Evans Blue dye removal from contaminated water on calcined and uncalcined Cu-Al-CO₃ layered double hydroxide materials prepared by coprecipitation

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Abstract. This work focuses on studying the removal of Evans Blue dye, which is a water pollutant, using Cu-Al-CO₃ anionic clay known also as layered double hydroxide (LDH) and its phase calcined at 500°C (Cu-Al-500). LDH is easy to synthesize by a coprecipitation method at a constant pH; it is non-toxic and non-expensive, constituted of plane sheets containing alternating octahedral stack M(OH)₆ formed by divalent (Cu²⁺) and trivalent (Al³⁺) cations and carbonate anions (CO₃²⁻) in the interfoliar space. The X-ray diffraction (XRD) pattern of the formed solids shows that the synthesized phase is the LDH type, and was confirmed by infrared spectroscopy (FT-IR). Thermogravimetric analysis (TGA) shows that the decarbonation of LDH begins at 500°C, thus this temperature is chosen for the calcination of this clay. XRD and FT-IR of the calcined phase confirm the obtaining of copper and aluminium oxides. The UV-visible study of the adsorption of Evans Blue is performed by varying different parameters such as the weight of LDH and its calcined phase, the concentration of the dye and the pH of the solution. The obtained isotherms from this kinetic study show that the adsorption of Evans Blue dye is more efficient in the calcined phase compared with the as-synthesized LDH.

Keywords. LDH; calcination; Evans Blue dye; adsorption; coprecipitation.

1. Introduction

Industrial activities, like the textile, paper, plastics, leather, agro-food and chemical industries, release effluent containing high concentrations of dyes that generate a visual and chemical pollution and that should be treated [1]. The choice of the method to remove this pollutant is very important and depends on some factors such as the composition of dyes, the quality and the use of water. Traditionally, mixed biological and chemical treatment processes have been used to reduce the dye concentration of wastewater, but their effectiveness seems limited because of the low biodegradability of most organic pollutants [2]. Part of current research is directed towards the development of low-cost treatment processes using materials such as activated carbon and clays [3]. In this perspective, many researchers have been interested in applications of layered double hydroxides (LDHs) with brucite as structure, which are known for their electrochemical [4,5] and anionic exchange properties in relation to its layered structure [6,7] for use in adsorption processes and removal of anionic dyes [8]. These materials have shown significant efficiency and performance in this area. Indeed, Yanwei *et al* used a mesoporous trimetal material based on LDH (Cu/Mg/Fe-LDH) to remove As(V) from aqueous solutions. The Cu/Mg/Fe-LDH showed good

adsorption ability for As(V) and it was able to reduce the As(V) concentration down to a final level of <10 µg l⁻¹ under the optimal conditions [9]. A magnetic Mg-Fe-Zr LDH/Fe₃O₄ composite was also developed as an adsorbent for As(V) removal using an external magnetic field [10]. The dye adsorption on these anionic clays is favoured by the nature and the accessibility of their structure. Martin and Pinnavaia [11] used the name 'lamellar double hydroxide' to show the presence of two types of metal cations in the sheets of these compounds. They are constituted by the alternate stacking of octahedral plane layers M(OH)₆ which are formed by divalent and trivalent cations, as well as hydrated anions in the interlayer region (figure 1). The compact hydroxylated layers are charged positively in proportion at a rate of substitution x in trivalent metals where $x = M^{III}/(M^{II} + M^{III})$ [12]. These materials as a part of divalent cations are replaced by trivalent cations creating a positive charge into layers; this excess charge is compensated by the negative charges of anions inserted into the interlayer regions. Large varieties of divalent and trivalent cation associations with inserted anions in the structure lead to a large variety of LDH [13]. Some authors studied the phases with monovalent and trivalent cations [14–16]. Anionic species that can be inserted into the interlayer space can be inorganic or organic anions, complex or polymers [17–20].

Figure 1. The LDH structure.

Figure 2. Chemical structure of Evans Blue dye.

