Original Article

Ni/Fe and Mg/Fe layered double hydroxides and their calcined derivatives: preparation, characterization and application on textile dyes removal

Rachid Elmoubarki\textsuperscript{a}, Fatima Zahra Mahjoubi\textsuperscript{a}, Alaâeddine Elhalil\textsuperscript{a}, Hanane Tounsadi\textsuperscript{a}, Mohamed Abdennouri\textsuperscript{a}, M’hamed Sadiq\textsuperscript{a}, Samir Qourzal\textsuperscript{b}, Abdeljalil Zouhri\textsuperscript{c}, Noureddine Barka\textsuperscript{a,∗}

\textsuperscript{a} Laboratoire des Sciences des Matériaux, des Milieux et de la Modélisation (LS3M), FPK, Univ Hassan 1, Khouribga, Morocco
\textsuperscript{b} Equipe de Catalyse et Environnement, Département de Chimie, Faculté des Sciences, Université Ibn Zohr, Agadir, Morocco
\textsuperscript{c} Laboratoire Chimie Appliquée et Environnement, FST, Univ Hassan 1, Settat, Morocco

Abstract

In this study, Mg/Fe and Ni/Fe layered double hydroxides (LDHs) with molar ratio (M\textsuperscript{2+}/Fe\textsuperscript{3+}) of 3 and intercalated with carbonate ions were synthesized by co-precipitation method. The as-synthesized materials and their calcined products (CLDHs) were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric and differential thermal analyses (TGA–DTA), transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM–EDX), inductively coupled plasma (ICP) and elemental chemical analysis CHNSO. The materials were used as adsorbents for the removal availability of textile dyes from aqueous solution. Methylene blue (MB) and malachite green (MG), representative of cationic dyes, and methyl orange (MO) representative of anionic dyes were used as model molecules. Adsorption experiments were carried out under different parameters such as contact time, temperature, initial dyes concentration and solution pH. Experimental results indicate that CLDHs had much higher adsorption capacities compared to LDHs. Adsorption kinetic data fitted well the pseudo-second order kinetic model. The process was spontaneous, endothermic for cationic dyes and exothermic for the anionic dye. Equilibrium sorption data fitted the Langmuir model instead of Freundlich model.

© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

∗ Corresponding author.
E-mail: barkanouredden@yahoo.fr (N. Barka).
http://dx.doi.org/10.1016/j.jmrt.2016.09.007
2238-7854/© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

The rapid economic growth has caused environmental disorder with huge pollution problems. The demand for water has increased tremendously in agricultural, industrial and domestic sectors. This has resulted in the generation of large amounts of wastewater containing a high number of contaminants. Many industries, such as textiles, paper and plastic, use dyes tufts in order to colour their products and they also consume substantial volumes of water [1,2].

Water polluted by organic dyes has attracted a global concern because of its harmful impact on public health [3,4]. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and difficult to biodegrade [5]. The removal of organic dye tufts from industrial polluted water has always been a difficult issue in the field of environmental remediation and pollution control.

Among various physical and chemical processes, the adsorption technique is the most widely used for being of low cost, simple and efficient for dyes removal [6]. Several types of porous materials such as natural phosphate [7], hydroxyapatite [8], natural clays [9], lignite [10], chitosan [11], silica [12], kaolinite [13], sepiolite [14], Fe3O4 nanoparticles [15] and some natural biosorbents have been reported [16,17]. However, studies in this field have not produced materials which meet all demands of adsorption activity.

Layered double hydroxides (LDHs) have received considerable attention due to their potential applications in catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical science and environmental applications. They are easy and inexpensive to synthesize in laboratory and industrial scales [18,19]. LDHs have many physical and chemical properties that are surprisingly similar to those of cationic clay minerals. Their layered structure, wide chemical composition (due to variable isomorphous substitution of metal cations), variable layer charge density, ion-exchange properties, reactive interlayer space, swelling in water, rheological and colloidal properties have made LDH clay-mineral-like [20]. The general chemical composition of LDH is \[ \text{M}^{2+} \times \text{M}^{3+} \times (\text{OH})_{2} \times (\text{A}^{n-})_{\text{n}} \times \text{H}_{2} \text{O} \], where \( \text{M}^{2+} \) and \( \text{M}^{3+} \) are divalent and typically trivalent metal cations, respectively, on the layer; \( x \) is the molar ratio of the trivalent cation \( [\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})] \); \( A^{n-} \) is the interlayer anions with the charge \( n \) and \( m \) is the amount of interlayer water [21].

