Article

Removal of Azo Dyes from Water Using Natural Luffa cylindrica as a Non-Conventional Adsorbent


1 Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca 62209, Mexico; ma.arandafig@uaem.edu.mx
2 Departamento de Ingeniería en Aeronáutica, Universidad Politécnica Metropolitana de Hidalgo, Tolcayuca 1009 Ex Hacienda San Javier, Tolcayuca 43860, Mexico; adrodri@upmhu.edu.mx
3 Centro de Investigación en Biotecnología, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca 62209, Mexico; alexis.rodriguez@uaem.mx
4 Dirección de Ciencias Básicas e Ingeniería, Universidad Popular de la Chontalpa, Carretera Cardenas-Huimanguillo Km 2.0, Cardenas 86500, Mexico; gloria.bolio@upch.mx
5 Centro de Investigación en Biodiversidad y Conservación, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca 62209, Mexico; davidos@uaem.mx
6 Centro de Investigación y Educación Ambiental Sierra de Huautla (CEAMISH), Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca 62209, Mexico; dulce@uaem.mx
7 Centro de Investigación en Ingeniería y Ciencias Aplicadas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca 62209, Mexico
8 Correspondence: rosenberg@uaem.mx (R.J.R.); mg.valladares@uaem.mx (M.G.V.-C.)

Abstract: Reducing high concentrations of pollutants such as heavy metals, pesticides, drugs, and dyes from water is an emerging necessity. We evaluated the use of Luffa cylindrica (Lc) as a natural non-conventional adsorbent to remove azo dye mixture (ADM) from water. The capacity of Lc at three different doses (2.5, 5.0, and 10.0 g/L) was evaluated using three concentrations of azo dyes (0.125, 0.250, and 0.500 g/L). The removal percent (R%), maximum adsorption capacity (Qm), isotherm and kinetics adsorption models, and pH influence were evaluated, and Fourier-transform infrared spectroscopy and scanning electron microscopy were performed. The maximum R% was 70.8% for 10.0 g L−1 Lc and 0.125 g L−1 ADM. The Qm of Lc was 161.29 mg g−1. Adsorption by Lc obeys a Langmuir isotherm and occurs through the pseudo-second-order kinetic model. Statistical analysis showed that the adsorbent dose, the azo dye concentration, and contact time significantly influenced R% and the adsorption capacity. These findings indicate that Lc could be used as a natural non-conventional adsorbent to reduce ADM in water, and it has a potential application in the pre-treatment of wastewaters.

Keywords: Luffa cylindrica; unmodified fiber; non-conventional adsorbent; azo dyes; dye removal

1. Introduction

Processing and manufacturing industries are sources of generated wastewater, which includes a mixture of pollutants, including heavy metals, pesticides, azo dyes, drugs, and oils. Wastewater can be classified depending on the type of compounds it contains. For instance, according to the World Bank, textile dyeing generates between 17% and 20% of industrial wastewater [1]. Mainly, textile wastewater contains dyes and salts and largely aqueous soluble inorganic-colored complexes. Some authors have reported that wastewater from the leather industry may contain up to 200 mg L−1 of dyes [2].
Most color-based industries commonly employ, at the end of the process, a wastewater treatment to reduce the pollutant concentrations before leaving water in open sources. However, the complexity and heterogeneity of the pollutants in wastewater need highly efficient technologies. Hence, water treatment plants are closely monitored and regulated by standard protocols to meet the required standards for water quality [3]. Higher pollutant concentration disposed in water is correlated with a huge risk and hazardous impacts on the environment and human health [2,4]. Consequently, water treatment is a leading factor in the accomplishment of sustainable water provision [5].

The presence of dyes in water is highly visible. Moreover, even at concentrations of <1.0 mg L$^{-1}$ [6], there can be significant changes in the physicochemical properties of water. For example, dyes reduce the transmission and penetration of sunlight into the water and thus affect the biochemical oxygen demand (BOD), chemical oxygen demand (COD), and pH [7,8]. Synthetic textile dyes are widely used due to their easy application and ability to give clothing brighter and more durable colors [9]. Azo dyes are the largest and the most important group of synthetic dyes [10]. They are highly toxic and stable under different environmental conditions (light, heat, etc.) and resist degradation processes (aerobic digestion and oxidizing agents) [11].

