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Fabrication of aluminum-based hybrid nanocomposite for photocatalytic degradation of methylene blue dye: A techno-economic approach

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Methylene Blue (MB) dye

- MB is a synthetic cationic thiazine dye
- Soluble in water (43,600 mg/L at 25 °C)

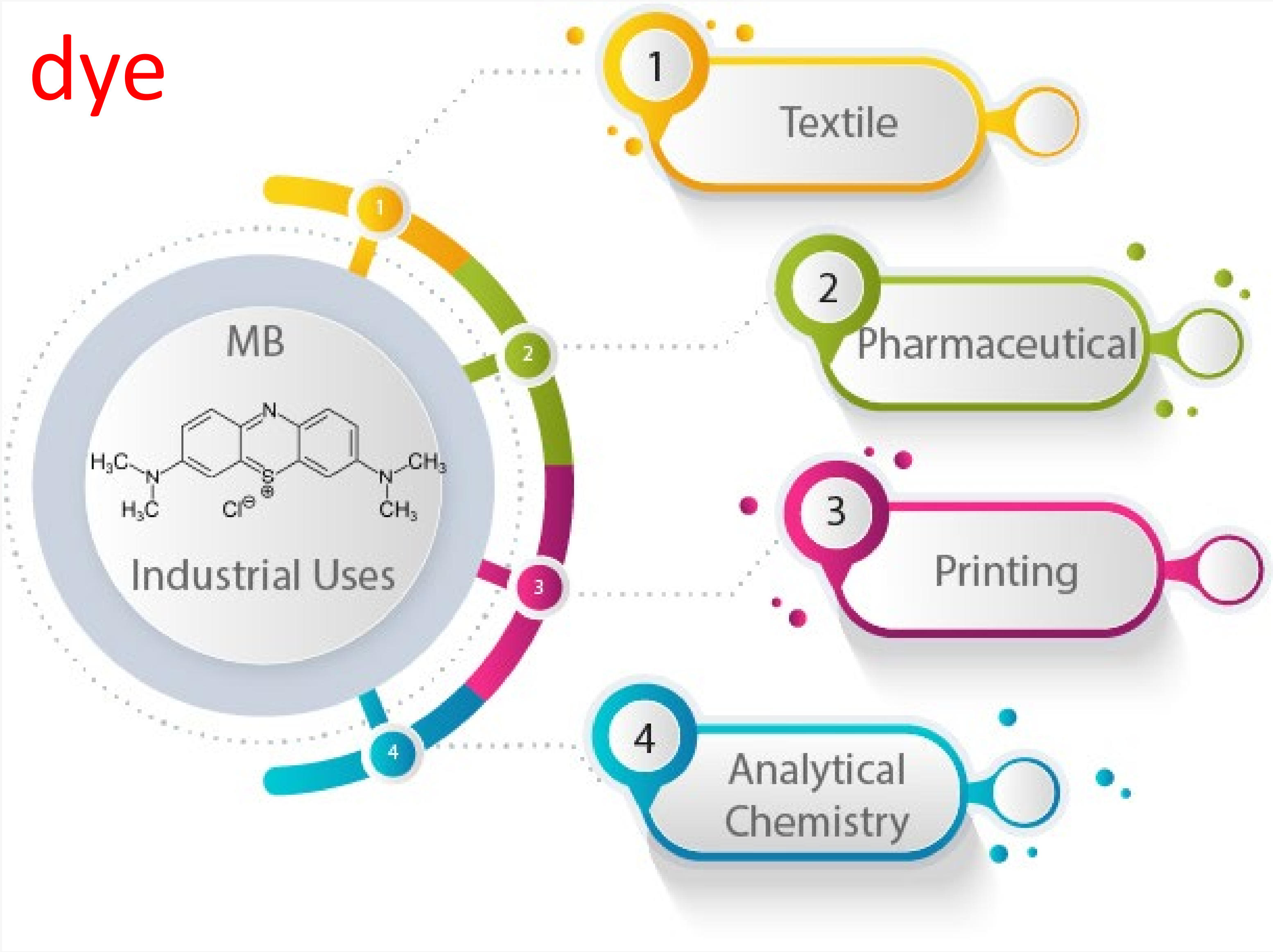

Figure 1. Industrial uses of MB dye

Toxicity of MB dye

- MB dye laden wastewater discharge in marine ecosystems:
  - ➢ Low sunlight transmittance for photosynthesis by aquatic plants
  - ➢ MB dye forms complex products leading to low dissolved oxygen and death of aquatic organisms
- MB is highly stable and cannot be removed by conventional wastewater treatment methods

