The Dual Roles of Activated Carbon as an Adsorbent and Photocatalyst for Azo Dye Removal

INTRODUCTION

- The growth of the **fast fashion** and **textile industries** has proliferated the **release of toxic azo dye effluent,** contributing to **20% of global industrial pollution** [1-3]
- **Industrial wastewater** consists of **many different azo dyes** [4]
  → **a universal treatment is urgently needed**
- **Mordant Orange 1 (MO1)** (Fig. 1A) and **Reactive Black 5 (RB5)** (Fig. 1B) are structurally **diverse** [5-8]
- Among conventional methods, **adsorptive removal** by **activated carbon (AC)** is **inexpensive** and viable for easy operation [9, 10]
- AC can generate **reactive radicals under UV light** [11-13]

How are AC's dual roles as an adsorbent and photocatalyst employed for MO1 and RB5 dye removals?

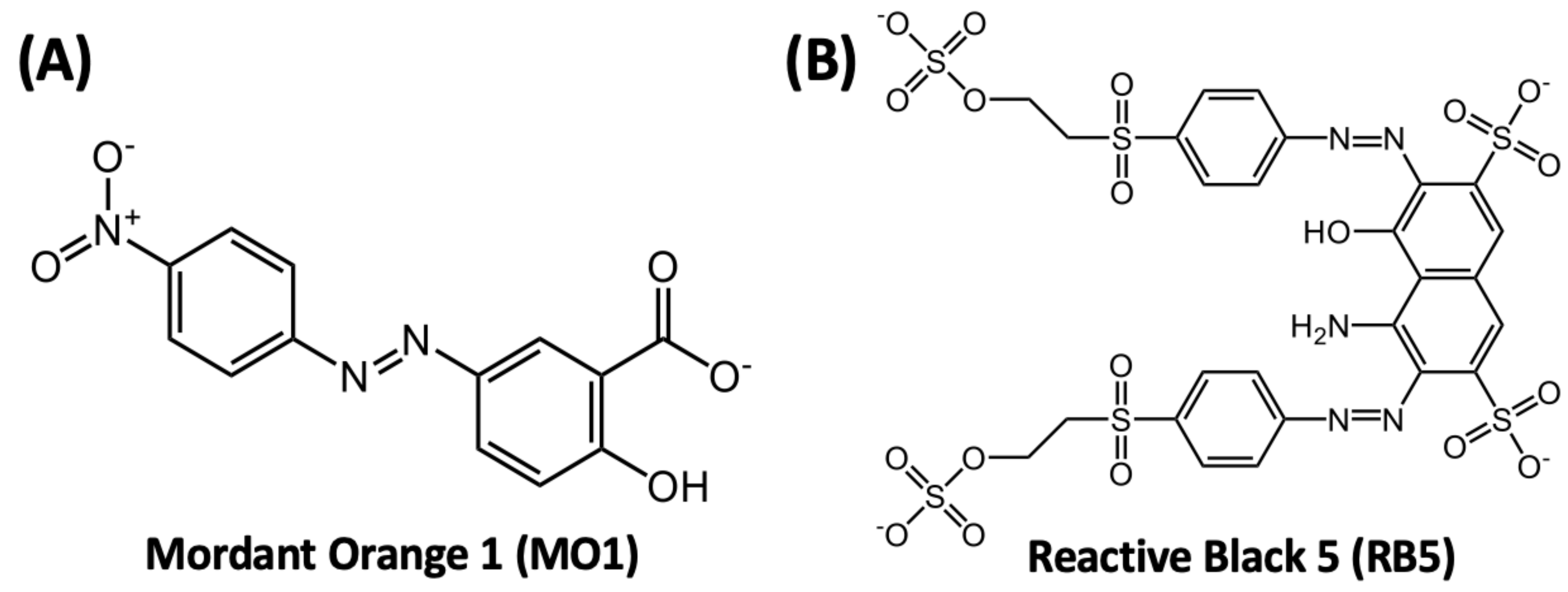

Fig 1. Chemical structures of (A) MO1 and (B) RB5. Image created by the student author.