Several technologies are being studied as part of wastewater treatment, including the combination of pre-treatments and primary treatments to reduce the organic load and improve the efficiency of secondary processes [12]. The most acceptable approaches should be eco-friendly and non-polluting. Moreover, the removal techniques that are used should consider the types of pollutants and their concentration [13]. Adsorption is a widely accepted technique because it is easy to apply, efficient for pollutant removal, does not require supplements, and can be low cost when a natural absorbent is applied [13–15]. The adsorbent, a highly porous material, has a large surface area and many free functional groups that provide adequate and selective adsorption [16–18]. To ensure sustainability in wastewater treatment, for nearly two decades, natural sources have been studied as non-conventional absorbent materials to remove or reduce pollutants in water, including dyes; they have demonstrated good adsorption capacity [19,20]. For example, Acid Blue 25 was removed using waste tea residue (50.8 mg g$^{-1}$) [21]. Crystal violet and methylene blue were removed using sugarcane bagasse (107.5 and 112.9 mg g$^{-1}$, respectively) [22]. Malachite green was removed by employing grape stalks (214.1 mg g$^{-1}$) [23]. Methyl red was removed using eggshell powder (1.26 mg g$^{-1}$) [24]. Cibacron blue was removed by utilizing pistachio shells (1.63 mg g$^{-1}$ untreated and 4.53 mg g$^{-1}$ chemically treated) [25]. Crystal violet was removed using activated carbon from pomegranate peels (23.26 mg g$^{-1}$) [26]. Tartrazine was removed with activated carbon powder from cola nut shells (19.26 mg g$^{-1}$) [27]. While these reports show that non-conventional absorbents represent emerging and eco-friendly alternatives for water decontamination, most of them focused on the removal of only one dye. The purpose of the present study was to establish the adsorption capacity of the non-conventional natural and green material Luffa cylindrica (Lc) to remove an azo dye mixture.

2. Results

2.1. Azo Dye Mixture Removal

Figure 1 shows the removal of ADM, considering 2.5, 5.0, and 10.0 g L$^{-1}$ Lc doses.
Figure 1. Removal of ADM using (a) 2.5; (b) 5.0; (c) 10 g L\(^{-1}\) of Lc.

2.2. The Effect of pH

The effect of pH is shown in Figure 2. pH 2.0 led to the lowest ADM removal (47.3%); there was 60%–70% ADM removal at pH 4.0–8.0. The highest removal (79.3%) occurred at pH 3.0.
2.3. Adsorption Capacity

The adsorption capacity for 2.5, 5.0 and 10.0 g L\(^{-1}\) Lc dose is showing in Figure 3a. The time effect respect to adsotprion capacity for 2.5 g L\(^{-1}\) Lc is showing in Figure 3b.
2.4. Adsorption Isotherms

Figure 5 shows how the adsorption isotherms fit the data. According to the correlation coefficient ($R^2$) values, the Langmuir model (Figure 5a) provided the best fit. Thus, ADM adsorbs to the Lc surface by forming a homogeneous monolayer.
2.5. Adsorption Kinetics

The kinetic parameters from the models evaluated using 2.5 g L\(^{-1}\) \(L_c\) are presented in Table 1, and Figure 6 shows the best fit for the data. Table 2 compares the results from the present study with other adsorption studies using \(Luffa\) spp. to remove dyes in water [28–33].

### Table 1. Kinetic parameters of the adsorption of ADM using \(L_c\) (ADM = 0.125 g L\(^{-1}\), \(L_c = 2.5\) g L\(^{-1}\), \(t = 24\) h, \(T = 298 \pm 2\) °K; pH = 7.0).