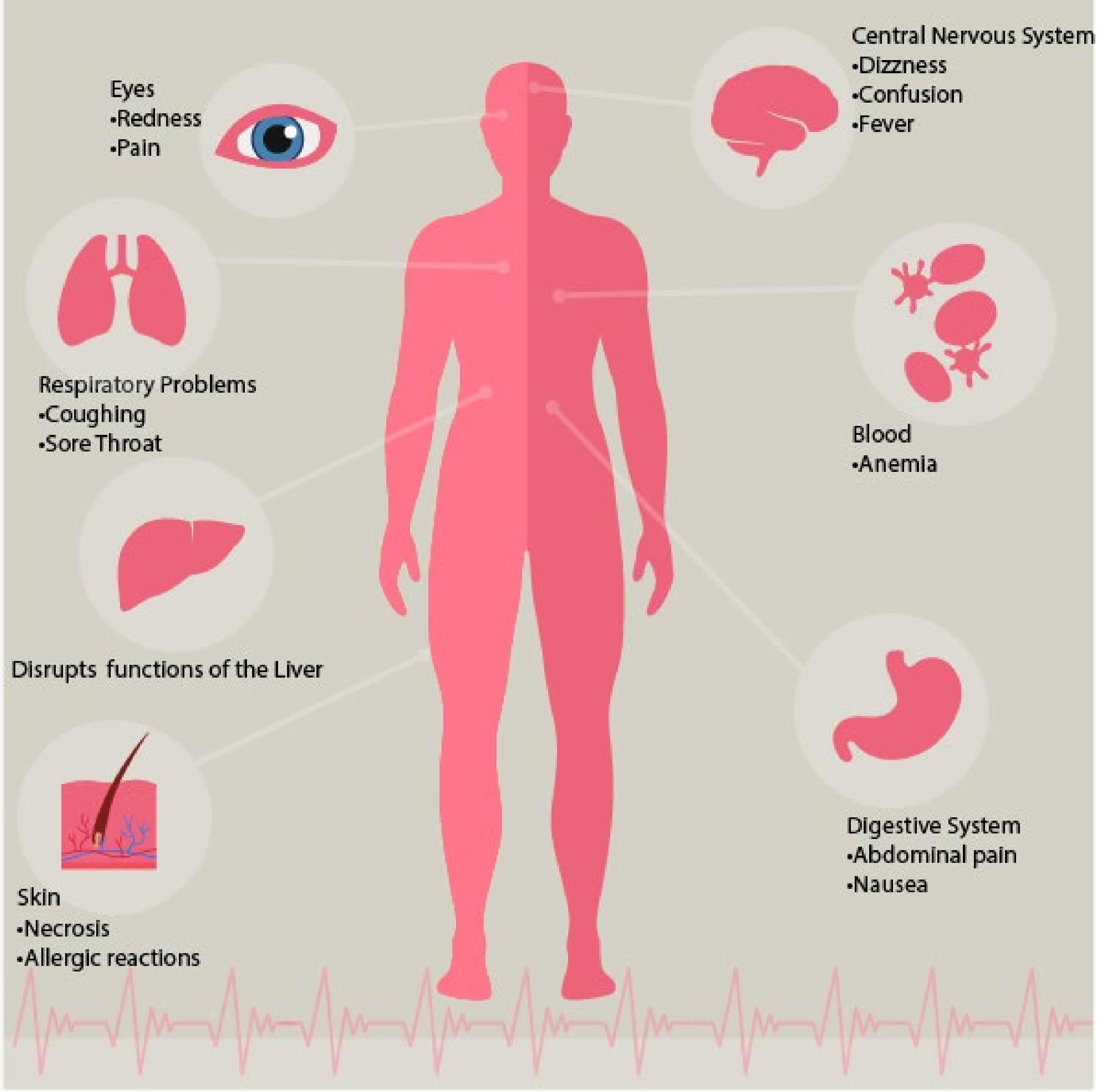

Figure 2. Effects of MB dye exposure on humans

Advanced Oxidation Processes

- Advanced Oxidation Processes(AOPs) are treatment techniques aimed at mineralizing refractory organic pollutants in wastewater mainly using OH•.
- AOPs are efficient technologies in the elimination of pollutants such as MB from wastewater
- AOPs include;
  - Photocatalysis
  - Ozonation
  - Photo-Fenton

Photocatalysis

- It is an AOP that utilizes catalysts and light irradiation for degradation of pollutants
- Heterogenous photocatalysis utilizes solid semiconductor catalysts such as TiO_2, ZnO for degradation of pollutants in aqueous phase
- Al_2O_3 has orderly nanopore structures and significant photocatalytic activity.
- Al_2O_3 can be synthesized from waste material such as aluminum cans, hence reducing costs in photocatalysis.
- Al_2O_3 nanocomposites can have higher photocatalytic activity due to formation of heterojunctions with other semiconductor materials.

Study Objectives

1. Synthesis of Al_2O_3-MgO nanocomposite
2. Investigate the effect of operating parameters in MB photodegradation
3. Estimate the economic feasibility of photocatalytic degradation of MB dye using Al_2O_3-MgO

Methodology: Al_2O_3-MgO photocatalyst synthesis

- Co-precipitation method was used for synthesis of Al_2O_3-MgO.

