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Photocatalytic Performance of Composites of Prussian Blue and Its Analogues with Anatase for UV-Driven Degradation of Aqueous Methylene Blue Solutions: Chemical and Ecotoxicological Evaluation

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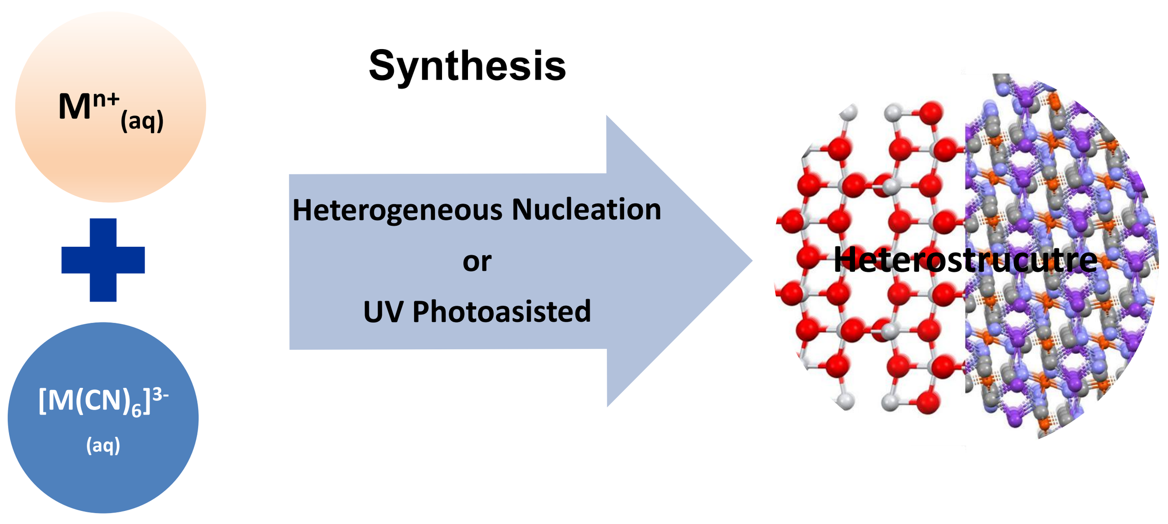
INTRODUCTION & AIM

Environmental motivation:
Methylene Blue (MB) is a chemically stable dye with high visible-range molar absorptivity, making it both persistent in aquatic systems and easily traceable by spectrophotometry. Even at low concentrations, MB disrupts photosynthesis and oxygen balance, posing ecotoxicological risks in textile wastewater.

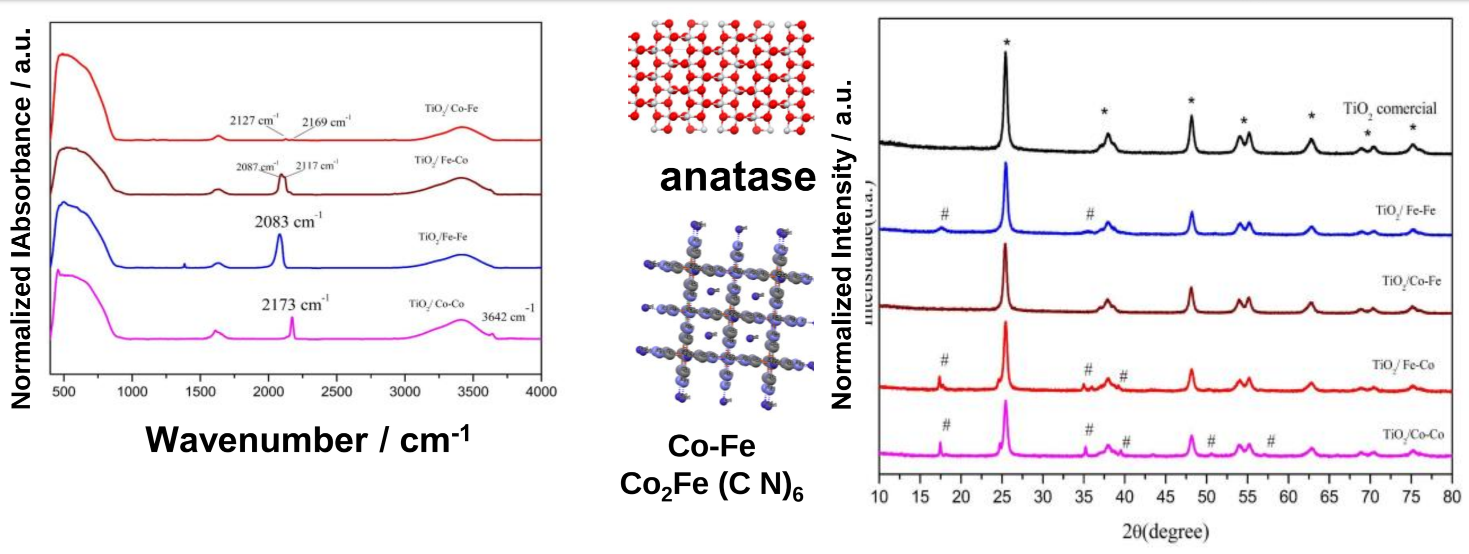
Sustainable Materials Strategy
Cost-effectivenes Scalable Synthesis
Abundant, non-noble transition metals (Fe, Co) and water as the primary solvent
Photoassisted and Precipitation Aqueous Green Synthesis