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Parameters</th>
<th>Value</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>(k_1) (min(^{-1}))</td>
<td>−0.0007</td>
<td>0.7974</td>
</tr>
<tr>
<td></td>
<td>(Q_{qe}), observed</td>
<td>24.8756</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Q_{qe}), calculated</td>
<td>26.7384</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>(k_2) (g min mg(^{-1}))</td>
<td>0.0008</td>
<td>0.9922</td>
</tr>
<tr>
<td></td>
<td>(Q_{qe}), calculated</td>
<td>15.0150</td>
<td></td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>(k_{id}) (mg min(^{1/2}) g(^{-1}))</td>
<td>0.3085</td>
<td>0.8456</td>
</tr>
<tr>
<td></td>
<td>(C)</td>
<td>4.0895</td>
<td></td>
</tr>
<tr>
<td>Elovich</td>
<td>(B) (g mg(^{-1}))</td>
<td>0.5967</td>
<td>0.9595</td>
</tr>
</tbody>
</table>

### Figure 6. Pseudo-second order model for the kinetic adsorption of ADM (\(L_c\) dose: 2.5 g L\(^{-1}\)).

### Table 2. Adsorption studies with \(Luffa\) spp. as adsorbent for dye removal.

<table>
<thead>
<tr>
<th>Study</th>
<th>Adsorbent (g L(^{-1}))</th>
<th>Dye (mg L(^{-1}))</th>
<th>pH</th>
<th>(T) (°K)</th>
<th>(t) (h)</th>
<th>(Q_m) (mg g(^{-1}))</th>
<th>Isotherm Model</th>
<th>(k_2) (g mg(^{-1}) min(^{-1}))</th>
<th>(R^2)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-Lc</td>
<td>0.05</td>
<td>20</td>
<td>5.0</td>
<td>308</td>
<td>5.0</td>
<td>29.40</td>
<td>L</td>
<td>0.013</td>
<td>0.996</td>
<td>[33]</td>
</tr>
<tr>
<td>MG-Lap</td>
<td>0.6</td>
<td>50</td>
<td>7.0</td>
<td>303</td>
<td>2.5</td>
<td>166.67</td>
<td>L</td>
<td>0.093</td>
<td>0.996</td>
<td>[31]</td>
</tr>
<tr>
<td>TB-Lc</td>
<td>1</td>
<td>10</td>
<td>7.0</td>
<td>303</td>
<td>0.5</td>
<td>45.60</td>
<td>L</td>
<td>0.0029</td>
<td>0.919</td>
<td>[29]</td>
</tr>
<tr>
<td>AB-Lc</td>
<td>1</td>
<td>20</td>
<td>2.0</td>
<td>293</td>
<td>4.0</td>
<td>9.63</td>
<td>F and T</td>
<td>0.004</td>
<td>0.999</td>
<td>[28]</td>
</tr>
<tr>
<td>MB-Lc</td>
<td>3</td>
<td>300</td>
<td>5.8</td>
<td>293</td>
<td>25.0</td>
<td>49.46</td>
<td>L</td>
<td>0.0051</td>
<td>0.999</td>
<td>[30]</td>
</tr>
<tr>
<td>MG-Lap</td>
<td>8</td>
<td>50</td>
<td>4.0</td>
<td>323</td>
<td>3.0</td>
<td>69.64</td>
<td>L</td>
<td>3.615</td>
<td>0.999</td>
<td>[32]</td>
</tr>
<tr>
<td>This study</td>
<td>2.5</td>
<td>250</td>
<td>7.0</td>
<td>298 ± 2</td>
<td>24</td>
<td>71.43</td>
<td>L</td>
<td>0.0008</td>
<td>0.954</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0002</td>
<td>0.973</td>
<td></td>
</tr>
</tbody>
</table>

\(L_c\): \(Luffa\) cylindrical; \(Lap\): \(Luffa\) aegyptica peel; TB: Trypan Blue; AB: Alpamide Blue; MG: Malachite Green; MB: methylene blue; L: Langmuiri; F: Freundlich; T: Temkin.
2.6. FTIR Spectroscopy

FTIR spectra (Figure 7) were acquired to analyze Lc with and without ADM and ADM only.

![FTIR spectra](image)

**Figure 7.** FTIR spectra of non-conventional and untreated Lc (pink line), ADM (reddish-brown line), and ADM adsorbed to Lc (blue-green line).

2.7. Morphology of Lc

The analysis of FESEM micrographs of the Lc surface before and after ADM adsorption is shown in Figure 8.

Based on energy-dispersive X-ray spectroscopy analysis (EDXA), before adsorption, Lc (Figure 8c) was composed of 56.2% carbon and 38.2% oxygen (Table 3).