In our work, a coloured dye named Evans Blue which has anionic properties is chosen to study its adsorption by LDH. In fact, Evans Blue (figure 2) is an azo dye which has the particularity of having four anionic sites, making it more difficult to adsorb. In order to remove this dye which is hazardous, two materials have been used as adsorbents. In this perspective, we divided this work into two parts: (1) the synthesis of LDH and its calcined phase by coprecipitation and their characterization using XRD, FT-IR and TGA and (2) then, the use of these materials in UV-visible study of the adsorption of Evans Blue dye by modifying various parameters such as adsorbent weight, dye concentration and the pH of the solution

to determine the efficiency of these materials under optimized conditions.

2. Experimental

2.1 Materials

The starting materials copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (Sigma-Aldrich, 99–104%) and aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (Sigma-Aldrich, $\geq 98\%$), sodium hydroxide (NaOH) (Riedel-de Haen) and sodium carbonate (Na_2CO_3) (Rectapur) are used as received

without further purification. Evans Blue ($C_{34}H_{24}N_6Na_4O_{14}S_4$) is used as a pollutant agent.

2.2 Preparation of LDHs

LDH ($Cu-Al-CO_3$) is prepared by coprecipitation of copper and aluminium nitrates. The synthesis procedure is briefly described as follows: $Cu(NO_3)_2 \cdot 3H_2O$ (0.2 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.1 mol) are dissolved in 400 ml of distilled water, at room temperature, with a molar ratio of $R = Cu^{II}/Al^{III} = 2$. Then, the obtained mixture is precipitated, under vigorous stirring, by adding dropwise a solution of metal salts composed of 1 M NaOH and 2 M Na_2CO_3 . The pH is maintained at 10. Next, the precipitate is aged at 65°C for 24 h in a hermetically sealed Pyrex glass flask in order to separate LDH, which is a gel, from the solution containing nitrates and water. After that, the gel is recovered by centrifugation and washed several times with distilled water to remove sodium nitrate traces that formed during the reaction. Finally, the gel is dried at 80°C for 12 h; then, the obtained $Cu-Al-CO_3$ is ground and characterized.

2.3 Calcination of LDHs

Calcination of LDH can give a better activity in the fields of catalysis and adsorption because it allows elimination by decomposition of a large part of carbonate ions which are in the interlayer space leading to mixed oxide formation which has a high specific surface area and a superior porous volume [21]. According to this effect, a part of the resulting material is calcined at 500°C.

2.4 Kinetic study of dye adsorption

Evans Blue is characterized by electronic absorbance at 600 nm [22]. The kinetic study of Evans Blue adsorption on LDH and its calcined phase is studied at room temperature. The adsorbent (80 mg) is mixed with 20 ml of dye solution of a known concentration. The pH values of a stirred solution are adjusted by adding a few drops of dilute NaOH or HCl. At different times of variable contact (from 5 to 360 min), the solution is centrifuged for 10 min at 3000 rpm and the residual concentration is determined by UV-Vis spectroscopy.

2.5 Characterization

Powder X-ray diffraction (PXRD) data are recorded on a Siemens D5000 $\theta/2\theta$ diffractometer, at room temperature, using Bragg-Brentano geometry with back monochromatized $CuK\alpha$ radiation. The diffraction data are scanned over the range of 5–60° in steps of 0.03°. FT-IR spectra are collected on a Perkin Elmer 16PC spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1} . UV-Visible spectroscopy analyses are performed using a Perkin-Elmer spectrometer (SpectroScan 80D).

3. Results and discussion

3.1 Characterization of LDHs and calcined LDHs

The XRD pattern (figure 3) of $Cu-Al-CO_3$ reveals the characteristic reflexions of LDH materials (JCPDS-ICDD 37-630); however, the traces of $Cu_2(CO_3)(OH)_2$ malachite (JCPDS-ICDD 41-1390) and $Cu_2(OH)_3 \cdot NO_3$ gerhardite (JCPDS-ICDD 14-687) are detected in the phase of $Cu-Al-CO_3$ due to the Jahn-Guichet effect of the Cu^{2+} ion. The measure of the peak positions gives access to values of interlamellar distances d_{hkl} , therefore to the parameters of the hexagonal crystal form. The calculated values are $a = 3.128 \text{ \AA}$ and $c = 22.107 \text{ \AA}$. They are similar to the often reported values in carbonated LDH containing CO_3^{2-} anions in interlayers [23–25]. Table 1 summarizes the crystallographic properties of the obtained LDH from the XRD pattern.