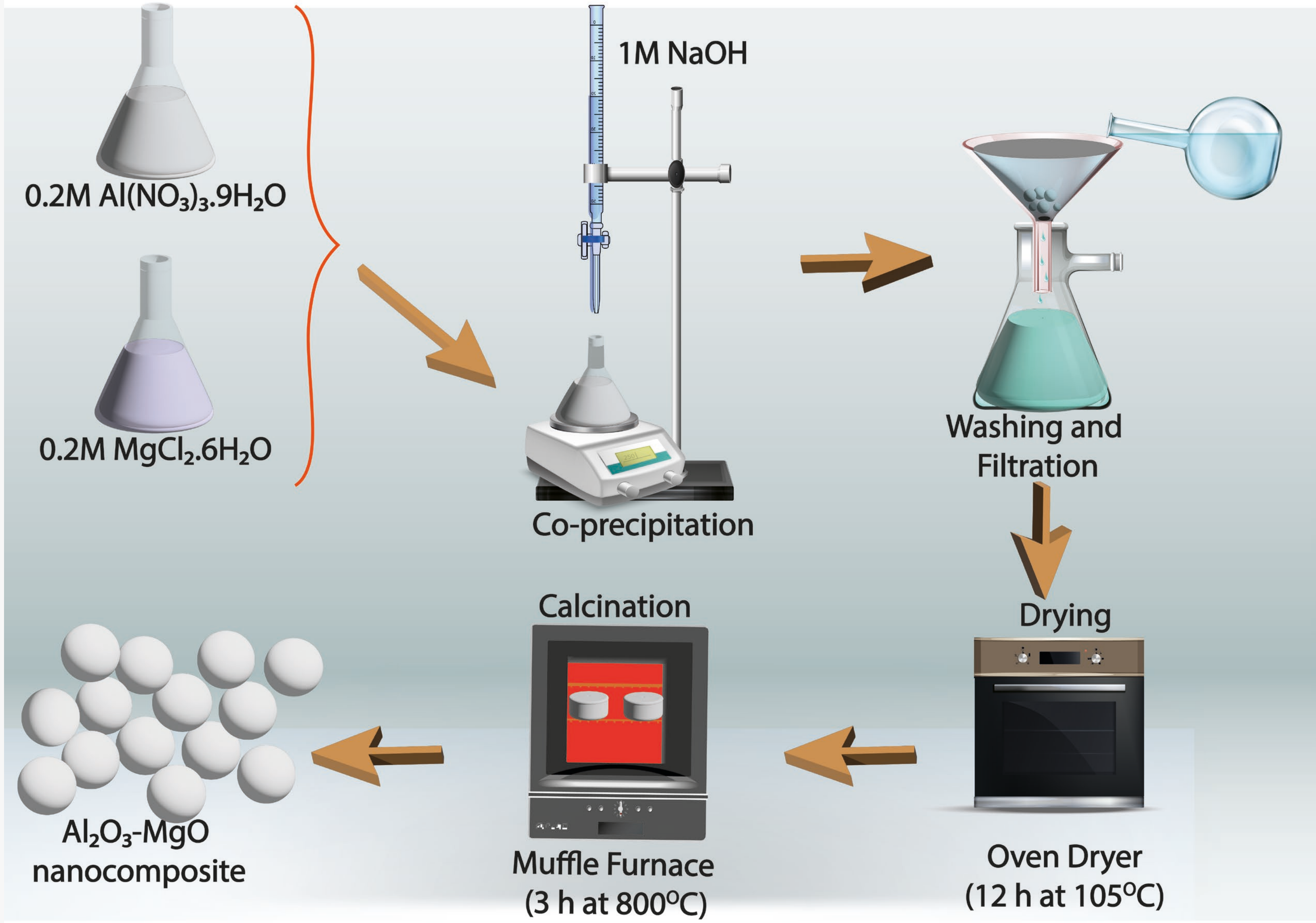

Figure 1. Synthesis method

Experimental setup

- Photoreactor with a 400 W metal halide lamp
- 60 min stirring in the dark to achieve adsorption/desorption. Light is turned on for MB dye photocatalytic degradation reaction.
- Initial(C_o) and final(C_f) concentrations of MB dye measured at 664 nm using UV-spectrophotometer.

Table 1. Experimental factors and limits for Box Behnken Design(BBD) in Response Surface Methodology(RSM)

Factor	Parameter	Unit	Levels		
			Low	Median	High
A	pH	-	3	7	11
B	Time	min	60	120	180
C	Photocatalyst dosage	mg/L	200	600	1000
D	Initial MB dye concentration	ppm	10	55	100

UV-DRS Analysis

- Band gap energy of Al_2O_3-MgO is 3.50 eV.
- This is higher than that of Al_2O_3 (5.97 eV).

