Insight of Anionic Dyes Adsorption from Their Aqueous Solutions onto MgAl LDH/Lignin: Characterization and Isotherm Studies

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Abstract
The removal of hazardous anionic dyes from wastewater is a critical environmental challenge due to their toxic effects and persistence in aquatic systems. This study investigates the adsorption performance of a new composite material, consisting of MgAl layered double hydroxide (LDH) and Lignin (MgAl LDH/Lignin), to remove three different anionic dyes: congo red, direct yellow, and procion red. The composite material was synthesized and thoroughly examined using various techniques, including X-ray diffraction, Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller, and Barrett-Joyner-Halenda. The adsorption isotherm studies indicate that the adsorption of congo red and procion red onto the MgAl LDH/Lignin composite follows the Langmuir isotherm model, suggesting a monolayer adsorption on a uniform surface. On the other hand, the adsorption of direct yellow conforms to the Freundlich isotherm model, indicating the possibility of multiple layers being adsorbed on a surface with varying properties. The maximum adsorption capacities for congo red and procion red were found to be 75.76 mg/g, 51.55 mg/g, and 74.63 mg/g, respectively. The results of this study demonstrate the promising capabilities of MgAl LDH/Lignin composites as highly efficient adsorbents for the treatment of wastewater contaminated with anionic dyes. This research provides valuable insights into the potential of these composites to address the pressing issue of water pollution in a sustainable manner.

Keywords
Layered Double Hydroxide, Anionic Dyes, MgAl, Isotherm, Adsorption

1. INTRODUCTION
Various industries, including textiles, printing, and plastics, utilize anionic dyes for their vibrant colors and strong binding properties. Examples of these dyes include congo red, direct yellow, and procion red (Doondani et al., 2024; Hasanah et al., 2022; Mahmoud, 2022). Nonetheless, the release of these substances into the environment presents considerable ecological and health hazards (Ibrahim et al., 2024). The solubility and stability of these dyes in water are well-documented, posing challenges for their removal in conventional wastewater treatments (Yao et al., 2022). The intricate molecular compositions of these substances contribute to their long-lasting presence in water ecosystems, resulting in significant environmental contamination (Zabibi and Motavalizadehakhkh, 2022). Obstruction of sunlight penetration in water bodies due to the presence of anionic dyes can have detrimental effects on photosynthesis in aquatic plants, ultimately impacting the entire aquatic ecosystem (Alabbad, 2021). In addition, certain anionic dyes have been recognized as possible carcinogens and mutagens, presenting a direct risk to human health when found in water sources that have been contaminated (Adeleke et al., 2024; Arab et al., 2022). Therefore, it is crucial to prioritize the elimination of anionic dyes from wastewater in order to protect the environment and public health.

Various techniques have been developed to address the presence of anionic dyes in wastewater. These methods encompass chemical precipitation, membrane filtration, photodegradation, and advanced oxidation processes (Dehingia et al., 2024; Javanbakht and Mohammadian, 2021; Priatna et al., 2024; Rohmatullaili et al., 2024a; Rohmatullaili et al., 2024b). Nevertheless, numerous approaches encounter drawbacks including expensive operations, production of additional pollutants, and inadequate elimination of dyes (Ba Mohammed et al., 2021). One method that has gained prominence is adsorption, which is known for its simplicity, cost-effectiveness, and remarkable efficiency in elimi-
nating dyes, even when present in low concentrations (Gao et al., 2022; Guo et al., 2022; Lv et al., 2019). The process of adsorption is highly advantageous due to its capacity to effectively treat large quantities of wastewater and its versatility in targeting various types of pollutants (Ribas et al., 2020). Adsorption is a highly effective method for reducing dye concentrations and has the added benefit of allowing for dye recovery and reuse (Siraromroj et al., 2022). This aligns perfectly with the principles of sustainable and green chemistry, making it a valuable technique to consider. As a result, the search for effective adsorbents to remove anionic dyes has become a central focus in environmental research.

Layered double hydroxides (LDHs) belong to a category of anionic clays known for their distinct layered structure, enabling the incorporation of different anionic species (Lesbani et al., 2024; Rohmatullaili et al., 2024c). LDHs, specifically MgAl LDH, are well-known for their remarkable anion exchange capacity, expansive surface area, and adjustable interlayer spaces, which render them highly suitable for the adsorption of anionic dyes (Ahmad et al., 2024a; Mohadi et al., 2023; Wibiyan et al., 2024). In addition, LDHs possess the benefits of being structurally flexible and environmentally friendly, making them highly suitable for practical use in wastewater treatment. When lignin is combined with LDHs, a biopolymer that is naturally abundant and renewable, the adsorption properties of LDHs can be greatly improved (Wang et al., 2022). The presence of various functional groups in lignin, such as hydroxyl and methoxy groups, enhances the binding affinity of the composite material towards anionic dyes (Dai et al., 2025; Guo et al., 2024). The incorporation of lignin enhances the adsorption capacity of the composite, while also promoting a more sustainable approach through the utilization of a byproduct from the paper and pulp industry (Li et al., 2023). Hence, the composites of MgAl LDH and lignin show great potential in efficiently removing anionic dyes.

