

Application of Atmospheric-pressure Non-equilibrium Microwave Discharge Plasma for Decomposition of Sodium Dodecyl Sulfate in Aqueous Solution

Abstract. The typical household uses dish detergent, laundry detergent, and other synthetic detergents that contain large amounts of surfactants. For example, in the laundry case, it is common to use a combination of detergents and fabric softeners, and the anionic surfactants contained in the detergent and cationic surfactants contained in the fabric softener is bonded together to create a condition where surfactants do not decompose easily in aqueous solutions. As a result, surfactants that are drained into the water without degradation can cause environmental damage and pollution to ecosystems, oceans, and waterways. In this study, an aqueous solution containing anionic surfactants was treated by an atmospheric-pressure non-equilibrium microwave discharge plasma jet using an Ar gas and an Ar + H₂ mixture gas to enable decomposition of the surfactants in the aqueous solution by the OH and H₂ radicals given off in the plasma.

Streszczenie. Typowe gospodarstwo domowe używa detergentów do naczyń, detergentów do prania i innych syntetycznych detergentów zawierających duże ilości środków powierzchniowo czynnych. Na przykład w przypadku prania często używa się kombinacji detergentów i zmiękczaczy do tkanin, a anionowe środki powierzchniowo czynne zawarte w detergencie i kationowe środki powierzchniowo czynne zawarte w środku do zmiękczenia tkanin są łączone razem, aby stworzyć stan, w którym środki powierzchniowo czynne nie ulegają łatwo rozkładowi w roztworach wodnych. W rezultacie środki powierzchniowo czynne, które są odprowadzane do wody bez degradacji, mogą powodować szkody w środowisku i zanieczyszczenie ekosystemów, oceanów i dróg wodnych. W tym badaniu wodny roztwór zawierający anionowe środki powierzchniowo czynne poddano obróbce strumieniem plazmy z wyładowaniem mikrofalowym o nierównowagowym ciśnieniu atmosferycznym przy użyciu gazu Ar i mieszaniny gazowej Ar + H₂, aby umożliwić rozkład środków powierzchniowo czynnych w roztworze wodnym przez OH i H₂ rodniki wydzielane w osoczu. (Zastosowanie plazmy wyładowczej mikrofalowej do rozkładu dodecylsiarczanu sodu w roztworze wodnym)

Keywords: Atmospheric-nonequilibrium plasma, Surfactant, pH value, Ar+H₂ mixture gas, Microwave discharge.

Słowa kluczowe: mikrofalowe wyładowanie plazmowe, detergenty.

Introduction

Today, the typical household uses various synthetic detergents, such as dishwashing detergent and laundry detergent. These synthetic detergents contain many surfactants as the main ingredient for cleaning in removing dirt [1-3]. Surfactants are widely used in almost every industry. For example, in typical households, it is common to use a combination of laundry detergent and fabric softener that contains surfactants. The anionic surfactants contained in laundry detergent and the cationic surfactants contained in fabric softener will bond together to form a state where their enhanced cleansing action and softening action cancel each other out, and the surfactants do not easily decompose in an aqueous solution. As a result, when surfactants are drained to waterways, they have not decomposed and can cause environmental damage and pollution to ecosystems, oceans, and waterways.

Most surfactants are sources of water pollution in rivers, streams, lakes, oceans, and other bodies of water, and this water pollution adversely affects aquatic life and harms the environment [4-5]. For this reason, the development of a method for easily decomposing surfactants from aqueous solutions containing surfactants is vital for reducing the future environmental impact on oceans and rivers. Sodium dodecyl sulfate (SDS) is an anionic surfactant and is used in household detergents, shampoos, and toothpaste.

Surfactants are one of the widespread xenobiotics that may enter wastewater and aquatic environments. They are responsible for foaming in rivers and treatment plants and reducing water quality. Therefore, surfactants are dangerous for humans and the ecosystem. Conventional treatment methods are not sufficient for treating wastewater with high concentrations of surfactants.

By their chemical structure, surfactants are classified as anionic, cationic, amphoteric. (zwitterionic) and non-ionic

surfactants. Surfactants are organic polar compounds composed of at least one hydrophobic molecule and one group of hydrophobic molecules. Surfactants are organic polar compounds composed of at least one hydrophobic molecule and one group of hydrophobic molecules.

Previously, the authors of this study conducted research where an atmospheric-pressure non-equilibrium plasma could be used to treat an organic matter aqueous solution containing pigments, and they were able to successfully control color changes of the pigments in the aqueous solution itself and the pH value within the aqueous solution by using the radicals (OH, O*, O₂, etc.) given off from the plasma [6].