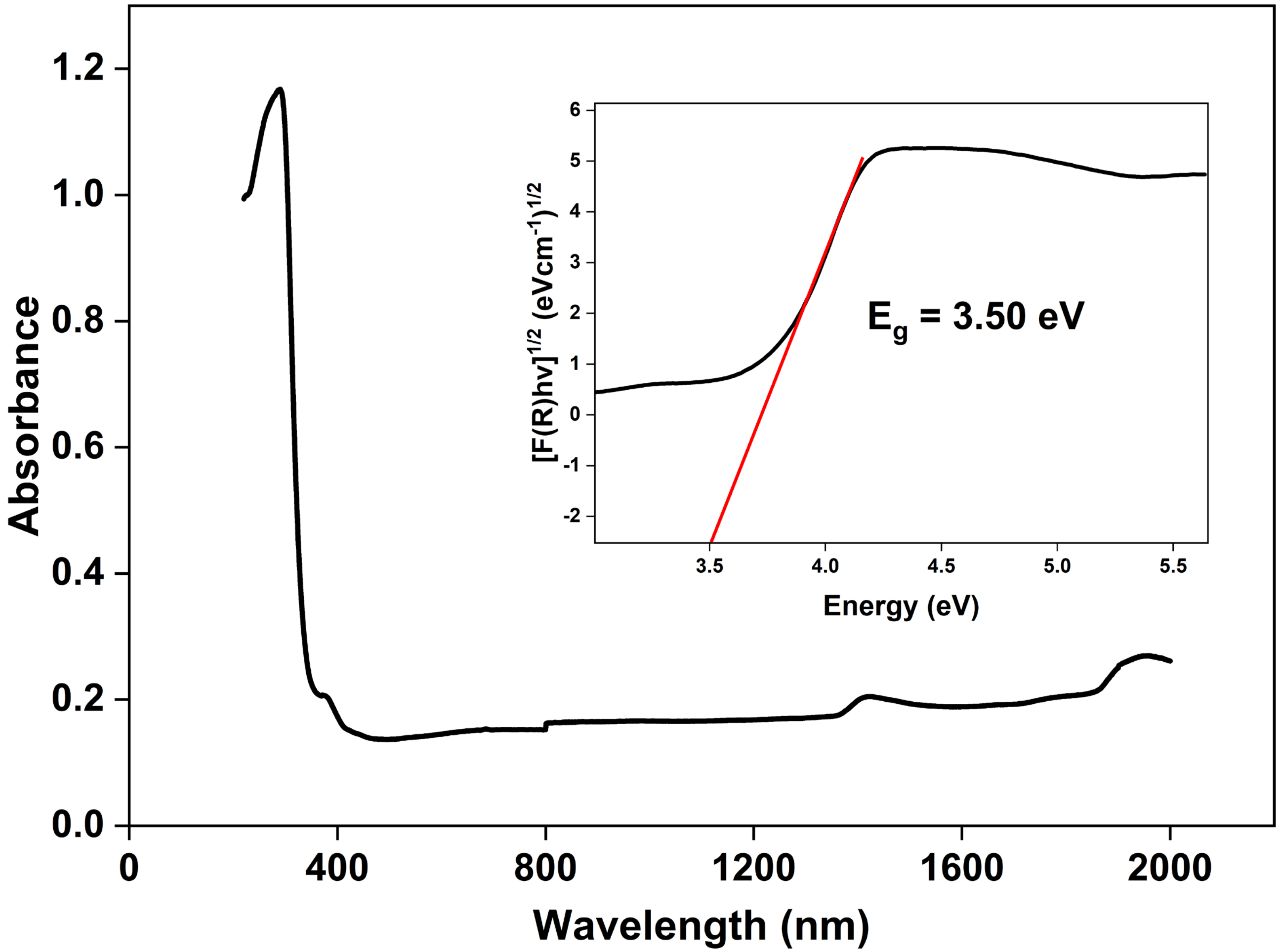

Figure 2. Absorbance plots for Al_2O_3-MgO

Initial catalyst tests

- Pure Al_2O_3 had photodegradation efficiency of 43,57% whereas Al_2O_3-MgO had 72.72%.
- Al_2O_3-MgO has lower band gap energy than Al_2O_3 hence higher photocatalytic activity.