The FT-IR spectrum of $Cu-Al-CO_3$ (figure 4) is similar to the spectra of phases of this type [26,27]. A large absorption band at 3417 cm^{-1} is attributed to the adsorbed interlayer water molecules and to the $\nu(OH)$ stretching modes of free and hydrogen-bonded hydroxyl groups. Indeed, the more this band is broad the more the number of hydrogen bonds is large and this is due to the result of links between the carbonate interlamellars, the water molecules and the OH structural ones. The absorption band at 1566 cm^{-1} is associated with the vibration of intercalated water deformation molecules of the layer. The band at 1358 cm^{-1} is attributed to the antisymmetric vibration mode of the interlayer carbonate anions. Other bands with weaker intensity are localized at 2359 and 848 cm^{-1} and are also attributed to the interlayer carbonate anion vibration. The bands in the range of 800–432 cm^{-1} are attributed to the frequencies of elongation of connections M–OH and to the vibrations of valence M–OH–M' forming the layers of the lamellate double hydroxides like Cu–OH, Al–OH and OH–Al–Cu–OH.

The obtained thermogravimetric curve (figure 5) corresponds to the relative weight loss depending on the heating temperature under an atmosphere of helium in an alumina fritted crucible. Three losses in weight are observed until 800°C. The first loss starts from 56 to 105°C due to adsorbed water. The second loss situated between 176 and 308°C is attributed to the departure of structural water molecules. The third loss between 500 and 800°C is attributed to the departure of a major part of carbonates with destruction of the lamellar phase and apparition of oxides. The last result allows to define the temperature (500°C) at which LDH should be calcined.

The PXRD pattern (figure 6) of the calcined LDH phase at 500°C, noted Cu-Al-500, reveals the dehydroxylation of the lamellar structure and the apparition of a CuO oxide (ASTM no. 01-074-1021) with an amorphous phase. Figure 7 shows the FT-IR spectrum of the calcined material and reveals a relative decrease in the intensity of the

Figure 3. XRD pattern of Cu-Al-CO₃ phase ($R = 2$).

Table 1. X-ray characteristics of Cu-Al-CO₃.

d_{hkl}	2θ	hkl
7.369	12.00	003
5.384	16.45	Malachite
5.006	17.70	Malachite
4.160	21.34	Gerhardite
3.704	24.00	006
3.572	24.90	Malachite
2.649	33.80	Gerhardite
2.590	34.60	009
2.561	35.00	012
2.390	37.60	014
2.279	39.50	015
2.220	40.60	Gerhardite
2.042	44.30	0012
1.935	46.90	018
1.893	48.00	Gerhardite
1.693	54.10	1010
1.564	59.00	110

characteristic absorption bands of water molecules at about 3417 cm⁻¹, as well as an increase in the intensity of the bands corresponding to the characteristic vibrations of the M–O bonds (M = Al or Cu) in the range of 400–700 cm⁻¹. In addition, it is observed that the band at about 1370 cm⁻¹ corresponding to the carbonate group CO₃²⁻ for calcined LDH is still detectable. Nevertheless, the low intensity of this band, compared with that observed for the starting material, suggests that carbonate ions are adsorbed on the surface of the grains of the calcined material caused by contamination with atmospheric carbon dioxide.

3.2 Adsorption kinetics

3.2a Time effect on the adsorption amounts of Evans Blue on LDHs and calcined LDHs: A kinetic study by UV–visible of Evans Blue adsorption on Cu-Al-CO₃ and Cu-Al-500 is performed. Figure 8 shows the adsorbed amounts of dye on both materials as a function of time. The adsorption curves are divided in two stages: the first stage is fast with the increasing of the adsorbed amounts of dye with increasing time. This rapid increase is due to a larger availability of the number of adsorption sites in these materials until they are saturated with dye. Indeed, the second stage, which is slower, shows that the amount of adsorbed dye begins to increase slowly until the equilibrium is reached at 60 min for Cu-Al-CO₃ and at 40 min for the calcined material Cu-Al-500. The yield of adsorbed dye is 77% for Cu-Al-CO₃ and 92% for Cu-Al-500 (figure 9). Thus, these results show that the adsorption of dye on the calcined material is faster with better retention compared with the starting material.

