Removal of Evans Blue and Yellow thiazole dyes from aqueous solution by Mg-Al-CO$_3$ Layered Double Hydroxides as anion-exchanger

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Abstract: Mg-Al-CO$_3$ Layered double hydroxide (LDH) was prepared by co-precipitation method at constant pH, and subsequently used to remove Evans Blue (EB) and Yellow thiazole (YT) dyes from aqueous solutions. The obtained material was characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), thermal analysis and BET. The kinetic and equilibrium aspects of sorption of the anionic dyes from aqueous solution by Mg-Al-CO$_3$ were investigated in batch mode. The sorption kinetic data were found to be consistent with the pseudo-second-order model. Data for YT and EB sorption by Mg-Al-CO$_3$ were fitted better by the Langmuir equation than by the Freundlich equation based on the determination coefficient values $R^2$. The maximum adsorption capacities of 222.2 mg g$^{-1}$ for Yellow thiazole and 107.5 mg g$^{-1}$ for Evans blue. The thermodynamic parameters including Gibbs free energy ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) for the process were calculated. The negative $\Delta G^\circ$ value indicates the spontaneity of the removal process.

Keywords: Mg-Al-CO$_3$ LDH, Removal dyes, Isotherms, Kinetics, Adsorption.

Introduction

Synthetic dyes are used extensively as dyeing agents in various industrial applications, such as textile, paper, leather, plastics and pharmaceutical industries$^{1,2}$, to colour their products, and they represent an important case of water pollution. Dye effluents from these industries cause certain hazards and environmental problems. Several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms$^{2,3}$.

The removal of textile dyes from wastewater is one of the most important environmental issues to be solved today. Many dyes used in textile industry are difficult to remove by conventional waste treatment methods since they are designed to be resistant to degradation or fading by oxidizing agents and light. Some azo dyes and their degradation products such as aromatic amines are highly carcinogenic.

Such conventional treatment techniques as chemical coagulation, flocculation, biodegradation, oxidation, membrane separation, have proven insufficient to purify a significant quantity of wastewaters after operations of textile dyeing and washing.
Since sorption-based technology seems to be a reliable alternative, many adsorbents have been proposed for this purpose. Dyes are generally removed from aqueous solutions by a sorption process using activated carbon. In recent years, many cheap and widely-available materials have been identified as suitable adsorbents for the removal of color from wastewaters. For example, the sorption of various dyes onto bottom ash (BA) and de-oiled soya (DOS), magnetic alginate beads, kudzu, organophilic bentonites, treated spent bleaching earth, templated crosslinked-chitosans was reported in the literature.

The application of adsorption based on the use of layered double hydroxides has been recognised as one of the most effective technologies for the removal of such organic compounds as dyes. Layered Double Hydroxides (LDHs), frequently called hydrotalcite-like compounds (HTc), represent a class of anionic clays that may be easily synthesized. Their structure can be visualised as derived from that of brucite in which the octahedral sites in metal hydroxides share their edges to form two-dimensional sheets. These sheets are positively charged due to the isomorphous substitution of a part of the divalent metal ions with trivalent ones. The simplified chemical structure of layered double hydroxide is represented by the chemical formula [M_{x+y}^{2+}\text{M}_{y}^{3+}(\text{OH})_z] (A^{n-})_y/m\text{H}_2\text{O} with M^{2+} and M^{3+} designating metal cations, A^{n-} being the exchangeable anions, and water molecules placed into the interlayer space; x represents the M^{2+} / (M^{2+} + M^{3+}) molar ratio. Layered double hydroxides (LDHs) also possess relatively large surface areas and high ion exchange capacities to adsorb/ion-exchange the variety of anionic polluting species. Because of these properties, LDHs have greater affinities for multivalent anions than for monovalent anions and have been considered in view of removing toxic anionic species from aqueous solutions. Layered double hydroxides (LDHs) constitute an important class of layered materials with potential applications for the wide range of areas as catalysts, anion exchangers, sorbents and antacids.

In the present study, Mg-Al-CO$_3$ LDH was synthesized, characterized and used as an adsorptive phase to remove Evans Blue (EB) and Yellow thiazole (YT) dyes from aqueous solutions. Carbonate ions could be exchanged with organic anions like acidic dye. The objectives of the present work were as follows: (i) study Mg-Al-CO$_3$ as anion exchanger material to remove EB and YT dyes from aqueous solution in a batch mode, (ii) the effect of various factors affecting sorption, including pH of aqueous solution, the time and temperature on anion-exchange have been investigated, respectively. The thermodynamic parameters including Gibbs free energy ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) for the process were calculated.