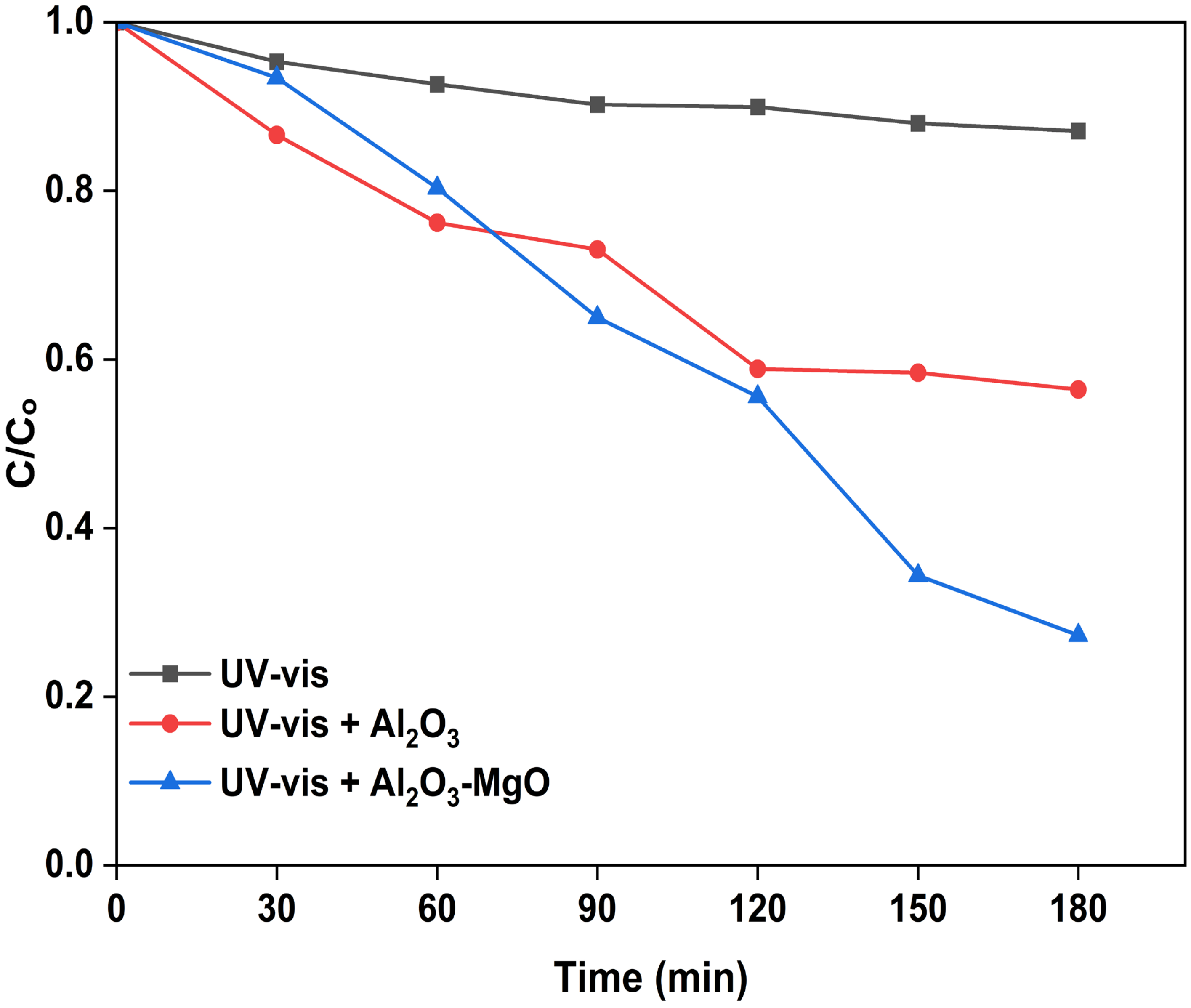

Figure 3. Initial photocatalyst test

Effect of operational parameters

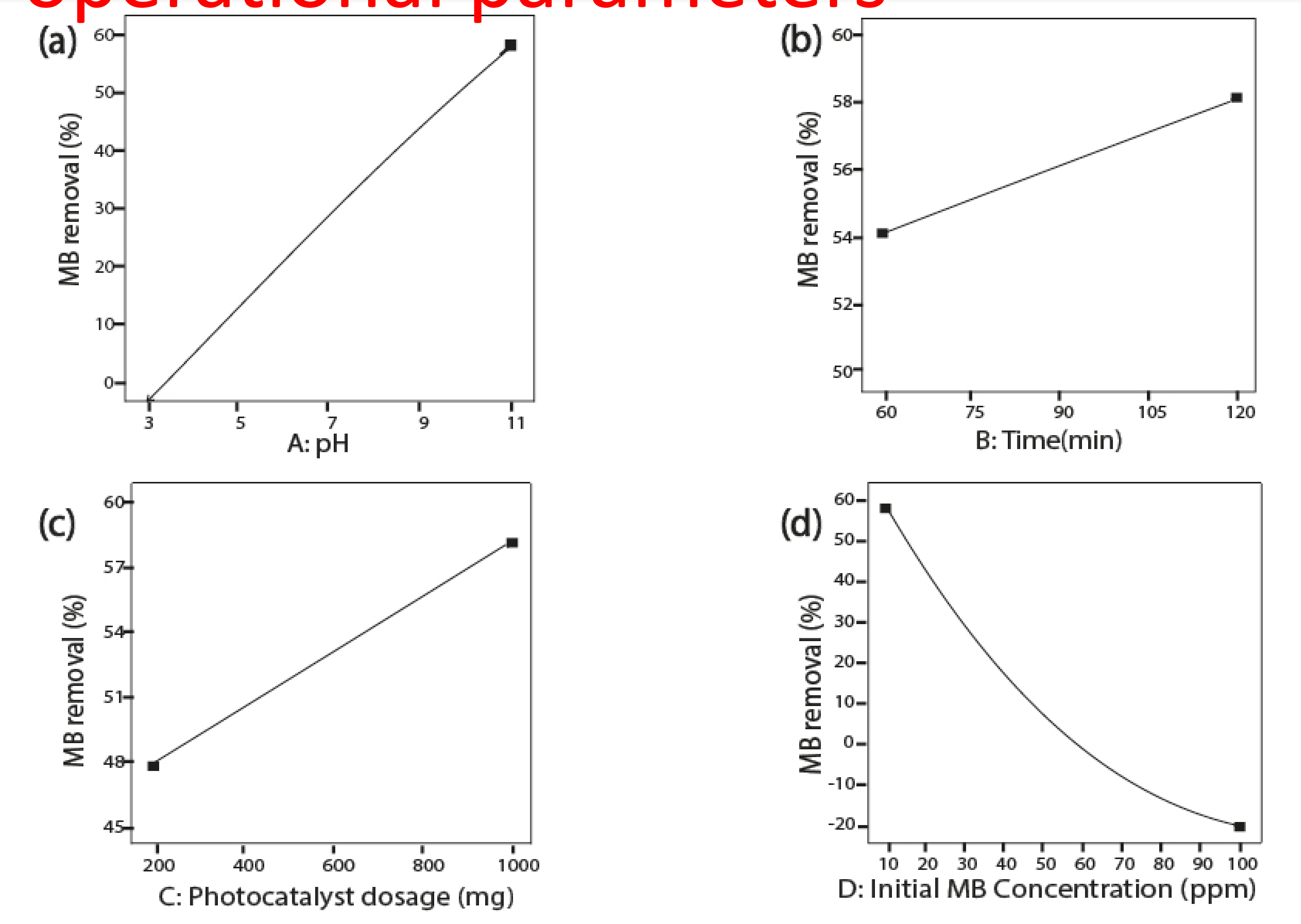

Figure 4. Effect of operational parameters

Effect of operational parameters

- Figure 4a shows effect of pH. In acidic pH, MB exists as a neutral molecule(pH< pKa (3.8)) below and surface of Al_2O_3-MgO is positively charged (pH_{zc} = 10.04) hence low adsorption on catalyst surface and low photodegradation efficiency.
- As the pH approaches the pH_{zc}, the repulsive force against MB cations is reduced . Above the pH_{zc}, Al_2O_3-MgO surface is negatively charged and attracts the MB cations hence higher photodegradation efficiency.
- In Figure 4b, at constant photocatalyst dosage, more electrons and holes are generated by Al_2O_3-MgO as irradiation time increases. This leads to production of more reactive radical species, leading to an increment in the photocatalytic degradation efficiency

Effect of operational parameters

- Figure 4c shows effect of photocatalyst dosage. Increasing Al_2O_3-MgO dosage leads to the generation of more active sites and subsequently leads to higher MB photodegradation efficiency.
- In Figure 4d shows effect of initial MB dye concentration. As MB dye concentration increase, there is limitation of photon influx on the Al_2O_3-MgO surface, resulting in low generation of electrons and holes.

Optimization of operational parameters

- Significant terms to the model have $p < 0.05$ ✓
- Model R^2 value of 0.9880 indicating good fit

Table 2. ANOVA analysis

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1029.44	14	73.53	81.99	< 0.0001	significant
A-pH	29.26	1	29.26	32.63	< 0.0001	✓
B-Time	11.41	1	11.41	12.73	0.0031	✓
C-Photocatalyst dosage	2.46	1	2.46	2.74	0.1198	
D-Initial MB dye concentration	348.8	1	348.8	388.92	< 0.0001	✓
AB	15.5	1	15.5	17.29	0.001	✓
AC	0.5407	1	0.5407	0.6029	0.4504	✓
AD	412.34	1	412.34	459.77	< 0.0001	✓
BC	4.39	1	4.39	4.9	0.0441	✓
BD	8.2	1	8.2	9.14	0.0091	✓
CD	4.11	1	4.11	4.59	0.0503	
A^2	12.29	1	12.29	13.7	0.0024	✓
B^2	0.0067	1	0.0067	0.0074	0.9325	
C^2	0.0006	1	0.0006	0.0006	0.9804	
D^2	152.97	1	152.97	170.57	< 0.0001	✓
Residual	12.56	14	0.8968			
Lack of Fit	10.6	10	1.06	2.17	0.2372	not significant
Pure Error	1.96	4	0.489			
Cor Total	1042	28				