In this study, an aqueous solution containing anionic surfactants was treated by an atmospheric-pressure non-equilibrium microwave discharge plasma jet using an Ar+H₂ mixture gas. The OH and H₂ radicals given off by the gases in the plasma caused a chemical reaction with the surfactants in the aqueous solution. It was found that this chemical reaction generated nitric acid within the aqueous solution, which facilitated decomposition of the surfactants and shifted the pH to a more acidic state.

Experimental setup

Figure 1 shows a diagram of the experimental equipment. In the experiment, a glass petri dish containing sodium dodecyl sulfate (SDS; CH₃(CH₂)₁₁OSO₃Na) aqueous solution (30 mL) classified as an anionic active agent was placed at a position 5.0 mm from the nozzle of the atmospheric-pressure non-equilibrium microwave discharge plasma jet (ADTEC Plasma Tech. Co.). At the surface of the aqueous solution, plasma was emitted to test whether the surfactants were decomposed by the plasma treatment for the aqueous solution containing surfactants.

The atmospheric-pressure plasma was generated using a plasma jet torch electrode, and a steady discharge was

maintained using a microwave power supply (2.45 GHz) for generating plasma. The transmission route of the microwaves used a coaxial cable (RG-393). The atmospheric-pressure non-equilibrium microwave discharge plasma jet torch electrode had a basic structure where the main material of the entire torch was aluminum, the torch discharge tube used quartz glass that was 13 mm in diameter and 170 mm in length, and the antenna used aluminum that was 7.0 mm in diameter and 23 mm in length [7-10]. The plasma input power for generating the plasma was 100-150 W, and the plasma used an Ar gas or an Ar + H₂ mixture gas (10-20 L/min).

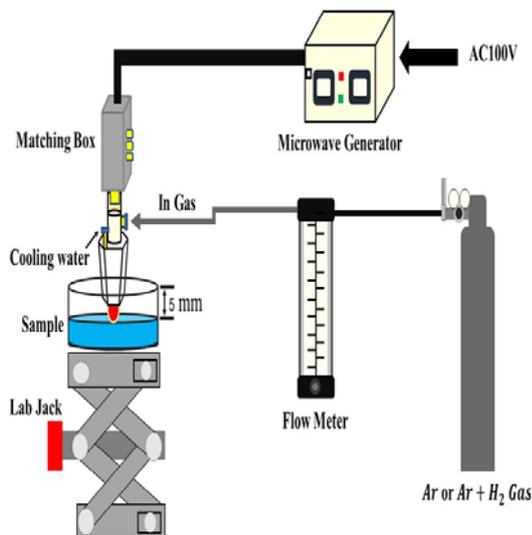


Fig. 1 Schematic diagram of the experimental setup

Figure 2 shows the chemical structures of the SDS surfactants and methylene blue. The SDS surfactants consist of a hydrophilic region and oil region. Normally, anionic surfactants generate cationic pigments and ionic associates and are extractable into chloroform and other organic solvents. Methylene blue, which is a cationic pigment, uses chloroform to extract SDS, which is an anionic surfactant, and ionic associates of methylene blue, and this absorbance can be measured [11]. From the 30 mL of aqueous solution containing surfactants treated by plasma, 15 mL was extracted and put into a screw cap bottle together with 5.0 mL of methylene blue aqueous solution (5.0 mL) and chloroform (10 mL). This bottle was mixed for 3 minutes and left to sit. Then, a volume of only 1.0 mL was extracted from the chloroform layer that had sunk to the downstream section, 9.0 mL of chloroform was added to this extracted volume to dilute it, and then the absorbance was measured. In the same way, a pH meter (HORIBA; pH / COND METER D-54) was used to measure the hydrogen ion concentration index in the aqueous solution after plasma treatment for confirming the change in the hydrogen ion concentration index. To find out the decomposition mechanism of the aqueous solution containing surfactants that was treated by plasma, the analysis method used the methylene blue absorptiometric method (JIS K 0102) with spectrophotometer (SHIMADZU; Multispec-1500).

Results

In Figure 3, a calibration curve was created for calculating the SDS concentration after plasma emission. The same figure shows the absorbance of SDS and methylene blue ionic associates based on the concentration of the SDS aqueous solution. To create this figure, SDS aqueous solutions with concentration 1.0×10^{-6} M and

5.0×10^{-6} M, 1.0×10^{-5} M, 5.0×10^{-5} M, and 1.0×10^{-4} M were prepared, and 15 mL of aqueous solution was extracted from each and put into a screw cap bottle together with 5.0 mL of methylene blue aqueous solution and 10 mL of chloroform. Next, a volume of 1.0 mL was extracted from this chloroform layer and 9.0 mL of chloroform was added to this extracted volume to dilute it.

