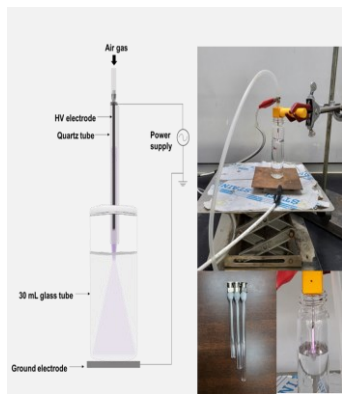


Jet-plasma catalysis system development for perfluorooctanoic acid removal: Mechanism studies via *in-situ* Raman spectroscopy analysis

ORAL
Ph.D. Student: N
Journal: Chemical
Engineering Journal

C.E. Choong^{1,2}, M. Jang^{1,2}. (1) Plasma Bioscience Research Centre, Plasma Bioscience Research Center, Kwangwoon University, Seoul 01897, Republic of Korea, cce@kw.ac.kr. (2) Kwangwoon University, Seoul 01897, Republic of Korea,



Air Jet plasma-coupled pseudo-photocatalysis is recognized as a novel approach for remediating PFOA-containing water. Particularly, pseudo-photocatalysis, propelled by UV-VIS range light sources generated from jet plasma, can enhance the formation of reactive species (RS). Herein, this study investigated PFOA removal using air jet plasma systems with the addition of plasma catalysts. As a result, the combination of the catalyst and air jet plasma system significantly improved the PFOA removal performance, and synergy between the jet plasma and catalysts was obtained up to 2.914. This is ascribed to the increased formation of hydroxyl radicals induced by the catalyst redox reaction, as evidenced by liquid spin resonance spectroscopy analysis and *in-situ* Raman spectroscopy measurement.

Introduction

Perfluorooctanoic acid (PFOA) has garnered significant attention and has been widely employed in fire-fighting foams, water-resistant products, and paint. Notably, PFOA is highly persistent with chemical and biological resistant properties, and it was found in soil, water bodies, wildlife, and human beings. Up to date, the available water treatment technologies via oxidation are ineffective for PFOA removal. Pseudo-photocatalysis driven by air jet plasma is recognized as a novel approach for remediating PFOA-containing water. Particularly, pseudo-photocatalysis, propelled by UV-VIS range light sources generated from jet plasma, can enhance the formation of reactive species (RS). Here, we investigated the synergistic effect between air jet plasma and catalyst for stimulating the hydroxyl radicals ($\cdot\text{OH}$) production for PFOA removal.

Material and Methods

The LaCoO_3 was prepared by sol-gel method followed by calcination (700°C for 2 h). The resultant grey color solid was pulverized into powder for further use. Various Ce_x , where X (0.5~5.0), indicated the weight ratio of Ce was prepared to determine the optimized doping ratio of Ce toward LaCoO_3 . In addition, the CeO_2 was also prepared for comparison via the calcination method. The plasma catalytic degradation of PFOA experiments were conducted using an atmospheric-pressure air plasma jet operated by an alternating current (AC) with a high voltage power source. Air gas flows into

the quartz tube with a flow rate of 2 LPM. Plasma was produced between the 2 electrodes when the sinusoidal voltage was applied. The plasma was produced from the inner quartz tube toward the lower tip and directly injected into the surface of the PFOA solution. In a typical run, 0.01 g of plasma catalyst was added to 30 mL of PFOA solution with an initial concentration of 25 mg L^{-1} . The obtained supernatants were analyzed using an HPLC. The electron paramagnetic resonance (EPR) analysis was conducted using air jet plasma catalysis system with DMPO solution to investigate the $\cdot\text{OH}$ formation. The *in-situ* surface-enhanced Raman spectroscopy of the air plasma catalysis was analyzed using a confocal Raman microscope with 532 nm laser.

Results and Discussion

Figure 1a showed the kinetic rate constants (k) for air jet plasma, $\text{LaCoO}_3/\text{Air jet}$, $\text{LaCoO}_3\text{-Ce}_{0.5}/\text{Air jet}$, $\text{LaCoO}_3\text{-Ce}_{1.0}/\text{Air jet}$, $\text{LaCoO}_3\text{-Ce}_{2.5}/\text{Air jet}$, $\text{LaCoO}_3\text{-Ce}_{5.0}/\text{Air jet}$ and $\text{CeO}_2/\text{Air jet}$, were 0.0163, 0.0232, 0.00411, 0.00514, 0.0304, 0.0025, and 0.015 min^{-1} , respectively. To investigate the synergistic effect between the air jet plasma system and catalysts, the synergistic factor (SF) was calculated, which stands for the ratio between the PFOA removal rate constant of the air jet plasma system with catalyst and the PFOA removal rate constant of the sole air jet plasma system. If $\text{SF} > 1$, there is a synergistic effect between the air jet plasma system and catalysts. The SF was obtained for LaCoO_3 (1.25),

