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Atmospheric Plasma Treatment of Methylene Blue: Role of Solution Chemistry

Presented by

Dr. Pallabi Pathak
Assistant Professor
Department of Physics
University of Science and Technology Meghalaya

Collaborators

Dr. N. Aomoa (CPP-IPR)
Dr. A. Boruah (Barkhetri College)
Mr. Kapani Ashiirhii (USTM)
Ms. Chandrika Barman (USTM)

OUTLINE

- Introduction
- Experimental Setup
- Results and analysis
- Conclusion



Industrial Dye Pollution: An Environmental Challenge

- Industrial dye effluents are major source of water pollution.
- Persistent dyes reduce light penetration in water, affecting aquatic photosynthesis.
- Their chemical stability makes conventional treatment and complete removal challenging.

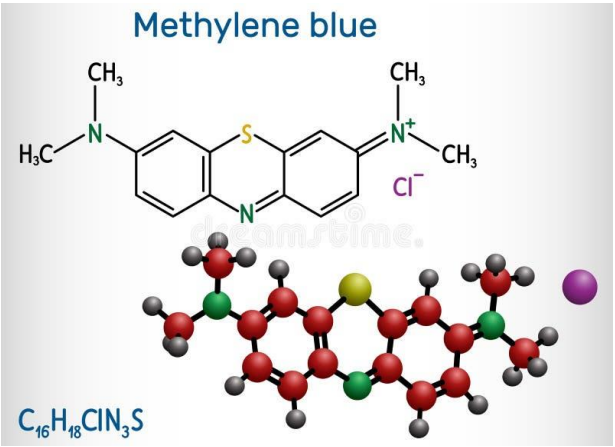






Why methylene blue?

- ✓ A commonly used cationic dye.
- ✓ Chemically stable and strongly coloured.
- ✓ Frequently employed as a model organic pollutant for studying wastewater treatment technologies.



Atmospheric Pressure Plasma for Water Treatment

Conventional Dye Wastewater Treatment Methods:

Physical: Adsorption, membrane filtration.

Chemical: Coagulation–flocculation, chemical oxidation.

Biological: Activated sludge, microbial degradation.

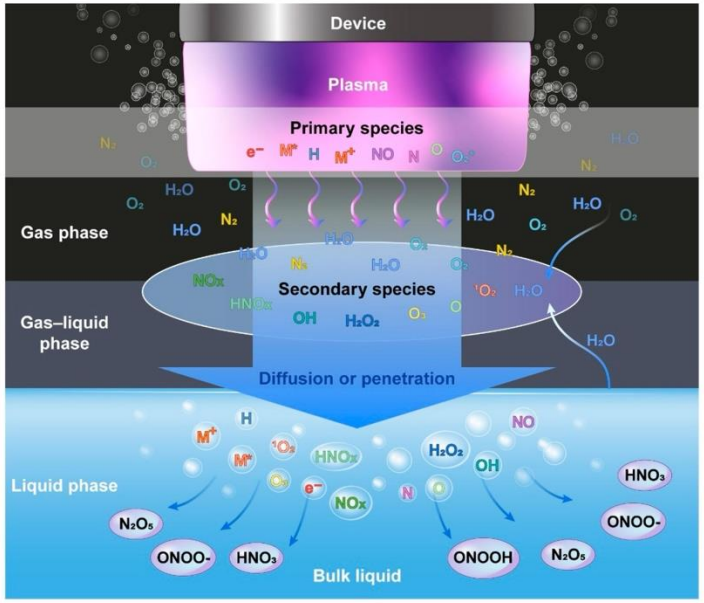
Advanced oxidation: Photocatalysis, Fenton oxidation.

Major limitations:

- ✓ Secondary sludge generation.
- ✓ Membrane fouling and waste disposal.
- ✓ Chemical consumption, secondary by-products.
- ✓ Limited efficiency for persistent synthetic dyes.