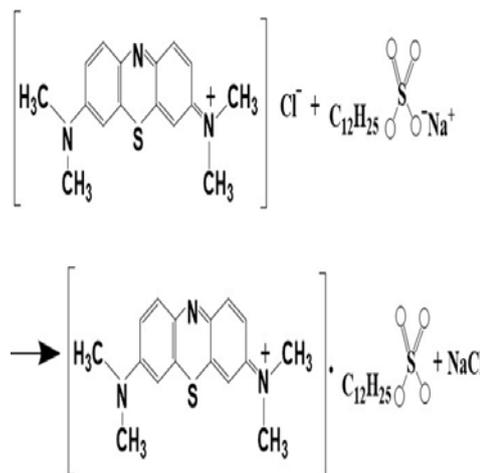


Fig. 2 Chemical bonds of SDS + Methylene blue

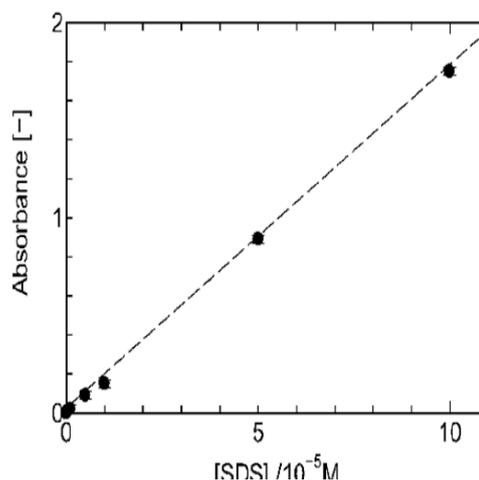


Fig. 3 Measurement of absorbance for concentration of SDS aqueous solution

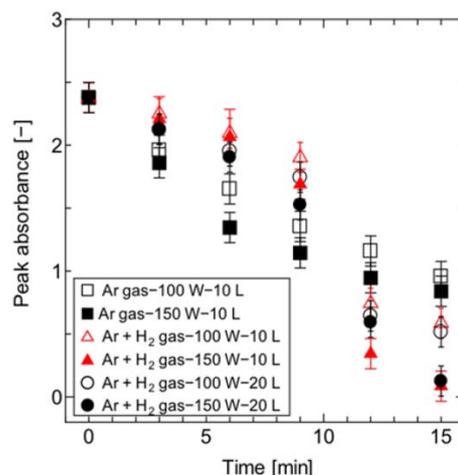


Fig. 4 Relationship between the maximum absorbance of plasma gas flow rate and plasma power and the plasma treatment time of the atmospheric-pressure non-equilibrium microwave discharge plasma jet.

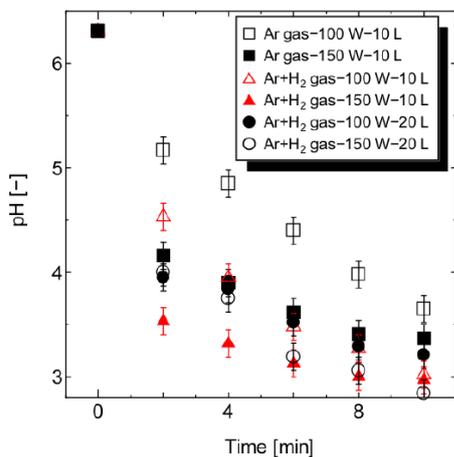


Fig. 5. Relationship between the pH value and plasma gas flow rate and plasma power and the plasma treatment time of the atmospheric-pressure non-equilibrium microwave discharge plasma jet.

Figure 4 shows the results when argon gas or argon-hydrogen mixture gas is injected and the absorbance of the ionic associations at a wavelength of 656 nm was measured for each plasma treatment time. This figure shows that the absorbance value decreased noticeably as the plasma treatment time increased.

Figure 5 shows the relationship with the pH value of aqueous solution containing surfactants for each plasma treatment time when an Ar gas or Ar+H₂ mixture gas is used. When plasma treatment was performed on purified water using an Ar gas or Ar+H₂ mixture gas, the pH value of the aqueous solution showed 3.0 to 4.0.

