Removal of Congo red by a synthesized layered double hydroxide ZN-AL-SO 4

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REMOVAL OF CONGO RED BY A SYNTHESIZED LAYERED DOUBLE HYDROXIDE ZN-AL-SO_4

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ABSTRACT

The colored wastewaters from the textile industries may show toxic or carcinogenic effects on the organism, when discharged into the rivers and lakes, which are changing their biological life. Therefore, in this study, the removal of Congo red by Zn-Al-SO_4 layered double hydroxide has been achieved. Zn-Al-SO_4 material was prepared by a facile co-precipitation method at constant pH, resulting in a suitable material for the adsorption of Congo red dye. The structure and morphology of the Zn-Al-SO_4 adsorbent were investigated using XRD, FT-IR, and BET and MEB techniques. Layered double hydroxides (LDHs) have been widely investigated in a wide range of applications in health, in the pharmaceutical industry and in the material of biotechnology industries. In this work the synthesis of Zn/Al double layered hydroxides by chemical co-precipitation method (molar ration 3). The samples were characterized and confirmed by X-ray diffraction (XRD), BET analysis, and infrared spectroscopy. A series of experiments was then carried out to study the influence on the adsorption capacity of certain parameters such as the amount of the adsorbent, the pH, the contact time, the initial dye concentration, the ionic strength effect and temperature. All the results obtained show that the adsorption kinetics of the dye on our material is well described by the second order model. The adsorption isotherms of the adsorbent / adsorbate systems studied are satisfactorily described by the Langmuir mathematical model. The intra-particle scattering model confirms the physisorption phenomenon Negative values of free energy prove that the phenomenon is physisorption. On the other hand, the thermodynamic study revealed that the adsorption is spontaneous and exothermic. The recovery of the material and reuse shows that the property of

being able to regenerate is remarkable.

Key words: LDH, Congo red, Adsorption, Regeneration.

INTRODUCTION

Increasing environmental pollution caused by the rapid growth of technology is one of the serious concerns of global societies (Boulaiche et al., 2019). The growth of civilization and industrialization has led to the destruction of water resources (Järup., 2003; Niazi et al., 2009; Sajid et al., 2018). More than 10,000 dyes have been widely used in textile, rubber, paper, plastics, leather, cosmetic, pharmaceutical, and food industries, which generated huge volume of wastewater every year (Tahmasebi et al.,2015; Luo et al.,2015; Qu et al., 2017; Zhao et al., 2016). Annually the production of dyes is estimated at around 1.6 million tons which 10–15% of this amount is discharged to sewage. Exposure to these species causes skin irritation, respiratory problems, and cancer (Carro et al., 2015; Wang et al.,2016). In addition, the produced colored wastewater from the dye manufacturing and textile industries effects on biological life when is discharged into rivers and lakes without wastewater treatment. The long history of red coloring elements are figured out in two periods separated by a approximately recent year, 1858, marked by the invention of the first synthetic red dye. Previously, in the 19th century, foods were colored with natural red dyes, including cochineal red, beetroot red, madder, and metal salts as well. Yet, it had been merely following the invention of red dyes resulting from chemical synthesis that their use within the food industry spread from 1880. If the fields of application of red dyes remain very varied (the textile industry remains the main sector making use of these compounds), we note that since a few decades, the global food industry uses more and more significant amount of natural or artificial red dyes, in particular in confectionery, desserts, drinks, but also in cold cuts, fruits and vegetables and sugar. Otherwise, these compounds have a toxic character causing significant disturbances in the various natural mechanisms existing in the flora (self-purification power of watercourses, inhibition of the growth of aquatic plants, etc.) and in the fauna (destruction of a category of fish, microorganisms, etc.) (Alipour et al., 2021) and can persist a long time in this environment.

Besides to the toxicity and health risks of these pollutants, the wide kinds of red dyes usually have complex structure and non-biodegradable molecular due to their high molecular weight, so that is very hard to eliminate from environments (Gong et al., 2011). These are the reasons that the effective removal of these pollutants from water and their treatment before discharging into the water stream is a great

subject of research nowadays (Sajid et al., 2018). Diff erent methods are used to remove organic pollutants, such as dyes from wastewater (Agarwal et al.,2017), like ozonation (Joshi et al.,2020), coagulation (Chen et al., 2010), electrocoagulation (Wang, K et al., 2016) photocatalytic removal (Ferrandon et al., 2001), membrane filter (Xu et al.,2015), and adsorption (Mnasri-Ghnimi et al., 2015; Naseem et al., 2019). Among various methods, and using a suitable adsorbent, adsorption is widely used as a reasonable technique due to its simplicity, ease of use, low cost, high efficiency and the availability of the materials (Lahreche et al., 2022).

The objective of this work is to prepare and characterize (ZnAl-SO_4) by co precipitation method. This green adsorbent has been used to study the effects of different parameters on Congo red adsorption, such as pH of the aqueous solution, quantity of hybrid material, initial concentration of heavy metal ion, adsorption equilibrium time, stirring speed, salts effects and temperature.

MATERIAL AND METHOD

Experimal Materials

The reagents used in this study were Zn Al-SO_4 synthesized in the laboratory (Kadari et al., 2017; Mahassene et al.,2016), the raw materials $ZnSO_4$ (Riedel De Haen), $Al_2(SO4)_3$ (Riedel De Haen), nitric acid (64% Riedel De Haen), Congo red (98%, Sigma Aldrich), NaOH (99%, Riedel De Haen), Na_2SO_4 , KNO_3 (99%, Riedel De Haen), UV/Vis spectra were obtained using a UV/Visible double beam type" OPTEZEN 3220" spectrometer to analyze the concentration of congo red in aqueous solution, a digital pH meter Consort C863 type.

