Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and retention mechanisms studies

R. Sadik, R. Lahkale, N. Hssaine, M. Diouri, E.M. Sabbar*
Laboratory of Physics and Chemistry of Materials (LPCM). Department of Chemistry, University Chouaib Doukkali, El Jadida, MOROCCO.

Abstract: The removal of the orange acid dye 7 was carried out by adsorption using a mixed oxide obtained after calcination of layered double hydroxide (LDH) also called anionic clay. This work requires the control and optimization of various parameters such as the contact time, the pH, the mass of adsorbent and the initial concentration of dye.

The removal of the orange acid dye 7 is an arapid adsorption process, the equilibrium temperature is reached after 34 min. The kinetic data were analyzed using the pseudo first-order and pseudo second-order models and they were found to fit very well the pseudo second order. This is confirmed with fast kinetics modeling of experimental data according to the pseudo-first-order. Furthermore, the adsorption of the dye follows the Langmuir isotherm, with an adsorption of about 328.94 mg/g capacity. This retention is far greater than that obtained by unburned HDL. In order to clarify the adsorption mechanism, we have also studied the intraparticle diffusion. The use of a mixed oxide as adsorbent has allowed us to regenerate a new dye-precursor HDL.

Keywords: Layered Double Hydroxides, Mixed Oxide, Orange Acid dye 7, Adsorption, Kinetic.

I. Introduction

Annually, approximately \(7 \times 10^5\) tons of dyes are produced, and approximately \(7 \times 10^4\) tons/year are discarded by industries, including the textile, rubber, food, paper and plastic industries [1-3].

Because of their high organic matter concentrations and their intense colors, the effluents discarded by the food industry are an important source of pollution for water bodies. When discharged into streams, these effluents reduce the transmission of sunlight into the depleted dissolved oxygen zone [4-6] and may cause changes in aquatic biota (particularly near the release point). Thus, it becomes necessary to remove these materials before they are mixed with natural and unpolluted water bodies [2].

The removal of color from wastewater is a major environmental problem because it is difficult to treat colored wastewaters with conventional methods [3].

Among the various types of processes for dye removal (physical, chemical, biological methods, electrochemical oxidation and adsorption methods), the adsorption process is one of the most efficient [7-10]. Activated carbon is the most popular adsorbent due to its high adsorption capacity for organic and inorganic pollutants [4]. Moreover, the use of low cost materials for adsorption has attracted attention as a color removal technique. For example, natural clays, bagasse fly ash, chitosan and other adsorbents have been used [10-14].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, have attracted considerable attention in recent years because of their potential industrial uses, which include their use as adsorbents, ion exchangers, catalysts and drug carriers [15-17].

It is from this perspective that our research is interested in the removal by adsorption of a class of textile dye that is common and widespread worldwide. Indeed bleaching is carried out using a mixed oxide of the LDH as adsorbent, given its high adsorption properties in comparison to its uncalcined precursor.

These compounds which are a class of layered compounds that are derived from the structure of mineral brucite, Mg(OH)\(_2\), can be represented with the general formula \([\text{M}^{\text{II}}\text{M}^{\text{III}}\text{O}_2\text{H}_2]^\text{n+} [\text{A}^{n-}\text{xH}_2\text{O}]^\text{x-}\) where \(\text{M}^{\text{II}}\) and \(\text{M}^{\text{III}}\) are any divalent and trivalent metal cations, \(\text{A}^{n-}\) is the interlayer anions, and \(x\) is \(\text{M}^{\text{II}}/\text{M}^{\text{III}} + \text{M}^{\text{III}}\) molar ratio, determining the charge density of the sheet, and therefore, the amount of interlayer sites that can be occupied by anions.

