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Synthesis and characterization of Zn_2AlCO_3 and application on methyl orange removal from aqueous solution

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Abstract

Zn_2AlCO_3 a layered double hydroxide (LDH) with molar ratio $\frac{Zn}{Al}$ of 2:1 was synthesized using a co-precipitation method at constant pH. The capacity of Zn_2AlCO_3 to adsorb anionic dye methyl orange (MO) from aqueous solution was investigated and factors influencing the sorption such as contact time, pH and initial dye concentration were studied too. The adsorption processes were supported by n value of the Freundlich equation and also by Langmuir dimensionless separation factor R_L. In addition, Zn_2AlCO_3 was characterized by XRD, FT-IR, XPS, TG and N_2-Adsorption Desorption.

1. Introduction

The release of large amounts of dyes into water resources from various industries caused grave environmental problems. Low biodegrability, complex ingredients and the high concentration of organic pollutants pose the difficulty of treating dyes wastewater by conventional treatment processes. Many approaches have been employed for the treatment of textile wastewater such as photocatalytic degradation [1] chemical oxidation [2] ion exchange [3] membrane filtration [4] and adsorption [5], Due to its effectiveness and economic [6] adsorption was the most method used for the removal of dyes from wastewater.

Layered Double Hydroxides (HDLs) are layered materials their structure is close to that of brucite $Mg(OH)_2$. The excess of positive charge in the layers is created by the substitution of divalent anions by trivalent ones, wich are stabilized by anions and water molecules intercalated in the interlayer space, with the general formula [7]:

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}\ (A^{n-})_{x/n}\ .\ mH_2O$$

Where A^{n-} is the interlayer anion with n- valence,

M^{3+} and M^{2+} are tri and divalent metal cations [8, 9] which are octahedral coordinated by hydroxide ions.

x: is the layer charge density of LDHs $x = \frac{M^{3+}}{M^{2+}+M^{3+}}$

m: is the number of interlayer water.

LDH have various properties: high anion exchange capacity, interlayer galleries, high surface area and high anion exchange capacity. Due for these properties LDH are excellent materials employed in varies fields such as adsorption [10], catalysis [11], polymer additive [12], drug delivery [13] and electrode [14]. Because of their properties and easy preparation these materials have attracted remarkable attention in recent decades.

The aim of this study was to investigate the capacity of Zn_2AlCO_3 in removing MO from aqueous solution. The effect of contact time, pH solution and also initial dye concentration were studied. The adsorption mechanism was understood by the equilibrium and kinetic study. Besides, $ZnAlCO_3$ was synthesized by co-precipitation method at constant Ph and then characterized by XRD, FTIR, TG, N_2-adsorption desorption and XPS.

2. Experimental

2.1 Synthesis of Zn_2AlCO_3-LDH

Materials:

Chemicals including $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, Na_2CO_3 and NaOH used in the synthesis of Zn_2AlCO_3 and methyl orange (MO) were purchased from Sigma ALDRICH, all chemicals are grade without further purification.

Preparation of Zn_2AlCO_3-LDH

The Zn_2AlCO_3–LDH material was synthesized using the co-precipitation method at constant pH equal to 10 and at 65 °C. A metal salt solution of molar ratio equal to 2 of volume 50 ml containing $Zn(NO_3)_2.6H_2O$ (0.5 M) and $Al(NO_3)_3.9H_2O$ (0.25 M). In parallel, another solution was prepared by dissolving Na_2CO_3 (0.1 M) and NaOH (0.1 M) dissolved in 100 ml distilled water. The first solution was added drop wise and under magnetic stirring to the second solution. The solution pH was controlled and adjusted to 10 by adding NaOH solution (2 M). The resulting slurry was aged for 24h at 65 °C to ameliorate the crystallinity of the LDH. After aging they formed precipitate was washed many cycles with distilled water and then dried in a vacuum oven for 24 h at 80 °C.

2.2 Characterization techniques

Zn_2AlCO_3-LDH was characterized using X-ray photoelectron spectroscopy (XPS) by a Kα (thermo) fitted with a monochromatic Al Kα x-ray source with spot size 300 µm.To analyse its elemental composition X-ray diffraction (XRD) patterns was applied to identify the phase and was detected using bruker D8 DAVINCI diffract meter equipped with equipped with Lynx eye detector and 9 positions sampler with Cu –Kα radiation (λ=1.5405 Å). The surface area and the pore size were determinate by the Brauner-Emmet-Teller (BET) method and the N_2-Adsorption-Desorption isotherms were performed using AutosorbiQ station 1 at 77.35 k for 12h. To identify the functional groups, the FTIR spectra of Zn_2AlCO_3 was collected applying thermo scientific Nicolet 8700 spectrometer over the

frequency range 4000-400 cm^{-1}. To perform thermogravimetric analysis a SETARAM instrument (LABSYSEVo1150) was used and Zn_2AlCO_3 was heated up from 80 to 800 °C under argon.