Discussions

As Fig. 3, a spectrophotometer was used to measure the absorbance of the SDS and methylene blue ionic associates. In the same way, the remaining concentration of SDS after plasma emission was found. The absorbance after 15 minutes of plasma emission was a value of 0.8 using argon gas, and the remaining concentration of SDS after plasma emission was found to be 4.8 M from the same figure. In the same way, when the argon-hydrogen mixture gas was used, we found an absorbance of 0.08, and the remaining concentration of SDS was found to be approximately 5.0 M.

In Fig. 4, in the same way, when examining the plasma input power and plasma generated gas, increasing the input power and plasma generated gas flow rate resulted in a significant decrease in absorbance by the ionic associates due to the increased generation of radicals and their longer lifetimes [12]. And so, it is thought that the oil component and hydrophilic group itself of the SDS aqueous solution are decomposed by the radicals that contribute to the generation of OH and H₂ [13-17] from the plasma due to the plasma treatment on SDS, which the associates are derived from.

As Fig. 5, this shows that, as the plasma input power and plasma gas flow rate increased, the pH value decreased, and the acidity became stronger. The primary reason for this is that the surfactants are decomposed by a chemical reaction with the aqueous solution due to OH radicals and H₂ radicals generated from the Ar or Ar+H₂ mixture gas. The mechanisms for generating OH radicals and H₂ radicals from the Ar or Ar+H₂ mixture gas are shown in the following three chemical formulas (1)-(4) [18-20]

The shift of the pH to a more acidic state is thought to be due to the generated OH radicals and H₂ radicals

reacting with nitrogen in the air for certain types of gases and radicals given off from the plasma so that a chemical reaction occurs between the hydrogen ions and nitrate ions in the aqueous solution to generate nitric acid [21-23].

- (1) $\text{H}_2\text{O} + e \rightarrow \text{H} + \text{OH} + e$
- (2) $\text{H}_2\text{O} + \text{Ar}^* \rightarrow \text{H} + \text{OH} + \text{Ar}$
- (3) $\text{H}_2\text{O}_2 + e \rightarrow \text{OH} + \text{OH} + e$
- (4) $\text{H}_2\text{O}_2 + \text{Ar}^* \rightarrow \text{OH} + \text{OH} + \text{Ar}$

The determination of the degradation of SDS in solutions containing inorganic salts is of practical importance. These solutions simulate the actual liquid sewage that occurs at a radiation chemical plant after equipment disinfection. By chemical structure, surfactants are classified as an anionic, cation, amphoteric and non-ionic surfactants [24]. Surfactants are organic polar compounds composed of one or more hydrophobic molecules and one group of hydrophobic molecules [25]. Surfactants are widely used in almost every industry [26].

Conventional treatment methods are not sufficient for treating wastewater containing high concentrations of surfactants. Biomolecular reactions between dissolved plasma and salts that result in plasma effects are observed at pH ~ 4.5. Moreover, at a certain concentration, the diameter of the bubbles decreases due to the strong inhibition of coalescence. As a result, the thickness of the diffuse film decreases, which can alter the kinetic strength. At the same time, the presence of nitrates, phosphates, sulfates, and chlorides in the plasma process of benzoic acid substitutes does not affect the selection. It may be suggested that in the presence of salts (pH ≈ 3.5–4.6), the dissolved compounds compete with each other in accessible plasma processes. With high salt concentrations, SDD foaming can be significantly reduced. This may be due to a decrease in the degree of SDD rupture. In an alkaline medium, a new chemical reaction appears, involving highly reactive radicals forming active particles, as salts are known to be the receptors of the above particles. Therefore, the reaction of OH radicals with SDS is more preferable. Indeed, leaching solutions containing NaNO₃ significantly increase the degradation of SDS. The intense OH reaction with the SDS molecules in the alkaline medium is the most efficient method for the decomposition of SDS. In conclusion, the presence of NaNO₃ influences both the physical nature of the process and its chemical nature, which is of great importance for the direct reaction of the plasma to sodium dodecyl sulfate.

Conclusions

In this study, we attempted to degrade surfactants in an aqueous solution containing anionic surfactants using atmospheric pressure plasma therapy. Plasma releasing unbalanced atmospheric pressure in mixed gas Ar or Ar + H₂ is used in the treatment of SDS aqueous solutions, and its adsorption is measured by a spectrophotometer. Our results show that over time, the SDS-dependent maximum value decreased, and the pH changed to make the solution more acidic.