Methods

Synthesis of the $ZnAlSO_4$

Zn-Al-SO_4 was prepared using a co-precipitation method similar to that described by Miyata (Miyata., 1975) with a Zn/Al ratio of 3 a. In a reactor, 150 mL of an aqueous solution of metallic sulphates (0.75 M in $ZnSO_4$ and 0.25 M in $Al_2(SO_4)_3$ was added drop wise, at 25°C and under magnetic stirring. 1.5 M NaOH was added to maintain the pH of the reaction mixture constant at 10.5 ± 0.1. When the reaction was achieved, the resultant gel was made under reflux at 60-70°C during 15 hours to permit crystal growth. After ripening, at room temperature for 24 h in mother liquors, the mixture was filtered, washed several times then dried, a white precipitate was obtained.

Adsorption experiment

The LDH of type ZnAl-SO_4 with a molar ratio of 3 has been prepared by the method of co-precipitation described by Miyata. In this work, we have chosen the method of spectrophotometry molecular absorption as colorful indicator for the determination of Congo red at λ_{max} = 500 nm (Guiza et al., 2022)

Several mixtures of solid phase (ZnAl-SO_4) and aqueous phase of the dye are subjected to magnetic stirring. After separating the two phases by centrifugation, the amount of Congo red remaining in the aqueous phase has been determined by spectrophotometry visible UV/V (double beam type" OPTEZEN 3220" spectrometer), The amounts of Congo red adsorbed are calculated from the following equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C0 and Ce are the initial and equilibrium concentrations of Congo red (mg L^{-1}) respectively; m the amount of adsorbent (g) and V the volume of solution (L). The efficiency percentage (Y) of dye removal was calculated as follows (equation (2):

$$Y\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Characterization techniques

XRD Analyses

Powder X-ray diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using Cu Kα radiation (1.5405980 Å). Scans were recorded from $5° \leq 2\theta \leq 100°$ with varying scan speeds and slit sizes. Samples were mounted on stainless steel sample holders.

FTIR Analyses

Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer 16 PC-FTIR equipped with a thermostat to maintain the temperature of the sample at 25.0 ± 01 °C on KBr pellets in the range of 4000-400 cm^{-1}.

BET analyses

Specific surface areas and pore size were analyzed using the Brunauer–Emmett–Teller (BET) method. The samples were measured from the N_2 adsorption and desorption isotherms at 77 K collected from a Quantachrome Autosorb-6 surface area and pore size analyzer.

UV/V analyses

A UV/Visible double beam type" OPTEZEN 3220" spectrometer was used for UV–vis spectral measurements.

The accuracy and the precision of the method on the instrument were determined by measuring the absorbance at 500 nm against the prepared standards in the concentration range of (10^{-3} to 10^{-6} mol/l) (Chen et al., 2010). A standard curve for UV-vis measurement demonstrated high degree of accuracy with a coefficient of regression, R^2=99.7 %, was used in the calculation of unknown UV-vis concentrations from absorbance readings.

RESULTS AND DISCUSSION

X-ray diffraction

The powder XRD pattern of Zn-Al-SO_4 is presented in figure (Figure 1). The diffraction peaks corresponding to the LDH phase are observed at the 2θ position 12.4, 20, 27.5, 37.2, 42. and 47.1 having the respective *d*-values 10.94, 5.47, 3.66, 2.66 and 2,.18 and the respective miller indices are 003, 006, 015, 018, 110 and 113 characteristic of an LDH phase with a basal spacing of 7.98 A° and an inter metallic distance of 1.52 A°. The XRD patterns corresponding to the rhombohedral symmetry (space group, R-3m) are indexed in an hexagonal lattice. The (a) and (c) lattice parameters are estimated using (110) and (003) reflections, respectively.

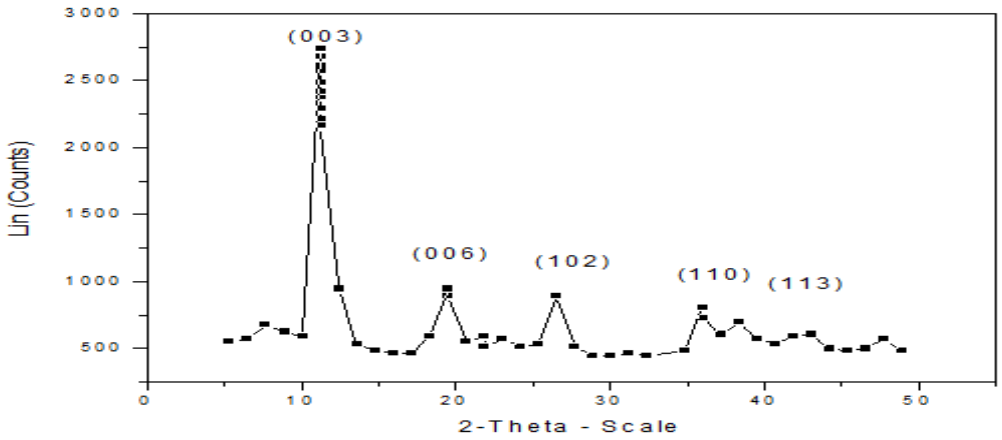

Figure 1. DRX pattern of ZnAl-SO4

Fourier transformed infrared spectroscopy analysis (FTIR)

The spectra FTIR of ZnAl-SO_4 is shown in Figure 2. The presence a very intense band peak around 3458 cm^{-1} corresponds to the vibration of the hydroxide

groups of the molecules water. The band recorded at 1620 cm^{-1} can be assigned to intercalated water molecules deformation. Lattice vibrations appear in the 430-559 cm^{-1} range. The weak band at 2100 indicates the binding vibration of SO_4^{2-}. The band at 1352 cm^{-1} indicates the presence of small amounts of carbonate in the galleries (Delgado et al., 2008).