Many researches have shown that LDHs can adsorb some inorganic or organic pollutants through exchange with interlayer anions. However, CO32− is preferentially attached and readily replaceable by other anions [22]. By heating LDHs, they are converted into mixed metal oxides which can easily reconstruct the original layered structure in an aquatic environment [23]. Used as sorbents, calcined LDHs receive more and more interests in the environmental studies.

The main objective of this study was to examine the feasibility of using Mg/Fe and Ni/Fe layered double hydroxides and their calcined products for the removal of dyes from aqueous solution. We chose in this study methylene blue (MB) as a reference dye because its strong adsorption study on solids and its use in characterizing adsorptive materials [24] and to determine specific surface area [25]. Two textile dyes were also used, malachite green (MG) and methyl orange (MO), representative of the two families of textile dyes (cationic and anionic dyes). The effect of different parameters including solution pH, dye concentration, temperature and contact time were studied to optimize the sorption process. Equilibrium, kinetic and thermodynamic parameters were explored to describe the adsorption process.

2. Experimental

2.1. Materials

Chemicals including Mg(NO3)2·6H2O, Ni(NO3)2·6H2O, FeCl3·6H2O, Na2CO3, methyl orange (MO), methylene blue (MB) and malachite green (MG) were purchased from Sigma–Aldrich (Germany). NaOH was purchased from Merck (Germany), and HNO3 from Scharlau (Spain). All solutions were prepared using distilled water. The molecular structures and some physicochemical characteristics of used dyes are shown in Table 1.

2.2. Preparation of LDHs and CLDHs

Layered double hydroxides were synthesized by co-precipitation method at room temperature. A solution containing 0.75 M of Mg(NO3)2·6H2O or Ni(NO3)2·6H2O and 0.25 M of FeCl3·6H2O was added at a rate of 1.0 mL/min, under vigorous stirring, to a solution of NaOH (2 M) and Na2CO3 (0.2 M). The resulting slurry was hydrothermally treated at 80°C for 24 h and then filtered and washed with deionized water until the pH of supernatant was 7.0. After that, the solids obtained were dried at 80°C for 24 h. The samples are hereafter referred to Ni-LDH and Mg-LDH. The Ni-CLDH and Mg-CLDH were obtained by heating for three hours Ni-LDH and Mg-LDH in a tubular furnace at 400 and 500°C, respectively. These temperatures were determined by the TGA/DTA analysis (see below). Both the calcined and uncalcined products were ground and passed through a 100-mesh sieve prior to analysis or use in adsorption experiments.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded from 2θ = 5–70° using a Bruker-axs D2-phaser advance diffractometer operating at 30 kV and 10 mA with Cu Kα radiations. The surface morphology of the samples was observed by transmission electron microscopy (TEM) at accelerating voltage of 120 kV using a Tecnai G2/FEI instrument. FTIR spectra were collected on a Nicolet Avatar 330 Fourier transform IR spectrophotometer. Samples were mixed with KBr at a mass ratio of 1:100 and finely powdered to prepare pellets. The spectra were recorded with 2 cm−1 resolution in the range of 4000–400 cm−1. Simultaneous thermogravimetric differential thermal curves (TGA–DTA) were recorded on a Setaram (SENSYS Evo) instrument under argon atmosphere in the temperature range of 30–700°C at a heating rate of 10°C/min. The metal composition of the synthesized materials was...
determined by Optima 2100DV inductively coupled plasma optical emission spectrometry (ICP-OES) after dissolving the samples in concentrated nitric acid. C, H and O content was determined by elemental chemical analysis using a CHNSO Thermo Scientific Flash 2000 EA 1112 analyzer.

2.4. Adsorption experiments

Stock solutions of 1 g/L of MB, MG or MO were prepared by dissolving the appropriate amount of each dye in distilled water and the used concentrations were obtained by dilution. The adsorption experiments were carried out at a constant agitation speed of 500 rpm by varying the initial solution pH from 2 to 12, the contact time from 20 to 480 min, the initial dye concentration from 20 to 200 mg/L and the temperature from 10 to 50 °C. The temperature was controlled using a thermostatically controlled incubator. The pH was adjusted to a given value by addition of HNO₃ (1N) and/or NaOH (1N) and was measured using an EZODO pH-Meter.

After each adsorption experiment completed, samples were centrifuged at 3000 rpm for 10 min to separate the solid phase from the liquid phase. The supernatants were analyzed for residual dye concentration using a Tomos V-1100 UV/Vis spectrophotometer.