**Experimental Section**

**Materials and reagents**

The reagents employed in this study were all > 98% pure and were not purified further prior to use. Dye sodium salts, Evans blue (EB), Yellow thiazole (YT), with a purity > 99%, were purchased from the Ciba Society (Zurich, Switzerland) and used as received. They are widely used in dyeing for textiles such as tissue, cotton and silk in textiles industries in Algeria. The two dyes are commercial grade and were used without further purification. The physico-chemical characteristics and molecular structures of EB and YT are shown in table 1 and (Figure 1) respectively. MgCl$_2$.6H$_2$O; Al(NO$_3$)$_3$.9H$_2$O (Merck), and NaOH; Na$_2$CO$_3$ (Riedel-de Haën).
Table 1. Physico-chemical characteristics of the dyes EB and TY.

<table>
<thead>
<tr>
<th></th>
<th>Evans blue (EB)</th>
<th>Yellow thiazole (YT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{34}H_{24}N_6Na_4O_{14}S_4</td>
<td>C_{27}H_{13}N_5Na_2O_6S_2</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>960.817</td>
<td>695.73</td>
</tr>
<tr>
<td>Color</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>Absorbance (\lambda_{max}) nm</td>
<td>610</td>
<td>406</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Figure 1. Chemical structure of (1a) Evans blue (EB) and (1b) Yellow thiazole (YT)

Preparation of Mg-Al-CO_3 LDH

The Mg-Al-CO_3 LDH containing carbonate as the interlayer anion was prepared by using a conventional co-precipitation method previously developed by Reichle with some modifications. A mixed solution containing 0.1 mol of MgCl_2.6H_2O and 0.05 mol of Al(NO_3)_3.9H_2O in 100 mL of deionized water was added drop wise under vigorous stirring to 100 mL of an aqueous solution containing 0.35 mol of NaOH and 0.09 mol of Na_2CO_3. During the co-precipitation process, the pH was maintained at a constant value equal to 10 by addition of 1N HNO_3 solution. The resulting precipitate was stirred during 20 hours at 65°C for maturation. The solid obtained was separated from the solution by centrifugation, washed thoroughly with deionized water several times until obtaining a Cl^- free LDH (AgNO_3 test), dried at 105°C during 18 hours. The resulting material, designated as Mg-Al-CO_3, was ground in an agate mortar and sieved with a 0.250 mm-sieve.

Characterization of the material

The powder X-ray diffraction (PXRD) patterns were recorded on a Phillips X’Pert MPD diffractometer with monochromatic CuK_\alpha = 1.5418 Å radiation (30 mA and 40 kV). FTIR spectra were obtained in the transmission mode on a Nicolet Avatar 330 Fourier transform IR spectrometer. Samples were mixed with KBr and finely powered in a mortar to prepare KBr pellets. The spectra were recorded with 2 cm\(^{-1}\) resolution in the range 4000-400 cm\(^{-1}\). Thermal analysis curves of the samples were recorded with a NETZSCH STA 409 PC / PG
BET analysis was performed on a Micromeritics ASAP 2010 apparatus.

**Study of Evans blue (EB) and Yellow thiazole (YT) removal with Mg-Al-CO$_3$**

_**Kinetic study on the removal of Evans blue (EB) and Yellow thiazole (YT)**_

The kinetic study was carried out in the batch mode on Mg-Al-CO$_3$. In this study, initial dyes concentration was fixed at 50 mg L$^{-1}$ and the adsorbent dose at 0.5 g L$^{-1}$. The pH of the solution was maintained at 6 for Yellow thiazole (YT) and 7 for Evans blue (EB). Suspensions were stirred at room temperature for different time intervals (10 min to 24 h). After agitation, the dye solutions were separated from the adsorbent by centrifugation for 5 min. The dye concentration in the supernatants was determined by visible spectrophotometer on (HACH DR/4000U) UV-vis spectrophotometer at 406 nm for Yellow thiazole (YT) and at 610 nm for Evans blue (EB).