Optimization of operational parameters

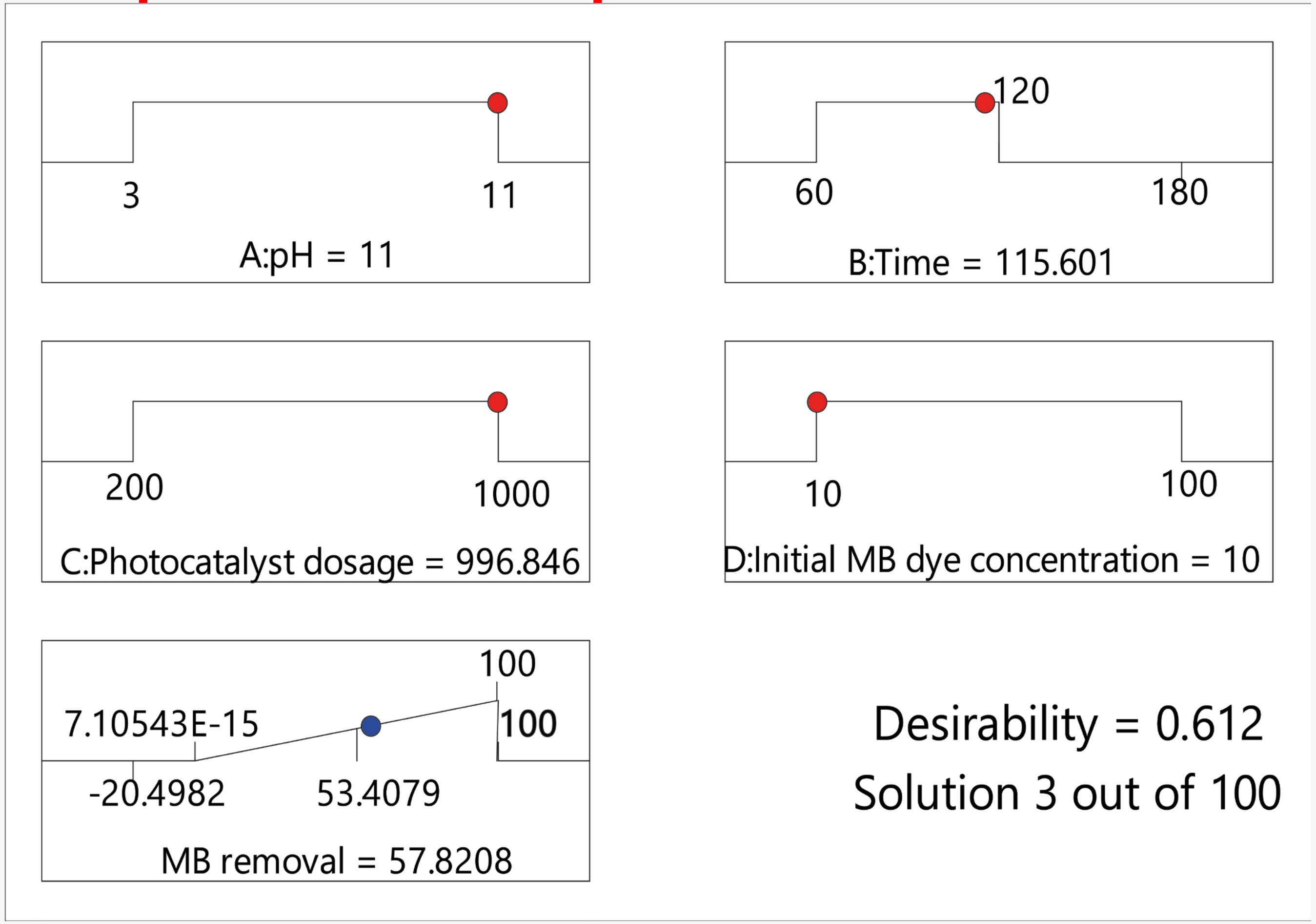

Figure 5. Optimized conditions

Coded Equation for MB removal:

$$(\text{MB removal} + 22.5)^{0.81} = 12.63 + 1.56A - 0.9753B + 0.4529C - 5.39D + 1.97AB + 0.3677AC - 10.15AD - 14.3BD - 1.01CD - 1.38A^2 - 0.0321B^2 - 0.0093C^2 + 4.86D^2$$

Model validation

- Verification experiment : 59.20 % MB removal
- Model prediction : 57.82 % MB removal
- Error : 1.68 %.