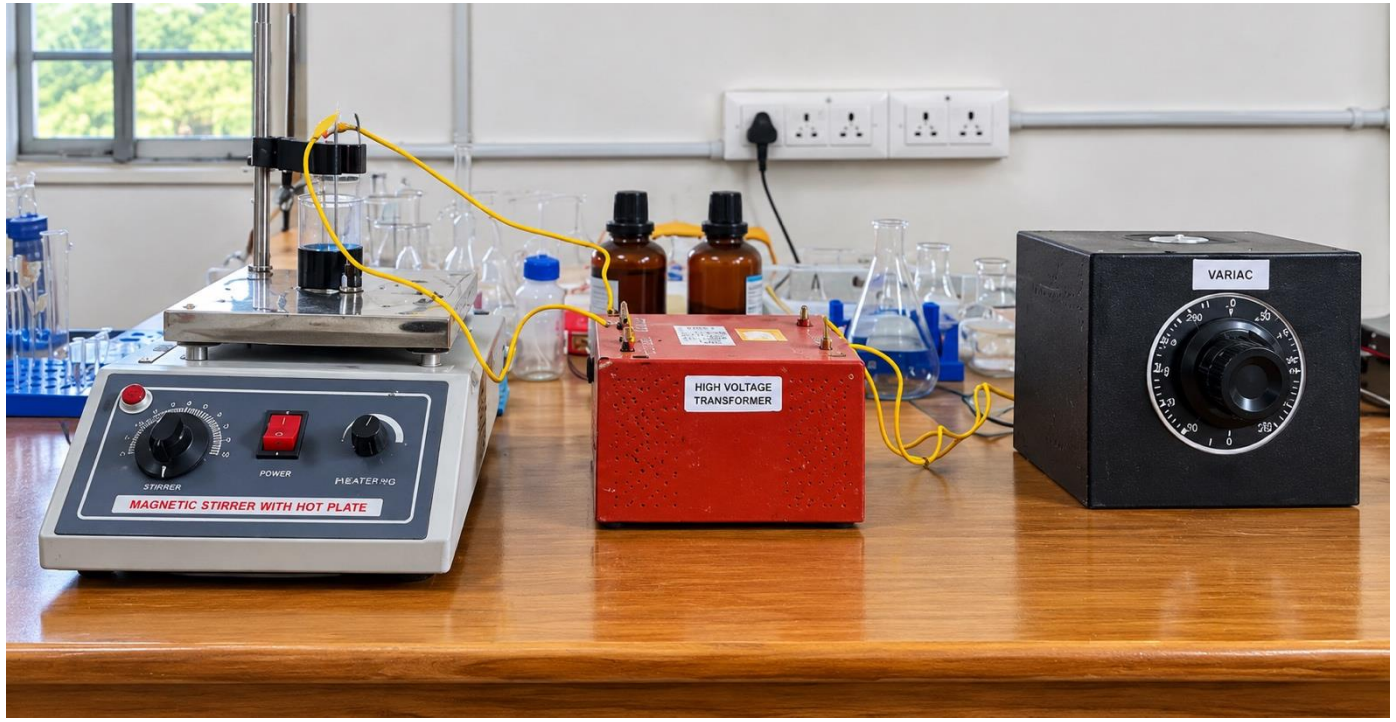
MOTIVATION

1. Atmospheric-pressure plasma generates reactive species capable of degrading organic pollutants.
2. Enables plasma-induced oxidation without necessarily requiring additional chemical oxidants.
3. Offers a potential alternative for the treatment of dye-containing wastewater.



