equation of T-H drug degradation.

Furthermore, the degradation rate of 63% was obtained at 33 kV applied potential and plasma exposure time of 20 min.

Fig.4 shows the % of degradation of T-H drug as a function of plasma exposure time and discharge potential as calculated using the following expression

$$\% \text{ of degardation } = \frac{C_0 - C_{at}}{C_0} \times 100\%$$

Where, $\eta$ is the degradation % of the T-H drug, $C_0$ and $C_{at}$ are the initial and final concentration of the T-H drugs in the sample before and after plasma treatment.

### 3.3 Kinetic equation of T-H aqueous solution degradation

The non-thermal plasma assisted degradation of commercially available T-H as a function of discharge potential and reaction time are shown in Fig 5. T-H degradation was carried out under various plasma parameters. The degradation of T-H was observed to follow a pseudo-first-order kinetics [10-11]. The following expression is used to calculate the degradation rate constant.
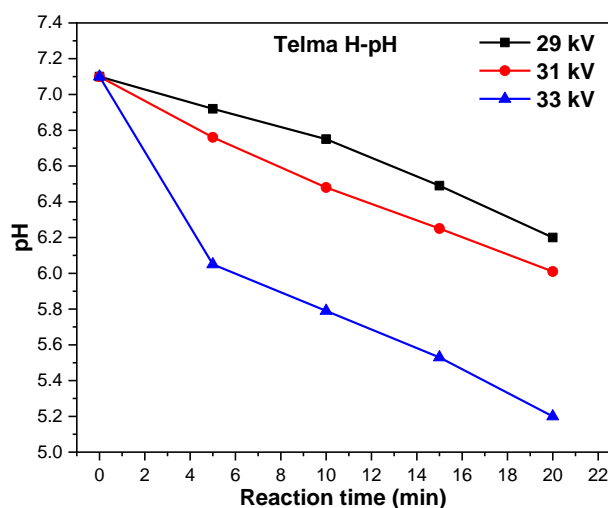
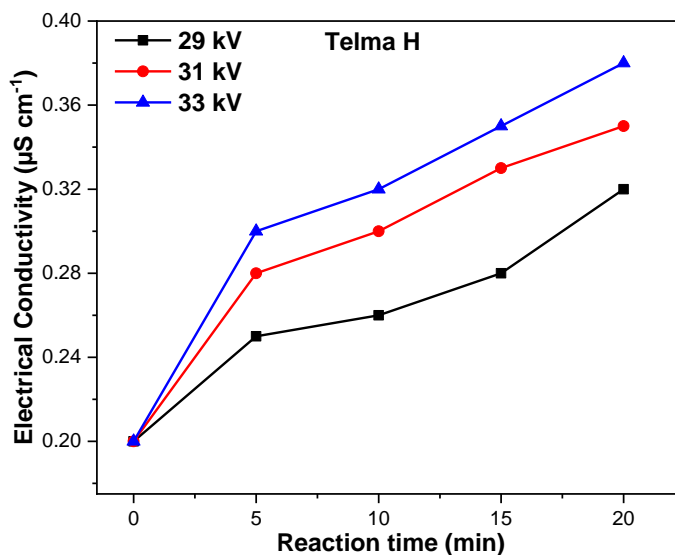**Fig 6.** Variation of H of plasma treated T-H solution as a function of various operating parameters



**Fige 7.** APPJ treated T-H aqueous solution Electrical conductivity graph

$$ln\frac{C}{C_0} = -kt$$

Where, k is the first order rate constant, t is the plasma treatment time (min) and C and $C_0$ are the T-H.

Concentration before and after plasma treatment. It is seen from Fig.5 that the extent of degradation increases with the discharge potential. Further, at a given discharge potential, the degradation rate is found to increase with plasma exposure time. Among the studies samples, maximum degradation (63%) of the drug was observed after 20 minutes exposure at the plasma discharge potential of 33 kV. The increase in degradation of the dye at increased discharge potential can be attributed to higher concentration and higher energy of the reactive species.

### 3.4 Temporal change of pH in T-H aqueous solution

Temporal value of pH of the aqueous T-H drug solution after plasma treatment was measured and the results are shown in Fig 6. Fig.6 clearly shows that the pH of the solution decreased with treatment time and applied potential [11], indicating that an acid is formed as one of the degraded products of T-H drug. It is observed from Fig.6 that the pH value decreased significantly (initial pH 7) with increasing applied potential. Furthermore, the aqueous solution plasma-treated at the higher applied potential of 33 kV had the lowest pH value of 4.8 obtained (Fig.6). The decrease in pH value after plasma exposure clearly shows formation of an acid as one of the degraded products of T-H drug. Formation of reactive nitrogen species (as observed in the OES) and decrease in pH after plasma exposure clearly indicate that

plasma treatment breaks down the T-H drug into simpler compounds.

