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Study of Organic Micropollutants Degradation by Atmospheric Pressure Plasma

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Abstract

This study is about the removal of organic micropollutants (OMP) by atmospheric pressure plasma as the effect of micropollutants to the environment and living things is severe. The impact of reactive oxygen and nitrogen on OMP is investigated to degrade it. OMP used in this study are methylene blue and phenol. Both samples are going through plasma treatment in a treatment beaker consisting of two electrodes, one at the bottom and another one on the top surface of water sample. The micropollutants are degraded by the reactive free radicals generated by plasma. The treated samples show a decrease in micropollutants after the analysis of Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV-Vis). Moreover, the findings indicates that the plasma treatment has reduced micropollutant concentration, although the micropollutant is incompletely degraded within 30. Therefore, plasma treatment is a reliable method and should be included as one of the the stages for water treatment.

1. Introduction

The presence of organic micropollutants (OMPs) in wastewater and aquatic environments is a growing concern due to their potential ecological and human health impacts. [1-3]. Traditional wastewater treatment methods have limited effectiveness in removing OMPs, leading to their widespread presence in surface water and drinking water reservoirs. [4, 5]. OMPs encompass a wide range of chemicals, including pharmaceuticals, pesticides, and personal care products, which can persist in the environment and adversely affect aquatic organisms. [6, 7].

Advanced oxidation processes, such as atmospheric pressure plasma, offer a promising approach for OMP degradation. Atmospheric pressure plasma generates reactive species that can efficiently degrade OMPs [8-10]. In this study, the researchers focus on the degradation of various OMPs using atmospheric pressure plasma and investigate the effects of different variables, such as degradation time, OMP concentration, and electrode discharges. The effectiveness of the plasma treatment is evaluated using via Ultraviolet–visible spectroscopy (UV-Vis) and other apparatus. The results of this study provide valuable insights into the potential of atmospheric pressure plasma as an effective method for OMP removal from wastewater.

This study aims to examine the impact of reactive oxygen and nitrogen species (RONS) on OMP and investigate the formation of radical ions through atmospheric plasma. The focus is the contaminated water containing OMP commonly found in plastic containers, particularly on the phenol-based organic compound. The compound phenol, which is released from plastic products is highly potentially harmful to human health when it contaminates food. Additionally, the study addresses organic dyes as another type of organic micropollutant. The objective is to assess the presence of micropollutants in water samples and explore the degradation potential using atmospheric plasma technology.

2. Material and Method

Firstly, the plasma treatment beaker is set up by using 2 copper electrodes which one positive and one negative sealing on the wall of beaker that one of it is under surface water and another one is on the surface water and there are connected to a Direct Current (DC) power source. The experimental setup is shown in Fig. 1. The concentration solutions of 0.0001 mol/dm^3 of methylene blue and 0.01 mol/dm^3 of phenol were prepared. About 0.0320g and 0.941g of methylene blue and phenol was used in this dilution solution (1L) as the standard solution. Then, three different diluted concentrations which are 25%, 50% and 75% were prepared. 10ml of each sample is collected before treatment as initial and after that each sample undergoes plasma treatment for 3 different periods which are 10, 20 and 30 seconds. Every 10ml of treated sample for every period is collected as well for further characterization and analysis. For precaution, the distance of the electrode between the surface of sample solution is fixed at 1cm. All steps are repeated by replacing methylene blue with phenol.