3.2b Mass effect on the adsorption amounts of Evans Blue on LDHs and calcined LDHs: Figure 10 shows the amount of adsorbed dye as a function of variation in adsorbent mass. It is noticed that when the mass of the material increases, the capacity of adsorption decreases. This result is explained by the fact that the aggregation of the LDH tablets generates a reduction in the total surface of particles in the material available for the adsorption of dye [28,29]. The yield of adsorbed dye is 73% for Cu-Al-CO₃ and 80% for Cu-Al-500 as shown in figure 11.

Figure 4. FT-IR spectra of Cu-Al-CO₃.

Figure 5. TGA/DTG thermograms of Cu-Al-CO₃.

3.2c Adsorption isotherms: The adsorption is studied with dye concentration varying between 50 and 1000 mg l⁻¹ for Cu-Al-CO₃ and Cu-Al-500 (figure 12). Isotherms are

L types of Langmuir classifications and present an initial slope indicating that the adsorbent is more efficient at weak concentrations. As the concentration at the equilibrium

Figure 6. XRD pattern of Cu-Al-500.

Figure 7. FT-IR spectra of (a) Cu-Al-CO₃ and (b) Cu-Al-500.

increases, the number of vacant sites decreases, and the dyes can have the possibility of adsorption horizontally or vertically. The quantity of the adsorbed dye on Cu-Al-500 is greater than that on Cu-Al-CO₃; the difference in adsorption between the two types of materials ‘carbonated’ and ‘calcined’ can be explained by the difficult displacement of anion carbonates in uncalcined LDH [30].

3.2d Adsorption model: The application of Freundlich and Langmuir models permits us to define the mechanism of interaction of dye/material. Data of the dye adsorption on Cu-Al-CO₃ and Cu-Al-500 are treated according to the linearized equations of the two models (table 2). The model of Langmuir seems more suitable [31]. The capacity of adsorption in the case of Cu-Al-500 is greater than the first one of Cu-Al-CO₃.

Figure 8. Effect of time on the adsorbed Evans Blue amounts on Cu-Al-CO₃ and Cu-Al-500.

Figure 9. The yield of adsorbed dye on Cu-Al-CO₃ and Cu-Al-500.

Figure 10. Effect of mass on the adsorbed Evans Blue amounts on Cu-Al-CO₃ and Cu-Al-500.

Figure 11. The adsorbed amount of dye on Cu-Al-CO₃ and Cu-Al-500.

Figure 12. Adsorption isotherms for Evans Blue on Cu-Al-CO₃ and Cu-Al-500.

Table 2. Constants of Langmuir and Freundlich.

	Langmuir			Freundlich		
	Q_m (mg g ⁻¹)	K_L	R^2	$1/n$	K_F	R^2
Cu-Al-CO ₃	100	0.71	0.95	0.050	71.44	0.86
Cu-Al-500	333.33	0.6	0.96	0.053	204.17	0.89

3.2e The pH effect on the adsorption amounts of Evans Blue on LDHs and calcined LDHs: The value of the pH is adjusted by the addition of HCl (0.1 N) or NaOH (0.1 N) and the results are shown in figure 13. It is seen that a maximum retention of dye is neighbouring pH = 7, a value close to the one of natural water. However, a decrease of the adsorption to acidic pH is observed; it is attributed to a partial dissolution of the mineral by acidic hydrolysis. For the basic pH, a weak retention is

observed; it can be due to the presence of OH^- and CO_3^{2-} ions adsorbed in competition with the anions of the dye on the adsorption sites [32–34].

3.2f Characterization of LDHs and calcined LDHs after the adsorption of Evans Blue: Figure 14 shows the diffractograms of the carbonated LDH Cu-Al- CO_3 used in the dye adsorption. The diffractograms clearly show that there is a shift towards smaller angles of 00L peaks (003, 006 and 009) indicating that the distance between the sheets of the LDH structure has increased due to the intercalation of dye

molecules in the interfoliar space. Indeed, the molecules of dye being larger than that of the carbonates (CO_3^{2-}) and hydroxyl ions (OH^-), their insertion by adsorption results in a larger separation of the sheets. The results in table 3 show the value evolution of the interlayer distance before and after the adsorption of dye. The structure of the calcined LDH is amorphous, that is why, evaluating the interlayer distance is not possible, nevertheless, the diffractograms in figure 15 show that the compound retain the same morphology even after the adsorption of dye. The same observation is noted for the diffractograms in figure 14. These results confirm that Cu-Al- CO_3 and Cu-Al-500 have preserved the same phase and that the adsorption of dye does not alter the final arrangement of these compounds.