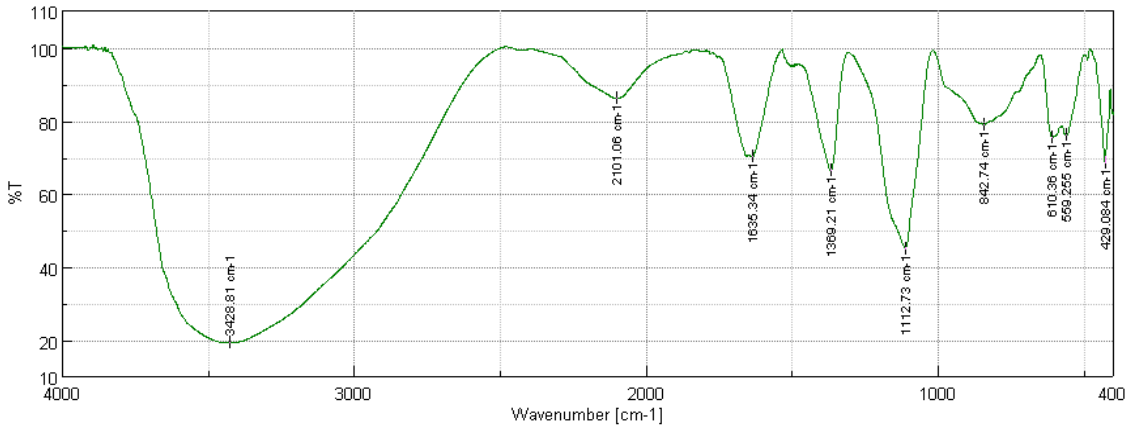

Figure 2. FTIR spectrum of Zn-Al-SO_4

Specific area

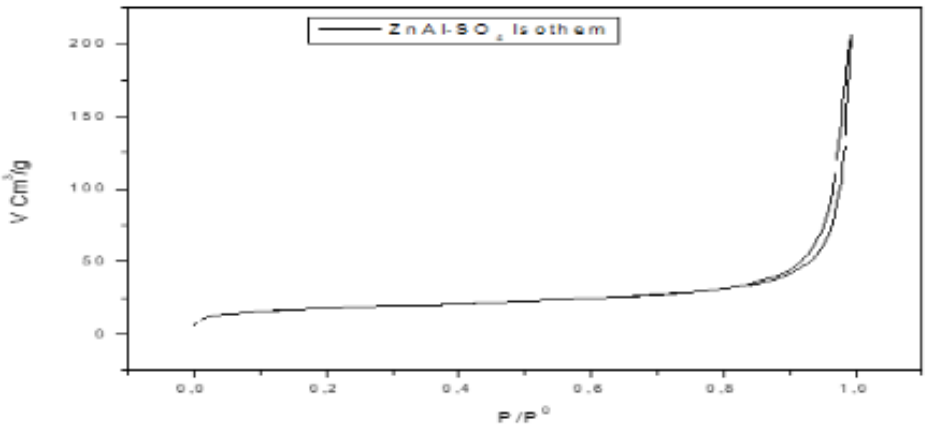

Figure 3. Adsorption isotherm for ZnAl-SO4

Table 1. Pore properties and specification surface area of ZnAl-SO4

	BETsurface area(m^2g^{-1})	Pore volume(cm^3g^{-1})	Average pore size(nm)
Zn/Al-LDH	62.5	0.29	18.6

Morphology

SEM images of ZnAl-SO_4-LDH are presented in Figure 4. The images clearly show that the sample existing lamellar particles with hexagon layer structure, which is the typical structure of the hydrotalcite-like material.

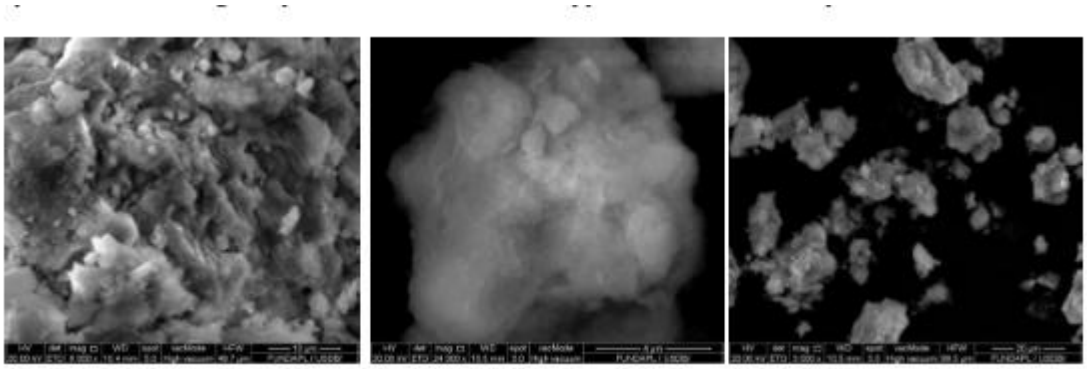

Figure 4. SEM image of ZnAl-SO4

Effect of various parameters on Congo red dye removal efficiency

Different parameters have been investigated to study the retention yield of Congo red dye

Effect of stirring speed

We observe that the adsorption rate depends on the stirring speed. On the other hand, it is fast for t < 10 min, then it remains constant (Figure 5). The agitation speed affects the resistance to the transfer of material outside the clay particle, this with accordance with literature (Guiza et al., 2019).