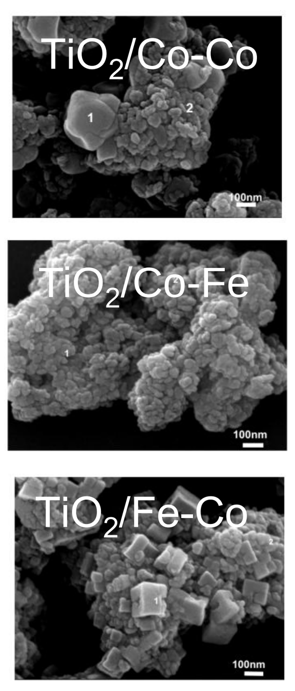
Scientific Objective
Develop Anatase/PB and Anatase/APB composites to promote interfacial charge separation and reactive oxygen species (ROS) formation for dye photodegradation.

METHOD



RESULTS & DISCUSSION

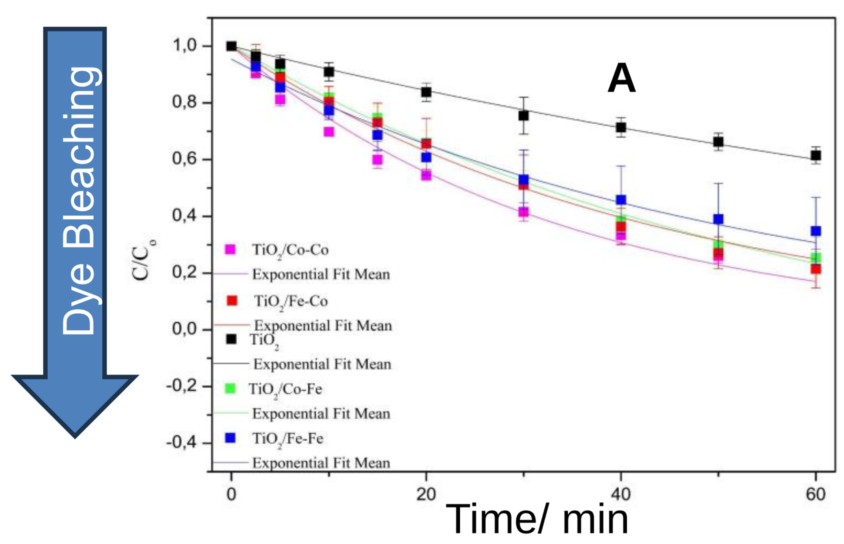


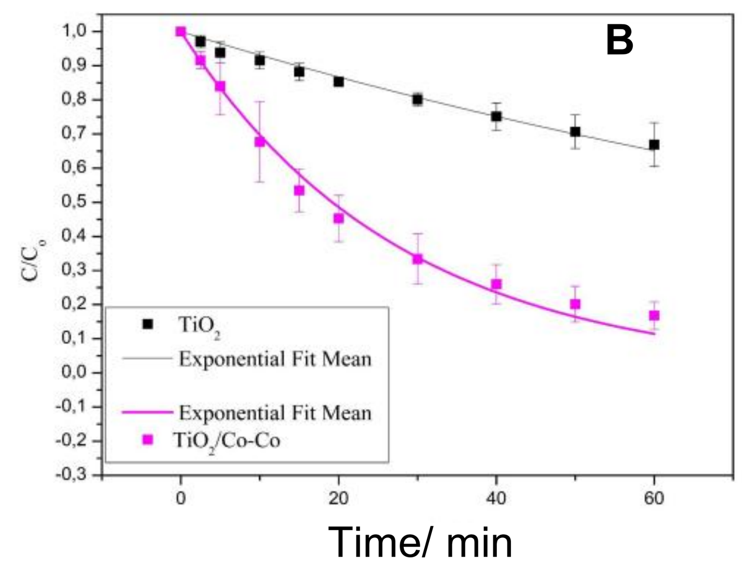


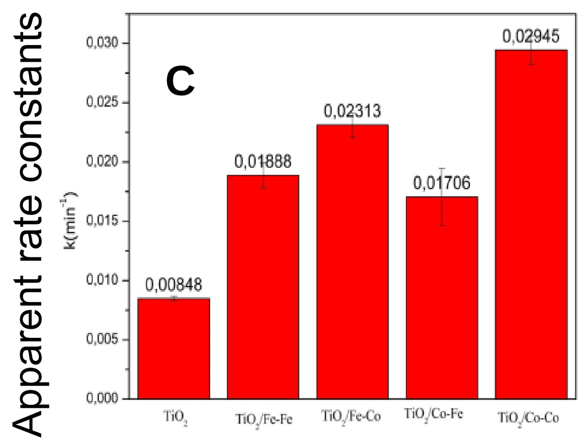
SEM micrographs (left) of selected TiO_2/APB composites showing distinct morphologies depending on the coordination polymer phase.

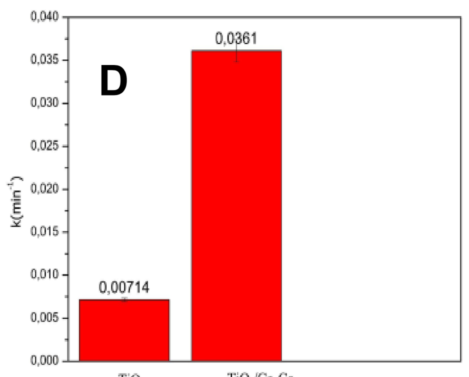
The table (right) summarizes estimated optical band gaps (E_g) for pure phases and TiO_2-based composites, revealing evidence of dual-band absorption behavior in heterostructures such as TiO_2/Fe-Co and TiO_2/Fe-Fe, likely arising from interfacial interactions or electronic decoupling between components.

Material	Eg (eV)
TiO_2	3,28
Co- Co	1,99
Fe-Co	2,45 ; 1,6
Fe-Fe	1,6
Co-Fe	2,78
TiO_2/Fe-Co	1,56 e 3,27
TiO_2/Fe-Fe	1,6 e 3,25
TiO_2/Co-Fe	3,2
TiO_2/Co-Co	3,3