The adsorbed quantity was calculated using the following equation:

\[ q = \frac{(C_0 - C)}{R} \] (1)

where, \( q \) (mg/g) is the quantity of dye adsorbed per unit mass of adsorbent, \( C_0 \) (mg/L) is the initial dye concentration, \( C \) (mg/L) is the dye concentration after adsorption and \( R \) (g/L) is the mass of adsorbent per litter of aqueous solution.

### Table 1 – Physicochemical characteristics of used dyes.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
<th>Nature</th>
<th>MW (g/mol)</th>
<th>( \lambda_{max} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene blue (basic blue 9)</td>
<td><img src="image1" alt="Methylene blue structure" /></td>
<td>Cationic</td>
<td>319.8</td>
<td>661</td>
</tr>
<tr>
<td>Malachite green (basic green 4)</td>
<td><img src="image2" alt="Malachite green structure" /></td>
<td>Cationic</td>
<td>329.5</td>
<td>621</td>
</tr>
<tr>
<td>Methyl orange (acid orange 52)</td>
<td><img src="image3" alt="Methyl orange structure" /></td>
<td>Anionic</td>
<td>327.3</td>
<td>461</td>
</tr>
</tbody>
</table>

![Fig. 1 – XRD patterns of LDHs and CLDHs samples.](image4)

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. XRD

Fig. 1, shows the XRD patterns of LDHs and CLDHs. The diffractograms for both Ni-LDH and Mg-LDH indicate a high degree of crystallinity. All the diffraction peaks can be indexed on a hexagonal structure with a space group R3m. Thus revealing that the LDHs are crystallized in a rhombohedral structure [26]. It can be found that the patterns show diffraction peaks corresponding to (003), (006), (012), (015), (018), (110) and (113) diffraction plans. The cell parameter “c” is commonly calculated as \( c = 3d_{(003)} \), assuming a 3R polytispism for the hydrotalcite [27], while the value of cell parameter “a” is calculated as \( a = 2d_{(110)} \) [28]. The calculated parameters were found to be 2.322 and 2.333 nm for “c” parameter; 0.308 and 0.311 nm for “a” parameter, respectively, for Ni-LDH and
Table 2 – Crystallite size in a and c directions calculated by Scherrer equation for LDHs.

<table>
<thead>
<tr>
<th>LDHs</th>
<th>Mg-LDH</th>
<th>Ni-LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size in a direction (nm)</td>
<td>24.19</td>
<td>19.36</td>
</tr>
<tr>
<td>Crystallite size in c direction (nm)</td>
<td>18.88</td>
<td>12.42</td>
</tr>
<tr>
<td>Aspect ratio (a/c) d_{10} (nm)</td>
<td>1.28</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Mg-LDH. Since the difference in the basal spacing can be reasonably attributed to the amount of the interlayer (CO$_3^{2-}$) anion, as confirmed by CHO and TGA–DTA analyze (see below). The difference in the lattice parameter a can be explained by the higher ionic radius of Mg$^{2+}$ (0.150 nm) compared to ionic radius of Ni$^{2+}$ (0.135 nm).

The crystallite size of LDH samples is calculated by the Scherrer equation:

$$D_{hkl} = \frac{R\lambda}{\beta \cos \theta}$$

(2)

where $R$ is the Scherrer number (0.89), $\lambda$ is incident ray wavelength (0.1542 nm), $\beta$ is peak width at half height (rad), $\theta$ is Bragg angle.

The crystallite sizes in the a/c direction calculated by Scherrer equation, which is appropriate for the crystal size range from 3 to 200 nm [29], are shown in Table 2. The widening of peaks ([110] and [003] planes) implies that the crystal sizes are reduced in both (a) and (c) directions. The crystallite size in the c direction is indicative of stacking thickness of LDH sheets.

Chemical composition of the samples obtained by ICP and CHO analyses is given in Table 3. The amount of interlayer water determined by TGA analysis is also given in the table. It is clear that the obtained values for $M^{2+}$/Fe$^{3+}$ molar ratio are in good agreement with the theoretical value of 3 used in the preparation. The table also indicates that, C, H and content are greater in Mg-LDH than in Ni-LDH. This result is in good agreement with TGA analysis, which indicates a mass loses for Mg-LDH greater than that of Ni-LDH. From the above cited results, the molecular formula of the two samples could be expressed as [Ni$_{0.75}$Fe$_{0.25}$OH]$_3$·(CO$_3$)$_{1.68}$·1.12H$_2$O and [Mg$_{0.73}$Fe$_{0.27}$OH]$_3$·(CO$_3$)$_{2.17}$·1.62H$_2$O, respectively, for Ni-LDH and Mg-LDH.