2.3 Adsorption experiments

Adsorption assays were carried out in a series of 100 ml beakers and at room temperature. A MO stock solution was prepared by dissolving amount of MO in water and diluted to obtain desired concentration. A 20 mg of Zn_2AlCO_3 was dispersed in 50 ml of MO solution with different concentrations and the solution was magnetically stirred for 180 min. After the adsorption process, the solid material was separated from the solution by filtration, and then the concentration of MO persisting in the filtrate was determined at 465 nm using a spectrophotometer.

The amount of MO adsorbed was calculated by using the following formula (2)

$$Q_{ads} = \left(\frac{C_0 - C_t}{m}\right) V \qquad (2)$$

Where : C_0 : the initial dye concentration ($mg.g^{-1}$),

C_t : the concentration of dye at any time t,

V : volume of the solution,

m : masse of LDH (mg).

The effect of initial dye concentration was determinate by varying the concentration from 50 to 250 $mg.L^{-1}$ the influence of pH on the adsorption of MO by Zn_2AlCO_3 was investigated by varying the pH from 4 to 10 by adding an amount of dilute NaOH or HCl solution. The contact time was investigated too.

3. Results and discussion

3.1 X-ray diffraction

The Zn_2AlCO_3 exhibited PXRD patterns **Figure 1** similar for those of hydrotalcite-like compounds. **Figure 1** shows Intense diffractions located at 11.58; 23.24; 32.00; 34.36; 39.08; 46.61; 60.13 and 61.51° wich corresponded to the diffraction plane of Zn_2AlCO_3 (003), (006), (012), (009), (015), (018), (110) and (113) this come to confirm that Zn_2AlCO_3 have a cristal structure [15] and rhombohedral lattice with space group R-3m, a=2d_{110} =3.07 Å and c= 3d_{003} =22.62 Å [16, 17].

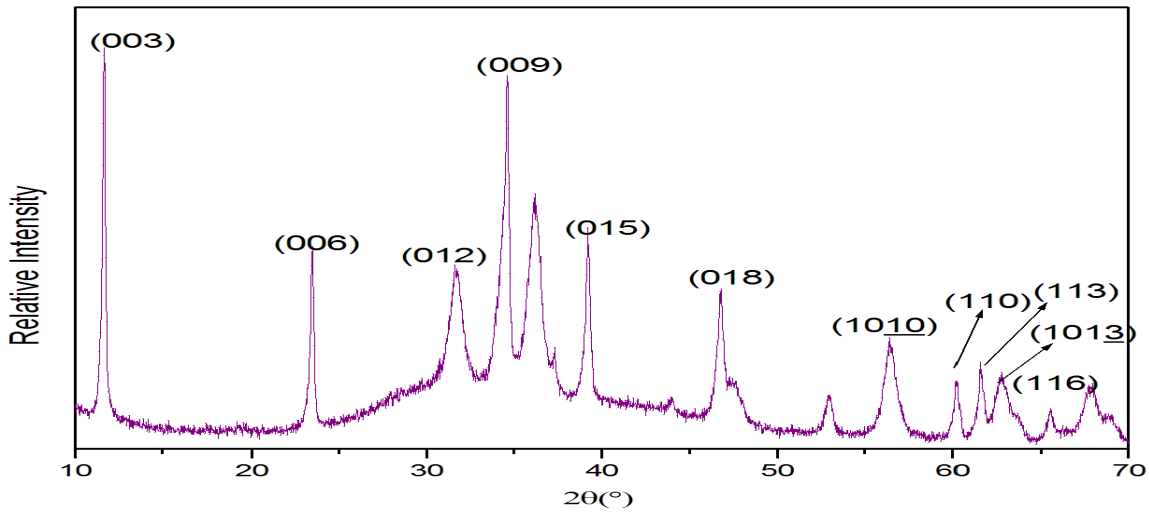

Figure 1. X-ray powder diffraction pattern of Zn_2AlCO_3-LDH

3.2 IR spectroscopy

Zn_2AlCO_3-LDH was analyzed by FTIR spectroscopy and the result is illustrated in **Figure 2**. **Figure 2** shows different bands. The band at 3471 cm^{-1} associated to O-H stretching and binding modes in LDHs of water molecules [18]. The asymmetric stretching mode of CO_3^{2-} group is showed at band located at 1360 cm^{-1} [19]. The band observed at 780 cm^{-1} is assigned to the interaction of CO_3^{2-} groups and the brucite-like layers [20]. The band located in the low frequency at 421 cm^{-1} is attributed to the stretching mode of M-OH.