LaCoO₃-Ce_{0.5} (2.37), LaCoO₃-Ce_{1.0} (2.914), LaCoO₃-Ce_{2.5} (1.715), LaCoO₃-Ce_{5.0} (1.455) and CeO₂ (0.597). The results showed that the composite of LaCoO₃ and CeO₂ catalysts exhibited high SF in air jet plasma system and PFOA removal performance compared to pure LaCoO₃ and CeO₂. The results showed the LaCoO₃-Ce_{1.0} as the optimized catalysts used in air jet plasma system for PFOA removal. The addition of LaCoO₃-Ce_{1.0} increased the formation of higher ·OH (Figure 1b), that improved the PFOA removal performance.

Figure 1c showed the setup for in-situ SERS analysis for LaCoO₃-Ce_{1.0}. Figure 1d showed the peaks at 443, 489 and 798 ~830 cm⁻¹ referred to F₂g of CeO₂, Co-O stretching and O-O stretch vibration from the adsorbed peroxy species, respectively. During the interaction of air jet plasma and LaCoO₃-Ce_{1.0}, the blue-shifted peroxy signal was obtained, revealing the aggregated peroxide species.

The power dissipation of air jet plasma system was calculated as 6.8 W, derived from the I-V curve. Table 1 showed the air jet plasma system (0.165kW/mgPFOA) exhibited a better energy consumption performance for PFOA removal

compared to air Jet plasma system (3.023kW/mgPFOA). Hence, the LaCoO₃-Ce_{1.0} plasma catalysis system exhibited considerably higher energy efficiency for PFOA removal.

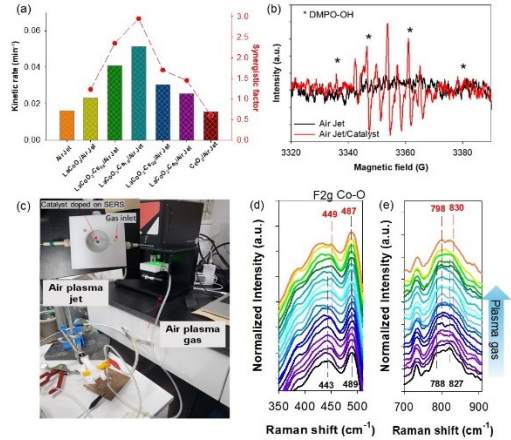


Figure 1. (a) the PFOA removal kinetic rate constant using air jet plasma and catalyst/air jet plasma. (b) EPR analysis for spin trapping of hydroxyl radicals. The SERS measurement setup (c) and raman spectrum (d).

Table 1.: Energy consumption comparison between this study and other commercial plasma system for PFOA removal

System	Treatment vol (mL)	PFOA initial (mg/L)	Treatment time (min)	Average power (W)	EEO (kW/mg)
7-wires' DC plasma reactor [1]	170	41.1	300	10	26.57
Hollow electrode' AC plasma reactor [1]	15	41.1	30	7	0.869
Self-pulsing discharge (SPD) plasma reactor [1]	15	41.1	30	19	0.797
DC plasma/Ar [2]	200	44.9	140	60	0.72
Air Jet plasma	25	20	30	6.8	3.023
Ar Jet plasma/catalyst (this study)	25	20	30	6.8	0.165
Plasma/MB/air [3]	300	30	120	38.9	0.33

Conclusions

In summary, we synthesized LaCoO₃ and CeO₂ composites via facile single-step calcination and applied them as catalysts in air jet plasma system to boost PFOA destruction. As a result, the optimum ratio of 1% CeO₂ composited with LaCoO₃ exhibited a high SF (2.91) for PFOA destruction in AP, whereas no enhancement was observed with pristine CeO₂ or LaCoO₃. Based on *in-situ* SERS and ESR spin-trap analysis results revealed that higher ·OH generated from the the redox reaction between LaCoO₃ and CeO₂ in the air jet system could increase the PFOA removal rate.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (Grant No. 2021R1A6A1A03038785, 2023R1A2C1003464 and RS-2023-00240726).

References

- [1] M. Saleem, O. Biondo, G. Sretenović, G. Tomei, M. Magarotto, D. Pavarin, E. Marotta, C. Paradisi, Chemical Engineering Journal 382 (2020) 123031.
- [2] H. Obo, N. Takeuchi, K. Yasuoka, IEEE Transactions on Plasma Science 41 (2013) 3634-3639.
- [3] H. Zhang, P. Li, A. Zhang, Z. Sun, J. Liu, P. Héroux, Y. Liu, Environmental Science & Technology 55 (2021) 16067-16077.
- [4] Q. Zhuo, S. Deng, B. Yang, J. Huang, G. Yu, Environmental Science & Technology 45 (2011) 2973-2979.