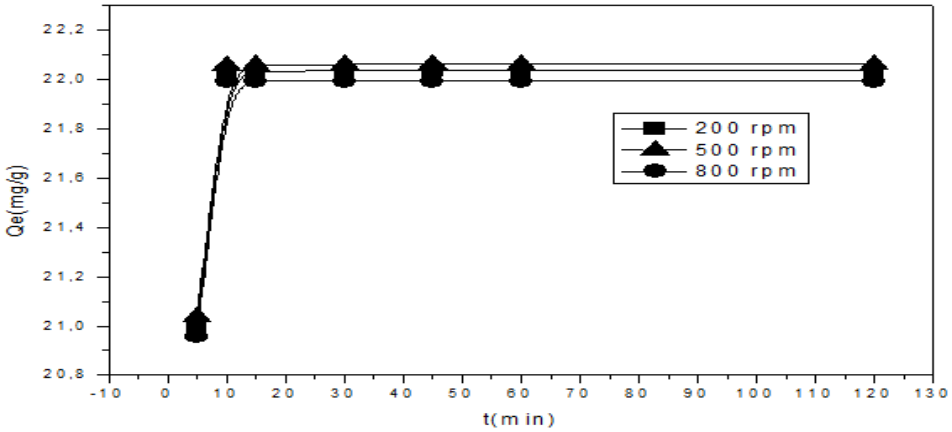

Figure 5. Effect of stirring speed on the retention of Congo red

M = 0,025g et C=55,74 mg/L .T=25°C

Effect of material amount on the efficiency of Congo red removal

Three volumes of the dye solution with 55,74 mg/L has been prepared and added to

four different amounts of ZnAl- SO_4 LDH: 0.025, 0,035, 0.045 and 0.055 g. The best yield has been obtained with a mass 0.025 g reaching 99,9 % with average stirring speed of 500 rpm as shown in the graphical representation on figure 6. This is explained by the attainability of the sites of the adsorbent. The mass transfer of the dye in the external film can be controlled by the LDH amount; the increase in the LDH dose contributes to the increase of the transfer coefficient in the liquid film.

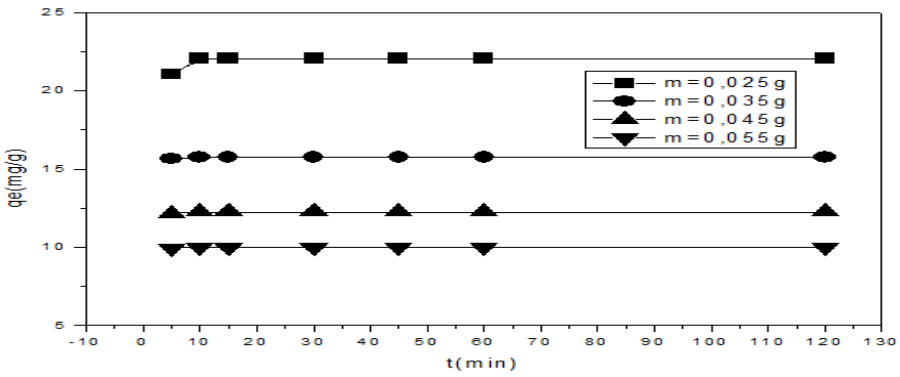

Figure 6. Adsorbent amount effect on the Congo red retention

T=25C°, [Dye] = 55,74 mg/L

Effect of dye concentration on the removal efficiency

Various concentrations of congo red dye was used: 5.57, 34.83 and 55.74 mg/L with an amount of (ZnAl-SO_4) adsorbent 0.025 g. and under 500 rpm. The results are presented in Figure 7. It has been shown that the best retention yield is obtained with a concentration 55, 74 mg/l. The results are gathered in figure 7.

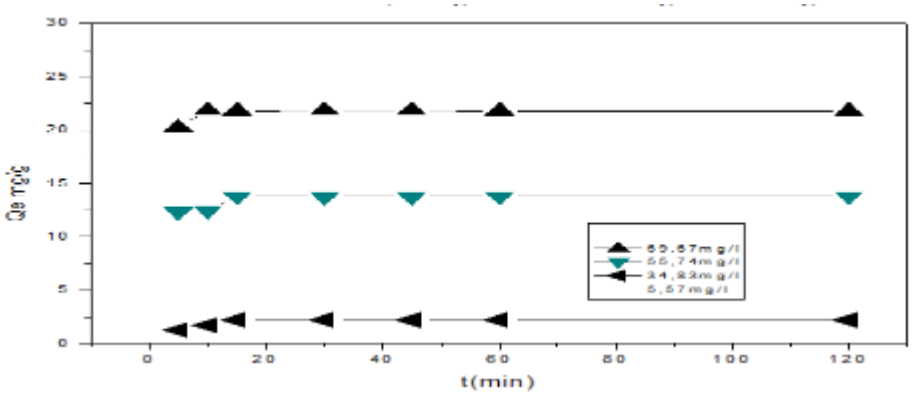

Figure 7. Concentration effect on the retention of Congo red. T = 25C°, m = 0,025 g

Effect of pH on the efficiency of Congo red removal

The removal of Congo red has been investigated in the pH range from 3.5 to 12 by adding nitric acid HNO_3 in different solutions with an adsorbent dose of 0.025 g. According to the results shown in Figure 8, we noted that the removal of dye by

the ZnAl-SO_4 is much more important at pH=8 with best adsorption capacity of 23 mg/g. That is to say the more acidic (pH = 3.5) is the solution, the less dye are extracted. This is probably due either to competition between the ionic organic pollutant dye in solution and the ions released by the nitric acid or to the non- stability of the LDH in acidic solution.