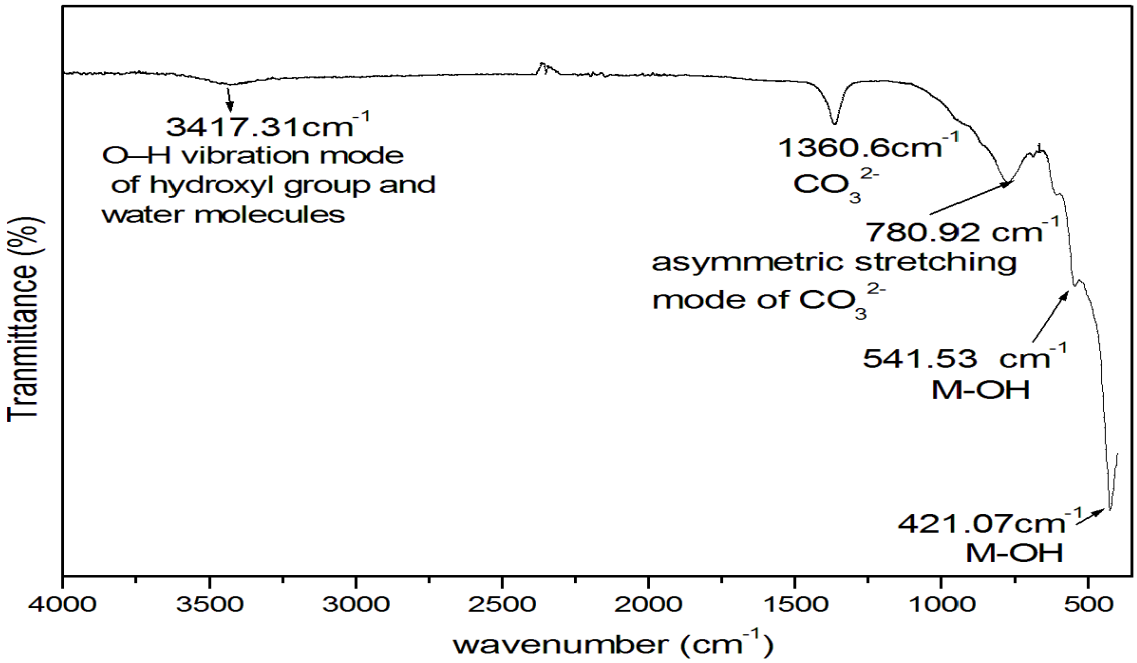

Figure 2. IR spectra of Zn_2AlCO_3-LDH

3.5 XPS analysis

To further study the surface chemical composition of Zn_2AlCO_3 a XPS analysis was used. **Figure 3** assemblies the analysis resultants and exhibits the resolution spectra of Zn 2p state at 2021.92 and 1044.98 e.v attributed to the binding energy of Zn $2p_{3/2}$ an Zn $2p_{1/2}$ respectively, implicating that Zn presented in a divalent oxidation state in LDH [21]. The analysis showed the binding states of major elements present in the material. The binding energy of 531.58 e.v can be associated to the hydroxyl form (OH-group) for pure LDH [22]. The binding energies at 286.7 and 74.04 e.v are attributed to C1s and Al 2p respectively [23, 24].

3.4 N2-Adsorption-Desorption

The surface area and pore size measurement are represented in **Figure 4a** and **Figure 4b** respectively. The surface area was calculated using the Brauner – Emmett - Teller (BET) method. The results revealed that the surface area of Zn_2AlCO_3 was 62.38 m^2/g having a pore volume of 0.148 cc/g wich are compatible with the range of values in the literature [25]. The Barret-Joyner-Halinda (BJH) method was used to determine the pore diameter and it was found to be 3.716 nm.