**Effect of solution pH on dye removal**

In order to check the effect of solution pH on Yellow thiazole (YT) or Evans blue (EB) uptake by the Mg-Al-CO$_3$ material, experiments were conducted on suspensions of 25 mg of Mg-Al-CO$_3$ in 50 mL of Yellow thiazole (YT) or Evans blue (EB) solutions with initial concentration of 50 mg L$^{-1}$. The initial pH values of each suspension were adjusted to values from 5 to 10 by adding 1M HCl or 1M NaOH solutions. The suspensions were stirred at room temperature during the equilibrium time, and then centrifuged. The dye concentration in the supernatants was determined as above.

**Sorption isotherms**

The sorption isotherms experiment was carried out by agitating 50 mL of dye solutions of various concentrations (solid-to-solution ratio = 0.5 g L$^{-1}$). The suspensions were stirred during equilibrium time at room temperature. After agitation, the dye solutions were separated from the adsorbent by centrifugation for 5 min. The dye concentration in the supernatants was determined as above.

**Effect of the temperature**

This effect was studied on suspensions of Mg-Al-CO$_3$ in a solid/solution ratio equal to 0.5 g L$^{-1}$ in 60 mg L$^{-1}$ and 100 mg L$^{-1}$ of dye solution of EB and YT with Mg-Al-CO$_3$, respectively. The suspensions were stirred at three constant temperatures (298, 308 and 318K) during equilibrium time then centrifuged. The supernatants were separated by centrifugation and the equilibrium concentrations were determined as above.

**Results and Discussion**

**Characterization of materials**

The X-ray powder diffraction pattern of Mg-Al-CO$_3$ (Figure 2) shows peaks at 7.59Å (d$_{003}$), 3.84Å (d$_{006}$), 2.58Å (d$_{012}$), 2.32Å (d$_{015}$), 1.97Å (d$_{018}$), 1.52Å (d$_{110}$), 1.49Å (d$_{113}$) and 1.41Å (d$_{116}$), which are similar to those reported by several authors.$^{15,30,31}$
Figure 2. Powder X-ray diffraction patterns of Mg-Al-CO₃

The FTIR spectra of Mg-Al-CO₃ (Figure 3) show the characteristic absorption bands of a hydrotalcite. The broad band at 3421 cm⁻¹ is due to the O–H stretching vibration of the metal hydroxide layer and interlayer water molecules. The shoulder near 3200 cm⁻¹ is caused by the interaction between the CO₃²⁻ and H₂O present in the interlayer region, which involves mostly hydrogen bonds. The bending vibration of the interlayer H₂O is also reflected in the broad bands at 1637 cm⁻¹. The strong peak at 1359 cm⁻¹ can be assigned to the vibration of carbonate species. The band characteristic to metal-oxygen bond stretching appears below 700 cm⁻¹. The sharp bands in the range of 500 - 700 cm⁻¹ are caused by various lattice vibrations associated with metal hydroxide sheets.

Figure 3. FT-IR spectra of Mg-Al-CO₃

The specific surface area (based on BET analysis) of synthesized a carbonated hydrotalcite was 69 m²/g for HT-CO₃. TGA and DSC plots of Mg-Al-CO₃ (Figure 4) show the most widely reported is a two-stage decomposition process: The first, endothermic, occurs at low temperatures on an interval of 50-200°C and can be attributed to the removal of surface adsorbed water and interlayer water molecules. A second weak endothermic weight loss at the temperature (300-500°C) is the result of the deintercalation of carbonate and dehydroxylation of the brucite-like layers.
Contact time effect on dyes sorption

Effect of sorption time on dyes (EB and YT) removal by Mg-Al-CO$_3$ is shown in (Figure 5). The percentage removal of each dye increased and remained almost unchanged after 18h, indicating an equilibrium state. Mao-Xu Zhu et al. reported that for acid dye Brilliant blue R (BBR) sorption on Mg-Al-CO$_3$ hydrotalcite, the equilibrium was reached after 20h$^{1}$. Moreover the percentage removal of Evans blue (EB) and Yellow thiazole (YT) on Mg-Al-CO$_3$ was 96.67% and 81.91%, respectively.

The percentage removal (R%) of dye was calculated using the following relationship:

\[
\text{Percentage removal} = \left( \frac{C_i - C_t}{C_i} \right) \times 100
\]

Eq. (1)

Where $C_i$ (mg L$^{-1}$) is the initial concentration of the dye solution, $C_t$ (mg L$^{-1}$) is the concentration of the dye solution at the adsorption equilibrium at time t.