Ref: *S. Kim and C-Ho Kim, Biomedicines, 2021, 9(11), 1700*

Experimental Setup: AtmoPlas Device

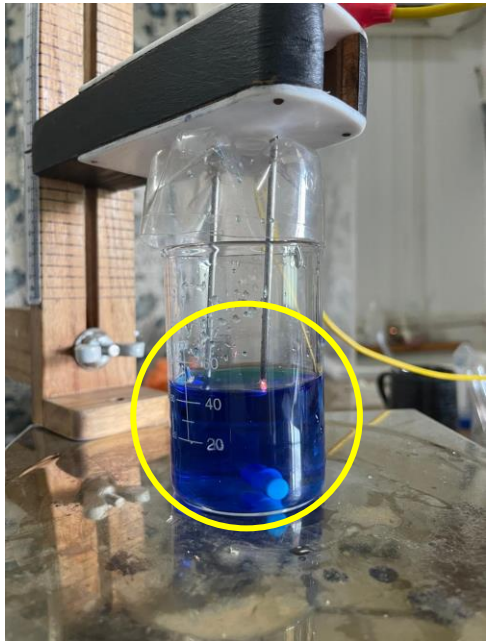


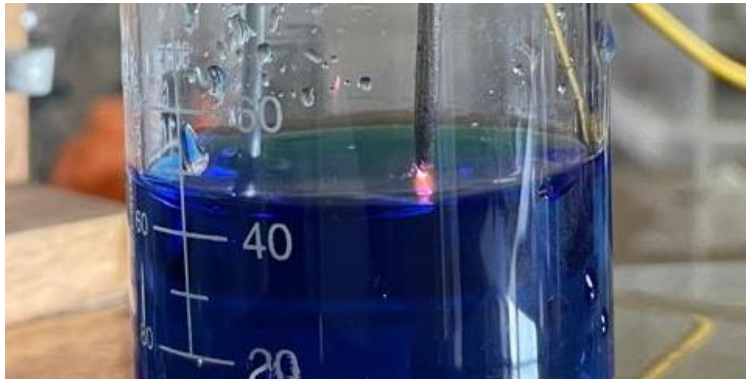
Photograph of the device

Electrode material: Stainless Steel

Gap between electrode and liquid: 2 - 4 mm

Applied voltage: 1.5 kV





Plasma formation above the liquid

Methodology

Preparation of Methylene Blue Standard Solutions:

- Prepared MB standard solutions of 5, 10, 15 and 20 ppm.
- Recorded UV–Visible absorption spectra over 200 to 800 nm.
- Identified the characteristic absorption peak of MB (~664 nm).
- Obtained a calibration curve (Absorbance vs. Concentration).