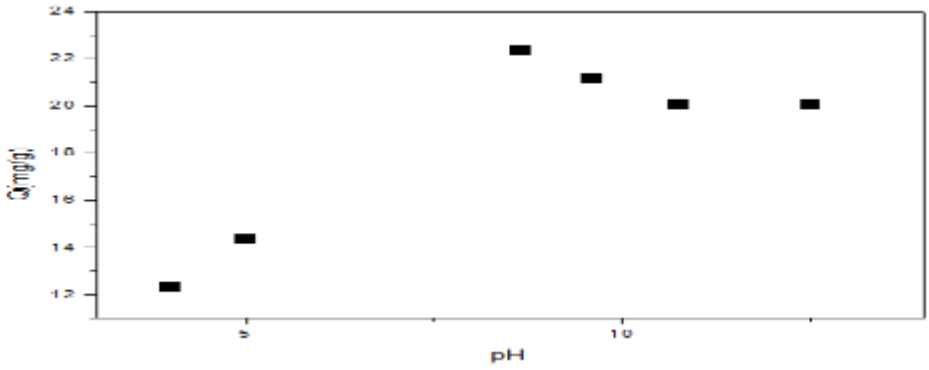

Figure 8. Effect of initial solution pH on the dye retention. T=25C°, m=0,025 [dye] = 55,74 mg/L

Effect of temperature on the efficiency of Congo red removal

The effect of temperature on the extraction yield has been studied in the temperature range from 40 to 60°C. Thermodynamic parameter, free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been determined; by the application, at the extraction equilibrium, of the following thermodynamic relations (Mahassene et al.,2016):

$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

$$\ln\Delta G° = -RT\ln K_d \quad (4)$$

From these two equations, the following expression was obtained:

$$\ln k_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (5)$$

The calculation of certain thermodynamic parameters is essential in determining the nature of the retention process. The equilibrium constant Kd, can be calculated from the following relation:

$$K_d = \frac{qe\left(\frac{m}{V}\right)}{\left[C0 - qe\frac{m}{V}\right]} \quad (6)$$

The capacity of adsorption (q) of the studied heavy metals by the LDH is determined by the following relation

$$q(mg/g) = \frac{(Co-Ce).V.M}{m} \quad (7)$$

q_e: the capacity of the adsorption at equilibrium
C_0: initial concentration of Cong red in mg/L
Ce: the concentration of the Cong red at equilibrium in mol/lL
V: the volume of the solution of the treated Cong red (10 mL)
M: the molar mass of Congo red dye
m: the mass of ZnAl-SO_4 (0.025 g)
R: the perfect gas constant (R= 8.314 J $mol^{-1}K^{-1}$)
Kd: the distribution coefficient between the aqueous and solid phases

The thermodynamics parameters are listed in Table 2, where ΔG^0 values were obtained by plotting lnK against 1/T for the Langmuir data.

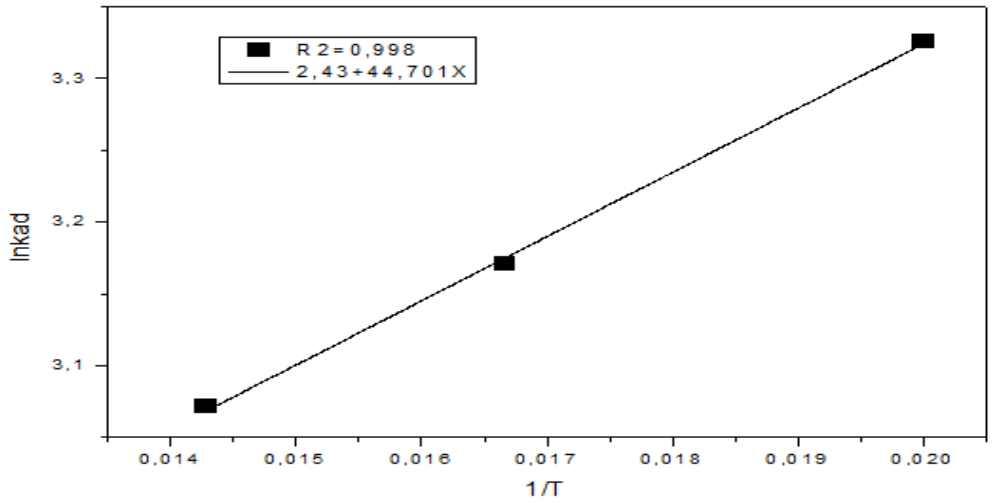

Figure 9. lnKads fonction of 1/T for the congo red retention

The results of the thermodynamic study show that in (Table 2):
The negative ΔH°value indicates the exothermic nature of adsorption of the Congo red and was less than 10 kcal/mol indicating physical adsorption. The ΔG°values obtained were negative meaning that the adsorption was spontaneous and positive value of ΔS° suggested a slight increase in the randomness at the solid/solution interface during adsorption of dye on to the adsorbent.

Table 2. Adsorption Thermodynamic parameters at 303K

Thermodynamic Parameters	ΔG° (kcal. mol^{-1})	ΔH°, (kcal.mol^{-1})	ΔS° (cal.m^{-1}.$kcal^{-1}$)
Values	-1.55	-0.088	4.83

Adsorption isotherm

The study of the adsorption isotherm is fundamental and plays an important

role in determining the maximal capacity of adsorption. In order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained, Langmuir, Freundlich and Dubinin-Radushkevich models have been considered.

In Figure 10, the quantities adsorbed according to the concentrations of the aqueous solution in equilibrium shows that the isotherm is of L-type which is obtained when the adsorption of the solvent is low and when the molecules are not oriented vertically but rather flat. In this case, the adsorption of the solute on the solid takes place in a monolayer.