METHODOLOGY

- MO1 and RB5 solutions were stirred with AC under UV light or no light for 60 min and 120 min, respectively
- Data on RB5 concentrations in solution overtime were fit to the Langmuir-Hinshelwood (LH) kinetic model
- **Lactone**, **carboxyl**, **hydroxyl**, and **aldehyde** groups were computationally added to AC's structure with the Amsterdam Modeling Suite

RESULTS AND DISCUSSION

MO1 Removal by AC with and without UV light

- Abs peak at **373 nm** attributed to the **azo bond** and its surrounding chemical moieties [14]
- **Under darkness,** Abs peak decreased over time (Fig. 2)

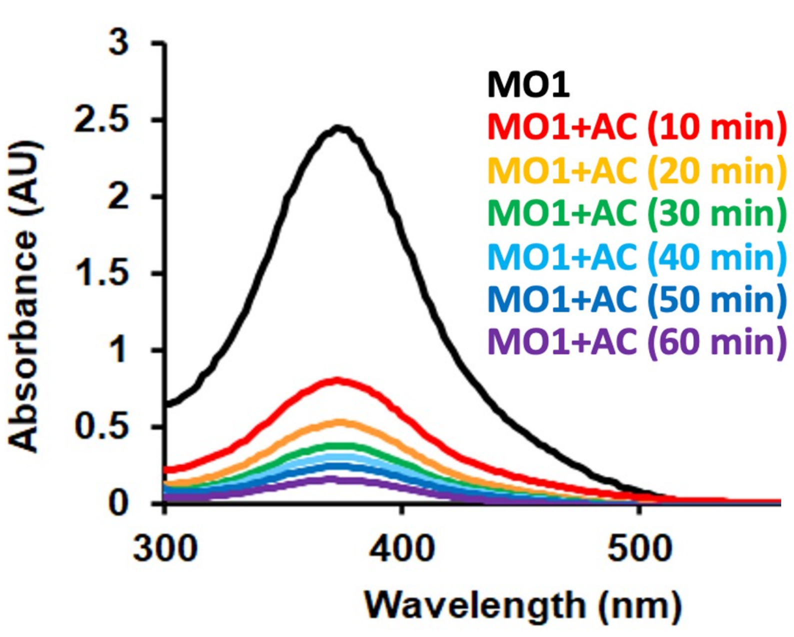

Fig. 2. Time-course removal of MO1 (430 mg/L at t=0) by AC (20 mg) under darkness at room temperature. MO1's absorbance peak at 373 nm decreased over time. Determined with UV-VIS spectroscopy. Image created by the student author.