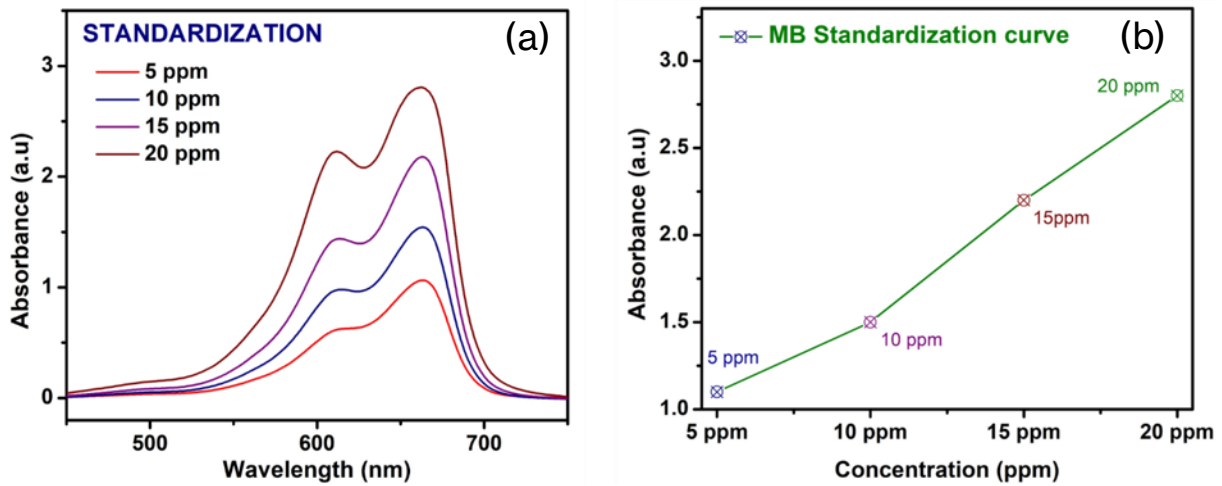


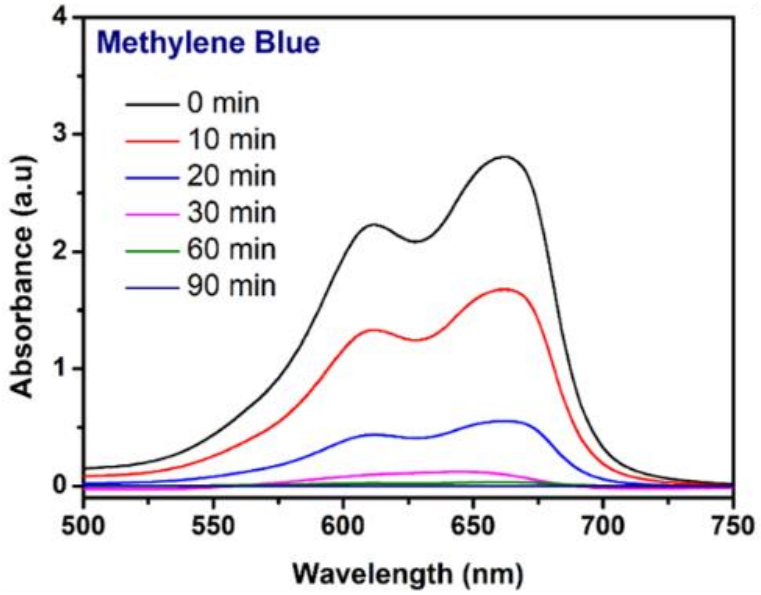
Fig. *(a) UV–visible absorption spectra of MB standard solutions with concentrations of 5, 10, 15 and 20 ppm and (b) corresponding MB standardization curve.*

Materials and Solution Preparation:

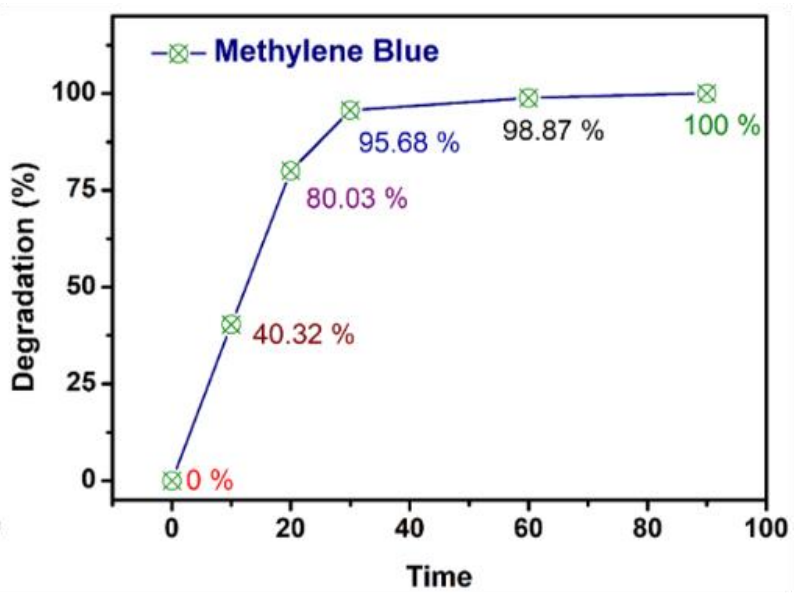
- Model dye pollutant: Methylene Blue (MB), initial concentration 20 ppm.
- Electrolyte: Sodium chloride (NaCl) – added at three different concentrations: 0.1g/L, 0.3g/L and 0.5g/L
- pH adjustment: Hydrochloric acid (HCl) added to adjust the MB solution to pH 3.
- Solvent: Deionized water.