We found that the amount of nitric acid increased due to the radicals, and this led to the degradation of aqueous surfactant solutions. In the future, we plan to test atmospheric pressure plasma therapy for the development of atmospheric pressure plasma treatment technology for the degradation process of aqueous solutions containing surfactants in which cationic surfactants and their additives. Reduce the surface tension, and anion has a bond.

Acknowledgments

This work was supported by King Mongkut's University of Technology Thonburi (KMUTT), Thailand, and under the project of the Research, Innovation, and Partnerships Office (RIPO), National Research University Project of Thailand's Office of the Higher Education Commission, and Faculty of Industrial Education for Financial Support.

Authors: Somchai Arunrungrusmi, Department of Electrical Technology Education, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd, Bang Mot, Thung Khru, Thailand, E-Mail: somchai_aru@yahoo.com; Wittawat Poonthong, Department of Electrical Technology Education, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd, Bang Mot, Thung Khru, Bangkok, 10140, Thailand, E-mail: poonthong_golf2538@outlook.com; Apidat Songruk, Department of Electrical Technology Education, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd, Bang Mot, Thung Khru, Bangkok, 10140, Thailand, E-Mail: songruk.apidat38@hotmail.com; Narong Mungkung, Department of Electrical Technology Education, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd, Bang Mot, Thung Khru, Thailand, E-Mail: narong_kmutt@hotmail.com; Nuttee Thungsuk, Department of Electrical Engineering, Dhonburi Rajabhat University, Thailand, E-Mail: tonsai8996@yahoo.com; Kongsak Anuntahirunrath, Department of Mechatronics Engineering, King Mongkut's University of Technology Ladkrabang, Thailand, E-Mail: konglek1@gmail.com; Toshifumi Yuji, Faculty of education, University of Miyazaki, Japan, E-Mail: yuji@cc.miyazaki-u.ac.jp.