![FESEM micrographs](image)

**Figure 8.** FESEM micrographs of (a) untreated natural Lc, (b) Lc after ADM adsorption, (c) amplification of untreated Lc (500), (d) amplification of Lc after ADM adsorption (500).
hydrogens of the aromatic ring of ADM involves stronger interactions with the adsorbent. The peaks at 3328, 2894, and 1732 cm\(^{-1}\) indicate characteristic vibrations for the sulfonate group present in the dye [53]. All of those vibrations are present in the FTIR spectrum of ADM adsorbed to the biomass surface (Figure 7). Moreover, the peaks at 1370, 1317, and 1243 cm\(^{-1}\) are attributable to N–H bonds for amines. The bands at 1370, 1316, and 1031 cm\(^{-1}\) are assigned to N=N stretching interactions. The azo group (–N=N) vibrates at 1580 cm\(^{-1}\), as confirmed by stretching vibrations at 1243 and 1158 cm\(^{-1}\). The signals at 1405, 1316, and 1031 cm\(^{-1}\) indicate the stretching vibrations for the sulfonate group present in the dye [53].

FTIR spectra of ADM adsorbed to Lc (reddish-brown line, Figure 7) show a broad signal at 3322 cm\(^{-1}\) assigned to N–H and O–H vibrations due to dye–adsorbent interactions. The azo group (–N=N) vibrates at 1580 cm\(^{-1}\), as confirmed by stretching vibrations at 1243 and 1158 cm\(^{-1}\). The signals at 1405, 1316, and 1031 cm\(^{-1}\) indicate the stretching vibrations for the sulfonate group present in the dye [53].


discussion

After 24 h as contact time, the highest Lc dose (10.0 g L\(^{-1}\)) had removed 70.8% of ADM azo dye (line blue, Figure 1c). Based on previous studies, other lignocellulosic adsorbents could remove approximately 90% of dyes; however, most of these studies focused on only one dye or used chemically modified adsorbents [34–36].

pH is a crucial parameter in the adsorption process [37,38] because it impacts the binding sites on the adsorbent and alters the electronic environment of dissolved molecules. In acidic media, the surface is positively charged, and H\(^{+}\) ions compete with dye cations, meaning that less adsorbent interacts with the adsorbate [39,40]. On the other hand, in basic media, the lignin and cellulose chains of Lc fibers become negatively charged, and thus, the azo dyes cannot interact well with the adsorbent. Analysis of variance showed that pH significantly affects ADM removal (\(p < 0.05\)).

The adsorption capacity is enhanced at the lowest Lc dose and the highest ADM concentration (Figure 3a), and it increases with respect to time (Figure 3b). The highest Q_e was obtained when using 2.5 g L\(^{-1}\) Lc.

The adsorption of ADM along the entire surface of Lc is mediated by the formation of multiple, different, and strong physicochemical interactions like van der Waals forces [41]. Similar observations have been reported when using natural adsorbents from agricultural waste such as Citrus limetta peel [42], wheat straw [43], shaddock husk [44], and cottonseed husk [45], to mention a few examples, to remove dyes in solution. In each of the aforementioned studies, the Langmuir isotherm provided the best fit for the data.

According to the \(R^2\) values (Table 1 and Figure 6), the pseudo-second-order model shows the best fit for the data. Hence, the removal process involves chemisorption [28]. In most of them, the Langmuir isotherm and the pseudo-second-order model best described the dye adsorption processes, even with other pollutants or adsorbents [14,46–48].

Unmodified Lc (green line, Figure 7) shows a broad absorption band at 3328 cm\(^{-1}\) characteristic of O–H. A broad shorter peak at 2894 cm\(^{-1}\) is attributable to C–H stretching vibrations. The bands at 1370, 1317, and 1243 cm\(^{-1}\) represent vibrations for –CH– and –CH\(_2–\) groups [49]. The peaks at 1620 and 1424 cm\(^{-1}\) show conjugated double bonds. The strong peak at 1027 cm\(^{-1}\) is attributed to C–O–C and to C–O vibrations, bonds present in polysaccharides [50]. All these signals describe a lignocellulosic material [51]. The FTIR spectrum of ADM (blue line, Figure 7) shows the vibrations of the \(\pi\) conjugation system of C=C bending (1606 cm\(^{-1}\)) and of N=N stretching (1482 cm\(^{-1}\)), characteristics of amines. The sulfonate group vibrations are observed at 1396 cm\(^{-1}\) (the S=O double bond) and 1052 cm\(^{-1}\) (the S–O bond) [52]. A broad signal at 3354 cm\(^{-1}\) is attributed to N–H bonds for amines. The FTIR spectra of ADM adsorbed to Lc (reddish-brown line, Figure 7) show a broad signal at 3322 cm\(^{-1}\) assigned to N–H and O–H vibrations due to dye–adsorbent interactions. The azo group (–N=N) vibrates at 1580 cm\(^{-1}\), as confirmed by stretching vibrations at 1243 and 1158 cm\(^{-1}\). The signals at 1405, 1316, and 1031 cm\(^{-1}\) indicate the stretching vibrations for the sulfonate group present in the dye [53].