Plasma Assisted Degradation of MB

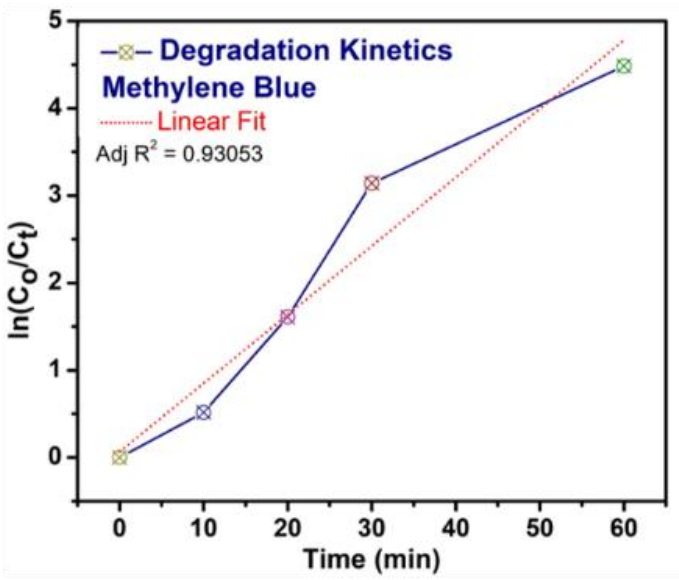
UV–visible absorption spectra



Degradation profile



Degradation kinetics



Beer–Lambert relationship:

$$\frac{C_t}{C_0} = \frac{A_t}{A_0}$$

The percentage degradation:

