Rapid Degradation of Coumarin via In Situ Hydroxyl Radical Generation Induced by Recycled Gas from a DBD Plasma Bubble Reactor

Kiran Ahlawat, Akshara Chithran, Mario Janda, Zdenko Machala

Division of Environmental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University Bratislava, Slovakia

Email: ahlawat.kiran@fmph.uniba.sk

Introduction

- Coumarin, a fluorescent aromatic compound widely used in dyes, pharmaceuticals, and optical brighteners, is frequently detected in industrial effluents and poses ecological risks due to its persistence, phototoxicity, and potential bioaccumulation in aquatic environments. This study presents a novel approach for the rapid degradation of coumarin using recycled gas from a dielectric barrier discharge (DBD) plasma bubble reactor.

- DBD based plasma-bubbled reactor was developed to simultaneously produce RONS-rich plasma activated water (bubble discharge enhances plasma-liquid interactions) for agricultural use and recycle the gas phase into a secondary reactor for coumarin degradation without direct plasma–liquid contact, demonstrating the dual functionality of the system. This integrated approach provides a sustainable pathway for coupling plasma agriculture with wastewater treatment.

Experimental Setup

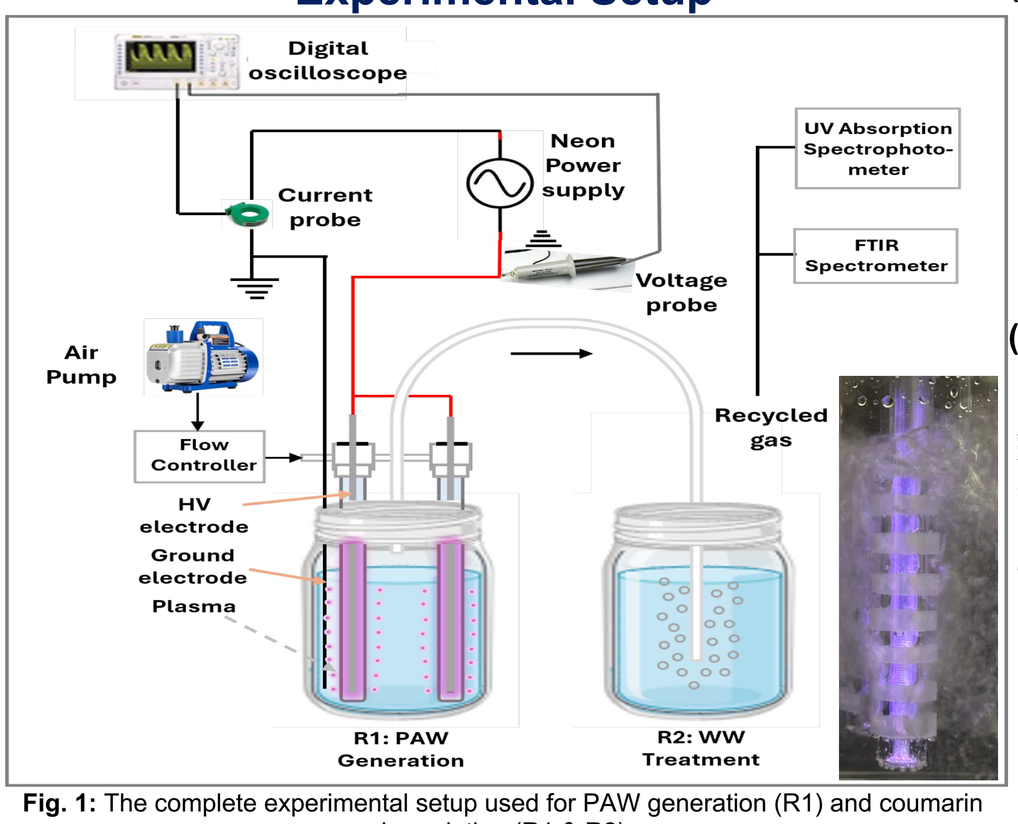


Fig. 1: The complete experimental setup used for PAW generation (R1) and coumarin degradation (R1 & R2).