II. Materials And Method

2.1 Material

2.1.1 Synthesis of the adsorbent

The preparation of the precursor was carried out by the method of coprecipitation described by Reichle[18]. (MgCl\(_2\), 6H\(_2\)O) and (AlCl\(_3\), 6H\(_2\)O) are dissolved in distilled water with a molar ratio (Mg/Al = 3). The pH of the reaction mixture was maintained constant at 10.0 by addition of a mixture of NaOH and Na\(_2\)CO\(_3\) ([NaOH]/[Na\(_2\)CO\(_3\)] = 4). The gel was stirred at room temperature for 48h. The clay obtained was washed by centrifugation with distilled water and dried at 60\(^\circ\)C for 48 h. The chemical formula of the clay prepared is
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and ....

Mg$_3$Al(OH)$_8$(CO$_3$)$_0.5$.3.1H$_2$O (noted HT). The adsorbent used in this study is obtained by calcination of HT at 500°C during 5 h. The formula of this mixed oxide is Mg$_{2.95}$AlO$_{4.45}$ (noted HT500).

2.1.2 Adsorbate

The adsorbate is a textile dye called orange7 acid (denoted AO7), the structural formula is schematized in Fig 1:

![Chemical structure of orange 7 dye acid (AO7)](image)

Figure 1. Chemical structure of orange 7 dye acid (AO7)

1.2. Analysis and characterization

Chemical compositions of metals were determined by ICP (Induced coupled plasma (ICP) measurements) Emission Spectrophotometer. IR spectra were recorded in the range of 4000–400 cm$^{-1}$ by FT-IR-8400S SHIMADZU spectrometer using KBr pellets (2%).

The anionic clay was characterized by X-ray diffraction using 2-D-diffractometer of Bruker-AXS PHASER using copper K$_{a1}$ radiation (1.54056 Å) and K$_{a2}$ (1.54439 Å) and Scanning Electron Microscopy (SEM) (type FEI Quanta 200). The dosage was carried ($\lambda=483$nm) out by spectrophotometry using a spectrophotometer type RAYLEIGH-Vis Spectrophotometer 7220G.

1.3. Batch Adsorption Studies

These experiments were performed by contacting 20 mg of HT500 with 50 ml of AO7 effluent at desired contact time, pH, adsorbent mass and initial AO7 concentration.

Once the equilibrium time was reached, the adsorbent was recovered by centrifugation. The amount of AO7 retained per unit mass of solid at equilibrium is calculated by:

$$q_e = (C_0-C_e)V/m$$

i.e., (1)

Where $q_e$ (mg/g) is the amount of AO7 adsorbed per gram of adsorbent; m (g) is the mass of the adsorbent, $C_0$ and $C_e$ (mg/L) are the AO7 concentrations respectively at $t = 0$ and at equilibrium.

The AO7 removal efficiency or AO7 uptake (%) is calculated by:

$$\% \text{ AO7} = 100 \frac{(C_0-C_e)}{C_0} \text{ i.e., (2)}$$

III. Results And Discussion

3.2. Characterization of LDH precursor

3.2.1. X-ray diffraction

The typical XRD pattern (Fig. 1) shows a lamellar structure of LDH material. The XRD patterns were indexed in the R-3m space group, c the lattice parameter corresponding to three times the interlayer distances ($c=3d_{003}$). The peak (110) indicates the intermetallic distance used to calculate a lattice parameter ($a=2d_{110}$).

The values of the parameters c and a are respectively 23.13 and 3.02Å. These values are similar to those reported in literature [19-20].
3.2.2. Infrared Spectroscopy

The IR spectra of synthesized anion clays (Fig 2) resemble those of other hydrotalcite-like phases [19]: The band at 3463 cm\(^{-1}\) which could be attributed to the stretching vibration of hydroxyl group. The low intensity band at 1637 cm\(^{-1}\) is assigned to bending vibration of strongly adsorbed water (solvation water for compensating anion vibration).

The band at 1381 cm\(^{-1}\) is assigned to carbonate vibration (CO\(_3^{2-}\)), the bands at 672 and 436 cm\(^{-1}\) are respectively due to M–O and O–M–O related to LDH layer (M is a divalent or trivalent metal).