Our study focuses on examining the adsorption capabilities of MgAl LDH/Lignin composites in the elimination of anionic dyes, such as congo red, direct yellow, and Procion red, from aqueous solutions. This study will encompass a thorough analysis of the composite material, utilizing advanced techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH) analysis. In addition, isotherm studies will be conducted to assess the adsorption behavior and capacity of the composite under different conditions. This will provide a more comprehensive understanding of the underlying mechanisms involved in dye adsorption. This study endeavors to create an adsorbent that is both highly efficient and environmentally friendly, thus making significant contributions to the field of environmental remediation.

2. EXPERIMENTAL SECTION

2.1 Chemicals

The chemicals used in the experiments were of high quality and did not require any additional purification, including magnesium nitrate, aluminum nitrate, sodium hydroxide, hydrochloric acid, and lignin. Deionized water was utilized throughout each stage of the experiment. In this study, congo red, direct yellow, and Procion red were employed as adsorbates.

2.2 Preparation of MgAl LDH/Lignin and Its Characterizations

A preparation of MgAl LDH/Lignin was achieved using the coprecipitation method (Palapa et al., 2023). In a solution of 60 mL of deionized water, both aluminum nitrate and magnesium nitrate were dissolved, with concentrations of 0.25 M and 0.75 M, respectively. The solutions were treated with a 2 M sodium hydroxide solution to adjust the pH to 10. The mixture was then stirred at a temperature of 80°C for a duration of 12 h. Subsequently, the MgAl LDH was mixed with 3 g of lignin and subjected to continuous stirring for a duration of 3 d. The resulting mixture was then filtered and dried. The MgAl LDH/Lignin was characterized using advanced analytical techniques including Fourier Transfer Infra-Red (FTIR) spectroscopy type Shimadzu, Brunauer–Emmett–Teller and Barrett–Joyner–Halenda (BJH) method type Quantachrome, and X-ray diffractometer (XRD) analysis type Rigaku.

2.3 Experiment Process of Anionic Dyes

An experiment was carried out using a shaker to conduct batch adsorption tests. Explorations were conducted to examine the impact of temperature (ranging from 30 to 60°C) and initial dye concentration (ranging from 60 to 100 mg/L). In the experiment, a beaker glass was filled with 25 mL of anionic dyes (congo red, direct yellow, and Procion red) solution and 25 mg of MgAl LDH/Lignin for 2 h at pH 8.86. After undergoing adsorption, the solution was obtained and subsequently subjected to centrifugation. Next, the anionic dye solution was analyzed using a UV-Vis spectrophotometer configured to the optimal wavelength for detecting the concentration of dyes. The concentration of dyes (q) was determined using Equation 1.

\[
q = \frac{C_0 - C \times V}{m} \tag{1}
\]

Where \(C_0\) and \(C\) are the initial concentration and concentration for \(t\) time of anionic dyes, respectively (mg/L); \(V\) is the volume of anionic dyes (L); \(m\) is the mass of MgAl LDH/Lignin (g).

3. RESULTS AND DISCUSSION

3.1 XRD Diffraction

This analytical technique, known as X-ray diffraction (XRD), plays a crucial role in revealing the crystal structure of materials. By examining the diffraction patterns that occur when X-rays interact with the atomic planes of a material, researchers gain valuable insights. The XRD analysis of MgAl LDH modified with lignin in Figure 1 shows clear hkl reflections at positions 003, 002, 006, 012, 015, 018, 110, and 113, suggesting the presence of a crystalline framework in the material (Ahmad et al., 2024a; Palapa et al., 2023). Reflections at 003 and 006, which are usually...
observed at lower diffraction angles, indicate the basal spacing between layers within the LDH structure (Hao et al., 2024). This phenomenon of reflections displaying shifts or changes in intensity can be attributed to the intercalation of lignin, which has the effect of increasing the distance between layers.