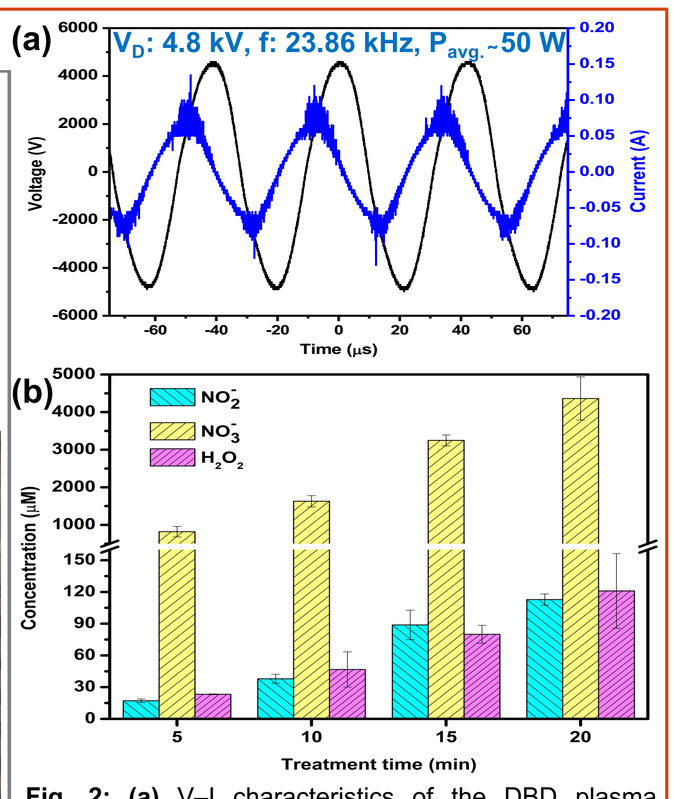
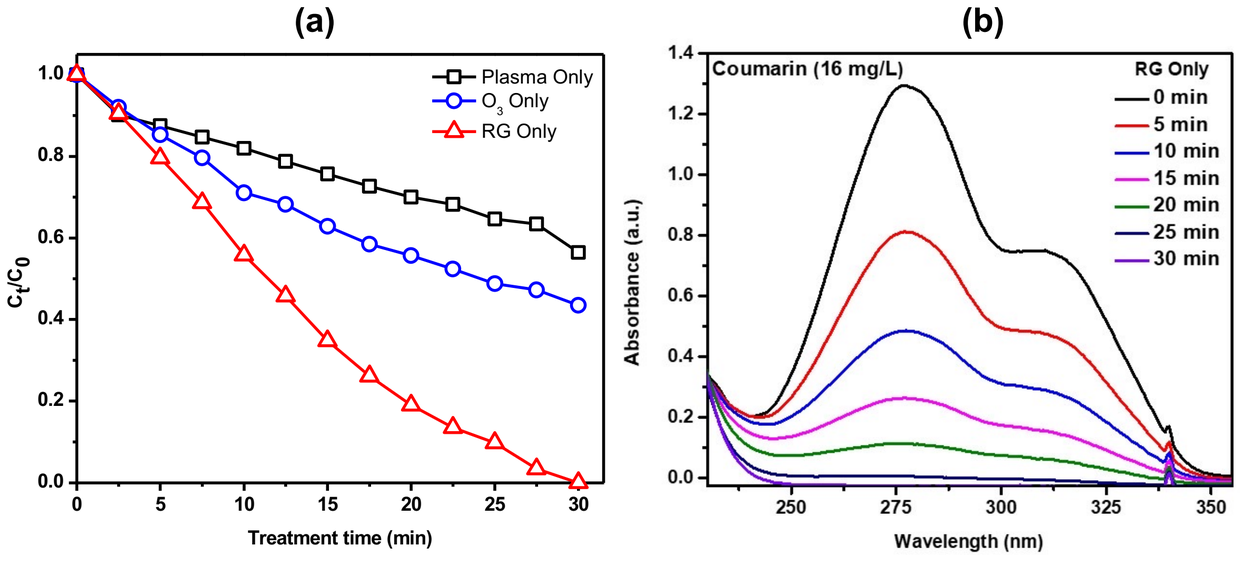