FTIR signals corresponding to hydroxyl, carbonyl, and alkyl functional groups, and aromatic vibrations are generally present in cellulose, hemicellulose, and lignin [54,55]. All of those vibrations are present in the Lc–ADM FTIR spectrum (reddish-brown line, Figure 7). Moreover, the peaks at 3328, 2894, and 1732–1482 cm\(^{-1}\) indicate that ADM involves stronger interactions with the hydroxyl and carbonyl groups of Lc and methylene hydrogens of the aromatic ring of ADM dye on the Lc surface.
Figure 8c (enclosed zone in yellow) shows the fibrous structure of \( Lc \) with many small holes (0.5–4 \( \mu \)m in diameter). The smooth amorphous waxy/gummy layer indicates the presence of lignin [56]. Porosity increases the surface area of adsorbent material [17]. Figure 8d (enclosed zone in yellow) shows the changes in the surface of \( Lc \) after ADM adsorption. It is possible to observe that the holes are occupied by the ADM molecules. The large, brilliant zones could correspond to salts [42,57].

The data of composition \( Lc \) obtained by EDXA (Table 3) are consistent with the composition of cellulosic and hemi-cellulosic materials [15]. After adsorption (Figure 8d), \( Lc \) exhibited a composition of 53.4% carbon, 15.2% nitrogen, and 24.7% oxygen as the chief elements, along with trace amounts of other elements.

Thus, azo dye mixture likely adsorbs to \( Lc \) via hydrogen, electrostatic, chemical, and van der Waals interactions [54,58]. In the literature, researchers have reported various adsorption mechanisms depending on the chemical composition of the adsorbent, the nature of the pollutant, and the environmental media [11,18,59]. The adsorption process in solution involves water molecules forming hydrogen bonds between dyes and free functional groups on the \( Lc \) lignin–cellulose surface [60–62]. In agreement with the results of the isotherms and the FTIR spectra of the adsorbent after ADM adsorption, it is necessary to consider that the molecules and free ions play an important role in the adsorption process. Figure 9 shows a general mechanism for the \( Lc \)-ADM interaction to understand how adsorption occurs.

![Figure 9. Mechanism of adsorption proposal to \( Lc \)-ADM in aqueous solution.](image)

### 4. Materials and Methods

#### 4.1. Luffa Cylindrica (\( Lc \))

\( Lc \) (Figure 10) is a fibrous, highly porous natural material composed of lignocellulose [13]. It has a large surface area with a large number of hydroxyl groups that can bind organic and inorganic molecules [63,64]. Dried \( Lc \) was acquired from Buenavista de Cuel- lar, Guerrero, Mexico (18°27′32″ N 99°24′20″ W). It was cleaned, the peel and seeds were removed, and it was cut into small 1 cm\(^3\) fragments, which were exhaustively washed using distilled water and dried using an oven (RIOSA made in Mexico) at 40 °C for 24 h. These \( Lc \) fragments were used in the subsequent experiments as untreated natural fiber.

![Figure 10. Luffa cylindrica; longitudinal and cross-sectional views of its structure.](image)
4.2. Azo Dye Mixture

A commercial mixture of azo dyes commonly used to renew the blue color of jeans at home was acquired from a local supermarket; the commercial mixture is commonly named ‘Indigo Blue’. Its formulation contains nine azo dyes: blue 71, 86, 102, 151, 200, and 201; black 22; red 23; and yellow 50 (Figure 11) as the major ingredients. They can be classified as mono-, di-, tri-, and tetra-azo dyes, one of which is a phthalocyanine class. This commercial azo dye mixture was renamed as ‘Azo dye mixture’ (ADM). A stock solution of ADM (1.0 g L\(^{-1}\)) was prepared and used for all experiments. The maximum absorbance of ADM was determined using an ultraviolet–visible (UV–vis) spectrophotometer; it was detected at 550 nm.