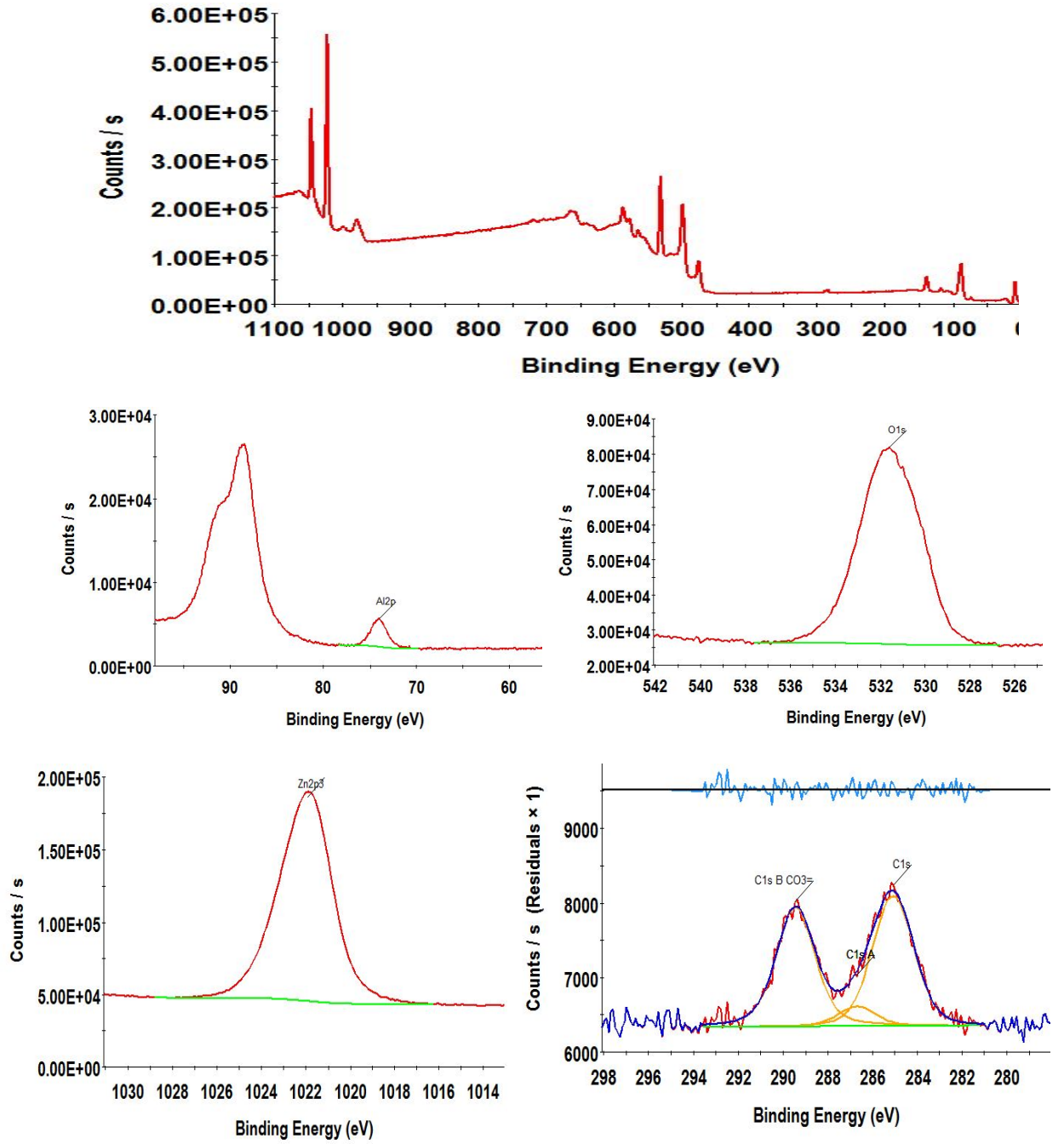

Figure 3. XPS spectra of Zn_2AlCO_3

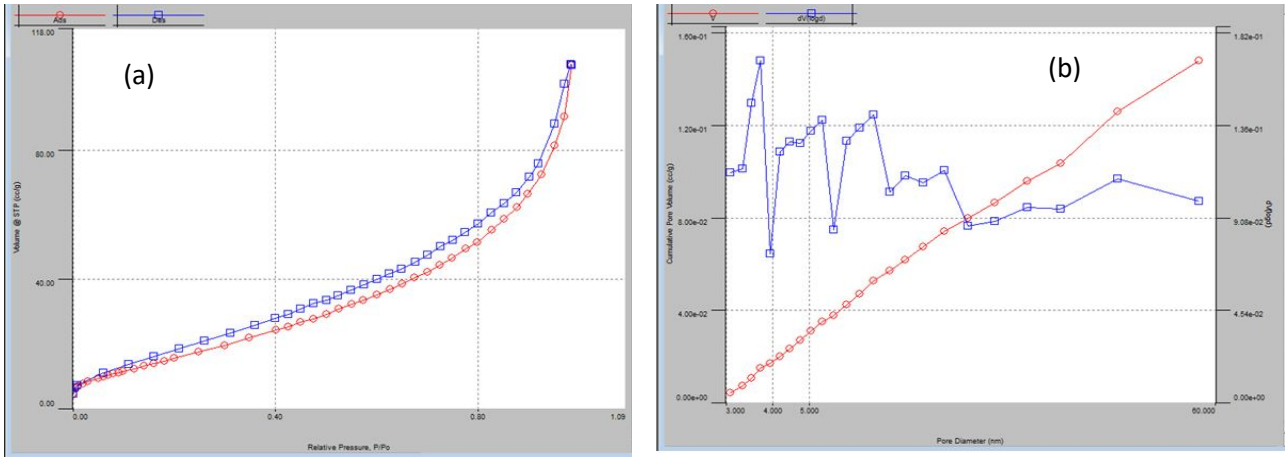

Figure 4: (a) Physisorption isotherms of Zn_2AlCO_3 and **(b)** physiodesorption isotherms of Zn_2AlCO_3

3.5 TGA analysis

The thermal behavior of Zn_2AlCO_3 was studied using thermogravimetric analysis and the resultat is illustrated in **Figure 5** also the weight loss percentage are calculated. Three major decomposition steps can be considered, the first step occurred at temperature ≤ 200 °C wich in generally attributed to the interlayer and physically adsorbed water with weight loss equal to 8.73%. The second weight loss ascribed to the decomposition of brucite like layers in the temperature range between 200 °C and 350 °C (5.64%). The last weight loss stage (1.17%) was between 350 °C and 560 °C is due to the removal of interlayer anions CO_3^{2-} [26].

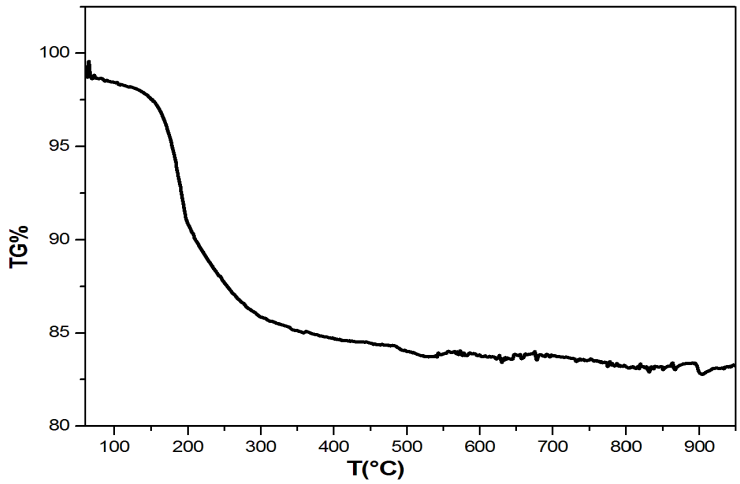

Figure 5. TGA spectra of Zn_2AlCO_3

4. Study of MO adsorption

4.1 effect of pH

In general, pH considered as a vital parameter to control the adsorption process. The solution pH modifies the chemistry of the adsorbents and also the dye molecules [27]. To evaluate the effect of pH, the adsorption experiments were studied varying the Ph from 4 to 10 under the same condition: contact time was 180 min, MO concentration was 10 $mg.L^{-1}$ and at 25 °C. The resultants are displayed in **Figure 6** as presented in these figures the amount of MO adsorbed increased when pH increased and reached the maximum at pH 6 equal to 9.6 $mg.g^{-1}$ this is explained by the positive charge of the Zn_2AlCO_3 surface and had resulted the electrostatic repulsion between the dye cations and the positively charged surface. Besides, at pH lower maybe hydroxylated metal salts was dissolved and the metal cations presented in the Zn_2AlCO_3 layers was released into solution which resulted a lower MO capacity. At high pH the competition between protons and metal ions for binding sites decrease.

4.2 effect of concentration of adsorbate

To investigate the effect of initial dye concentration on the removal of MO by Zn_2AlCO_3. The initial concentration of MO was varied from 50 to 250 $mg.L^{-1}$. It is shown from **Figure 7** that the amount of dye adsorbed increase from 7.7 to 73.21 $mg.g^{-1}$. This increase is probably due to the major interaction between adsorbent and adsorbate. The greater percentage of removal dye at higher concentrations is maybe due to decreased resistance and increased diffusion to dye removal. In addition, the increase of the dye concentration above 250 $mg.L^{-1}$ contributes to a few increase in the amount of MO adsorbed, signifying saturation of the adsorption sites.