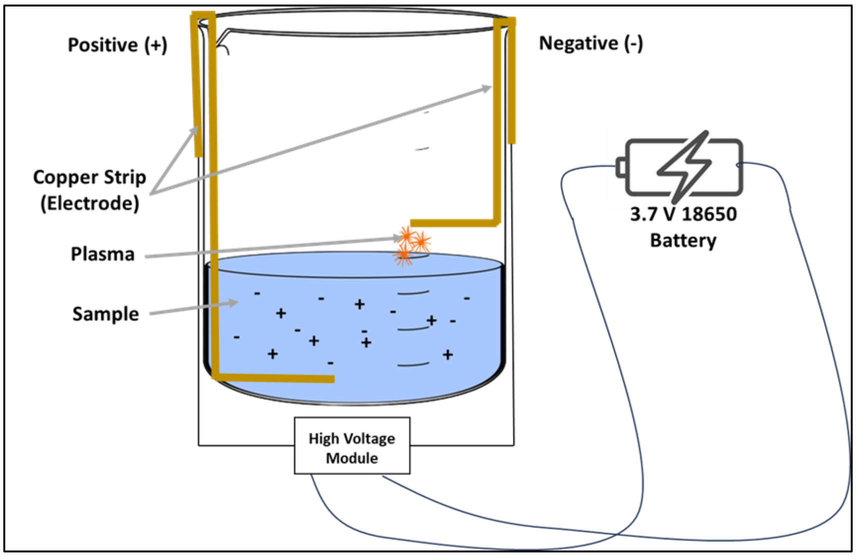

Fig. 1 *Schematics of experimental setups used in studies of liquid treatments with cold plasma*

UV-Vis and Fourier-transform Infrared spectroscopy (FTIR) are employed to confirm the degradation of OMPs in a sample. UV-Vis enables the measurement of light absorption, providing information about electronic structure and compound concentrations. UV-Vis is vital for analyzing chromophores and studying reaction kinetics and stability. FTIR, on the other hand, identifies chemical bonds, functional groups, and molecular structure through infrared light absorption. It is useful for characterizing complex molecules and determining the composition of substances. By observing changes in transmittance peaks, FTIR confirms the degradation of OMPs as their quantity decreases and they transform into simpler substances. Both techniques contribute to understanding the degradation process of OMPs in the sample.

3. Result and Discussion

3.1 Methylene Blue

Dyes are organic micropollutants commonly utilized in industries such as textiles, paper, plastics, and leather. However, the release of these dyes into wastewater has posed significant challenges due to their resistance to conventional treatment methods. Moreover, concerns arise regarding their toxicity and potential harm to aquatic ecosystems, as some dyes have been identified as potential carcinogens. As a result, numerous researchers have focused on the development of efficient wastewater treatment processes to eliminate dyes and address these environmental issues. One of the treatments will be plasma treatment, which applies the high voltage or non-thermal plasma to the surface of liquid sample, degrading the micropollutants by generating high-energy electrons that collide with micropollutants molecules.

Table 1 *Resultof UV-Vis analysis for methylene blue degradation under plasma treatment*

Concentration (%)	25%				50%				75%			
Time (s)	0	10	20	30	0	10	20	30	0	10	20	30

Absorbance UV-Vis (ppm)	1.310	0.098	0.134	1.288	2.063	0.480	1.870	0.342	2.301	1.843	0.909	2.157
Degradation rate (%)	-	92.5	89.8	1.69	-	76.7	9.36	83.4	-	19.9	60.5	6.24

The result for methylene blue under analysis of UV-Vis shows positive feedback which the concentration (ppm) of methylene blue decrease, this can be prove by the absorbance peak of methylene blue in spectrum (664nm) drops after the plasma treatment in Fig. 2. For example, the concentration of methylene degradation rate also increases when the treatment time increases, which 76.7% for 10s, 9.36% for 20s and 83.4% for 30s, the sudden decrease in degradation rate for 20s treatment shows errors occurring in this plasma treatment. The overall result shows that the concentration of the sample decreased after plasma treatment.

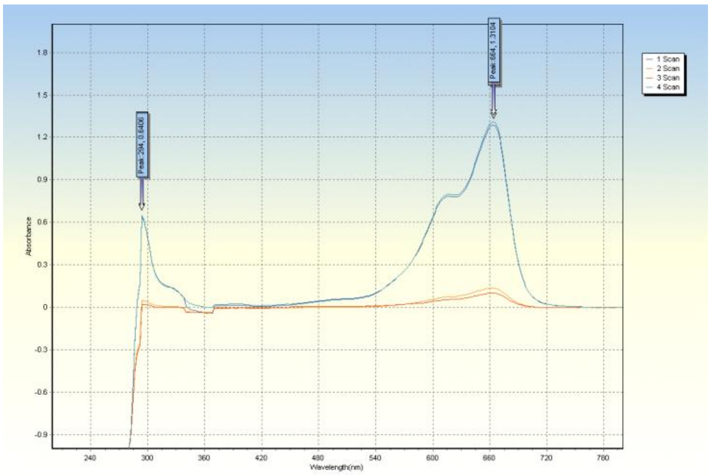

Fig. 2 *UV-vis analysis for methylene blue 25%*

Table 2 *Degradation of methylene blue analyzed by FTIR*

Concentration Percentage (% v/v)	Duration of Plasma Treatment (s)	Wavemeter (cm^{-1})	Peak height (T)	Percentage of Height Decrement (%)
25	0 30	1500-1700cm^{-1}	0.49 0.12	75.51
50	0 30		0.89 0.65	26.96
75	0 30		1.42 1.07	24.64

