

## ADSORPTION OF ANIONIC AMIDO BLACK DYE BY LAYERED DOUBLE HYDROXIDE, ZnAlCO<sub>3</sub>-LDH

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### Abstract

A layered double hydroxide anionic clay (ZnAlCO<sub>3</sub>-LDH) with molar ratio Zn/Al of 4:1 was synthesized by co-precipitation method. The ability of ZnAlCO<sub>3</sub>-LDH to adsorb anionic Amido Black dye from an aqueous and factors affecting the sorption efficiency were investigated. Results indicate that ZnAlCO<sub>3</sub>-LDH is an attractive candidate for removing organic anionic Amido Black from solution. The sorption process was also found to be influenced by contact time, initial concentration, adsorbent dosage, particle size, temperature and solution pH. The favorability of the adsorption process is reflected by the Langmuir dimensionless separation factor  $R_L$  and also the  $n$  value of the Freundlich Equation.

**Keywords:** adsorption; layered double hydroxide; Langmuir separation factor, Freundlich Equation

### Abstrak

Anionik dwi hidroksida berlapis (ZnAlCO<sub>3</sub>-LDH) pada nisbah molar Zn/Al 4:1 telah disintesis melalui kaedah pemendapan bersama. Kajian mengenai keupayaan ZnAlCO<sub>3</sub>-LDH untuk menyerap bahan pewarna, Amido Black daripada larutan akuas dan faktor-faktor yang mempengaruhi keberkesanan proses penyerapan telah dilakukan. Hasil kajian mendapati ZnAlCO<sub>3</sub>-LDH mempunyai potensi sebagai penyerap berkesan untuk menyahwarna bahan pewarna organik anionik Amido Black daripada larutan. Proses penyerapan ini juga didapati telah dipengaruhi oleh waktu sentuh, kepekatan, dos penyerap, saiz partikel, suhu dan pH. Keberkesanan penyerapan telah dapat diukur melalui nilai faktor pemisah Langmuir,  $R_L$  dan  $n$  daripada Persamaan Freundlich.

**Kata kunci:** penyerapan; dwi hidroksida berlapis; faktor pemisahan Langmuir, persamaan Freundlich

### Introduction

Wastewater containing dyes pose grave problems to the environment as dyes normally constitute synthetic organic molecules which are recalcitrant to biodegradation [1,2] and difficult to treat by conventional water treatment. Besides, colored water is aesthetically displeasing and unacceptable as it is perceived as pollution, and in aqueous medium, they reduce light penetration vital for photosynthesis by aquatic plants [3,4].

Worldwide production of dyes especially from textile industry has increased in terms of volume, types and complexity. A total of 30% of world production of dyes may be lost during dyeing process [5]. Dyes in wastewater is normally the result of inefficient dyeing processes, which cause as much as 10-15% unused dyestuff entering the watercourse directly [6]. Dye effluent normally contain about 10-50 mg/L, but even at 1 mg/L dyes are easily noticeable [7,8] and thus may be perceived as being contaminated and unacceptable. This poses challenge to colour removal methods from wastewater and dyehouse effluent. Conventional methods of water treatment such as coagulation [9], chemical precipitation [10], ozonation [11], membrane filtration [12] and reverse osmosis [10] are not effective in removing colour from waste effluent. Adsorption, on the other hand has been regarded as the most effective technique for colour removal from aqueous solution as a result of its simplicity in design, relatively low cost and high efficiency [13]. Among the most established adsorbents, activated carbon is the most widely used [10,14], mainly because of its efficiency and widescale application. However, activated carbon is an expensive material [10], and difficult to regenerate [15]. As a result research into relatively cheaper and efficient materials has opened up to a host of potential new adsorbents. One of these promising classes of adsorbents are synthetic anionic clays called hydrotalcites (HT) or hydrotalcite-like compounds (HTlc) or layered double hydroxide (LDH), of which the most famous class is Mg-Al hydrotalcites [7].