Remarkable changes are observed for CLDHs. The well-defined diffraction peaks of the parent samples were replaced by broad peaks, thus indicating a poor long-range ordered phase. These broad peaks suggest a nanocrystalline material with very small nanoparticles or even an amorphous phase [30]. Layered structure of the original samples is completely destroyed and replaced only by MgO and NiO peaks at 2$\theta$ = 43.06° and 62.48° for Mg-CLDH and at 2$\theta$ = 36.97°, 43.26° and 62.8° for Ni-CLDH [31]. There are no peaks present.
and 

3.1.3. 

The 

loss 

associated 

water. 

Ni-LDH 

4000 

x 

CHO 

3 

phases 

by 

str 

broad 

is 

and 

which 

the 

interlayer 

are 

associated 

and 

restrained 

under 

the 

influence 

of 

electrostatic 

interaction. 

Another 

absorption 

band 

at 1640 cm−1 

correspond 

the 

water 

deformation, 

H(H2O). 

The 

bands 

at 

low 

frequency 

region 

(below 

1000 cm−1 

except 

carbonate) 

are 

related 

with 

metal–oxygen 

and 

metal–oxygen–metal 

vibrational 

modes 

in 

brucite-type 

layer [34]. 

The 

absorption 

band 

observed 

at 

1390 cm−1 

was 

the 

v5 (asymmetric 

stretching) 

of 

the 

CO32− ion 

in 

the 

interlayer [37]. 

The 

FT-IR 

spectrum 

of 

calcined 

products, 

shows 

three 

major 

differences; 

first, 

the 

O–H 

stretching 

at 

3500–3600 cm−1 

band 

observed 

in 

spectra 

of 

Ni-LDH 

and 

Mg-LDH 

is 

slightly 

narrowed 

after 

calcinations. 

The 

decrease 

in 

the 

intensity 

of 

the 

O–H 

stretching 

is 

elucidated 

after 

calcinations 

in 

which 

the 

layered 

structure 

of 

LDH 

collapses 

owing 

to 

the 

thermal 

dehydroxylation 

of 

the 

double 

hydroxide, 

secondly, 

the 

sharp 

band 

at 

1640 cm−1 

disappears, 

and 
in 

thirdly, 

the 

band 

at 

around 

1390 cm−1 

of 

the 

CO32− ion 

in 

the 

interlayer 

disappears, 

693 and 670 cm−1 are the out-of-plane deformation stretching vibration and in-plane bending vibration of CO32− ions [35,36], respectively. Usually, the later position is interpreted as the crystal lattice stretching vibration of M-O bond and the antisymmetric v4 vibration of CO32− anions. Such result proposes that the hydroxyl groups in the brucite layer and interlayer are associated and restrained under the influence of electrostatic interaction. Another absorption band at 1640 cm−1 correspond the water deformation, \( \delta (H_2O) \). The bands at low frequency region (below 1000 cm−1 except carbonate) are related with metal–oxygen and metal–oxygen–metal vibrational modes in brucite-type layer [34]. The absorption band observed around 1390 cm−1 was the v5 (asymmetric stretching) of the CO32− ion in the interlayer [37]. The FT-IR spectrum of calcined products, shows three major differences; first, the O–H stretching at 3500–3600 cm−1 band observed in spectra of Ni-LDH and Mg-LDH is slightly narrowed after calcinations. The decrease in the intensity of the O–H stretching is elucidated after calcinations in which the layered structure of LDH collapses owing to the thermal dehydroxylation of the double hydroxide, secondly, the sharp band at 1640 cm−1 disappears, and in thirdly, the band at around 1390 cm−1 of the CO32− ion in the interlayer disappears,

3.1.4. Morphological characterization (TEM-EDX)

TEM micrographs of Mg-LDH and Ni-LDH are presented in Fig. 4(a, c). The figure indicates that, LDHs have hexagonal platelet morphology, having some small cracks at the edge of hexagonal sheets and part of sheets presenting vertical crossing at hexagonal sides. From the micrographs, the crystallite size varied from 15 to 88 nm. The crystal size of stacked-disc-shaped observed in the Mg-LDH was larger than that in the Ni-LDH. This result is in good agreement with XRD analysis. The micrographs of calcined products shown in Fig. 4(e, g) indicate a very rough surface while their sheet/disc-like shape remains unchanged, there are numerous pores in the structure, originating from the interparticle voids.