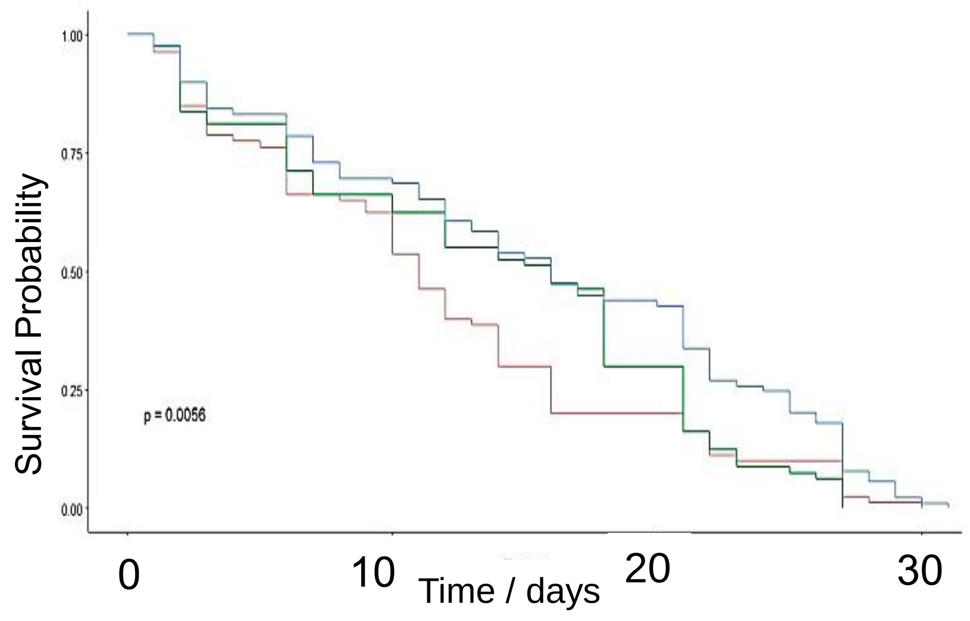






Material	Initial TOC (mg/L)	Final TOC (mg/L)
TiO_2/Co-Co	66.24	60.00 (after 1 h)
TiO_2		63.01 (after 1 h)

Photocatalytic degradation of methylene blue (MB).(A) MB concentration (C/C_0) vs. time for TiO_2 and its composites with PB and analogues. (B) Comparison of dye bleaching between TiO_2 and a TiO_2 + Co-Co physical mixture.(C) Apparent rate constants (k, min^{-1}) for TiO_2 and composite materials.(D) Comparison of k values for TiO_2 and TiO_2 + Co-Co physical mixture. Table: TOC values before and after 1 h of irradiation. Conditions: 20 mg catalyst in 35 mL H_2O (pH 5.6) + 35 mL MB (10 ppm); sonicated 1 h, stirred 30 min in the dark. UV irradiation applied via optical fiber from a Xe/Hg lamp, 6 cm from a borosilicate reactor. Aliquots (800 µL) collected over 1 h. Error bars represent SD (n = 3).



TL_{50} (C) = 16 days; TL_{50} (E1) = 11 days; TL_{50} (E2) = 12 days

Kaplan–Meier survival curves for stingless bees (Scaptotrigona postica) exposed to: control diet (C, red), methylene blue-contaminated syrup (E1, green), and photodegraded methylene blue syrup (E2, blue). The assay included 240 bees from four unrelated colonies (A–D), with 20 individuals per treatment group per colony (10 bees per replicate). No feeding deterrence was observed during the pilot assay. Survival was monitored daily over 31 days, and forid (parasite) presence was recorded. The log-rank test yielded p = 0.0056, indicating a statistically significant difference in survival among the groups.

CONCLUSION

- **TiO_2/Co-Co** composite showed **best photocatalytic rate** for MB degradation but **very small mineralization**;
- **Physical mixture** (TiO_2 + Co-Co) showed comparable activity, suggesting non-heterojunction effects (e.g., surface co-catalysis or additive ROS generation)

⚠️ Low TOC removal indicates incomplete mineralization despite discoloration

🐝 Significant reduction in ecotoxicity observed in Brazilian stingless bee, *Scaptotrigona postica*, assays (partial detoxification)

FUTURE WORK

- Identify dominant **ROS species** (e.g., •OH vs. $O_2^{\bullet-}$)
- Correlate **composite morphology** with ROS profile and degradation efficiency
- Differentiate **heterojunction effects** from physical mixing via mechanistic tools (e.g., EPR, scavenger tests)
- **Enhance mineralization** by favoring hydroxyl radical formation (e.g., surface modification, light intensity tuning)
- Expand **ecotoxicological assessment** to aquatic and multi-trophic models