REFERENCES

- [1] E. Andrews, S. M. Larson, "Effect of surfactant layers on the size changes of aerosol particles as a function of relative humidity", *Environ. Sci. Technol.*, 27(1993), 5, 857- 865.
- [2] Evrim Yüksel, Ayhan S, engil, Mahmut Özacar, "The removal of sodium dodecyl sulfate in synthetic wastewater by peroxi-electrocoagulation method," *Chemical Engineering Journal* 152 (2009), 347–353.
- [3] Ayla Arslan, Eylem Topkaya, Deniz Bingöl, Sevil Veli, "Removal of anionic surfactant sodium dodecyl sulfate from aqueous solutions by O₃/UV/H₂O₂ advanced oxidation process: Process optimization with response surface methodology approach," *Sustainable Environment Research* 28 (2018), 65-71.
- [4] M. Soda, H. Okochi, H. Ogata and H. Okawa, "Rapid determination of anionic surfactants in atmospheric aerosol in an urban area using an improved methylene blue method", *BUNSEKI KAGAKU*, 62(2013), 7, 589-594.
- [5] Jamie E.Rossi, Karen J.Soule, ErinCleveland, Scott W.Schmucker, Cory D.Cress,Nathanael D.Cox,AndrewMerrill, Brian J.Landi, "Removal of sodium dodecyl sulfate surfactant from aqueous dispersions of single-wall carbon nanotubes", *Journal of Colloid and Interface Science*, 495, 1(2017),pp. 140-148
- [6] T. Yuji, "Dyeing Technology for Textile Using Atmospheric Plasma", *J. Surf. Finish. Soc. Jpn.* 68(2017), 551-555.
- [7] T. Yuji, T. Urayama, S. Fujii, N. Mungkung and H. Akatsuka, "Temperature behavior of atmospheric-pressure nonequilibrium microwave discharge plasma jets for poly(ethylene naphtharate)-surface processing", *Surface and Coatings Technology*, 202(2008), 5289-5292.
- [8] T. Yuji, S. Fujii, N. Mungkung and H. Akatsuka, "Optical Emission Characteristics of Atmospheric-Pressure Nonequilibrium Microwave Discharge and High-Frequency DC Pulse Discharge Plasma Jets", *IEEE Trans. on Plasma Science*, 37(2009), 839-845.
- [9] T. Yuji T, Urayama, S. Fujii, Y. Iijima, Y. Suzaki and H. Akatsuka, "Basic characteristics for PEN film surface modification using atmospheric-pressure nonequilibrium microwave plasma jet", *Electron. Commun. Jpn.* 93(2010), 42-49 .
- [10] J. Sukhapan and P. Brimblecombe, "Source apportionment of surfactants in marine aerosols at different locations along the Malacca Straits", *The Scientific World Journal*, 2(2002), 1138 1138-1146.
- [11] P. Attri, Y. H. Kim, D. H. Park, Ji H. Park, Y. J. Hong, H. S. Uhm, K.-N. Kim, A. Fridman and E. H., "Choiinfluence of ionic liquid and ionic salt on protein against the reactive species generated using dielectric barrier discharge plasma", *Scientific Reports*, 5, (2015), 1-13.
- [12] S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, J. C.r Whitehead, A. B. Murphy, A. F. Gutsol and S. Starikovskaia, "The 2012 Plasma Roadmap", *Journal of Physics D: Applied Physics*, 45(2012), 253001.
- [13] T. Atsushi, Y. Ono, S. Fukui, S. Ikawa and K. Kitano, "Free radicals induced in aqueous solution by non-contact atmospheric-pressure cold plasma", *Applied physics letter*, 100(2012) , 254103.
- [14] B. Pateyron, M.-F. Elchinger, G. Delluc, and P. Fauchais, Thermodynamic and transport properties of Ar-H₂ and Ar-He plasma gases used for spraying at atmospheric pressure. I: Properties of the mixtures, *Plasma Chemistry and Plasma Processing*, 12(1992),421-448.
- [15] H. Kuwahata and T. Yamaguchi, "Two-Dimensional Concentration Distribution of Hydrogen Peroxide Generated by Atmospheric-Pressure Plasma Jet Irradiation", *e-J. Surf. Sci. Nanotech.* 13(2015) , 474-480.
- [16] T. Yuji, H. Kawano, S. Kanazawa, T. Ohkubo and H. Akatsuka, "Laser-Induced Fluorescence Image of OH Radicals for Atmospheric-Pressure Nonequilibrium Dry Air Gas DC Pulse Plasma Jet", *IEEE Transactions on Plasma Science*, 36(2008), 976-977.
- [17] Dariusz CZYLIKOWSKI, Mariusz JASIŃSKI, Jerzy MIZERACZYK, "Novel low power microwave plasma sources at atmospheric pressure", *PRZEGLĄD ELEKTROTECHNICZNY (Electrical Review)*, ISSN 0033-2097, R. 88 NR 8/2012
- [18] H. Inui, K. Takeda, H. Kondo, K. Ishikawa, M. Sekine, H. Kano, N. Yoshida and M. Hori, "Measurement of Hydrogen Radical Density and Its Impact on Reduction of Copper Oxide in Atmospheric-Pressure Remote Plasma Using H₂ and Ar Mixture Gases", *Appl. Phys. Express*, 3(2010). 126101.
- [19] Y. Itikawa and N. Mason, "Cross Sections for Electron Collisions with Water Molecules", *J. Phys. Chem. Ref. Data*, 34(2005), 1-23.
- [20] M. Kirkpatrick, B. Dodet and E. Odic, "Atmospheric Pressure Humid Argon DBD Plasma for the Application of Sterilization Measurement and Simulation of Hydrogen, Oxygen, and Hydrogen Peroxide Formation", *International Journal of Plasma Environmental Science and Technology*, 1(2007) , 96-101.
- [21] K. Tachibana and K. Yasuoka, "Chemical Reactions Induced by Atmospheric Pressure Hydrogen Plasma", *International Journal of Plasma Environmental Science & Technology* 8(2014), 117-122.
- [22] A. A. Joshi, B. R. Locke, P. Arce, and W. C. Finney, "Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution", *Journal of Hazardous Materials*, 41(1995), 3-30.
- [23] C. Douat, S. Hübner, R. Engeln and J. Benedikt, "Production of nitric/nitrous oxide by an atmospheric pressure plasma jet", *Plasma Sources Science and Technology*, 25(2016), 025027.
- [24] Panich, N.M., Ershov, B.G., Seliverstov, A.F., and Basiev,A.G., *Zh. Prikl. Khim.*, vol. 80, no. 11, pp. 1787–1790.
- [25] A.M. Amat, A. Arques, M.A. Miranda, R. Vincente, and S. Seguí, Degradation of Two Commercial Anionic Surfactants by Means of Ozone and/or UV Irradiation, *Environ. Engin. Sci.*, , vol. 24(2007), no. 6, pp. 790–794.
- [26] Hoigne, J., and Bader, H., "The role of hydroxyl radical reactions in ozonation processes in aqueous solutions", *Water Res.*, 1976, vol. 10(1976), no. 5, pp. 377–386.