Moreover, the analysis of methylene blue under FTIR shows the presence of aromatic rings that showing peak at 1500cm^{-1} in Fig. 3. These bands arise from vibrations related to C-C and C-H bonds in aromatic rings. The spectrums show that the concentration of methylene blue decreases as the peak decreases for the treated samples. For example, the 25% methylene blue sample shows a decrease of peak height from 0.49 to 0.12 and a percentage of decrement of height at 75% as indicated in Table 2.

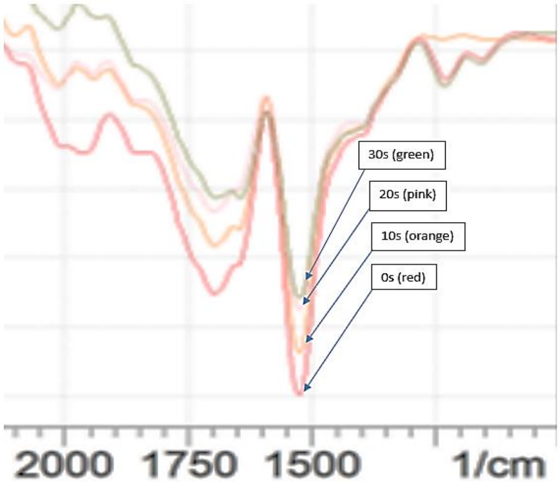

Fig. 3 *FTIR graph for 50% methylene blue solution under plasma treatment for 0s, 10s, 20s, and 30s*

3.2 Phenol

Phenol is a substance that falls within the category of aromatic organic compounds. It is also known as hydroxybenzene or carbolic acid. Phenol is an alcohol derivative made composed of a benzene ring with a hydroxyl group (-OH) linked to it. At room temperature, phenol is a colourless or white crystalline solid with a strong odour. It can be dissolved in ether, alcohol, and water. Due to the hydroxyl group, which can engage in a few chemical processes like esterification, oxidation, and halogenation, it is extremely reactive. The uses for phenol are numerous. It serves as a raw ingredient for the manufacture of plastics, resins, detergents, drugs, and a variety of compounds. Additionally, it is employed in medical and personal care goods as an antiseptic and disinfectant. The uses for phenol are numerous. It serves as a raw ingredient for the manufacture of plastics, resins, detergents, drugs, and a variety of compounds. Additionally, it is employed in medical and personal care goods as an antiseptic and disinfectant. Due to their toxicity and estrogenic nature, their presence in ground, surface, and drinking water and their extremely low biodegradability has been of major concern. Therefore, investigation in finding better method to remove phenol is necessary.

Table 3 *Result plasma treatment for phenol with different concentration and treatment time*

Concentration (%)	25%				50%				75%			
Time (s)	0	10	20	30	0	10	20	30	0	10	20	30
Concentration UV-Vis (ppm)	0.017	0.017	0.016	0.016	0.017	0.017	0.017	0.017	0.017	0.017	0.017	0.017
Degradation rate (%)	-	0.58	1.17	1.75	-	0.58	0.58	1.16	-	0	0	0.58

The concentration of phenol under analysis of UV-Vis does not drop as much as methylene blue, for example the concentration of phenol only decreases from 0.0171 ppm to 0.0168 ppm only for 25% of phenol solution as depicted in Table 3. This can be seen in the spectrum, in which the peak at 280 nm decreases after treatment as depicted in Fig. 4. The degradation rate is 0.58%, 1.17% and 1.75% respectively. The most effective treatment time for phenol within 0 to 30s is 30s, which the 30s for each concentration of phenol shows a great degradation rate.

FTIR analysis shows a peak at around 1600cm^{-1} which proves that the presence of aromatic ring C-C or C=C bond that supposed to present at 1600-1400cm^{-1}. By comparing the spectrums, the peak becomes smaller or decreases for all 3 concentrations of treated samples shown in Fig. 5. For example, the 25% of phenol showing the most obvious change after plasma treatment, which its peak height drop from 220.79 to 61.53 and showing the highest decrement of height which around 72.13%.