The EDX spectrum shown in Fig. 4(b, d, f, h) clearly indicate the presence of magnesium, iron and nickel within walls. The molar ratios of Mg/Fe and Ni/Fe were found to be 2.81 and 2.93 respectively, which is in good agreement with the ratio of 3 used in the preparation and confirmed by ICP analysis. The analysis also confirmed the presence of carbon.

3.2. Dyes removal performance

3.2.1. Effect of solution pH

pH of the solution is an essential parameter for the control of the adsorption process, given that it may affect at the same time the surface charge of the adsorbents and the ionization behaviour of the dyes [38]. Figs. 5–7 shows the effect of solution pH on the adsorption of MB, MG and MO by LDHs and CLDHs. For Ni-LDH and Mg-LDH, with the increase of solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg (%)</th>
<th>Ni (%)</th>
<th>Fe (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>O (%)</th>
<th>H2O (%)</th>
<th>M2+/Fe2+ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-LDH</td>
<td>0.73</td>
<td>–</td>
<td>0.27</td>
<td>2.17</td>
<td>3.81</td>
<td>37.75</td>
<td>1.62</td>
<td>2.70</td>
</tr>
<tr>
<td>Ni-LDH</td>
<td>–</td>
<td>0.75</td>
<td>0.25</td>
<td>1.68</td>
<td>2.84</td>
<td>35.41</td>
<td>1.12</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Table 3 – Chemical composition of the samples.
pH, the removal of MO decreased gradually. The high adsorption was obtained at the pH of 4.0, and the least removal was observed at pH of 10. At the lower solution pH, more hydrogen ions were in the solution making the surface of the adsorbent with more positive charges, which promoted the electrostatic attraction between the negatively charged dye molecules and the surface of the adsorbent [39]. Hence, the weak acid or neutral is the ideal condition for MO adsorption. The MB and MG adsorption capacities, present a significant increasing trend with the increase of pH values. For Ni-LDH and Mg-LDH, the removal efficiencies can reach up to 35 mg/g and 10 mg/g for MB, 90 mg/g and 100 mg/g for MG respectively, when the pH of
solution is 10. Lower adsorption capacities of these dyes are registered at low pH values.

Theoretically, at pH < point of zero charge (PZC) of the adsorbent, the surface gets positively charged, which enhances the adsorption of the negatively charged dyes through electrostatic forces of attraction. At pH > PZC, the surface of particles gets negatively charged, which favours the adsorption of cationic dyes [40]. The point of zero charge (PZC) of Ni-LDH, Mg-LDH, Ni-CLDH and Mg-CLDH, were 8.16, 9.0, 8.9 and 9.6 respectively. Furthermore, the structure of layered materials with hydroxide sheets will be destroyed when pH was below 4 [41].

For the calcined products, by varying the pH from 4.0 to 11.0, the removal efficiency can reach up to 55 and 25 mg/g for MB, 125 and 175 mg/g for MG, 100 and 140 mg/g for MO, respectively for Ni-CLDH and Mg-CLDH. Generally, the adsorbed amounts of MB and MG were lower than of MO. Also, the removal efficiency was higher than that of the LDHs. The probable reason was due to the reconstruction of the LDH structure with the intercalation of dyes into the CLDH in aqueous solutions [42]. It suggests that CLDH can be a high efficiency adsorbent for the adsorption of MB and MG in basic solutions [43].

3.3. Adsorption kinetics

Figs. 8–10 show the adsorption kinetics of dyes by LDHs and CLDHs. It is evident that the adsorbed amount of MB, Mg and MO increased rapidly in the initial 60 min. Thereafter, it becomes slower and almost unchanged after 240 min, indicating that equilibrium has been achieved. Dyes sorption by CLDHs was higher than by LDHs. The difference between equilibrium times obtained with LDHs and CLDHs can be explained by the fact that dyes adsorption on LDHs may occur via exchange mechanism. But on CLDH, it occurs probably by both surface and by reconstruction phenomena (memory effect) [42]. This property is typical to LDHs make them able to recover the original lamellar structuring after calcination induced complete loss of its original layered organization.