The presence of the 002 reflection, although not as prevalent in typical MgAl LDH, indicates the possibility of structural alterations caused by lignin (Du et al., 2022). These reflections at 012, 015, and 018, located at intermediate diffraction angles, offer valuable insights into the changes in interlayer spacing and ion distribution resulting from lignin modification (Abushawish et al., 2024). These observations indicate changes in the internal structural organization of the MgAl LDH. On the other hand, the reflections at 110 and 113, found at higher diffraction angles and linked to the distances between atoms in a single layer of the metal hydroxide, remain consistent. The stability of the metal hydroxide layers remains largely unchanged with the addition of lignin, suggesting that the fundamental structure remains intact.

The presence of absorption bands at specific wavenumbers indicates the occurrence of C–O stretching vibrations (He et al., 2022). This suggests that the functional groups of lignin have been integrated into the LDH matrix. There is a band observed at 1381 cm\(^{-1}\), which indicates the presence of nitrate ions (Ahmad et al., 2024b). This suggests that these ions may be located within the interlayer spaces. The band observed at 1512 indicates the presence of aromatic C=C stretching, suggesting that the composite material incorporates the aromatic components of lignin (Wang et al., 2024). At a frequency of 1627 cm\(^{-1}\), a distinct band is observed, suggesting the involvement of O–H bending vibrations (Amri et al., 2024). This band serves as evidence for the existence of water molecules and hydroxyl groups, which in turn indicate the occurrence of hydrogen bonding interactions between lignin and LDH.

The presence of absorption bands at 2854 cm\(^{-1}\) and 2924 cm\(^{-1}\) indicates the occurrence of C–H stretching vibrations in aliphatic chains, which confirms the incorporation of aliphatic components in lignin (Du et al., 2024). The presence of a wide band at 3448 cm\(^{-1}\) suggests strong O–H stretching, indicating the formation of extensive hydrogen bonding (Mahmoud et al., 2024). This bonding greatly enhances the overall stability of the composite structure. This study presents FTIR findings that show the successful integration of lignin into the LDH framework. This integration improves the functional properties of the composite without compromising the structural integrity of the LDH. This incorporation of lignin into the LDH structure represents a collaborative improvement, potentially expanding the potential uses of this composite material in areas such as environmental remediation and catalysis.
3.3 Pore Properties
The composite material generated from MgAl LDH/Lignin is analyzed using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) techniques (Figure 3). These analyses provide important information about the structural and surface properties of the material, which are crucial for understanding its possible uses. The composite has a specific surface area of 4.870 m$^2$/g, which, while not extremely high, is important for catalytic and adsorptive reactions since it offers plenty of surface locations for chemical interactions. The composite’s average pore size of 2.398 nm classifies it as mesoporous, enabling the transport and adsorption of bigger molecules (Clark et al., 2019). This characteristic makes it well-suited for applications such as pollutant adsorption.

The average pore volume of 0.006 cm$^3$/g indicates a moderate capacity for pore volume, suggesting that the structure is composed of a combination of materials, with lignin potentially occupying or blocking part of the mesopores within the LDH matrix. The inclusion of lignin in the composite causes changes in the distribution of pores, which might potentially improve the stability of the composite and introduce functional groups that enhance its reactivity and interaction capabilities. In summary, the BET and BJH data highlight the potential of the composite material. Based on the results, it can be concluded that adsorption takes place on a surface with evenly distributed and equally energetic sites, where each site can only hold one adsorbate molecule (Khan et al., 2024). This implies that there is a limited and uniform number of adsorption sites available. On the other hand, the Freundlich isotherm model considers adsorption on surfaces that have different energy sites, allowing for the potential of multiple layers of adsorption and indicating a more intricate interaction environment (Semwal et al., 2023). Langmuir and Freundlich models use Equation 2 and Equation 3 to collect data.

$$C_e = C_0 + \frac{1}{q_m K_L}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where $q_e$ is the adsorption efficiency at the equilibrium (mg/g); $C_e$ is the final concentration (mg/L); $q_m$ is the maximum adsorption capacity (mg/g); $K_L$ and $K_F$ are isotherm constants of Langmuir and Freundlich, respectively; and $n$ is adsorption intensity.

The adsorption of anionic dyes onto the MgAl LDH/Lignin, the adsorption characteristics of congo red, direct yellow, and procion red were analyzed using the Freundlich and Langmuir models at different temperatures (30°C, 40°C, 50°C, and 60°C) (Table 1). The study revealed notable variations in the adsorption patterns of the dyes, suggesting unique interactions with the composite material. Based on the results, it can be concluded that the Langmuir isotherm model exhibited a strong fit ($R^2$ values ranging from 0.974 to 0.991) for both congo red and procion red. This indicates that the adsorption process mainly involves the formation of a monolayer on a uniform surface of the composite. The adsorption capacity remains consistent, with $q_m$ values ranging from 72-75 mg/g for both dyes at different temperatures (Figure 4). The rising values of the Langmuir constant as temperature increases suggest that it is an endothermic process. Higher temperatures improve the composite’s attraction to the dye molecules, possibly because of increased molecular mobility and diffusion rates, resulting in improved interaction with the adsorption sites (Banerjee and Chattopadhyaya, 2017).