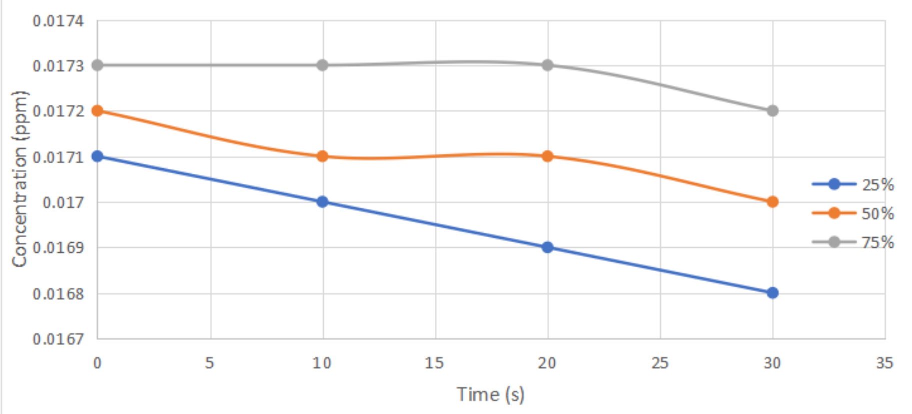

Fig. 4 *Three types of phenol concentration over plasma treatment time as analyzed by UV-Vis*

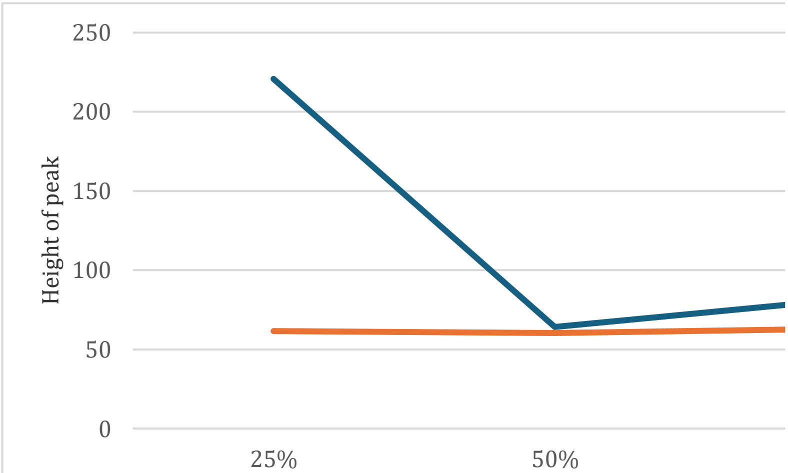

Fig. 5 *Graph of phenol concentration vs height of peak as analyzed by FTIR*

The results showed a significant reduction in micropollutant concentrations after treatment, indicating the effectiveness of atmospheric pressure plasma in degradation. However, the result also proves that OMP cannot be fully degraded by atmospheric pressure plasma within the period of 30s but decrease in amount, therefore suggesting the need for optimization and longer treatment durations. The findings aligned with previous studies, highlighting the potential of atmospheric pressure plasma for micropollutant removal. The spectrum or data in this study is not perfectly aligned with expectations due to some experimental errors occurring such as inappropriate of preservation method. Overall, the findings are reliable which degradation of OMP occurs for most of the samples.

4. Conclusion

In conclusion, this study demonstrated the potential of atmospheric pressure plasma as an effective method for organic micropollutant degradation. The findings underscored the need for further research and development to optimize the efficiency and practicality of this technique. By addressing the identified limitations and continuing to explore its applications, atmospheric pressure plasma holds promise for improving water purification systems and reducing the negative impacts of micropollutants on the environment and human health.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Phang Sheng Shan, Cha Kai Quan, Muhammad Sufi Bin Roslan;* ***data collection:*** *Phang Sheng Shan, Cha Kai Quan, Muhammad Sufi Bin Roslan;* ***analysis and interpretation of results:*** *Phang Sheng Shan, Cha Kai Quan, Muhammad Sufi Bin Roslan;* ***draft manuscript preparation:*** *Phang Sheng Shan, Cha Kai Quan, Muhammad Sufi Bin Roslan. All authors reviewed the results and approved the final version of the manuscript.*

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