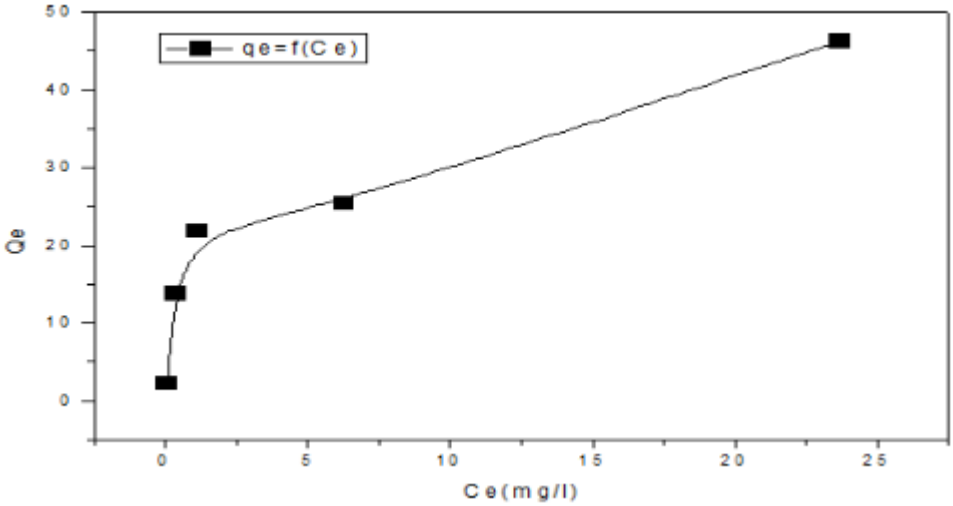

Figure 10. Graphical representation of the isotherm of the Congo red aqueous solution

Langmuir isotherm model

Mathematically, Linearization of Langmuir isotherm model is defined as:

$$\frac{1}{qe} = \frac{1}{qm \cdot KL \cdot Ce} + \frac{1}{qm} \qquad (8)$$

Where q_m is the monalayer capacity of the adsorbent, and K_L is the Langmuir adsorption constant. qm and K_L can be determined from the slope and intercept, respectively from the plot of 1/qe versus 1/Ce (figure 11).

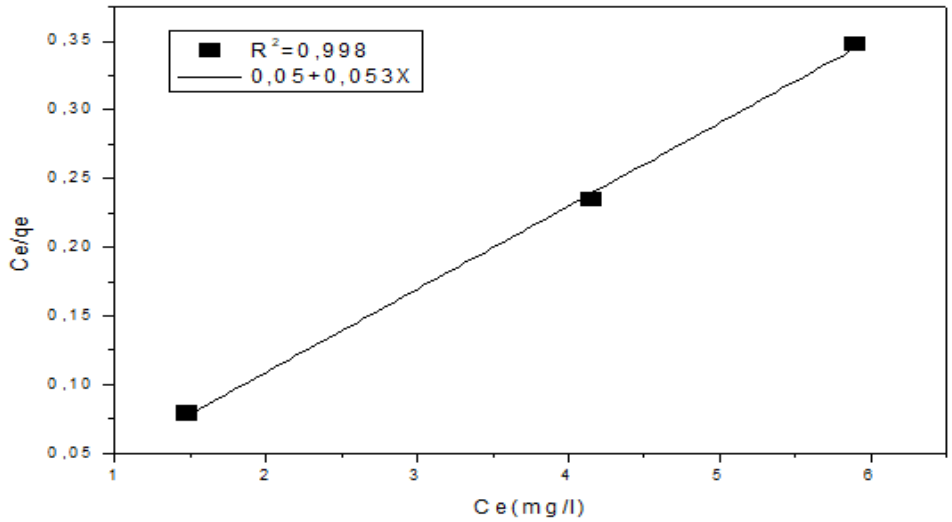

Figure 11. Langmuir linearization

Freundlich isotherm model

This model describes systems where the adsorption is done on heterogeneous surfaces with interactions between the adsorbed molecules; the linear form is given by:

$$\log q_e = \log Kf + 1/n \log C_e \qquad (9)$$

The constant (Kf), due to the bond energy, and the heterogeneity factor (1/n) which measures the deviation from the linear part are determined from the plot log qe versus log C_e. The experimental results obtained at ambient temperature are presented in Figure 12. The Freundlich equation (8) is applied for the adsorption of the Congo red dye on our prepared LDH.

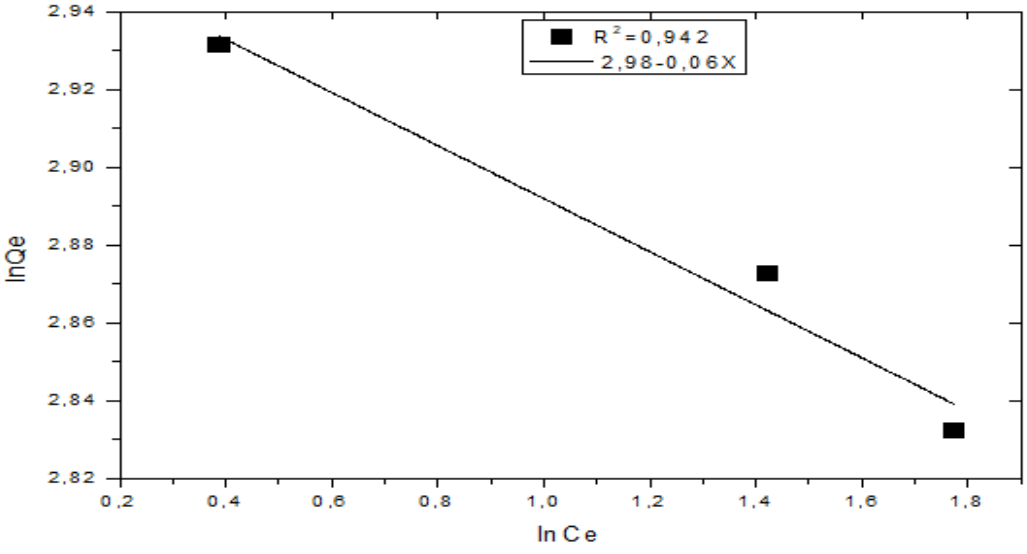

Figure 12. Freundlich linearization

Table 3. Langmuir and Freundlich constants for the elimination of Congo red on ZnAl-SO4

Langmuir model		Freundlich model	
Qm (mg/g)	KL (l/mg)	1/n	KF
22.22	0.52	-0.023	21.75

Dubinin – Radushkevich Isotherm

Plotting ln q_e = f (ε^2) gives us the line of the slope β, and qs is the y-intercept. The results obtained are gathered in Table 4 and Figure 13 shows a linear adjustment.