LDH belongs to a class of ionic lamellar solids with positively charged layers consisting two kinds of metallic cations and charge balancing exchangeable hydrated gallery anions located in the interlayer region [16]. This compound is also referred to as an anionic clay to differentiate it from a cationic clay. It is also referred to as a hydrotalcite-like compound in reference to structural similarities to hydrotalcite whose general formula is  $[Mg_6Al_2(OH)_{16}(CO_3)_4 \cdot 4H_2O]$ . LDH is commonly represented by the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} (A^{n-})$

$x/n$ ·mH<sub>2</sub>O, where M<sup>2+</sup> is a divalent metal (Mg, Zn, Cu), M<sup>3+</sup> is a trivalent metal (Al, Cr, Fe,...), and A<sup>n-</sup> is an n-valent anion (CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). x is a fraction of M<sup>2+</sup> ions substituted by a trivalent ion M<sup>3+</sup> [17].

The crystal structures of LDH is similar to that of brucite, Mg(OH)<sub>2</sub>, in which the Mg cations occupy the centers of hydroxy octahedral, joined along their edges, forming a layered structure consisting hexagonal platelets [18]. The divalent ions, M<sup>2+</sup> can be replaced by trivalent ions M<sup>3+</sup>, thus inducing a net positive charge in the cation layers. This positive electrical charges are balanced by intercalating anions, A<sup>n-</sup> (usually CO<sub>3</sub><sup>2-</sup> and water molecules) which are incorporated in the interlamellar layers. These interlayer anions can generally be easily exchanged by other wide variety of anions ranging from simple inorganic and organic anions and also complex biomolecules [19].

The presence of these highly interchangeable interlayer anions and the Brönstedt basicity of the layer surfaces have generated considerable interest in wide ranging applications of LDH such as direct catalysis or catalyst support, ion exchange, molecular stabilization, separation, membrane technology, and controlled release of anions. In environmental cleanup, anion adsorption by LDH has been subjected to investigations such as removal of phenolic compounds, heavy metals, pesticides and dyes [7].

Amido black is considered an anionic dye since it has a sulphonic group attached to the molecular structure. Commercially, it is usually in the forms of sodium salt, which in water renders this dyes soluble. Although amine group present, the overall charge on the molecule is negative. Therefore it presents a potential candidate for anion exchange with anionic layered double hydroxide.

The objectives of this study are to 1) evaluate the adsorption potential of ZnAlCO<sub>3</sub>-LDH towards coloured compounds such as Amido Black (AB), which was chosen as a model dye, 2) study the influence of contact time, initial dye concentration, adsorbent dosage, particle size, pH and temperature on the adsorption process performance. The data was fitted into Langmuir and Freundlich isotherms.

## Experimental

### Sample preparation

The sorbent was prepared in the laboratory by coprecipitating mixed metal solutions of zinc nitrate, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1M) and aluminum nitrate Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.25M) in a molar ratio (Zn/Al) of 4:1. The solution mixture was raised to pH 10 ± 0.2 by the addition of sodium hydroxide (1M) and sodium carbonate (0.25M) solution mixture under vigorous stirring at room temperature (27 °C ± 0.1) for about 3 h. The slurry was then aged at approximately 70 °C for 24 h in a thermostated oil bath. The filtrate was then filtered and washed with excess water, dried at 80 °C in an oven for 24 h to a constant weight. The resulting filter cake was pulverized in a mortar and ready for use for characterization and chemical analysis.

An anionic dye, Amido black (AB) was chosen as adsorbate. It was supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia and was used without any further treatment. The chemical structure and specifications of AB are shown in Figure 1.

A stock solution of 1000 mg/L was prepared from which initial dye concentrations (50-300 mg/L) were obtained by diluting necessary aliquots of stock solution using ultra pure water to desired concentrations. The pH measurements were carried out using a Mettler Toledo pH meter, while the concentration residual of AB in solution was determined at a maximum wavelength, λ<sub>max</sub> = 518 nm using a UV-VIS spectrophotometer, Secomam Uvikon XS.