3.3 Regeneration of LDHs and calcined LDHs after the adsorption of Evans Blue

The reuse of anionic clays after the adsorption process makes them even more important, given their low cost and their ability to regenerate [35]. In order to study the procedure of

Figure 13. Effect of the pH on the adsorbed Evans Blue amounts on Cu-Al- CO_3 and Cu-Al-500.

Table 3. Values of interlayer distances in Cu-Al- CO_3 before and after the adsorption of dye.

Phase	Initial Cu-Al- CO_3	Cu-Al- CO_3 after adsorption
$d_{(003)}$ (Å)	7.36	7.90
$d_{(006)}$ (Å)	3.704	3.86
$d_{(009)}$ (Å)	2.590	2.90

Figure 14. XRD pattern of (a) initial Cu-Al- CO_3 and (b) Cu-Al- CO_3 after adsorption.

Figure 15. XRD pattern of (a) initial Cu-Al-500 and (b) Cu-Al-500 after adsorption.

Figure 16. Recycling and reuse of Cu-Al- CO_3 after adsorption of Evans Blue.

Cu-Al- CO_3 regeneration after dye adsorption, 1.2 g of this material are dispersed in the coloured solution at an initial concentration of 500 mg l^{-1} . The sample is stirred for 3 h. After that, the material is recovered and then dried, ground and calcined at 500°C . The obtained product is reused by dispersing it in new dye solutions at the same concentration. This procedure is repeated until the adsorption capacity of the material is reduced. The same regeneration test is performed for Cu-Al-500 after adsorption at an initial concentration of

the dye at 750 mg l^{-1} . Figures 16 and 17 show the reuse tests in the dye adsorption on these materials.

The reuse of the carbonate material Cu-Al- CO_3 for dye adsorption is carried out after three calcination cycles. In the first test, the adsorbed amount of the dye is 94.7 mg g^{-1} on Cu-Al- CO_3 . There is also an increase in the amount of the adsorbed dye of 252.2 mg g^{-1} between the second and third tests. However, for the fourth test, the adsorption capacity decreases to 218.3 mg g^{-1} . The obtained results from the

Figure 17. Recycling and reuse of Cu-Al-500 after adsorption of Evans Blue.

regeneration of the calcined material Cu-Al-500 after dye adsorption shows that three calcination tests are possible. The best result is obtained in the second test. In the fourth test, the adsorption capacity decreases and the colour of the material changes. This can be explained by the decrease in crystallinity of the LDH material, which is one of the most important factors responsible for reducing the adsorption capacity of these materials [36]. Other authors explain this phenomenon by the decomposition of a certain quantity of the dyes within the framework of the mixed oxides [37].

4. Conclusions

LDHs are found to be effective adsorbents for the removal of various dyes from an aqueous solution. These adsorbents showed their potential to be applied in the purification of water or in the treatment of effluents. In this work, LDH constituted of copper and aluminium has been used in the treatment of water polluted by Evans Blue, a dye of the textile industry. Firstly, Cu-Al- CO_3 is successfully prepared by coprecipitation. Its structure is confirmed by FT-IR and a good crystallinity of the powder is observed by XRD. Then, a thermal calcination at 500°C gives the Cu-Al-500 material. During the adsorption on LDH, several parameters influencing the ability of elimination of the dye are examined. The obtained isotherms reveal excellent adsorption levels observed for the calcined material (Cu-Al-500) which is evacuated from carbonate anions (CO_3^{2-}) that occupy the interlayer space of Cu-Al- CO_3 . Furthermore, XRD analysis shows that both compounds preserve their structural integrity even after the adsorption of dye. In addition, these

materials are regenerable and reusable even after several adsorption/calcination cycles.

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