Kinetic modelling of the adsorption process provides a prediction of adsorption rates, and allows the determination of fitting rate expressions characteristic for possible reaction
where the pseudo-first-order mechanisms. The most frequently used models are the pseudo-first-order [43] and the pseudo-second-order [44].

The pseudo-first-order rate expression of Lagergren based on solid capacity is generally expressed as follows:

$$q = q_e(1 - e^{-k_1t})$$  \hspace{1cm} (3)

where $q_e$ and $q$ (both in mg/g) are respectively the amounts of dye adsorbed at equilibrium and at any time $t$, and $k_1$ (1/min) is the rate constant.

The pseudo-second-order model proposed by Ho and McKay [44] is based on the assumption that the adsorption follows second order chemisorption. This model can be expressed as:

$$q = \frac{k_2q_e^2t}{(1 + k_2q_e t)}$$  \hspace{1cm} (4)

where $k_2$ (g/mg min) is the rate constant of pseudo-second order adsorption.

Parameters of the pseudo-first-order and pseudo-second-order kinetic models were estimated with the aid of the non-linear regression. The obtained values and correlation coefficients are presented in Table 4. It is obvious that the determined coefficient $r^2$ for the pseudo-second-order kinetic model are higher than those for the pseudo-first-order kinetic model, and the calculated $q_e$ values are closer with the experimental values compared to the pseudo-first-order kinetic models. The results mentioned above indicated that the adsorption of MB, MG and MO onto LDHs and CLDHs followed pseudo-second-order kinetics, suggesting that a chemisorption may be the rate-limiting step in the adsorption process [45]. The low values obtained for dyes removed by LDHs, can be explained by the strong carbonate affinity for LDHs compounds. However, on CLDHs it is much higher, because the adsorption occurs probably by both surface adsorption and reconstruction mechanism [39]. The pseudo-second order model is also presented as the best model to describe dyes adsorption by other adsorbents like hydrotalcite-iron oxide magnetic [46], clays [9], uncalcined and calcined MgNiAl layered double hydroxide [47], and native zeolite [48].

### 3.4. Adsorption isotherm

To analyze the characteristics of the adsorption equilibrium, the adsorption isotherms were studied, as this provides information about the surface properties of adsorbent, the adsorption behaviour and the design of adsorption systems. Adsorption equilibrium is a dynamic concept achieved as the rate of dye adsorption is equal to the desorption rate [49]. Several models including, Langmuir, Freundlich and Dubinin–Radushkevich have been used to analyze the equilibrium adsorption data.

The Langmuir adsorption model [49] is established on the following hypotheses: (1) uniformly energetic adsorption sites, (2) monolayer coverage, and (3) no lateral interaction between adsorbed molecules. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site.

The Freundlich isotherm [50] endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites
with different energy of adsorption. The energy of adsorption varies as a function of surface coverage.

The Dubinin–Radushkevich (D–R) isotherm model [51] does not assume a homogenous surface or constant sorption potential as other models. It can be noted that the (D–R) isotherm is more general that the Langmuir fit.

The adsorption isotherms of MB, MG and MO onto LDHs and CLDHs are shown in Figs. 11–13. It was found that the CLDHs showed much higher adsorption capacities than that of LDHs. The adsorption isotherm of LDHs was more scattered than that of the CLDHs. The possible reason was associated to the complexity of intercalated ions after adsorption on the LDHs materials. For the CLDHs, the reconstructed layered structure after adsorption of MB, MG and MO did not contain carbonate anions in the interlayer [39].