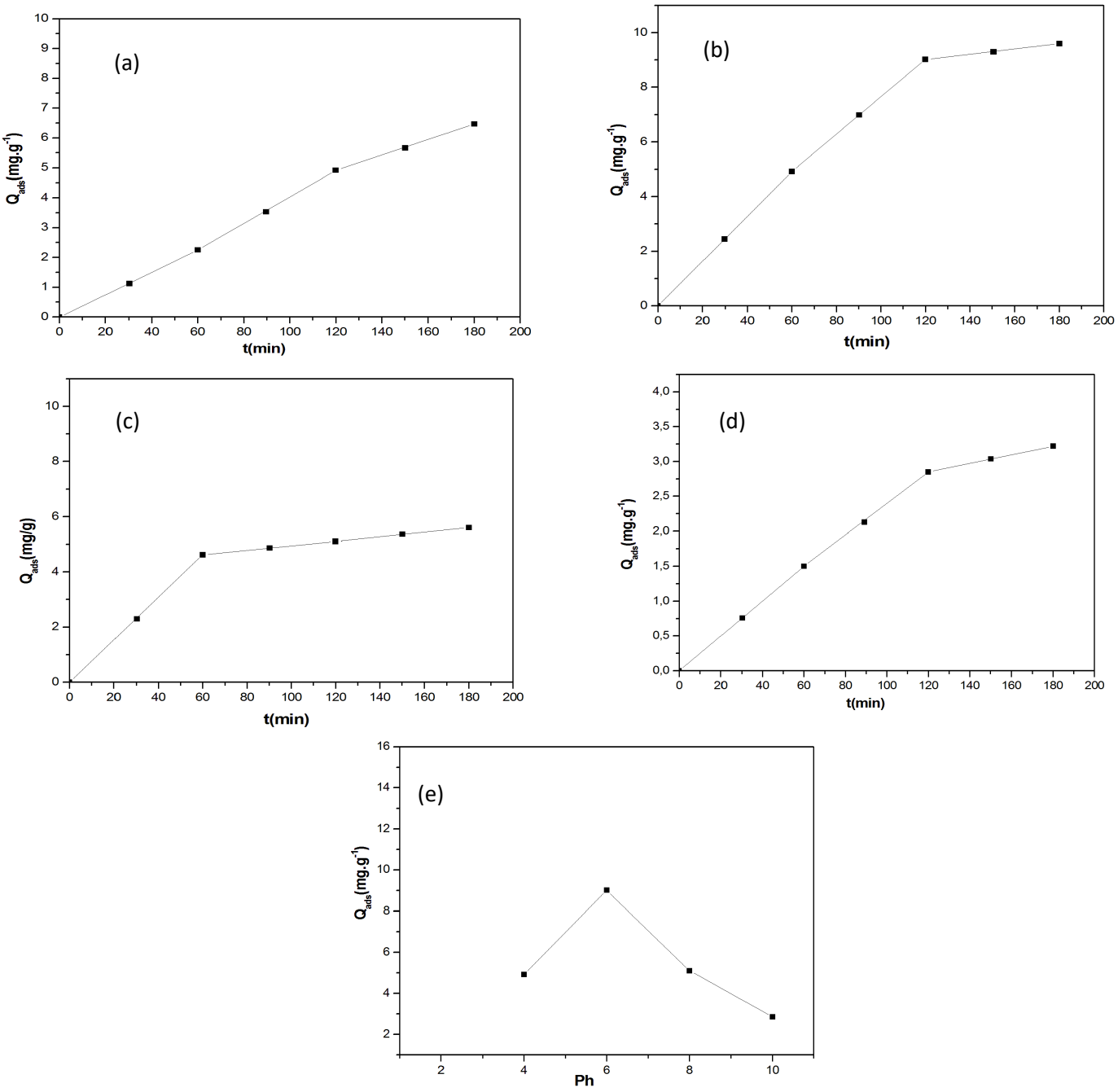

Figure 6. Effect of pH on methyl orange adsorption by Zn_2AlCO_3 at **(a)**: pH=4 ; **(b)**: pH=6 ; **(c)**: pH=8 ; **(d)**: pH=10 with: C_{MO}=10 mg.L-1, m_{LDH}=20 mg, V=50 ml and T=25 °C