![Figure 11. Chemical structure of dyes contained in ADM. Description: Monoazo dye: Disperse Blue 102 and Direct Red 23; Diazo dye: Direct Blue 151 and 201 and Direct Yellow 50; Triazo dye: Direct Blue 71 and Disperse Blue 200; Tetra-azo dye: Direct Black 22; and Phthalocyanine dye: Direct Blue 86.](image)

4.3. Experimental Design

In prior studies of adsorbents, researchers have generally used azo dye concentrations <0.100 g L\(^{-1}\) [28–30,65]. However, in real-world scenarios, dye concentrations are commonly >0.100 g L\(^{-1}\). For this study, it was necessary to establish a factorial experimental design for batch adsorption kinetic assays considering several azo dye and \(L_c\) doses (Table 4).

<table>
<thead>
<tr>
<th>Independent Variables</th>
<th>Level of Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_c) (g L(^{-1}))</td>
<td>Low (−1)</td>
</tr>
<tr>
<td>ADM (g L(^{-1}))</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Table 4. Experimental design.
4.4. Adsorption Kinetics

The experiments were carried out in conical borosilicate glass flasks with a 50 mL working volume in static conditions at 28 ± 2 °C and pH 7.0; the contact time was 24 h. The residual ADM concentration was measured at 550 nm. All experiments were performed in quadruplicates, and the results were processed using Origin Pro-8 version 2018 and Minitab version 20 software.

The removal percent (R%) of ADM was calculated with Equation (1):

\[ R\% = \frac{C_0 - C_f}{C_0} \times 100 \]  

where \( C_0 \) is initial concentration, \( C_f \) is final concentration, and R% is the removal percent.

The adsorption kinetics was evaluated to understand ADM removal. The amount of ADM adsorbed by \( Lc \) (mg g\(^{-1}\)) was calculated with Equation (2):

\[ Q = \frac{C_0 - C_f}{m} \times V \]  

where \( Q \) is the adsorption capacity (mg g\(^{-1}\)), \( C_0 \) and \( C_f \) are the initial and final concentrations (mg L\(^{-1}\)), respectively, \( V \) is the volume (L) used, and \( m \) is the \( Lc \) mass (g) employed [28].

Several kinetic models were analyzed with the degree of adsorption controlled as a function of time. Equation (3) was used for the pseudo-first-order model:

\[ \ln(Q_e - Q_t) = \ln Q_e - k_1t \]  

where \( Q \) is the ADM amount adsorbed by \( Lc \) at time \( t \) (mg g\(^{-1}\)), and \( k_1 \) is the adsorption rate constant (min\(^{-1}\)).

The pseudo-second-order kinetic assumes that chemisorption is the rate-limiting step; it is represented in Equation (4) [34,42]:

\[ \frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e} \]  

where \( t \) is the time (min), and \( k_2 \) is the rate constant of pseudo-second order (g min mg\(^{-1}\)).

Weber and Morris [66] proposed a theory based on interparticle diffusion and mentioned that adsorption occurs through a diffusion mechanism, as represented by Equation (5):

\[ Q_t = k_{id} t^{1/2} + C \]  

where \( k_{id} \) is a rate constant of intraparticle diffusion (mg min\(^{1/2}\) g\(^{-1}\)), and \( C \) is a dimensionless constant.

The Elovich model provides an explanation for adsorption of an adsorbate on the surface of an adsorbent. This model assumes that adsorbents have heterogeneous active sites with different active energies [67]. The model is represented in Equation (6):

\[ Q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta} \ln t \]  

where \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) is initial adsorption rate, \( \beta \) (g mg\(^{-1}\)) is desorption constant, and \( t \) (min) is time [67,68].

4.5. Adsorption Isotherms

Adsorption equilibrium was analyzed to determine the adsorption capacity of \( Lc \) for ADM in aqueous solution. The amount of ADM adsorbed at equilibrium is expressed by Equation (7):

\[ Q_e = \frac{C_0 - C_e}{m} \times V \]
where $Q_e$ and $C_e$ are the adsorption capacity and adsorbate concentration at equilibrium, respectively.