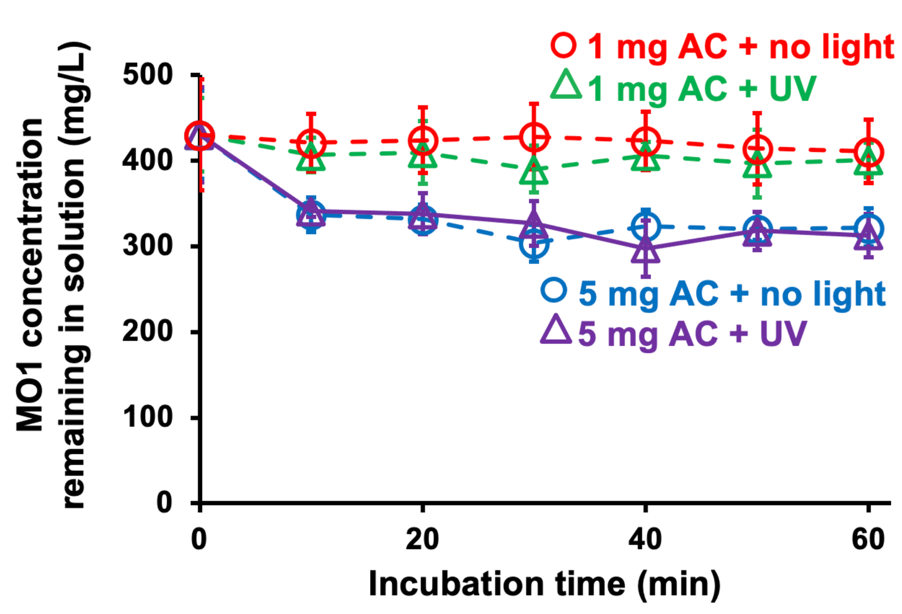

Fig. 3. Comparison of MO1 (430 mg/L at t=0) removals by 1 and 5 mg AC under darkness vs. UV irradiation at room temperature. MO1 removal was similar with and without UV light inclusion. Error bars: 1 SD for triplicate measurements. Image created by the student author.

- MO1 removal by AC was **similar** under **UV light and no light** (Fig. 3)
- MO1 is a **salicylic acid**, a group known for its **radical scavenging** activity → diminishes the effects of reactive radicals [15-17]

MO1 removal with AC occurs by a non-light assisted mechanism → ADSORPTION

Impacts of Chemical Modifications on AC's Band Gap

- AC's photocatalytic ability is determined by the **band gap** → a **smaller band gap energy** enhances photocatalytic properties [21]
- Difference in band gap varied with the **identity** and **quantity** of **chemical groups** added (Fig. 6)

Band gap energy decreased by adding aldehyde groups

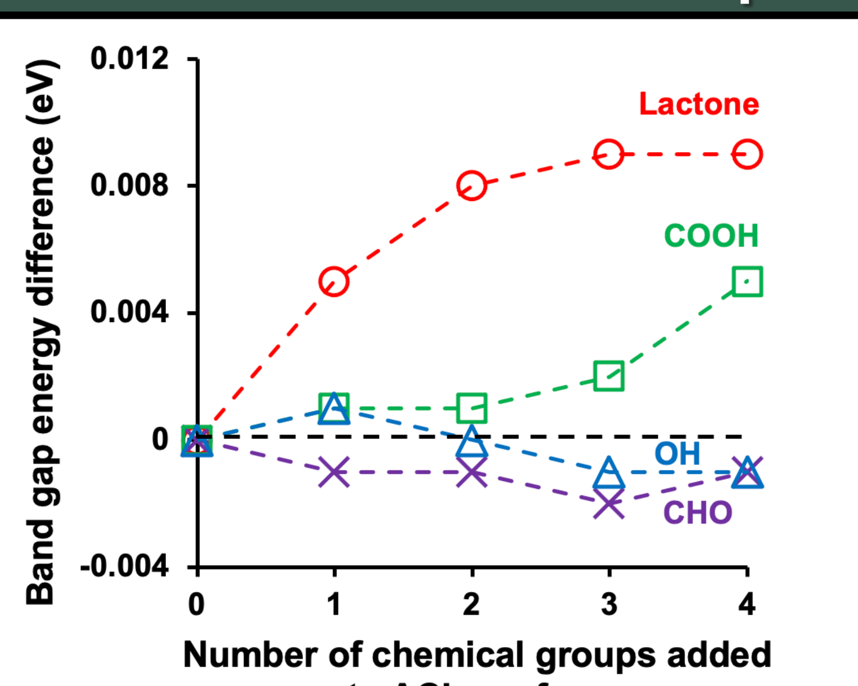

Fig. 6. Effects of various chemical modifications on band gap energy of AC. Band gap energies of AC and AC derivatives containing varying numbers of chemical groups (lactone: $C_9H_{16}O_2$, carboxyl group: COOH, hydroxyl group: OH and aldehyde: CHO) at the four corners of AC were calculated by the Amsterdam Modeling Suite and BAND. Image created by the student author.