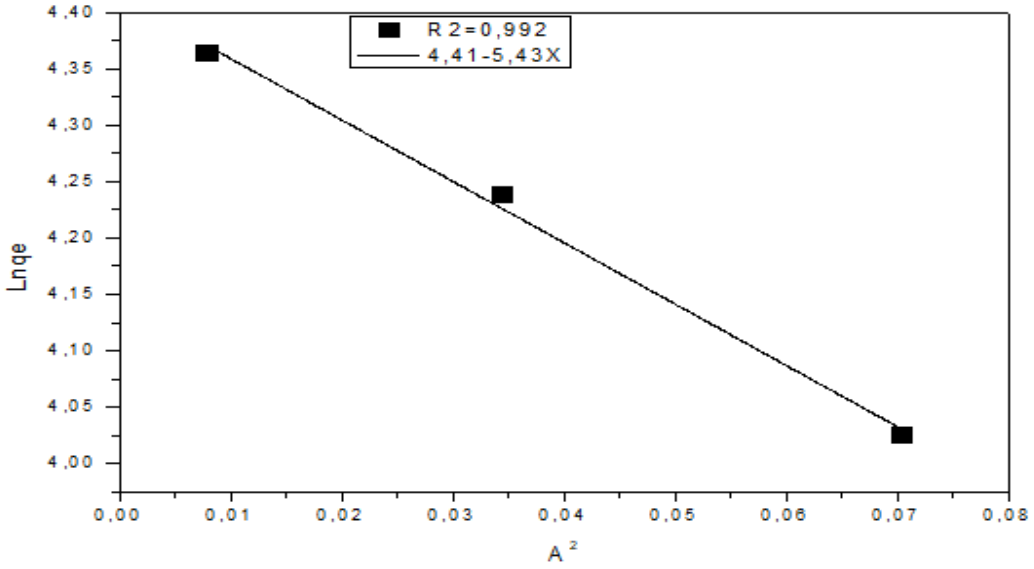

Figure 13. Dubinin–Radushkevich model for dye retention

Table 4. Dubinin–Radushkevich parameters for the elimination of Congo red on ZnAl-SO4

Dubinin Radushkevich model			
qs (mg/g)	β ($mol^2.kJ^{-2}$)	E (kj/mol)	R^2
82,27	5,43	0 ,130	0,992

These values indicate the predominance of physical adsorption (E < 8 kJ/mol)

Kinetic study

The kinetic adsorption of Congo red dye by ZnAl-SO4 is studied at different contact times in the batch system and has been tested with pseudo first order pseudo second order and Intra particles diffusion model.

Pseudo-first-order model

The fitting results based on the pseudo-first order kinetic model are shown in Figure 14. The values for the kinetic models are shown in Table 5

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (10)$$

Where q_e and q_t refer to the amount of mercury adsorbed per unit weight of Zn-Al-SO4 respectively at equilibrium and at any time:

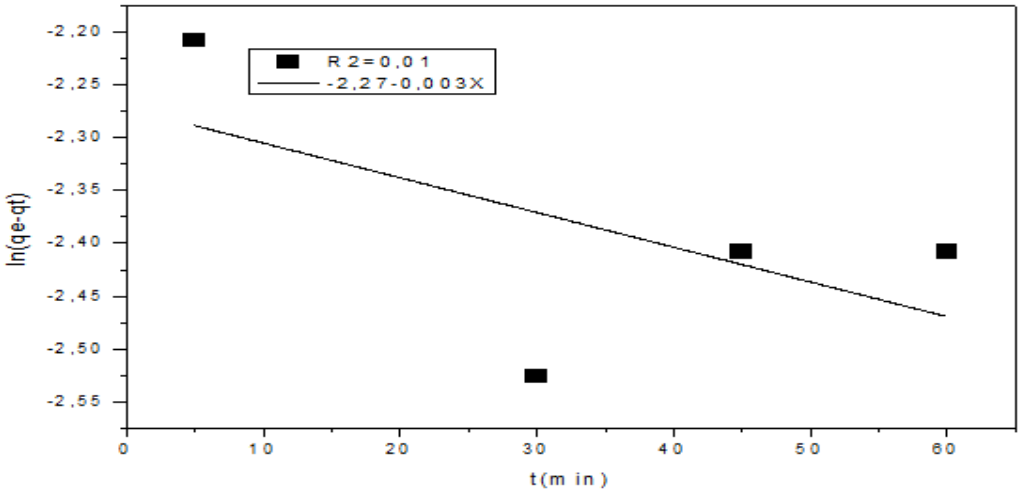

Figure 14. Kinetics of pseudo first-order for congo red retention

Pseudo-second-order

Using the pseudo-second-order equation also, the adsorption process may be described. The differential equation is the following:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{1}{q_{eq}^2} t \qquad (11)$$

The results obtained (Figure 15) show that the pseudo-second-order model is more suitable to describe the kinetics of the retention of Congo red toxic dye by ZnAl-SO_4.