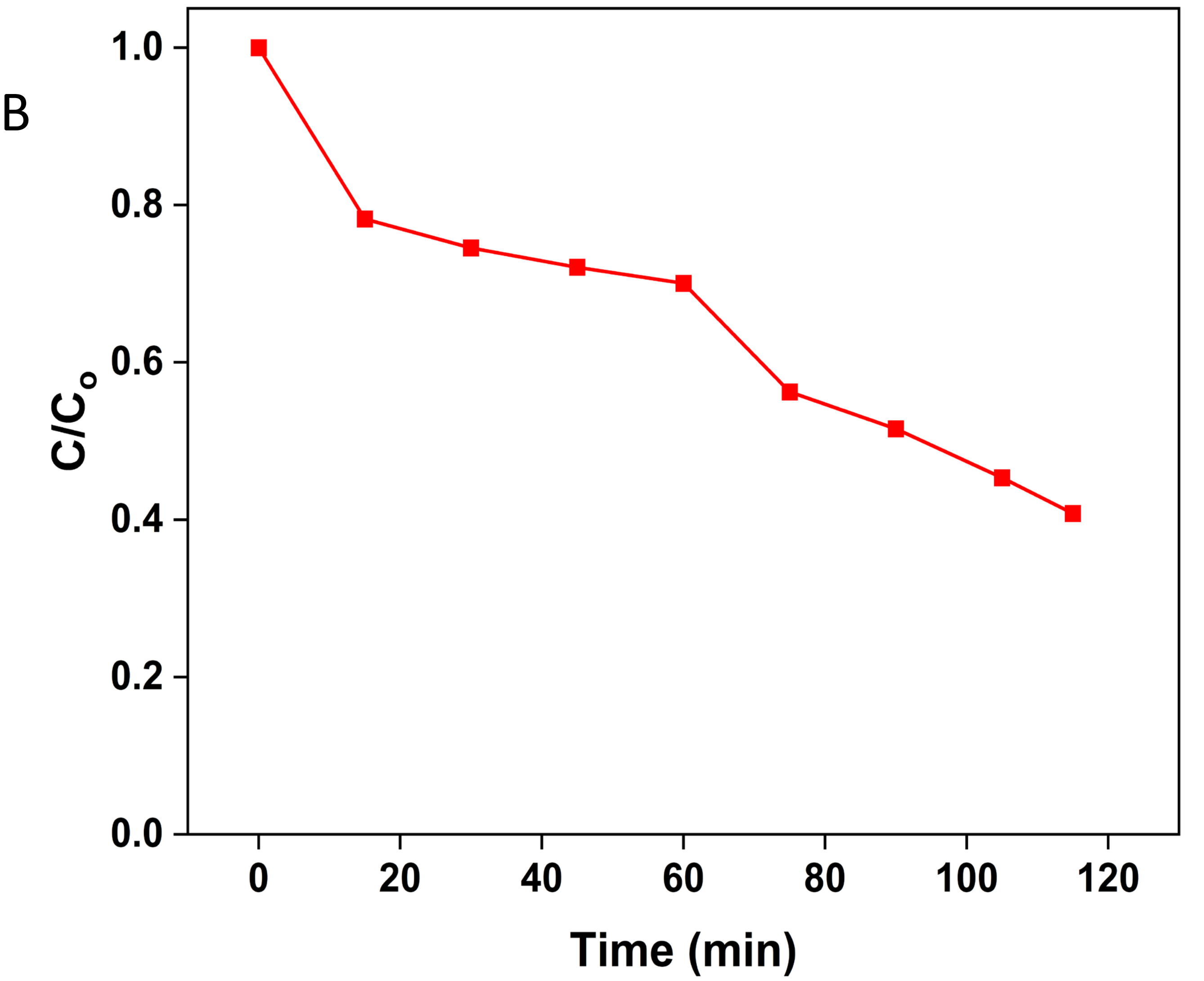

Figure 6. Optimized conditions

Model kinetics

- Model best fits first order kinetics

$$\ln C_t = \ln C_o - k_1 t$$

C_t (ppm) Concentration of MB at time **t(min)**

C_o(ppm) Initial concentration of MB dye

k_1(min^{-1}) First order rate constant

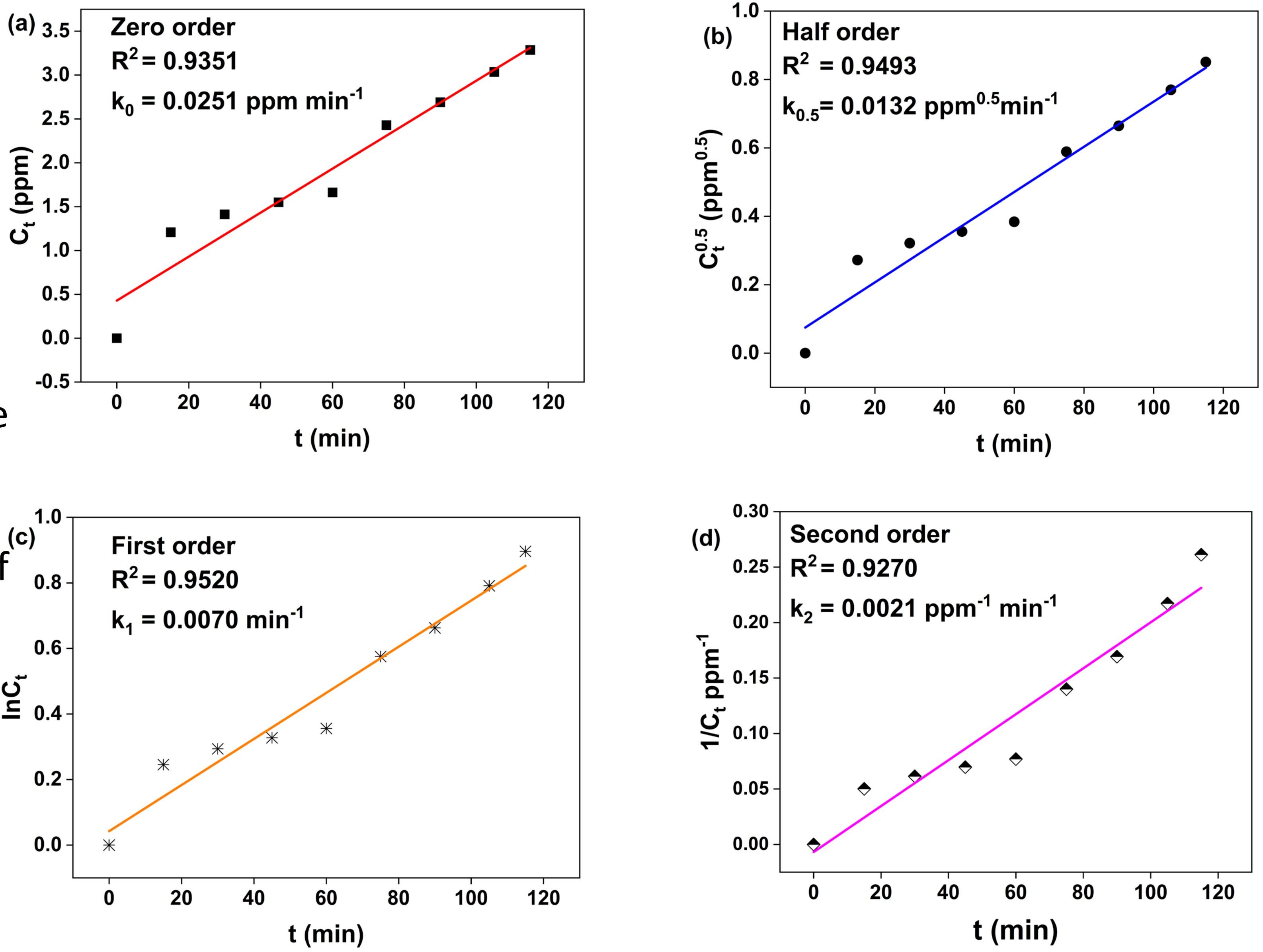

Figure 7. Kinetic models

Suggested removal mechanism

- Generation of electron-hole combinations from light photons
- OH• and O_2^{-}• responsible for MB degradation
- Mechanism summarized in Equations 1-5.