### 3.5. Electrical conductivity measurement of APPJ treated T-H aqueous solution.

Electrical conductivity (EC) is frequently used as an index to measure water quality as conductivity is directly related to the ion concentration in the aqueous solution [12]. The electrical conductivity of plasma-treated T-H aqueous solution is shown in Fig.7, which shows that the conductivity increases with treatment time and discharge potential. The variation in electrical conductivity with the processing parameters is similar to the variation of pH with the processing parameters. The increase in conductivity is due to an increase in the concentration of ionic species which are formed as degradation products of the drug. The results are in agreement with the observation that the pH value of the drug solution decreased with plasma exposure due to formation of acid species. The increase in conductivity of the drug solution after plasma exposure can be attributed to the presence of $H^+$ ions (of the acid) produced as a result of fragmentation and degradation of the T-H drug.

## 4. Conclusion

Degradation of T-H drug solution by non-thermal atmospheric pressure plasma jet is presented in this paper. Plasma degradation of T-H aqueous solution was carried out under different applied potentials and plasma treatment times. Extent of degradation of the drug was followed by UV-Visible spectroscopic studies. Higher degradation rate of T-H was observed at higher applied potential and treatment time. It was found that plasma degradation followed pseudo first order kinetics. Reactive OH radicals were found to be the species responsible for degradation of the drug. This was confirmed by optical emission spectra recorded during plasma treatment of T-H drug solution. Electrical conductivity and pH measurements of the drug solution after plasma treatment confirmed the formation of acid molecules as a fragmented compound from the T-H drug. Finally, the above results showed that the non-thermal APPJ treatment process is efficient and eco-friendly process that destroys the T-H drug forming simpler molecules.

## Reference

[1] K. Syam, E.Ceriani, E.Marotta, A. Giardina, P. Špatenka, and C. Paradisi, Products and mechanism of verapamil removal in water by air non-thermal plasma treatment, *Chem. Eng. J.* 292 (2016) 35-41.

[2] A. Kosar, H. Hama, H. Miessner, S. Mueller, D. Kalass, D. Moeller, I. Khorshid, M. Amin and M. Rashid. Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma, *Chem. Eng. J.* 313 (2017) 1033-1041.

[3] K. Edvinas, D. Martuzevicius, M. Tichonovas, D. Jankunaite, I. Rumskaite, J. Sedlina, V. Racys and J. Baltrusaitis, Decomposition of 2-naphthol in water using

a non-thermal plasma reactor, *Chem. Eng. J.* 260 (2015) 188-198.

[4] Magureanu, Monica, D. Piroi, N. Bogdan Mandache, Victor David, A. Medvedovici, and V.I. Parvulescu, Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment, *Water Res.* 44 (2010) 3445-3453.

[5] B. Radu and B. Locke, Pulsed plasma gliding-arc discharges with water spray, *IEEE transactions on industry applications*, 44 (2008) 482-489.

[6] K. Gajanan and M. Farooqui, Development and validation of a stability indicating RP-HPLC method for the simultaneous determination of related substances of albuterol sulfate and ipratropium bromide in nasal solution, *J Pharm Biomed Anal.* 52 (2010) 19-29.

[7] M.T. Jamil, J. Ahmad, S. H. Bukhari, M. E. Mazhar, U. Nissar, A. J. RAOb, H. Ahmad, and G. Murtaza, Atmospheric pressure glow discharge (apgd) plasma generation and surface modification of aluminium and silicon si (100), *Dig J Nanomater Bios.* 12 (2017) 595-604.

[8] K.Y. Hee, Y.J. Hong, K.Y. Baik, G.C. Kwon, J.J. Choi, G.S. Cho, H.S. Uhm, and E.H, Choi. Measurement of reactive hydroxyl radical species inside the bio solutions during non-thermal atmospheric pressure plasma jet bombardment onto the solution, *Plasma Chem Plasma P.* 34 (2014) 457-472.

[9] Attri Pankaj, Yong Hee Kim, Dae Hoon Park, Ji Hoon Park, Young J. Hong, Han Sup Uhm, Kyoung-Nam Kim, Alexander Fridman, and Eun Ha Choi, Generation mechanism of hydroxyl radical species and its lifetime prediction during the plasma-initiated ultraviolet (UV) photolysis, *Sci Rep.* 5 (2015) 9332.

[10] Gerrity Daniel, Stanford, Trenholm, and Snyder, An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation, *Water Res.* 44, 2 (2010): 493-504.

[11] Bradu, Magureanu, and Parvulescu, Degradation of the chlorophenoxyacetic herbicide 2, 4-D by plasma-ozonation system, *J. Hazard. Mater.* 336 (2017) 52-56.

[12] Rusydi, Correlation between conductivity and total dissolved solid in various type of water: A review, In *IOP Conference Series: Environ Earth Sci.*, 118 (2018) 012019.

## Funding

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