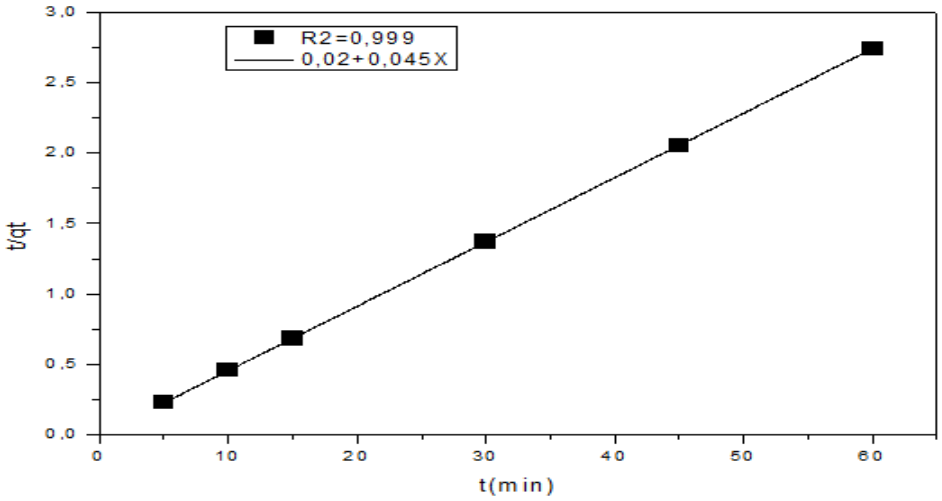

Figure 15. Kinetics of pseudo second order for Congo red retention

Intra particles diffusion model

Solute transfer is generally characterized by either the external mass transfer step or intra particle diffusion or both. To study the existence of intraparticle diffusion during adsorption, the most widely used equation (12) is that given by (Abdel-Ghani et al ., 2016).

$$q_e = K_I C^{0.5} + C \qquad (12)$$

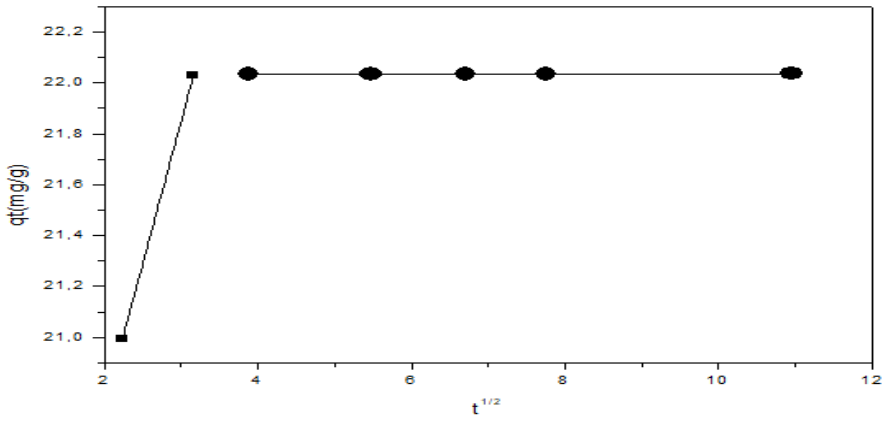

Figure 16. Diffusion model of Congo red dye particles

From figure 16, we distinguish a double linearity reflecting the existence of two stages: firstly, the high adsorption rate, resulting from the diffusion of the outer film and through the boundary layer of the outer surface of the adsorbent. Second, the adsorption process is controlled by intra-particle diffusion, which is characterized by slowing the rate of adsorption, and it is known as the rate-limiting step. These two phases are involved simultaneously during adsorption.

Tableau 5. Parameters of kinetic models of adsorption of Congo red dye on ZnAl-SO4

	Qe exp (mg/g)	K_1(l/min),K_2(g/min .mg)	Qe (mg/g)	R^2
Pseudo 1st order	22,08	0,003	0,10	0,01
Pseudo 2nd order	22,08	9,87	22,22	0,999
diffusion model	Qe exp(mg/g)	Kint(mg/g /$min^{1/2}$)	Ci(mg/g)	R^2
Step 1	22,03	$3{,}55\times10^{-4}$	22,03	0,97
Step 2	22,03	1,12	18,50	-

Material Regeneration

The economic and environmental aspect of the use of adsorbent materials makes it important to reuse anionic clays, given their low cost and their ability to regenerate. After an adsorption with a yield R of almost 100%, desorption has been carried out using a solution of NaOH of known concentration C = 5×10^{-3} M which is chosen after many trials using different NaOH concentrations.

The material used has been used for seven cycles showing best performance at each cycle.

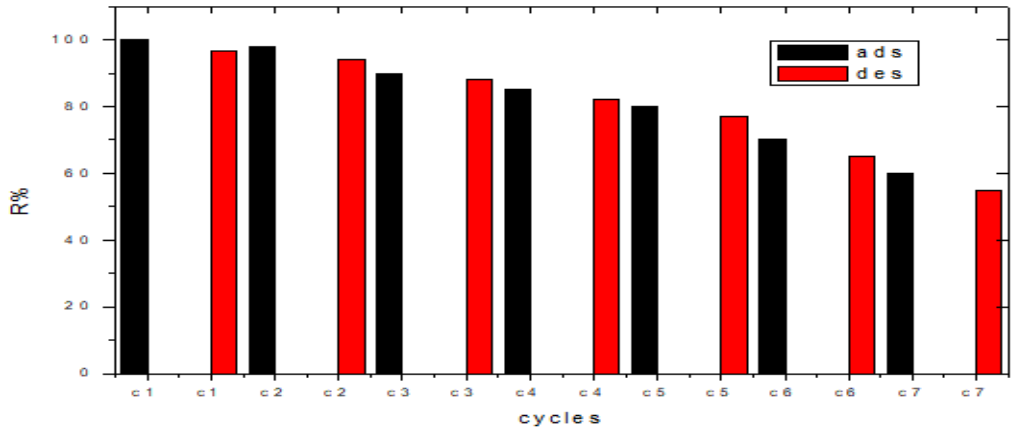

Figure 17. Recycling and reuse of ZnAl-SO4 towards adsorption of Congo red

CONCLUSION

Our prepared material (ZnAl-SO4) was found very effective adsorbent for the removal of Congo red dye from aqueous solutions. The synthetic method used to synthesize this adsorbent by chemical co-precipitation method is highly efficient and very low cost. This compound adsorbent showed that elimination can reach 100% under the optimal conditions and can be used at least for seven cycles. This can allow us to provide this adsorbent (Zn-AlSO4) for the waste water treatments.

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