Fig. 2: **(a)** V–I characteristics of the DBD plasma device, and **(b)** concentrations of RONS in PAW generated in reactor 1 (R1) while coumarin degradation was simultaneously performed in reactor 2 (R2).

Coumarin degradation



$$O_3 + H_2O \rightarrow H_2O_2 + O_2$$

$$\boldsymbol{O_3 + H_2O_2 \rightarrow \cdot OH + HO_2\cdot + O_2}$$

$$O_3 + HO_2^- \rightarrow \cdot OH + O_2^- + O_2$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2$$

$$O_3 + HO_2^- \rightarrow O_3^{\cdot -} + HO_2^{\cdot}$$

$$O_3^{\cdot -} \leftrightarrow O_2 + O^{\cdot -}$$

$$O^{\cdot -} + H_2O \rightarrow \cdot OH + OH^-$$

Fig. 3: **(a)** Degradation profile of coumarin under different treatment methods (Plasma Only, Ozonation Only, and Recycled Gas (RG) Only), **(b)** UV–Vis absorbance spectra showing the decrease in peak intensity and area with increasing treatment time in the case of RG, and **(c)** concentration of hydroxyl radicals under different methods using the same volume of water (550 mL).

- **Recycled Gas (RG) system** shows the fastest degradation, with C_t/C_0 decreasing rapidly and approaching complete removal by around 30 minutes, indicating highly efficient pollutant breakdown driven by enhanced •OH formation at the microbubble interface.
- **Ozonation system** exhibits moderate efficiency, with a steady but slower decline in C_t/C_0 compared to the RG system.
- The **plasma-only system** displays the slowest degradation, with a gradual decrease in C_t/C_0 over the treatment period, reflecting limited breakdown under plasma–liquid interaction alone.
- Overall, the degradation efficiency follows the order: **RG > ozonation > plasma-only.**

Conclusions

- ✓ A DBD-based plasma-bubbled reactor was developed to generate RONS-rich plasma-activated water (PAW) for potential applications in agriculture and wastewater treatment.
- ✓ Simultaneously, recycled gas containing reactive species enabled rapid coumarin degradation in a separate reactor without direct plasma–liquid contact.
- ✓ With RG, the microbubble interface promotes peroxone reaction (H_2O_2 + O_3 solubilization), thereby facilitating higher •OH formation and explaining the fast degradation kinetics.
- ✓ This approach highlights the dual functionality of plasma-bubbled reactors:
  (i) sustainable PAW production for agriculture and
  (ii) advanced oxidation of pollutants for wastewater treatment.
- ✓ Test on diverse pollutants (biological and chemical) and real wastewater will be conducted in future.

Methods used for characterization of PAW

- ✓ **H_2O_2:** $TiOSO_4$ colorimetry (yellow pertitanic complex, A_{407}).
- ✓ **NO_2^-**: Griess assay (azo dye formation, A_{540}).
- ✓ **Total NOx**: Dimethylphenol probe (DMP) assay.
- ✓ **Dissolved O_3**: Indigo trisulfonate method (decolorization, A_{600}).
- ✓ **•OH**: aqueous Terephthalic acid probe (Ex/Em = 310/425 nm).

FAKULTA MATEMATIKY, FYZIKY A INFORMATIKY
Univerzita Komenského v Bratislave

MATFYZ CONNECTIONS

Acknowledgement

This work was funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. **09I03-03-V03-00033** EnvAdwice.

RECOVERY AND RESILIENCE PLAN