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

Samuel Demarema ¹, Amal Abdelhaleem ¹, Shinichi Ookawara ², and Mahmoud Nasr ¹,³

¹Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, 21934, Egypt; ²Department of Chemical Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152-8552, Japan; ³Sanitary Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, 21544, Egypt; Correspondence: samuel.demarema@ejust.edu.eg
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$_2$O$_3$ has orderly nanopore structures and significant photocatalytic activity.
- Al$_2$O$_3$ can be synthesized from waste material such as aluminum cans, hence reducing costs in photocatalysis.
- Al$_2$O$_3$ nanocomposites can have higher photocatalytic activity due to formation of heterojunctions with other semiconductor materials.
Study Objectives

1. Synthesis of Al$_2$O$_3$-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$_2$O$_3$-MgO
Methodology: $\text{Al}_2\text{O}_3$-$\text{MgO}$ photocatalyst synthesis

- Co-precipitation method was used for synthesis of $\text{Al}_2\text{O}_3$-$\text{MgO}$.

**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)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Parameter</th>
<th>Unit</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>A</td>
<td>pH</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>Time</td>
<td>min</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td>Photocatalyst dosage</td>
<td>mg/L</td>
<td>200</td>
</tr>
<tr>
<td>D</td>
<td>Initial MB dye concentration</td>
<td>ppm</td>
<td>10</td>
</tr>
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</table>
Band gap energy of $\text{Al}_2\text{O}_3$-MgO is 3.50 eV.

This is higher than that of $\text{Al}_2\text{O}_3$ (5.97 eV).

**Figure 2.** Absorbance plots for $\text{Al}_2\text{O}_3$-MgO
Initial catalyst tests

- Pure Al$_2$O$_3$ had photodegradation efficiency of 43.57% whereas Al$_2$O$_3$-MgO had 72.72%.
- Al$_2$O$_3$-MgO has lower band gap energy than Al$_2$O$_3$ hence higher photocatalytic activity.

Figure 3. Initial photocatalyst test
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$_2$O$_3$-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$_2$O$_3$-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$_2$O$_3$-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 $\text{Al}_2\text{O}_3$-$\text{MgO}$ 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 $\text{Al}_2\text{O}_3$-$\text{MgO}$ 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>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1029.44</td>
<td>14</td>
<td>73.53</td>
<td>81.99</td>
<td>&lt; 0.0001 significant</td>
</tr>
</tbody>
</table>
| 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 conc   | 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 |
| A²                      | 12.29          | 1  | 12.29       | 13.7    | 0.0024 |
| B²                      | 0.0067         | 1  | 0.0067      | 0.0074  | 0.9325 |
| C²                      | 0.0006         | 1  | 0.0006      | 0.0006  | 0.9804 |
| D²                      | 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 |             |         |         |

Table 2. ANOVA analysis
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
  \[ \ln C_t = \ln C_0 - k_1 t \]

- \( C_t \) (ppm) Concentration of MB at time \( t \) (min)
- \( C_0 \) (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 O₂•- responsible for MB degradation
- Mechanism summarized in Equations 1-5.

\[
\text{Al}_2\text{O}_3-\text{MgO} + \text{hv} (\text{vis region}) \rightarrow \text{Al}_2\text{O}_3-\text{MgO} (\text{e}_{\text{cb}}^- + \text{h}_{\text{vb}}^+) \quad (1)
\]

\[
\text{h}_{\text{vb}}^+ + \text{H}_2\text{O(OH)}^- \rightarrow \text{OH}• + \text{H}^+ \quad (2)
\]

\[
\text{e}_{\text{cb}}^- + \text{O}_2 \rightarrow \text{O}_2•^- \quad (3)
\]

\[
\text{O}_2•^- + \text{MB} \rightarrow \text{degradation products} + \text{CO}_2 + \text{H}_2\text{O} \quad (4)
\]

\[
\text{OH}• + \text{MB} \rightarrow \text{degradation products} + \text{CO}_2 + \text{H}_2\text{O} \quad (5)
\]
Economic Evaluation

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

Table 3. Economic feasibility

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of wastewater treated</td>
<td>80 m³ per day</td>
</tr>
<tr>
<td>Number of operating days in year</td>
<td>300 days</td>
</tr>
<tr>
<td>Capital costs</td>
<td>US$ 3,896,428.57</td>
</tr>
<tr>
<td>Amortization Cost (25 years at 6% per annum interest rate)</td>
<td>US$ 365,765.78</td>
</tr>
<tr>
<td>Operational expenses</td>
<td>US$ 30,250</td>
</tr>
<tr>
<td>Wastewater Treatment Cost</td>
<td>US$ 16.50/ m³</td>
</tr>
<tr>
<td>Profits (Wastewater re-use, color removal and Al₂O₃-MgO sales)</td>
<td>5.20/ m³ of wastewater treated</td>
</tr>
<tr>
<td>Payback Period</td>
<td>3.17 years</td>
</tr>
</tbody>
</table>
Conclusion

- **Al$_2$O$_3$-MgO** nanocomposite was prepared using co-precipitation technique.
- UV-DRS analysis showed that the band gap energy was of Al$_2$O$_3$-MgO is 3.50 eV.
- RSM model had $R^2$ of 0.9880 for photocatalytic degradation of MB dye.
- MB photocatalytic degradation using Al$_2$O$_3$-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