The experimental adsorption isotherms obtained were compared with the adsorption isotherm models and the
| Adsorbent | T (°C) | q_e (mg/g) | K_D (l/mol) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/Kmol) | q_e (mg/g) | K_D (l/mol) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/Kmol) | q_e (mg/g) | K_D (l/mol) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/Kmol) |
|----------|--------|------------|-------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|-------------|-------------|
| Ni-LDH   | 10     | 83.10      | 12.56       | −5953.64    | −27.10      | 74.60       | 7.68       | 0.41        | 2122.95     | 38.34       | 128.58      | 33.10      | 2.23        | −1881.77    | 16.85       | 66.14       |
|          | 20     | 73.07      | 8.89        | −5321.67    |             |             | 14.38      | 0.83        | 449.90      |             |             | 41.85      | 3.11        | −2761.04    |             |             |
|          | 30     | 60.11      | 5.84        | −4444.67    |             |             | 20.96      | 1.29        | −641.69     |             |             | 40.06      | 2.91        | −2691.79    |             |             |
|          | 40     | 50.46      | 4.26        | −3772.78    |             |             | 30.53      | 2.07        | −1898.96    |             |             | 53.82      | 4.66        | −4002.36    |             |             |
|          | 50     | 40.82      | 3.05        | −2994.67    |             |             | 41.30      | 3.18        | −3104.95    |             |             | 59.20      | 5.53        | −4594.15    |             |             |
| Ni-CLDH  | 10     | 107.15     | 9.45        | −5283.96    | −22.23      | 60.22       | 30.73      | 1.74        | −1296.69    | 36.31       | 129.45      | 54.37      | 3.44        | −2904.80    | 18.41       | 75.10       |
|          | 20     | 79.57      | 5.87        | −4312.62    |             |             | 56.19      | 3.59        | −3110.23    |             |             | 65.76      | 4.41        | −3615.27    |             |             |
|          | 30     | 73.26      | 5.21        | −4159.57    |             |             | 65.76      | 4.41        | −3738.66    |             |             | 72.94      | 5.09        | −4098.52    |             |             |
|          | 40     | 57.71      | 3.77        | −3455.16    |             |             | 90.88      | 7.05        | −5080.67    |             |             | 95.67      | 7.64        | −5292.57    |             |             |
|          | 50     | 44.65      | 2.73        | −2699.26    |             |             | 104.04     | 8.78        | −5834.68    |             |             | 104.04     | 8.78        | −5834.68    |             |             |
| Mg-LDH   | 10     | 71.91      | 8.55        | −5050.13    | −36.53      | 111.17      | 3.55       | 0.18        | 4022.98     | 38.82       | 124.24      | 44.92      | 3.46        | −2920.25    | 23.92       | 95.61       |
|          | 20     | 59.88      | 5.80        | −4280.41    |             |             | 7.76       | 0.41        | 2171.36     |             |             | 62.19      | 6.08        | −4398.96    |             |             |
|          | 30     | 36.63      | 2.61        | −2413.43    |             |             | 11.35      | 0.62        | 1210.58     |             |             | 68.17      | 7.36        | −5028.07    |             |             |
|          | 40     | 28.85      | 1.89        | −1651.39    |             |             | 16.73      | 0.96        | 115.46      |             |             | 78.93      | 10.47       | −6110.96    |             |             |
|          | 50     | 22.33      | 1.37        | −837.86     |             |             | 24.51      | 1.51        | −1103.74    |             |             | 84.32      | 12.62       | −6809.04    |             |             |
| Mg-CLDH  | 10     | 138.11     | 15.58       | −6460.76    | −22.65      | 55.99       | 18.91      | 1.01        | −31.98      | 29.95       | 111.41      | 86.29      | 6.50        | −4405.51    | 10.51       | 52.62       |
|          | 20     | 137.08     | 15.32       | −6648.40    |             |             | 40.64      | 2.40        | −2135.02    |             |             | 98.06      | 7.96        | −5052.09    |             |             |
|          | 30     | 113.75     | 10.52       | −5928.15    |             |             | 51.41      | 3.20        | −2931.43    |             |             | 95.67      | 7.64        | −5123.48    |             |             |
|          | 40     | 85.88      | 6.58        | −4904.34    |             |             | 69.35      | 4.74        | −4050.91    |             |             | 111.22     | 9.87        | −5956.91    |             |             |
|          | 50     | 74.14      | 5.30        | −4479.70    |             |             | 96.86      | 7.80        | −5515.64    |             |             | 121.98     | 11.72       | −6608.77    |             |             |
constants appearing in each equation of those models were determined by nonlinear regression analysis. The results of this analysis are tabulated in Table 5. The square of the correlation coefficient ($r^2$) are also shown in this table.

The methyl orange isotherms show an important adsorption with almost weak concentration in the solution. It is an isotherm of the type I in Giles classification [52]. This occurs when the interactions between the adsorbed molecules and the solid surface are very strong. A chemical adsorption of negatively charged functional groups of MO on the positively charged surface groups of the LDHs and CLDHs is proposed. The best fit of experimental data in the case of MO was obtained with the Langmuir model. This result suggests that the adsorption process of MO by the LDHs and CLDHs was monolayer adsorption, and the maximum monolayer adsorption capacities were found to be 783.65, 859.47, 576.00, and 717.73 mg/g, respectively, for Ni-LDH, Ni-CLDH, Mg-LDH and Mg-CLDH. The adsorption isotherm forms of methylene blue and malachite green are type I in Giles classification. The forces of attraction between the adsorbed molecules are low. This is due to the fact that methylene blue and malachite was a cationic molecule that has the same charge of LDHs surface. Therefore, low adsorption affinity is observed. A physisorption assured by van der Waals interactions is suggested. The best fit of experimental data in the case of MB was obtained with the Langmuir model, with maximum adsorption capacities of 23.39, 32.48, 13.64 and 20.79 mg/g, respectively, for Ni-LDH, Ni-CLDH, Mg-LDH and Mg-CLDH. For MG, the experimental result was good fitted with both Langmuir and Dubinin–Radushkevich isotherm models. The Langmuir adsorption capacities were found to be 320.03, 438.85, 383.40 and 619.46 mg/g, respectively, for Ni-LDH, Ni-CLDH, Mg-LDH and Mg-CLDH.