$$\text{Degradation (\%)} = 1 - \frac{C_t}{C_0} \text{ x } 100$$

For kinetic analysis:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

C_0 = Initial MB concentration

C_t = Concentration at treatment time t

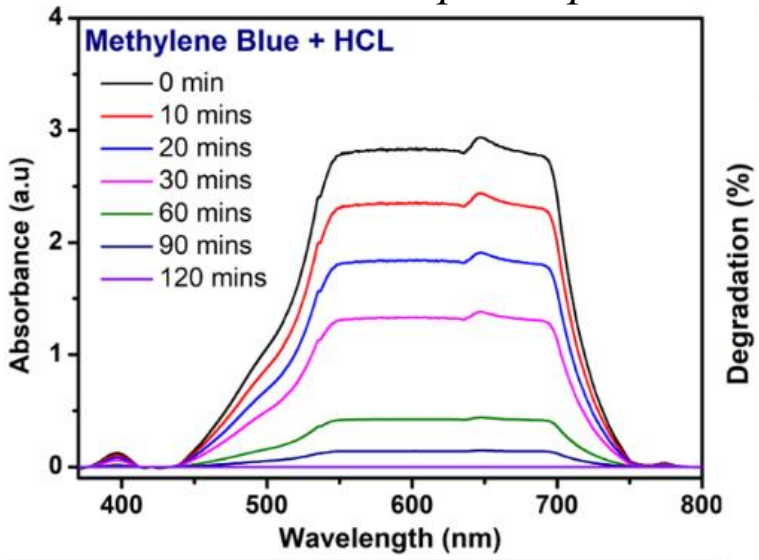
A_0 = Initial absorbance

A_t = Absorbance after plasma treatment

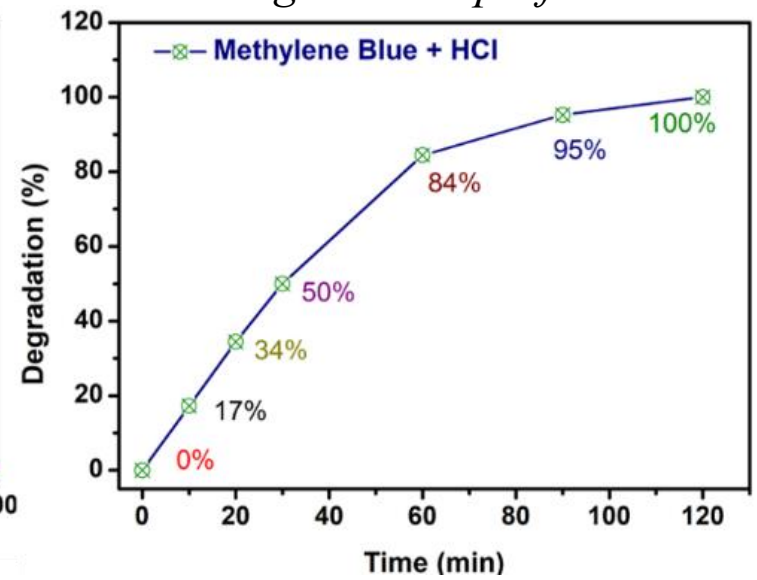
k = Rate constant (min^{-1})

Effect of Acidic Medium on MB Degradation

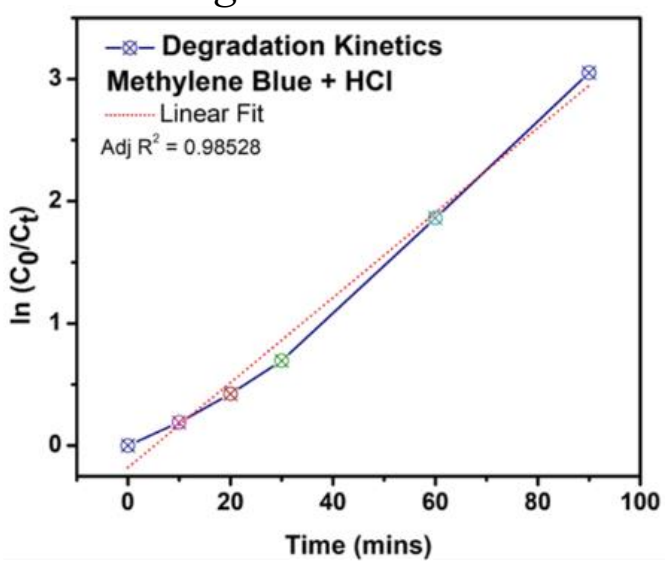
UV–visible absorption spectra



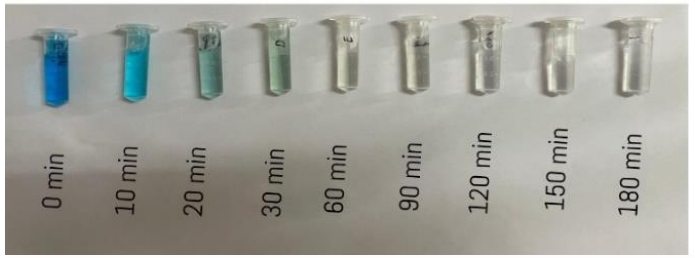
Degradation profile



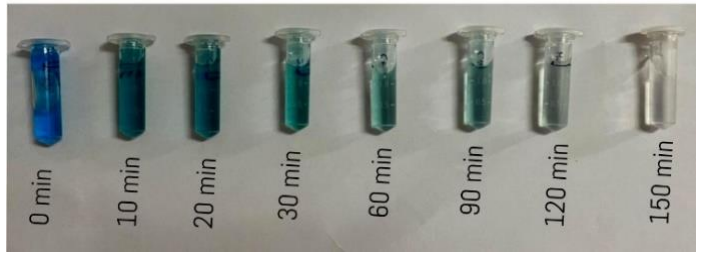
Degradation kinetics



Methylene Blue



Methylene Blue + HCl (pH-3)