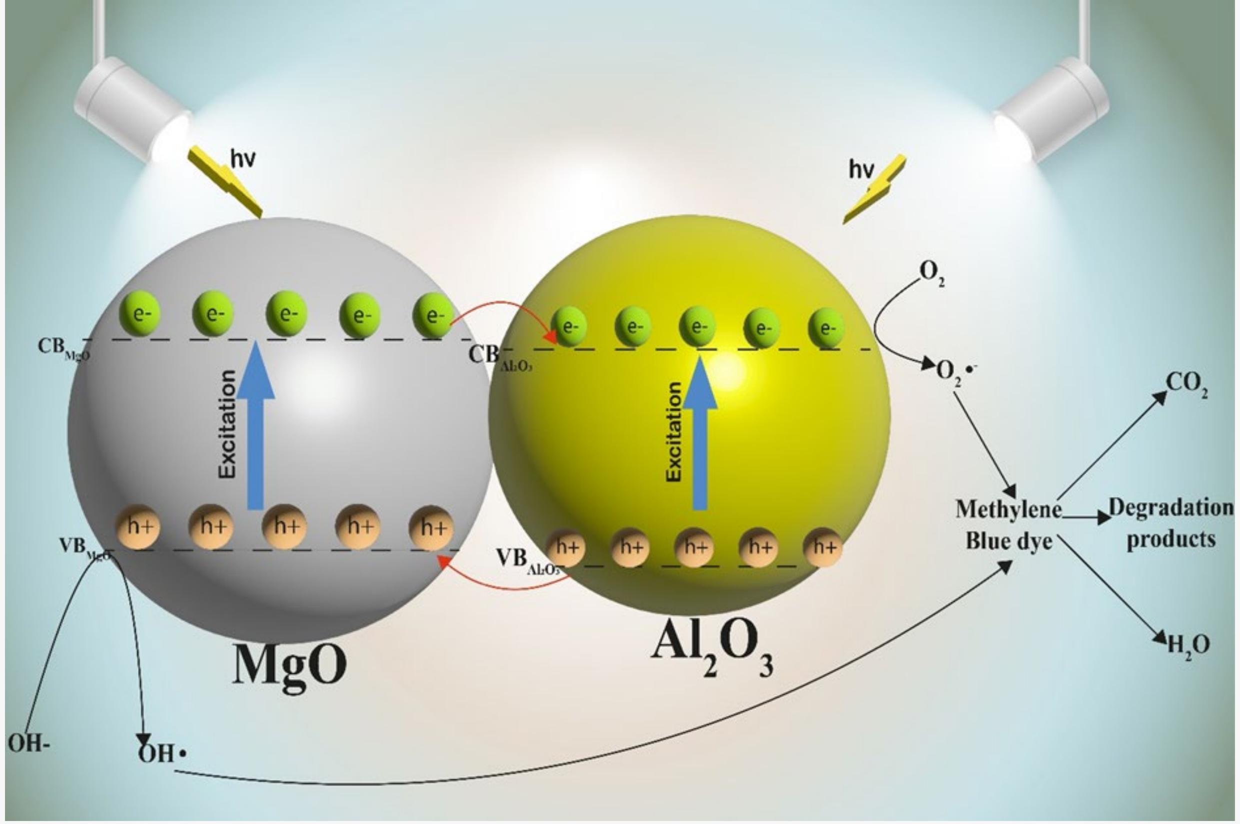

Figure 8. Suggested Removal mechanism

$$Al_2O_3\text{-}MgO + h\nu \text{ (vis region)} \rightarrow Al_2O_3\text{-}MgO\ (e_{cb}^{-} + h_{vb}^{+}) \qquad (1)$$

$$h_{vb}^{+} + H_2O(OH^-) \rightarrow OH\bullet + H^{+} \qquad (2)$$

$$e_{cb}^{-} + O_2 \rightarrow O_2^{-}\bullet \qquad (3)$$

$$O_2^{-}\bullet + MB \rightarrow \text{degradation products} + CO_2 + H_2O \qquad (4)$$

$$OH\bullet + MB \rightarrow \text{degradation products} + CO_2 + H_2O \qquad (5)$$

Economic Evaluation

- Cost estimates based on textile wastewater treatment using the optimized conditions

Table 3. Economic feasibility

Item	Value
Volume of wastewater treated	80 m^3 per day
Number of operating days in year	300 days
Capital costs	US$ 3,896,428.57
Amortization Cost (25 years at 6% per annum interest rate)	US$ 365,765.78
Operational expenses	US$ 30,250
Wastewater Treatment Cost	US$ 16.50/ m^3
Profits (Wastewater re-use, color removal and Al_2O_3-MgO sales)	5.20/ m^3 of wastewater treated
Payback Period	3.17 years

Conclusion

- Al_2O_3-MgO nanocomposite was prepared using co-precipitation technique
- UV-DRS analysis showed that the band gap energy was of Al_2O_3-MgO is 3.50 eV.
- RSM model had R^2 of 0.9880 for photocatalytic degradation of MB dye.
- MB photocatalytic degradation using Al_2O_3-MgO followed first order kinetics.
- Economic estimation revealed that the wastewater treatment cost was US$ 16.50/ m^3 with a payback period of 3.17 years.

THANK YOU