RB5 Removal by AC with and without UV light

- Abs peak at **310 nm** attributed to **aromatic and naphthalene rings** and Abs peak at **596 nm** attributed to **azo bonds** [18]
- **Under UV light,** Abs peaks decreased over time (Fig. 4)

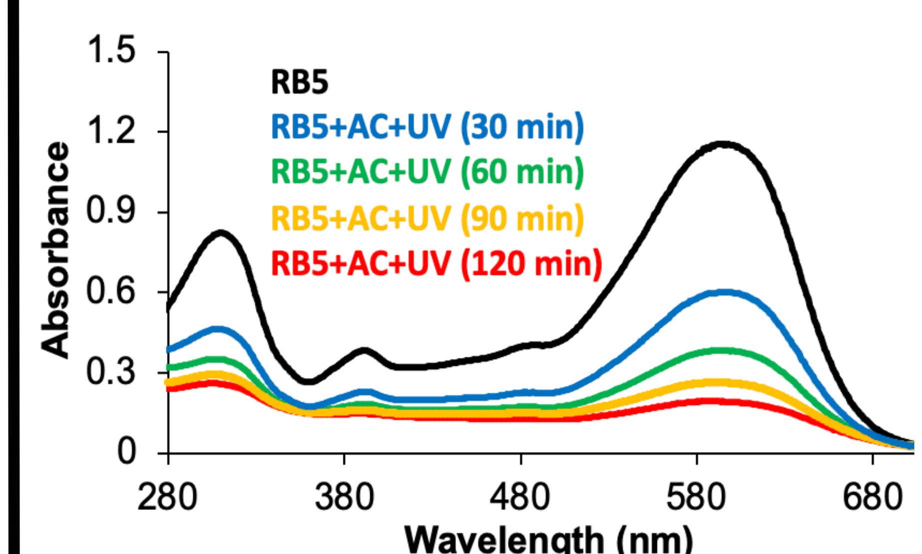

Fig 4. Decolorization of RB5 (77mg/L at t=0) by AC (0.1g) under UV light at room temperature. Image created by the student author.

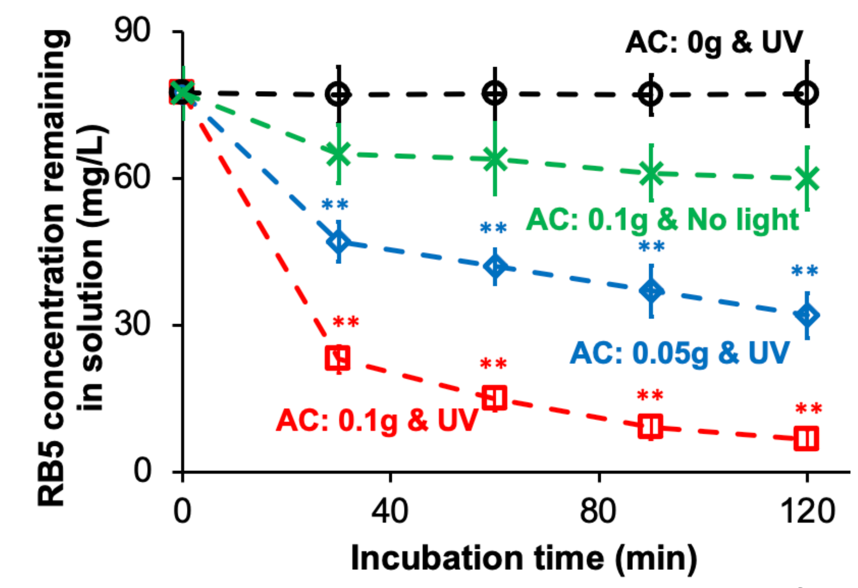

Fig 5. RB5 removal with various amounts of AC under UV light or no light at room temperature. [RB5] at $_{t=0}$ = 77 mg/L. **: $p < 0.01$ relative to (AC: 0g & UV) and (AC: 0.1g & Dark) for triplicate measurements. Error bars: 1 SD. Image created by the student author

- RB5 removal was **faster** with **greater amounts of AC under UV irradiation** (Fig. 5)
  - 92% removal for 100 mg of AC and UV light
  - 22% removal for 100 mg of AC only
- LH kinetic model: $\ln\left(\frac{[RB5]}{[RB5]_{t=0}}\right) + K_L([RB5] - [RB5]_{5=0}) = -K_L \cdot k_{LH} \cdot t$ [19]