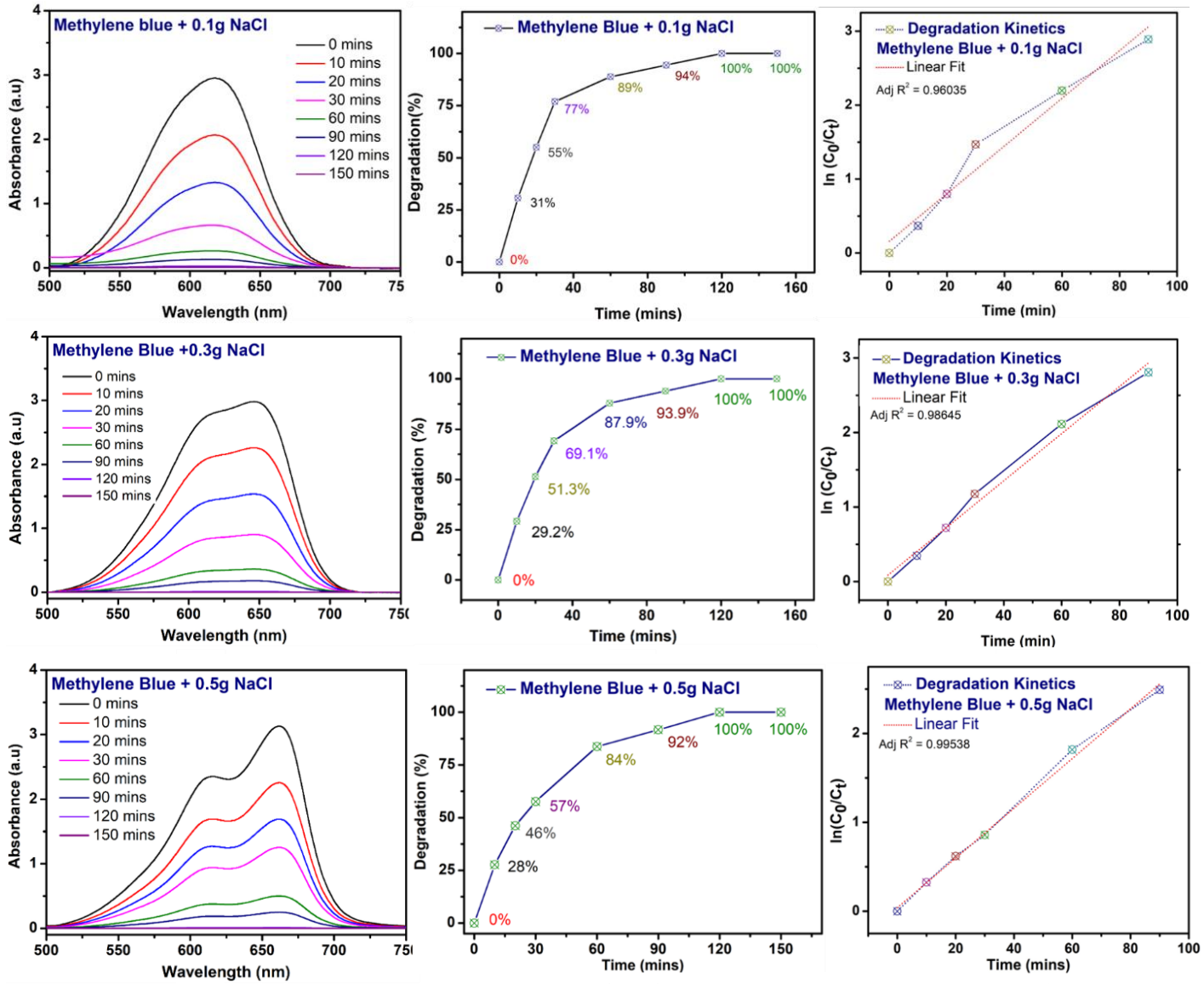


Observations:

1. Progressive decrease in MB absorbance with increasing plasma-treatment time
2. Degradation efficiency increased with treatment duration.
3. Solution pH influences plasma-assisted MB degradation and its apparent kinetics.