The type of adsorbent–adsorbate interaction, as well as the experimental conditions, is vital to determine which isotherm best fits the data. The equilibrium data were analyzed by considering the linearized Langmuir, Freundlich, and Temkin isotherms. The Langmuir isotherm has been commonly used to discuss various adsorbate–adsorbent combinations (liquid and gas phase adsorption) [29,30,65,69] and is represented by Equation (8):

$$\frac{C_e}{Q_e} = \frac{1}{Q_mK_L} + \frac{1}{Q_mC_e}$$

where $Q_e$ (mg g$^{-1}$) is the adsorption capacity of the material at equilibrium; $Q_m$ (mg g$^{-1}$) is the maximum adsorption capacity to form a complete monolayer on the surface at the adsorbate concentration at equilibrium $C_e$ (mg L$^{-1}$); and $K_L$ (L mg$^{-1}$) is the Langmuir constant related to the affinity between the adsorbate and adsorbent [26].

The essential characteristics of the Langmuir isotherm model are known as the separation factor $R_L$, which can be expressed by Equation (9):

$$R_L = \frac{1}{1 + K_L C_0}$$

If $R_L$ is > 1, the adsorption is unfavorable. The adsorption is linear if $R_L$ is 1. When $R_L$ is >0 but <1, the absorption is favorable. Finally, if $R_L$ is 0, then absorption is irreversible [31].

The Freundlich isotherm is represented by Equation (10):

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

where $K_F$ is the Freundlich constant [(mg g$^{-1}$) (L mg$^{-1}$)$^n$], and $n$ is a dimensionless constant that is related to the absorption intensity of the adsorbent–adsorbate relationship, sometimes called the adsorption intensity or surface heterogeneity [26,70].

The Temkin isotherm is presented in Equation (11):

$$Q_e = B \times \ln C_e + B \times \ln K_T$$

where $B$ (J mol$^{-1}$) is the Temkin constant, obtained from $RT/b$, where $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the temperature in Kelvin (298 °K), $b$ is the variation in the absorption energy, and $K_T$ is the Temkin equilibrium constant (L mg$^{-1}$) [70].

4.6. Influence of pH on ADM Removal

The pH effect of ADM removal was evaluated. A solution of 0.500 g L$^{-1}$ ADM was prepared using 0.01 M KNO$_3$ as a buffer [28,30]. Then, the pH was adjusted between 2 and 12 by adding 0.1 M NaOH or HCl. $L_c$ (2.5 g L$^{-1}$) was added to each flask and incubated for 24 h. Samples were taken at 0 and 24 h and analyzed to calculate the percent ADM removal.

4.7. Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectra were obtained with a Spectrum One FTIR spectrophotometer (Perkin Elmer, Wellesley, MA, USA). The spectra included 128 scans from 500 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.


The internal three-dimensional (3D) morphology and the surface of $L_c$ before and after dye adsorption were obtained with FESEM coupled to energy-dispersive X-ray spectroscopy using a Hitachi SU5000 microscope manufactured in Tokio, Japan. The fiber samples were sprayed with gold coating, and the analysis of samples was acquired by topographic contrast and registered at 100 and 500 magnification.
5. Conclusions

Lc could remove 70.8% of ADM dissolved in water in static conditions at 25 ± 2 °C, pH 7.0, and a contact time of 24 h. The adsorption capacity of Lc was 161.29 mg g⁻¹; adsorption occurs according to the Langmuir isotherm, and the kinetics obeys the pseudosecond-order model. The statistical analysis showed that the adsorbent dose, the azo dye mixture concentration, pH, and contact time significantly influence azo dye mixture removal and the adsorption capacity. Lc is an eco-friendly and sustainable adsorbent. It acts as a non-conventional material to reduce azo dyes dissolved in water. It could be applied to coupled treatments to ensure pollutant concentrations are sufficiently reduced and that wastewater treatment performs efficiently.


Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors are grateful to CONACyT (Consejo Nacional de Humanidades, Ciencia y Tecnología) from Mexico for the fellow scholarship to student M.G.A. (CVU:861755), and the authors acknowledge to Luis Maya and Julio Najera for technical helping the laboratory.

Conflicts of Interest: The authors declare no conflicts of interest.

References


Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.