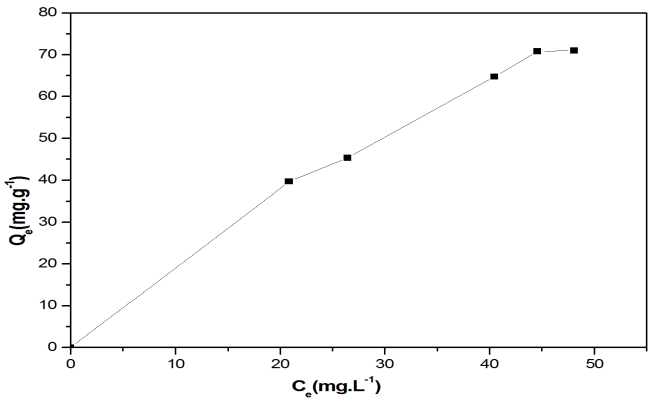

Figure 7. Effect of initial MO concentrations on MO adsorption by Zn_2AlCO_3 with: pH=6, C_{MO}=10 mg.L^{-1}, m_{LDH}=20 mg, V=50 ml and T=25 °C

4.3 effect of contact time

To find the equilibrium time for maximum dye removal a contact time study was investigated by varying the contact time from 0 to 180 min with adsorbent dose of 20 mg at pH 6 and dye concentration equal to 10 mg.L^{-1}. The result is shown in **Figure 8**. The amount of adsorbed dye increases and attains the equilibrium at 120 min and then remains constant this maybe explained that in the initially the surface had a large number of vacant sites and above period of time the molecules of MO get adsorbed at the surface awing to repulsive forces between MO adsorbed and the surface of Zn_2AlCO_3 it becomes heavy to occupy vacant sites.

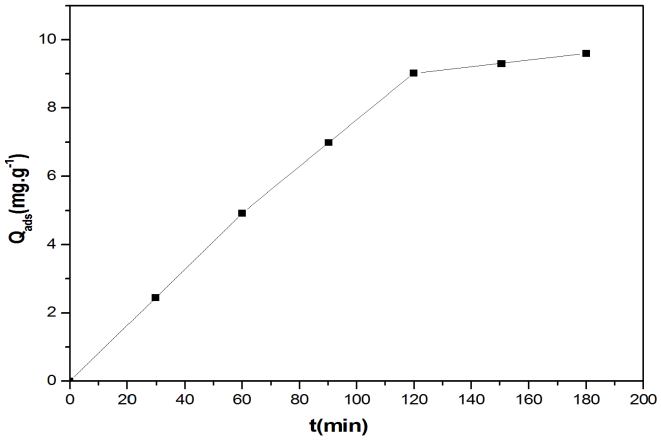

Figure 8. Effect of contact time on MO adsorption by Zn_2AlCO_3 with: pH=6, V=50 ml C_{MO}=10 mg.L^{-1}, m_{LDH}=20 mg, and T=25°C

4. Study of MO adsorption

The adsorption isotherm models are usually employed to describe the interaction between adsorbates and adsorbents bringing most important parameters for designing a desired system of adsorption [28] for that in the adsorption process, adsorption isotherms are important parameters [29]. The removal capacity of Zn_2AlCO_3 to remove MO was investigate, where the Langmuir and Freundlich adsorption models were used to evaluate the effectiveness of Zn_2AlCO_3.

The Langmuir model is centered on the supposition that the maximum adsorption happens when the surface is covered with a monolayer of the adsorbate. The sorption energy is constant and the adsorption takes place with no interaction between molecules of the adsorbate [30, 31]. The Langmuir isotherm is expressed as following:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where qe (mg.g^{-1}) and Ce (mg.L^{-1}) are the equilibrium adsorbate concentration of solute in the solid and aqueous phases, qm (mg.g^{-1}) is the maximum sorption capacity and b is Langmuir constant.

The dimension less constant separation factor RL is the most important characteristics of the Langmuir isotherm [32]. The value of R_L indicates the shape of the isotherm to be ether irreversible (R_L=0), linear (R_L=1), favorable (0‹R_L‹1) or unfavorable (R_L ›1).

$$R_L = \frac{1}{1 + bC_0}$$

The experimental data are shown in **Figure 9** and **Table 1**. The correlation coefficient of the isotherms relative high (R^2=0.992) wich proved that the Langmuir model is appropriate for describing the adsorption equilibrium of MO onto Zn_2AlCO_3. The maximum adsorption capacity calculated from the Langmuir isotherm is 250 $mg.g^{-1}$. The calculated R_L values at different initial MO concentration are lie between 0 and 1, wich confirm that the adsorption is a favorable process.