Effect of NaCl Concentration on MB Degradation

UV–visible absorption spectra *Degradation profile* *Degradation kinetics*



Effect of NaCl Concentration on MB Degradation

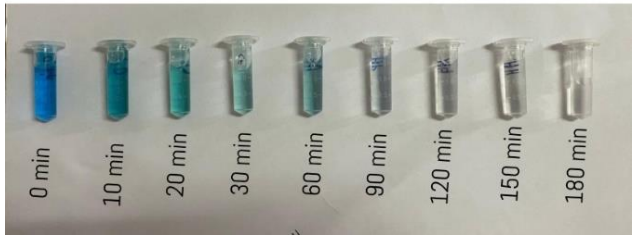
Degradation Behavior

Treatment time	0.1 g NaCl	0.3 g NaCl	0.5 g NaCl
10 min	31%	29.2%	28%
20 min	55%	51.3%	46%
30 min	77%	69.1%	57%
60 min	89%	87.9%	84%
90 min	94%	93.9%	92%
120 min	100%	100%	100%

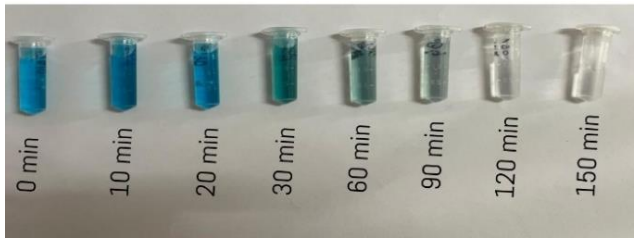
Pseudo-First-Order Kinetic Analysis

NaCl addition	k (min^{-1})	Half-life (min)	Adjusted R^2
0.1 g	0.0344	20.16	0.9604
0.3 g	0.0314	22.11	0.9865
0.5 g	0.0274	25.30	0.9954

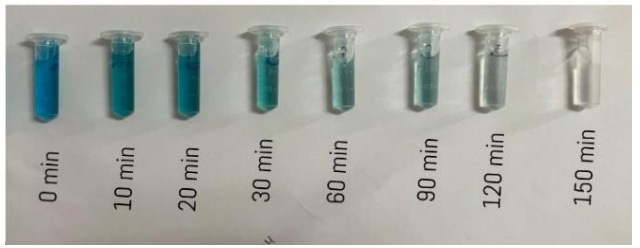
Methylene Blue + 0.1g NaCl



Methylene Blue + 0.3g NaCl



Methylene Blue + 0.5g NaCl



Increasing NaCl concentration decreases the apparent pseudo-first-order rate constant and increases the degradation half-life.

Conclusion

- Atmospheric-pressure plasma treatment promotes MB degradation through simultaneous physical and chemical processes involving energetic electrons, excited species and reactive intermediates.
- Plasma–liquid interactions may generate highly reactive species, particularly hydroxyl radicals (•OH) and hydrogen peroxide (H_2O_2), which contribute to dye degradation.
- The progressive decrease in UV–Visible absorbance indicates the destruction or transformation of the MB chromophore.
- HCl and NaCl containing systems exhibit slower initial degradation, suggesting an inhibitory influence of chloride ions on the degradation process.
- Chloride ions may scavenge hydroxyl radicals, forming less reactive or differently reactive chlorine-based species and reducing the availability of •OH for MB degradation.
- Changes in solution pH may also influence the plasma–liquid interaction and degradation kinetics.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