3.3. Batch Adsorption Studies

3.3.1. Effect of contact time

The contact time between the pollutant and the adsorbent is an important parameter in treatment by adsorption. Fig. 4 shows the effect of contact time between the HT500 and AO7 dye solutions (40 and 80 mg/L). Thus, Rapid adsorption and equilibrium in a short period of time is related to the efficacy of the adsorbent, especially for wastewater treatment [10,11]. Rapid absorption can be associated with the existence of a large number of vacant sites at the surface of HT500 and available for adsorption. Equilibrium is reached after saturation of the entire surface. Furthermore, most of the adsorbate species are physically adsorbed within a short time frame. However, strong chemical bonds between the adsorbat and the adsorbent require a longer contact time to achieve equilibrium [11].
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and ...

The adsorption kinetic was analyzed by the pseudo first-order equation [21], i.e., (3) or pseudo-second order [22-23], i.e., (4).

\[
\ln(q_e - q_t) = \ln(q_e) - t \cdot K_{1,ads} \quad \text{i.e., (3)}
\]

\[
v\frac{q_t}{q_e} = t \cdot K_{1,ads} + \frac{1}{K_{2,ads}} \quad \text{i.e., (4)}
\]

$q_e$ and $q_t$ are the amounts of AO7 adsorbed by HT500 respectively at equilibrium and $t$, $K_{1,ads}$ and $K_{2,ads}$ the adsorption constants. The experimental equilibrium data can be fitted by i.e., (3) and (4), the value of $R^2$ indicates that AO7 adsorption is successfully fitted by pseudo-second-order model.

Table 1. Fitting parameters for the AO7 adsorption kinetic models

<table>
<thead>
<tr>
<th></th>
<th>Pseudo first-order model</th>
<th>Pseudo-second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{1,ads}$ (min⁻¹)</td>
<td>$q_e$ (mg/g) R²</td>
<td>$K_{2,ads}$ (g/mg/min) $q_e$ (mg/g) R²</td>
</tr>
<tr>
<td>0.047</td>
<td>131.82</td>
<td>0.94</td>
</tr>
</tbody>
</table>

![Figure 5. Pseudo-first-order kinetic plots of sorption of AO7 on HT500](image)

![Figure 6. Pseudo-second-order kinetic plots of sorption of AO7 on HT500](image)

By comparing the two models, we can say that the adsorption kinetics of AO7 by HT500 obeys a law of pseudo-second order.

3.3.2. Intradiffusion

The intra-particle diffusion approach [24] can be used to predict if intra-particle diffusion is the rate-limiting step. The experiment data exhibit multi-linear plots, revealing that the process is governed by two steps (Fig. 6). The first linear portion (phase I) at both concentrations can be attributed to the immediate utilization of the available sites on the sorbent surface. In contrast the phase II may be attributed to very slow diffusion of the sorbate from the surface site into the inner pores. Thus the initial portion of AO7 dye sorption by HT500 may be governed by the initial intra-particle transport of AO7 dye controlled by surface diffusion process and the later
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and ....

part controlled by pore diffusion. The values of \( k_{ip1} \) and \( k_{ip2} \) (diffusion rate constants for phases I and II, respectively) obtained from the slope of linear plots are listed in Table 2 (Weber and Morris model).

![Figure 7. Intra-particle diffusion plots of sorption of AO7 on HT500.](image)

**Table 2. Parameters of Weber and Morris model**

<table>
<thead>
<tr>
<th>Phase</th>
<th>( k_{ip} )</th>
<th>( R^2 )</th>
<th>( k_{dp} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>17.496</td>
<td>0.96</td>
<td>0.59</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.3. Effect of adsorbent mass

The influence of adsorbent mass was studied in the range 5 to 100 mg. Fig 8 shows that, for a concentration of AO7 40 mg/l, for a time equilibrium (\( t_e = 34 \text{ mn} \)), an increase of adsorbent mass from 5mg to 100 mg causes a decrease of the residual concentration (\( C_e \)) from 16 mg to 0.46 mg/l. Thus, optimal adsorbent mass of HT500 is 20 mg to remove 97% of AO7.