Kinetic models

Several models must be checked for suitability and consistency over a broad range of system parameters. The key features of the two different kinetic models used to fit the experimental data can be summarized as follows:

The pseudo- first order kinetics adsorption model was suggested by Lagergren for the sorption of solid / liquid systems$^{34}$. It has been used by many authors$^{35-37}$ and can be expressed in integrated form:

\[
\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \times t
\]

Eq. (2)

Where $k_1$ is the rate constant of adsorption (min$^{-1}$) and $Q_e$ and $Q_t$ are the adsorption capacity of dye (mg g$^{-1}$) at equilibrium and at time t (min), respectively. When plotting $\ln(Q_e - Q_t)$ against t, (Figure 6) a straight line is obtained and the value of the rate constant $k_1$ and the equilibrium removal capacity $Q_e$ can be calculated.
Figure 6. First order plot for dye removal from aqueous solutions with Mg-Al-CO₃

These parameters (k₁, Qₑ) calculated for the sorption of EB and YT onto Mg-Al-CO₃ systems, as well as their respective correlations, are shown in Table 2.

Table 2. Kinetic parameters for the dyes EB and YT adsorbed on Mg-Al-CO₃.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Experimental</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qₑ(exp) (mg.g⁻¹)</td>
<td>Qₑ(cal) (mg.g⁻¹)</td>
<td>K₁ (min⁻¹)</td>
</tr>
<tr>
<td>EB</td>
<td>84.24</td>
<td>63.97</td>
<td>0.003</td>
</tr>
<tr>
<td>YT</td>
<td>97.05</td>
<td>66.85</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The calculated values from the first order kinetic model show that large differences between experimental and calculated values of the equilibrium sorption capacities are observed (Table 2). This means that the first order kinetic model is not adequate to describe the sorption process studied in the present paper.

The pseudo-second order kinetics model[^38-40] is expressed as

\[
\frac{t}{Q_t} = \frac{1}{Q_e}t + \frac{1}{k_2Q_e^2} \\
\text{Eq. (3)}
\]

Where k₂ (g.mg⁻¹.min⁻¹) is the rate constant of pseudo-second order adsorption.

Figure 7. show the fitting of the present experimental data to this model, and the calculated values for k₂ and Qₑ parameters are reported in Table 2. A good correlation is observed between the experimental data and the pseudo second order kinetic model with the correlation coefficient being higher than 0.99. It has been concluded that the kinetics of the present adsorption systems was best described by the pseudo-second order model, when based on the value of the correlation coefficient R² and the small differences between the experimental and the calculated values of the equilibrium removal capacity.
Effect of solution pH on dye removal

The pH value of the solution was an important parameter for controlling the sorption process. The effect of pH on the adsorption of dyes by Mg-Al-CO$_3$ was studied by varying the pH of the dye solution from 5 to 10 for an initial concentration of 50 mg L$^{-1}$ and the adsorbent dose at 0.5 g L$^{-1}$ at room temperature (Figure 8). The maximum adsorption occurs at pH = 6 and 7 was found to be equal to 87.1 mg g$^{-1}$, and 96.9 mg g$^{-1}$ for Evans blue (EB) and Yellow thiazole (YT), respectively. A similar result was observed by various authors.

Sorption isotherm

For the liquid–solid system, the Langmuir and Freundlich isotherm equations are usually employed. The well-known Langmuir equation, which is obtained by combining the adsorption and desorption rate equations, can be described as following Eq (4).

$$Q_e = \frac{Q_{\text{max}} K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} \text{Eq. (4)}

Where $K_L$ is the Langmuir constant related to the loading and energy of adsorption; $Q_{\text{max}}$ the maximum loading capacity; $Q_e$ the adsorption loading at equilibrium (mg g$^{-1}$), and $C_e$ is the equilibrium concentration of dye in the solution (mg L$^{-1}$).

The Langmuir equation can be rearranged as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}}$$  \hspace{1cm} \text{Eq. (5)}

The values of $Q_{\text{max}}$ and $K_L$ can be calculated from the slope and the intercept of the linear plots $C_e/Q_e$ versus $C_e$.