Table 1. Fitted RB5 removal rate data to the LH kinetic model

AC (mg)	50	50	100
$[RB5]_{t=0}$ (mg/L)	58	77	77
K_L (L/mg)[a]	2.1 ± 0.2 ×10^{-2}	1.4 ± 0.7 ×10^{-2}	1.6 ± 0.5×10^{-2}
k_{LH} (mg/L/min)[a]	0.8 ± 0.2 ×10^{-1}	1.3 ± 0.5×10^{-1}	7.4 ± 2.0×10^{-1}
R^2	0.9990	0.9942	0.9981

[a]Best fit value ± 95 % confidence interval

- K_L (Equilibrium constant for RB5 adsorption on AC) is **AC amount-independent** [20]
  - **Statistically similar K_L values** and **high R^2 values** suggest that the LH model is a good RB5 removal model (Table 1)
- k_{LH} (reaction rate constant) **increases** with **greater amount of AC** (Table 1) → **AC** acts a **photocatalyst** in **RB5 removal**

RB5 removal with AC occurs synergistically with UV irradiation → PHOTOCATALYSIS & ADSORPTION

CONCLUSION

AC is universal, versatile, and efficient for azo dye removal through its mechanisms of adsorption and photocatalysis

Proposed Reaction Mechanism for RB5 Removal

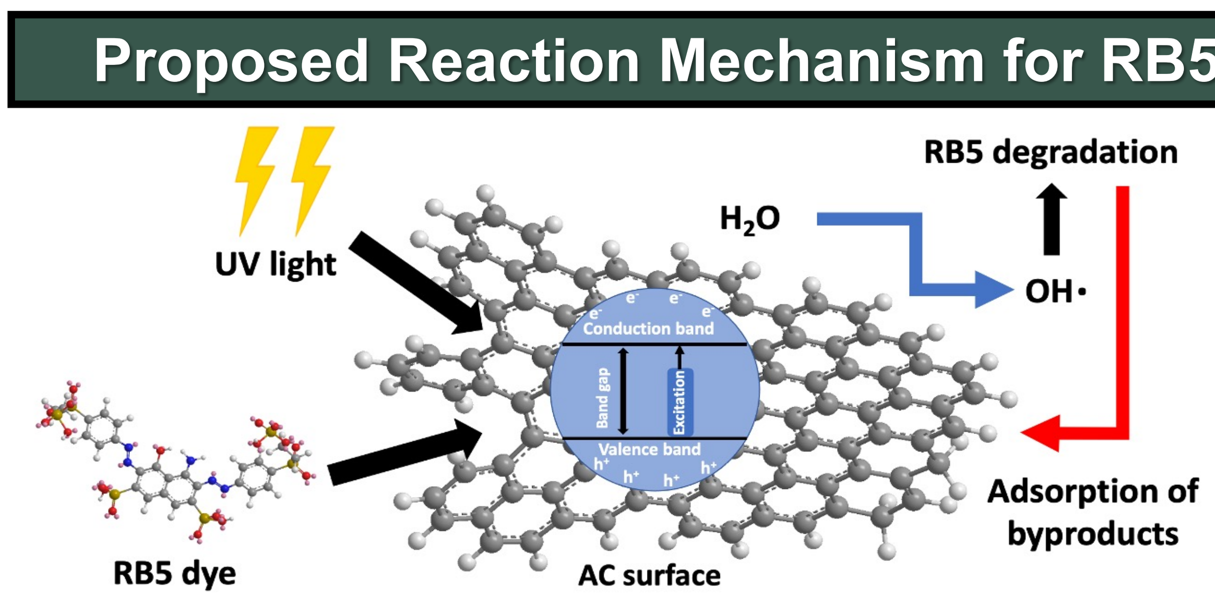

Fig. 7. An RB5 removal mechanism by AC under UV light. Image created by the student author.