![Figure 8. Effect of dose adsorbent on the adsorption of AO7 by HT500, \( te = 34 \text{ mn} \), \( AO7 = 40 \text{ mg/L} \), pH=6, \( T: 25^\circ \text{C} \)](image)

3.3.4. Effect of pH

Several parameters such as adsorption capacity of adsorbent, surface charges and active sites may be attributed to the adsorption behavior of the adsorbent at various pH.

The surface of HT500 contains a large number of active sites. The dye uptake can be related to the active sites and also to the chemistry of the dye in the solution. Theoretically, at pH < point of zero charge (PZC), the surface gets positively charged, which enhances the adsorption of the negatively charged dye anions through electrostatic forces of attraction. At pH >(PZC), the surface of HT500 particles gets negatively charged, which favors the adsorption of cationic dye [25]. These results are similar to the adsorption of Congo Red onto Mg–Fe–CO$_3$-LDH.[26].
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and ....

Figure 9. Effect of initial pH on the adsorption of AO7 by HT500. te = 34mn [AO7] = 80 mg/L
mHT = 20 mg, T = 25°C

3.3.5. Adsorption isotherm

Fig. 10 shows the behavior of the adsorption isotherm of AO7 dye in HT500. We observe that the adsorbed amount of AO7 increased rapidly from 74,58 to 148,37 mg/g at a relatively low AO7 initial concentration (from 30 to 60 mg/L). The initial sharp rise in the isotherm indicates the availability of readily accessible sites for adsorption. However, site saturation occurs as the AO7 concentration increases (from 80 to 120 mg/l) and a plateau is reached indicating that no more sites remain available for adsorption following the saturation of the adsorbent sites taken at a fixed dose, and this happens when the adsorption equilibrium is reached [27]. The model of the isotherm (isotherm type I) obtained is similar to the mathematical model of Langmuir. The sorption data was further analyzed using Langmuir model (Fig. 11), which can be expressed as follows:

\[
\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{K Q_m} e^{-K Q_m} \quad (5)
\]

\(Q\) (mg/g): denotes the adsorbed amount of AO7 per unit mass of adsorbent HT500.
\(Q_m\) (mg/g): the Langmuir constant representing maximum monolayer sorption capacity of HT500.
\(C_e\) (mg/L): the equilibrium adsorption concentration of AO7 in solution.
\(K\) (L/mg): Langmuir constant related to energy of sorption.

Figure 10. Isotherms of AO7 adsorption onto HT500 at 25°C and pH 6
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and....

Figure 11. Fitting lines of the Langmuir adsorption isotherms of AO7 on HT500

Table 3 shows values of constants of Langmuir. The maximum amount absorbed per unit mass of our adsorbent which is in the order of 328.94 mg/g is large enough compared to those found in the literature (Table 4).

Table 3. Parameters of Langmuir for the retention of AO7 by HT500

<table>
<thead>
<tr>
<th>Qm (mg/g)</th>
<th>K (L/mg)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>328.94</td>
<td>1.4</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The influence of adsorption isotherm shape has been discussed to examine whether adsorption is favorable in terms of \( R_L \), a dimensionless constant referred to as separation factor or equilibrium parameter. \( R_L \) is calculated using the equation below:

\[
R_L = \frac{1}{1 + KC_0}
\]

Where \( K \) (L mg\(^{-1}\)) is the Langmuir constant and \( C_0 \) (mg L\(^{-1}\)) is the initial concentration in the liquid phase. \( R_L \) represents the dimensionless parameter of the equilibrium or adsorption intensity. The value of \( R_L \) indicates the type of the isotherm to be either favorable (0 < \( R_L < 1 \)), unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)) or irreversible (\( R_L = 0 \)). The \( R_L \) value obtained (8.84 10\(^{-3}\)) shows a type of favorable equilibrium. This value which is close to the irreversible type is consistent with the type of interaction between adsorbate-adsorbent that is usually done in the case of HDL by hydrogen bonds which lies at the border of the physical link and the chemical.