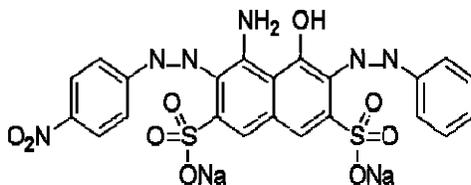


Figure 1: Chemical structure of Amido Black (C.I No.: 34140),  
Formula: C<sub>4</sub>0H<sub>28</sub>N<sub>7</sub>NaO<sub>13</sub>S<sub>4</sub>, Molecular weight: 965.94), λ<sub>max</sub> = 518 nm

### Characterization of ZnAlCO<sub>3</sub>-LDH

Characterization was carried out using a Fourier transform infrared (FTIR), powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). FTIR spectrum was obtained using a Perkin Elmer 1725X spectrophotometer. The sample was finely ground, mixed with spectroscopic grade KBr and pressed into a disc. The spectrum of sample was scanned at 2 cm<sup>-1</sup> resolution between 400 and 4000 cm<sup>-1</sup>.

PXRD was performed using a Shimadzu XRD-6000 diffractometer, with Ni-filtered Cu-K $\alpha$  radiation ( $\lambda=1.54$  Å) at 40 kV and 200 mA. Solid samples were mounted on alumina sample holder and basal spacing (d-spacing) was determined via powder technique. Samples scan was carried out at 10- 60<sup>0</sup>, 2 $\theta$ /min at 0.003<sup>0</sup> steps.

The surface morphology of adsorbent was characterized by scanning electron microscopy (FEI QUANTA 200F). SEM has been primarily used for determining the particle shape, and is particularly useful for characterizing fundamental physical properties including surface morphology of an adsorbent [13].

### Batch sorption experiment

The batch experiments were carried out using a constant sample volume of 25 ml in a series of stoppered glass bottles in a temperature-controlled thermostat bath shaker operating at 100 rpm. at 25  $\pm$  1 °C (except for experiment on temperature effect), with a constant sorbent dosage of 0.250 g (except for experiment on dosage effect) using different initial dye concentrations (50-300 mg/L) at predetermined contact time (0-480 min). The pH of the dye solution was unmodified except for the study on pH effect on dye uptake. The equilibrium time to reach equilibrium was then estimated, and this time period was chosen when investigating other operating variables on removal efficiency. The effect of initial dye concentrations (50-400 mg/L), sorbent dosage (0.1-0.3 g), particle size ( $\leq$ 212 to  $\leq$ 600  $\mu$ m), temperature (25-35 °C) and pH (2-12) on dye removal were investigated at predetermined equilibrium time (6 h) using 100 mg/L dye solution. The final dye solution was centrifuged for 5 min at 5000 rpm and the clear solution was extracted for UV measurement. All experiments were done in duplicate and the average value was used in the evaluation. A blank sample containing no dye and another containing dye solution only was run together with every batch of sample run.

### Analysis of data

The amount of dye adsorbed by the adsorbent was calculated by applying the mass balance equations:

$$\% \text{ dye uptake} = (C_0 - C_t / C_0) \times 100 \quad (1)$$

$$\text{Adsorption capacity, } q_e \text{ (mg/g)} = (C_0 - C_t) V / M \quad (2)$$

where  $C_0$  is the initial dye concentration (mg/L);  $C_t$  is the concentration of dye (mg/L) at any time  $t$ ;  $V$  is the volume of solution (L) and  $M$  is the weight (g) of the LDH.

To investigate the adsorption isotherm, two commonly used Langmuir and Freundlich expressions were used to fit the data. Langmuir isotherm model assumes that intermolecular forces between adsorbing molecules are negligible and that once available sites on adsorbent are fully occupied, no further adsorption take place. The equation reduces to Henry's law at low initial concentration, while at higher concentration monolayer adsorption is predicted [20]. The Langmuir expression is given by Equations (3) and its linearized form in Equation (4) :

$$q_e = Q_0 b C_e / (1 + b C_e) \quad (3)$$

$$C_e / q_e = (1 / Q_0 b) + (C_e / Q_0) \quad (4)$$

where  $q_e$  (mg/g), is the amount of solute (AB) adsorbed per unit weight of adsorbent (LDH) at equilibrium,  $C_e$  is the equilibrium concentration of the solute in the bulk solution (mg/L),  $C_e$  (mg/L) is the equilibrium dye concentration in solution,  $Q_0$  (mg/g) is the amount of dye adsorbed at complete monolayer coverage and  $b$  (L/mg) is the Langmuir adsorption constant, which is related to the affinity of the adsorption. The values of  $b$  and  $Q_0$  are obtained from the intercept and slope, respectively of a straight line plot of  $C_e / q_e$  versus  $C_e$ .