In contrast, the adsorption behavior of direct yellow showed a distinct pattern that did not align well with either the Freundlich or Langmuir models. The correlation coefficients ($R^2$ values) were particularly low, reaching as low as 0.143 for the
Table 1. Isotherm Study of Anionic Dyes in MgAl LDH/Lignin

<table>
<thead>
<tr>
<th>Anionic Dyes</th>
<th>Temperature (°C)</th>
<th>$n$</th>
<th>$K_F$</th>
<th>$R^2$</th>
<th>$q_m$</th>
<th>$K_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congo red</td>
<td>30</td>
<td>2.318</td>
<td>8.833</td>
<td>0.930</td>
<td>72.993</td>
<td>0.037</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.452</td>
<td>10.231</td>
<td>0.908</td>
<td>72.464</td>
<td>0.044</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.591</td>
<td>11.844</td>
<td>0.921</td>
<td>72.993</td>
<td>0.052</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.627</td>
<td>12.785</td>
<td>0.945</td>
<td>75.758</td>
<td>0.055</td>
<td>0.991</td>
</tr>
<tr>
<td>Direct Yellow</td>
<td>30</td>
<td>0.466</td>
<td>40.096</td>
<td>0.699</td>
<td>39.841</td>
<td>0.016</td>
<td>0.414</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.484</td>
<td>24.468</td>
<td>0.663</td>
<td>44.643</td>
<td>0.017</td>
<td>0.368</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.481</td>
<td>20.483</td>
<td>0.525</td>
<td>45.249</td>
<td>0.019</td>
<td>0.254</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.507</td>
<td>11.450</td>
<td>0.387</td>
<td>51.546</td>
<td>0.020</td>
<td>0.143</td>
</tr>
<tr>
<td>Procion Red</td>
<td>30</td>
<td>2.304</td>
<td>8.660</td>
<td>0.964</td>
<td>72.464</td>
<td>0.036</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.387</td>
<td>9.759</td>
<td>0.913</td>
<td>72.993</td>
<td>0.042</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.516</td>
<td>11.189</td>
<td>0.933</td>
<td>73.529</td>
<td>0.048</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.650</td>
<td>12.712</td>
<td>0.905</td>
<td>74.627</td>
<td>0.054</td>
<td>0.979</td>
</tr>
</tbody>
</table>

Figure 4. Maximum Adsorption Capacity of Anionic Dyes in MgAl LDH/Lignin

Langmuir model at 60°C. The Freundlich constants and n values for direct yellow indicate a less favorable and heterogeneous adsorption process (Hidayat et al., 2021). The consistently low n values suggest weaker interactions between the adsorbate and adsorbent. The relatively low adsorption capacity (around 39-51 mg/g) (Figure 4) and the inadequate fit of the model indicate that the adsorption mechanism for direct yellow may involve intricate interactions that are not fully captured by simplistic monolayer or heterogeneous surface models. This behavior may be due to certain factors, such as steric hindrance or unique chemical properties, which hinder the effective interaction between direct yellow and the composite material. The adsorption characteristics of these dyes highlight the specificity of the interaction between the MgAl LDH/Lignin composite and different molecular structures. This emphasizes the importance of tailored approaches in designing adsorbents for different pollutants.

4. CONCLUSIONS

This study describes the preparation of MgAl LDH/Lignin using the coprecipitation method. The success of the preparation is attributed to the support provided by the XRD, FTIR, BET, and BJH tests. The analysis of the isotherm indicates that the composite of MgAl LDH/Lignin shows encouraging adsorptive characteristics for specific anionic dyes, specifically congo red and procion red. This suggests that there could be potential uses in the fields of wastewater treatment and environmental remediation. The study emphasizes the composite’s aptness for capturing dyes through monolayer adsorption, showcasing improved performance at elevated temperatures. Nevertheless, the inadequate suitability for direct yellow suggests the need for additional research into the composite’s compatibility with various dye molecules in terms of structure and chemistry. This analysis enhances our comprehension of the interplay between intricate adsorbent materials and specific pollutants, opening up possibilities for refining the adsorbent design to effectively and selectively eliminate various contaminants.

5. ACKNOWLEDGEMENT

This research is supported by the Research Center of Inorganic Materials and Complexes, Universitas Sriwijaya.

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