1. RB5 dye adsorbs on AC (Fig. 7) [22]
2. HO· are generated from $H_2O \leftrightarrow H^+ + OH^- \rightarrow OH\cdot$ under UV light [22], catalyzed by AC [23, 24]
3. HO· reacts with and degrades RB5 adsorbed on AC [25]

Future Investigations & Applications

- Integration of a process to **separate** and **recycle AC** after azo dye removal (Fig. 8) [26]
- Azo dye removal via AC should be tested **in situ** [27]
- AC can be used to treat **diverse azo dyes** used in the **fast fashion** and **textile** industries with a **large-scale reactor** [28, 29]

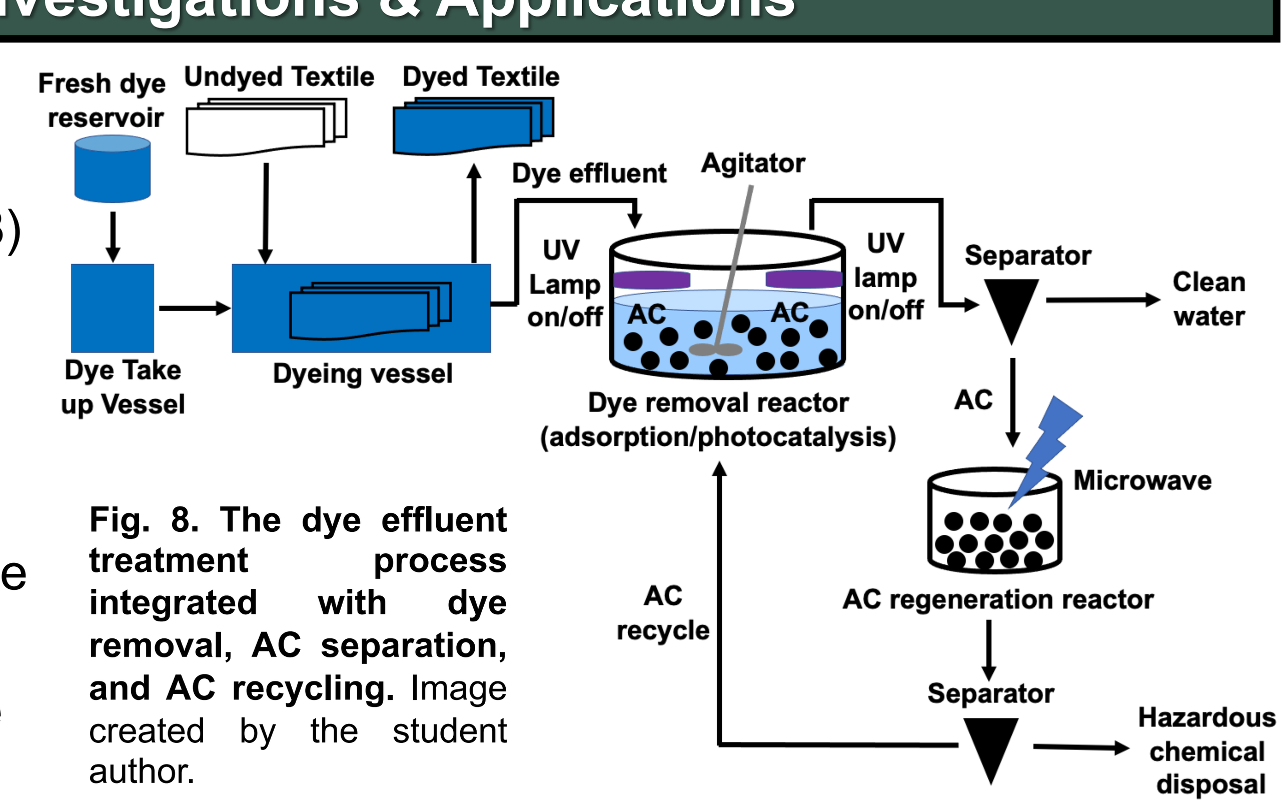

Fig. 8. The dye effluent treatment process integrated with dye removal, AC separation, and AC recycling. Image created by the student author.