The other expression is Freundlich Adsorption Isotherm given by Equation (5) and its linearised form in Equation (6):

$$q_e = K_F C_e^{1/n} \quad (5)$$

$$\log q_e = \log K_F + (1/n) \log C_e \quad (6)$$

$K_F$  and  $1/n$  are Freundlich equilibrium coefficients related to the adsorption capacity and adsorption intensity respectively [20]. A plot of  $\log q_e$  versus  $\log C_e$  gives a straight line with a slope ( $1/n$ ) and an intercept at  $\log K_F$ . A larger value of  $K_F$  indicates good adsorption efficiency for a particular LDH, while a larger value of  $1/n$  indicates a larger change in effectiveness over different equilibrium concentrations [21].  $n$  values between 1 and 10 represent beneficial adsorption [22].

The favorability of the sorption system in the batch process was estimated from the shape of the isotherm which may be indicated by an essential characteristics of the Langmuir isotherm, expressed in terms of a dimensionless constant separation factor  $R_L$ , given by Equation (7) [23]:

$$R_L = 1 / (1 + bC_0) \quad (7)$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial dye concentration (mg/L). The value of  $R_L$  indicates whether the isotherm follows the characteristic [23] as shown in Table 1.

Table 1: The characteristic of value  $R_L$

Nature of adsorption process	$R_L$ Value
Unfavourable	$R_L > 1$
Linear	$R_L = 1$
Favourable	$0 < R_L < 1$
Irreversible	$R_L = 0$

## Results and Discussion

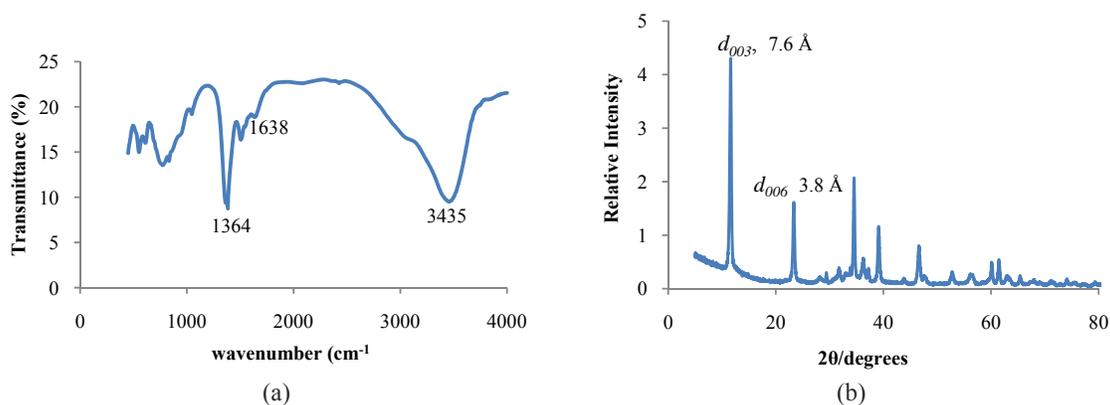
### Characterization of ZnAlCO<sub>3</sub>-LDH

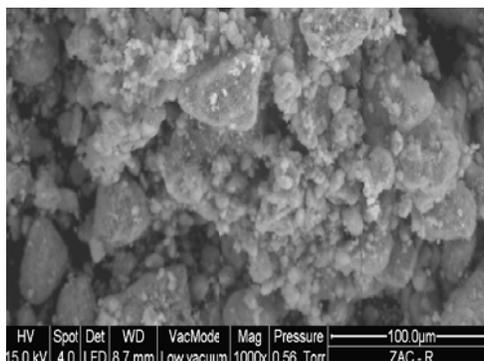
The results of FTIR, XRD, and SEM pattern analyses for ZnAlCO<sub>3</sub>-LDH are shown in Figures 2(a)-2(c).