An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter $R_L$ which was defined by:

$$R_L = \frac{1}{1 + K_L C_i}$$  \hspace{1cm} \text{Eq. (6)}

Where $K_L$ is the Langmuir isotherm constant and $C_i$ is the initial dye concentration (mg L$^{-1}$). The value of $R_L$ indicates the shape of the isotherms to be either unfavourable.
(\(R_L > 1\)), linear (\(R_L = 1\)), favourable (\(0 < R_L < 1\)) or irreversible (\(R_L = 0\)). Our results, reported in Table 3, were found to be between zero and one for each dye.

**Table 4.** Comparison of the maximum monolayer sorption capacities of some dyes on Mg-Al-CO₃

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Sorption capacity (Q_{\text{max}} \text{(mg g}^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow thiazole (YT)</td>
<td>222.2</td>
<td>This work</td>
</tr>
<tr>
<td>Evans blue (EB)</td>
<td>107.5</td>
<td>This work</td>
</tr>
<tr>
<td>Brilliant Blue R (BBR)</td>
<td>54.6</td>
<td>1</td>
</tr>
<tr>
<td>Green Bezanyl-F2B</td>
<td>52.1</td>
<td>15</td>
</tr>
<tr>
<td>Acid Blue 113</td>
<td>46.9</td>
<td>42</td>
</tr>
<tr>
<td>Acid Blue 9</td>
<td>139.4</td>
<td>13</td>
</tr>
<tr>
<td>Acid orange 7 (O-I1)</td>
<td>176.8</td>
<td>43</td>
</tr>
<tr>
<td>Reactive dye Yellow LS-R</td>
<td>92.2</td>
<td>44</td>
</tr>
</tbody>
</table>

Indeed, the equilibrium parameters in Table 3 indicate a favorable adsorption (\(0 < R < 1\)) process of the both dye for Mg-Al-CO₃ adsorbent, reflecting the validity of using Langmuir as a model for characterizing such adsorbate-adsorbent systems.

The Freundlich isotherm is purely empirical and commonly presented as Eq. (7):

\[
Q_e = k_F \times C_e^{1/n} \tag{Eq. (7)}
\]

Where \(Q_e\) is the amount of solute adsorbed per unit weight of adsorbent (mg g\(^{-1}\)), \(C_e\) the equilibrium concentration of solute in the bulk solution (mg L\(^{-1}\)), \(K_F\) the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mgg\(^{-1}\)) and \(1/n\) is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the nonlinear form:

\[
\log Q_e = \log k_F + \frac{1}{n} \log C_e \tag{Eq. (8)}
\]

A plot of \(\log Q_e\) versus \(\log C_e\) enables the constant \(K_F\) and exponent \(1/n\) to be determined from the intercept and slope of the line, respectively.

The Sorption isotherms of Evans blue (EB) and Yellow thiazole (YT) onto Mg-Al-CO₃ are shown in (Figure 9).

![Figure 9. Sorption isotherms of EB and YT onto Mg-Al-CO₃.](image-url)
Greater quantities of Yellow thiazole (YT) are sorbed than those Evans blue (EB) by Mg-Al-CO₃. The sorption isotherm data for each dye onto Mg-Al-CO₃ were fitted to both the Langmuir (Figure 10) and Freundlich isotherm (Figure 11) equations.

The resulting Langmuir parameters ($Q_{max}$ and $K_L$), Freundlich constants ($k_F$ and $n$) and correlation coefficients are listed in Table 3. The $R^2$ values obtained point out the good correlation between the Langmuir model and the experimental results. It can be seen that the Langmuir equation fits the experimental isotherms better than the Freundlich equation does. The maximum sorption capacity, $Q_{max}$, was found equal to 222.2 mg g⁻¹ for yellow thiazole (YT) and 107.5 mg g⁻¹ for Evans blue (EB). Table 4 shows the sorption capacity values of various anionic dyes toward Mg-Al-CO₃. It can be seen that our results are better than most of the results shown in the references¹,¹³,¹⁵,⁴²-⁴⁴ cited in Table 4.