The Freundlich isotherm is an empirical relationship [33] assuming that the adsorption process occurs on heterogeneous surfaces, and the concentration of dye at equilibrium affecting the adsorption capacity. The Freundlich isotherm is expressed by the following equation [34]:

$$q_e = K_F C_e^{\frac{1}{n}}$$

Where: 1/n: is the adsorption intensity of the dye molecules onto the sorbent or surface heterogeneity wich becomes more heterogeneous.

When the 1/n value becomes closer to zero a value for 1/n below represents a normal Freundlich isotherm, while 1/n above 1 indicates a cooperative adsorption, and for favorable adsorption conditions the value of n must be less than 10 and higher than 1 [35].

K_F: is the value for the system associated to the bonding energy it can interpreted as the adsorption or distribution coefficient and indicates the quantity of dye adsorbed or fixed onto adsorbent for unit equilibrium concentration.

As shown in **Figure 9** and **Table 1** the correlation coefficient (R^2=0.994) improve that the experimental data agree with the Fleundlich model. For favorable adsorption conditions, the value of n must be higher than 1 and less than 10, in this case, the value was found to be greater than 1, showed the adsorption of Mo by Zn_2AlCO_3 favorable.

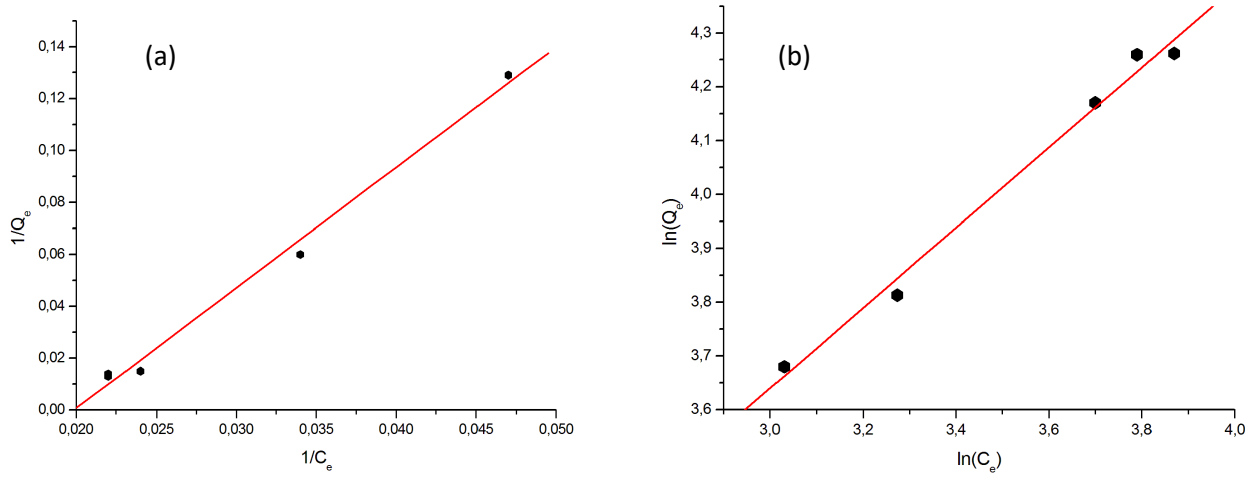

Figure 9. Adsorption isotherm for the adsorption of MO by Zn_2AlCO_3: **(a):** Langmuir model and **(b):** Freundlich model

Table 1. Isotherm parameters for the adsorption of MO by Zn_2AlCO_3

Freundlich	Langmuir
K_F : 4.075 $mg.g^{-1}$	**K_L:** 0.009 $L.mg^{-1}$
n : 1.34	**Q_m:** 250 $mg.g^{-1}$
R^2 : 0.994	**R^2 :** 0.992

Conclusion

In summary, we have investigated the efficient adsorptive of MO from aqueous solution with the synthesized Zn_2AlCO_3. The effects of contact time, pH solution, and initial dye concentration on the adsorption process of MO by Zn_2AlCO_3 were studied. The equilibrium data were studied by various isotherm models such as Langmuir and Freundlich wich fit the experimental data well. The maximum sorption capacity of the Zn_2AlCO_3 toward MO was calculated to be 250 $mg.g^{-1}$. This work indicated that Layered Double Hydroxide could be employed as a potential adsorbent for the removal of anionic dye in wastewater.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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