3.5. Effect of temperature on the adsorption

Temperature is a highly significant parameter in the adsorption process. To assess the capacity of LDHs and CLDHs in the removal of dyes in the case of different types of effluents, experiments were performed at different temperatures in the range of 30–50 °C. The quantities of MB, MG and MO adsorbed as function of solution temperature are shown in Table 6. The Table indicates that the increase in solution temperature increases the adsorbed quantities of MB and MG. However, the adsorbed quantity of MO decreases with the increase in temperature. From these results, the experimental data obtained for MB, MG and MO adsorption on LDHs and CLDHs adsorbents at different temperatures were used for calculation of thermodynamic parameters, such as Gibbs free energy ($\Delta G^\circ$), enthalpy variation ($\Delta H^\circ$) and entropy variation ($\Delta S^\circ$), by using the following equations.

For such equilibrium reactions, $K_D$, the distribution constant, can be expressed as:

\[
K_D = \frac{q_e}{C_e}
\]

The Gibbs free energy is:

\[
\Delta G^\circ = -RT \ln(K_D)
\]

where $R$ is the universal gas constant (8.314 J mol/K) and $T$ is solution temperature in K. The enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of adsorption were estimated from the slope and intercept of the plot of $\ln K_D$ versus $1/T$ yields, respectively.

\[
\ln K_D = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

The thermodynamic parameters calculated from the values of the slopes and intercepts are reported in Table 6. For the anionic dye the experimental results indicated that the amount adsorbed increased with decreasing temperature. The physical bonding between the MO molecules and the active sites of the LDHs and CLDHs is probably reduced with increasing temperature. The negative values of $\Delta G^\circ$ and the negative value of $\Delta H^\circ$ indicate that the adsorption of the dye was spontaneous and exothermic. For the cationic dyes the amount adsorbed increased with increasing temperature. The negative values of $\Delta G^\circ$ and positive values of $\Delta H^\circ$ indicate that adsorption of MB, MG on both LDHs and CLDHs are spontaneous and endothermic process. The low values of enthalpy indicated that the dyes are adsorbed via physical interactions. Entropy has been defined as the degree of chaos of a system. The positive values of $\Delta S^\circ$ indicate an increasing randomness at solid–solution interface during adsorption process. From all this results, it could be concluded that adsorption of MO was more influenced by the change in solution temperature, and the negative values of $\Delta G^\circ$ confirm the feasibility of the process and the spontaneous nature of adsorption with a high preference of MO by LDHs and CLDHs.

4. Conclusions

In this study, adsorption experiments for the removal of methylene blue (MB), malachite green (MG), and methyl orange (MO) from aqueous solutions have been carried out using Mg/Fe and Ni/Fe layered double hydroxides (LDH) with molar ratio (M²⁺/Fe²⁺) of 3 and intercalated with carbonate ions (Ni-LDH, Mg-LDH), and their calcined products (Ni-CLDH, Mg-CLDH). The obtained results show that the materials were found to be excellent adsorbents for the used dyes. The adsorption system reaches equilibrium in 240 minutes. The pH experiments showed that significant adsorption takes place at pH of 4 for MO and pH of 8 for MB and MG. The equilibrium uptake was increased with increasing the initial concentration of dye in solution. Experimental data were better described by pseudo-second-order model with initial adsorption rate on CLDHs higher than that on LDHs. The adsorption isotherm could be well fitted by the Langmuir equation. The sorption capacity decreases for MO and increases for MB and MG with an increase in solution temperature up to 50 °C. The values of the thermodynamic parameters obtained indicated that the MO sorption was spontaneous and endothermic in nature.

Conflicts of interest

The authors declare no conflicts of interest.