**Table 4.** Comparison of the maximum monolayer sorption capacities of some dyes on Mg-Al-CO₃

<table>
<thead>
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<th>Dyes</th>
<th>Sorption capacity $Q_{max}$(mgg⁻¹)</th>
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<tr>
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<td>107.5</td>
<td>This work</td>
</tr>
<tr>
<td>Brilliant Blue R (BBR)</td>
<td>54.6</td>
<td>1</td>
</tr>
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</tr>
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<td>Acid Blue 9</td>
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<td>92.2</td>
<td>44</td>
</tr>
</tbody>
</table>

Comparison of sorption capacities between our data and those previously reported by other authors is due to the different structures and molecular size of the inspected dyes. The main conclusion resulting from the above discussion is that the Mg-Al-CO₃ material may be used to remove anionic dyes from wastewater streams of relatively high concentrations.

**Determination of the thermodynamic parameters**

The thermodynamic parameters, such as the enthalpy ($ΔH^°$) and the entropy ($ΔS^°$) for the sorption of EB and YT onto HT are calculated by using the following equation:
\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  
Eq. (9)

Where \( T \) is the absolute temperature (K), \( R \) is the gas constant \((8.314 \text{ J mol}^{-1} \text{K}^{-1})\), and \( K_d \) \((\text{cm}^3 \text{g}^{-1})\) is the distribution coefficient which is calculated with the following expression:

\[ K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \]  
Eq. (10)

The standard free energy change \((\Delta G^0)\) is calculated from the following equation:

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  
Eq. (11)

The Van’t Hoff plot of \( \ln K_d \) as a function of \( 1/T \) (Figure 12) yielded a straight line from which \( \Delta H^0 \) and \( \Delta S^0 \) were calculated from the slope and intercept, respectively (see Table 5).

![Figure 12. Van’t Hoff plots for the dyes removal by Mg-Al-CO₃](image)

<table>
<thead>
<tr>
<th>Dyes</th>
<th>( \Delta S^0 ) ( \text{(Jmol}^{-1}\text{K}^{-1}) )</th>
<th>( \Delta H^0 ) ( \text{(KJmol}^{-1}) )</th>
<th>( \Delta G^0 ) ( \text{(KJmol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB</td>
<td>420</td>
<td>102,01</td>
<td>-23,59</td>
</tr>
<tr>
<td>YT</td>
<td>380</td>
<td>93,03</td>
<td>-20,73</td>
</tr>
</tbody>
</table>

Generally, the change in the adsorption enthalpy on physisorption is in the range of \(-20 \) to \(0\) kJ mol\(^{-1}\), but it ranges between \(-400\) and \(-80\) kJ/mol in the case of chemisorptions\(^{45,46}\).

The \( \Delta G^0 \) values for the used temperatures are negative, which indicate that the nature of adsorption is spontaneous and that the affinity of Mg-Al-CO\(_3\) material toward the anionic organic dyes is strong. The positive value of \( \Delta H^0 \) indicates that the adsorption is endothermic and further suggests that the interaction type is a combination of physical and chemical adsorption due to the adsorption on the external surface of the adsorbent and dye intercalation in the interlayer space of the layered double hydroxide Mg-Al-CO\(_3\). The positive value of \( \Delta S^0 \) indicates a rather good affinity of the material with dye molecules and is a sign of an increase in the degree of freedom of the adsorbed species\(^{47,48}\).

**Conclusion**

The layered double hydroxide Mg-Al-CO\(_3\) was synthesized by co-precipitation method, characterized and used as anion-exchanger in the removal of such anionic dyes as Evans blue.
and Yellow thiazole from aqueous solutions. The sorption isotherm was best defined by the Langmuir isotherm model and the adsorption capacity was found to be equal to 222.2 mg g⁻¹ and 107.5 mg g⁻¹ for Yellow thiazole and Evans blue, respectively. The $R_L$ values indicated the preferential dye adsorption in all cases. The pseudo-second order kinetic model was found to well describe the kinetic behaviour of the systems. The negative $\Delta G^\circ$ values indicated the spontaneity of the removal process. The positive values of $\Delta H^\circ$ pointed out the endothermic nature of the sorption mechanism. The positive values of $\Delta S^\circ$ suggested an increase in disorder accompanying the sorption process. Further study is in progress in view of extending to the present removal process to other anionic dye molecules from aqueous solutions. The removal technology will soon be tested on real wastewater streams containing such toxic molecules.

Work is in progress to explore other applications for the same dye (EB, YT) on another material synthesized LDH type, called ktenasite and to compare its sorption efficiency with Mg-Al-CO₃.

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