Table 4. Adsorption capacity obtained with other adsorbents eliminating FCF (C\(_{14}\)H\(_{10}\)N\(_{2}\)Na\(_2\)O\(_7\)S\(_2\)) dye which is similar to AO7

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>pH</th>
<th>Concentration range (mg/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite FPA51</td>
<td>130.6</td>
<td>-4.87</td>
<td>100-1500</td>
<td>[30]</td>
</tr>
<tr>
<td>Maggrove bark</td>
<td>12.72</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(OH)(_2)-NW-AC</td>
<td>76.92</td>
<td>1</td>
<td>50-200</td>
<td>[31]</td>
</tr>
<tr>
<td>Ag-NP-AC</td>
<td>37.04</td>
<td>1</td>
<td>50-200</td>
<td>[32]</td>
</tr>
<tr>
<td>CdTN-AC</td>
<td>181.81</td>
<td>1</td>
<td>25-150</td>
<td>[33]</td>
</tr>
<tr>
<td>CaAl-LDH-NO(_3)</td>
<td>398.41</td>
<td>4</td>
<td>10-1000</td>
<td>[29]</td>
</tr>
<tr>
<td>HT500</td>
<td>328.94</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

AC: activated carbon; CdTN: cadmium telluridenanoparticles; NW: nanowires; NP: nanoparticles

3.3.6. Retention mechanism

The intraparticle diffusion, the maximum absorbed and obtained amount and the calculated value of \( R_L \) (Type equilibrium) assume that the retention of AO7 by HT500 is a reconstruction reaction, usually encountered when contacting a HDL mixed oxide based on magnesium and aluminum with an anion [34]. In this case the retention mechanism makes a dye adsorption at the surface and by intercalation within the regenerated HDL.

This result is confirmed by the characterization of the product recuperated after adsorption by SEM and XRD. In effect, the X diffractogram obtained (Fig 12) shows the shape type of a HDL. Thus, the interlamellar distance of the order of 7.9406 Å is raised in accordance with a parallel arrangement by the interposed HDL and AO7.

Regeneration HT-AO7 was also confirmed by SEM. Indeed, SEM photographs taken at the same scale, obtained before and after adsorption, are reported respectively (Fig 13 and 14). The SEM micrograph of the HT500 revealed the collapsed layer structure, which further indicated that the HT transforms to mixed magnesium and aluminum oxides. While the plate of Fig 14 corresponding to the after adsorption of AO7 shows the presence of interlamellar sheet confirming the formation of HT after reaction of reconstruction.
Removal of textile dye by mixed oxide-LDH: kinetics, isotherms of the adsorption and ....

Figure 12. XRD pattern of HT500 after adsorption

Figure 13. SEM images of HT500
Figure 14. SEM images of HT500 after adsorption

IV. Conclusion

The results of the tests conducted during this study allowed us to optimize the parameters of adsorption of the dye AO7 by HT500 prepared, namely the equilibrium time, pH, dose of the adsorbate and the mass of the adsorbent.

The results related to the kinetics and adsorption isotherms have been exploited to clarify the method of fixing the dye on the adsorbent. Adsorption of AO7 on HT500 follows the pseudo second-order model. The intra-particle diffusion approach can be used to predict if intra-particle diffusion is the rate-limiting step. The adsorption isotherm results could be fitted by the Langmuir isotherm model, which is a better model. The equilibrium parameter $0 < R_L < 1$ represents a favorable adsorption. The dye molecules are then adsorbed monolayers, without dye-dye interactions, thereby increasing the order of their distribution on the surface. The maximum amount of dye retained mg/g of adsorbent which is in the order of 328 mg/g shows a high efficiency of our adsorbent. The results of XRD, and SEM, demonstrate that the main adsorption mechanism involves the rehydration of mixed metal oxides and concomitant intercalation of AO7 dye into the interlayer to reconstruct the initial HT structure.

References

[7]. U. V. Ladhe, P. R. Patil, Removal of Yellow 2G dye from aqueous solutions using activated carbon prepared from mosambi and cotton an agricultural waste, IOSR-JESTFT 8(1) (2014), 49-54

www.iosrjournals.org
Removal of textile dye by mixed oxide-LDH: kinetics, isothersms of the adsorption and ....