The FTIR spectrum shows a broad peak at 3435 cm<sup>-1</sup>. This is due to the presence of O-H stretching of hydroxyl group of LDH. A small peak around 3000 cm<sup>-1</sup> was due to hydrogen bonding between H<sub>2</sub>O and anions in the interlayer region. Sharp peaks at 1364 cm<sup>-1</sup> and 1638 cm<sup>-1</sup> represent symmetric and asymmetric stretching absorption of the C=O group. The peaks below 1000 cm<sup>-1</sup> correspond to Zn-OH or Al-OH stretching absorption. Metal-oxygen stretching mode is represented by peaks below 800 cm<sup>-1</sup>.

The formation of LDH can be identified easily by XRD study. Sharp peaks indicate that the material obtained is ordered and broadened peaks shows disordered crystal arrangement. The most intense peaks of the LDH at 7.6 Å, and 3.8 Å are typical characteristics of a LDH structure corresponding to the distance between the hydroxyl layers and interlayer spacing [24] ZnAlCO<sub>3</sub>-LDH.

The SEM image shows that LDH particles are mainly composed of irregular and porous particles. In general, the LDH has plate-like morphology and hexagonal crystallite.





(c)

Figure 2: Characterization of ZnAlCO<sub>3</sub>-LDH (a) FTIR spectrum (b)XRD diffractogram (c) SEM image

### Effect of pH

The effect of initial pH of dye solution on the percentage removal of AB was investigated by varying the initial pH under constant operating parameters. The result is shown in Figure 5 for 100 mg/L. The effect observed at 6 h shows that maximum removal was observed at optimum pH around 6.0, which is the natural pH of AB dye solution (6.4). At this pH, the ionic character of dye molecule and LDH was optimum for adsorption. The dye uptake shows a dip at a neutral pH, 7, indicating a sharp decrease of adsorption. As a result all subsequent experiment on the effect of adsorption variables on AB removal were carried out without any pH modification.

### Effect of contact time

The effect of contact time between AB and ZnAlCO<sub>3</sub>-LDH, was studied on various concentrations (50-300 mg/L) for at least 6 h as shown in Figure 3. Typically, rapid uptake was observed, gradually decreasing with time as equilibrium was reached. The rate of removal was higher initially due to greater available sites for adsorption at high concentration at the beginning of contact time. As time progressed, the active sites became less accessible, and eventually became saturated. After the initial adsorption, the rate of dye removal was controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent until all available surface sites were occupied [25,26]. This feature is typical in batch type systems, in which, for monolayer adsorption, the rate of adsorbate removal from aqueous system is controlled by the rate of transport of adsorbate species from the exterior to the interior sites of the adsorbent [16]. In addition, in the case of ZnAlCO<sub>3</sub>-LDH, two types of adsorption sites are available [27]; firstly, the external surface which leads to surface adsorption, and secondly, within the interlayer region of the host molecule (LDH), where ion exchange between NO<sub>3</sub><sup>-</sup> in its interlayer region and the guest ion, AB is possible. Such property is unique for anionic clays which are well known for their intercalation chemistry. Equilibrium adsorption was achieved at about 6 h with maximum removal of 99 % for a range of concentration of 50-150 mg/L using 0.25 g sorbent.

### Effect of initial dye concentration

The effect of initial concentration was investigated using various dye concentrations (50-400 mg/L) in a fixed time (6 h). The results are shown Figure 4. The percentage removal decreased exponentially with the increase in initial dye concentration as a result of reduction of available active sites for adsorption at high concentration, leading to reduced dye removal. The same pattern was also obtained using different initial concentrations, as depicted in Figure 3, in which increased initial concentrations at a particular time interval resulted in the decreased of AB removal.

### Effect of adsorbent dosage

The effect of adsorbent dosage on dye removal efficiency is represented by Figure 6 which shows an increase in adsorption with increased the adsorbent dosage. For 100 mg/L initial dye concentration, the adsorption efficiency is 96% using 0.3 g LDH compared to 74 % removal using 0.1 g. It may be discerned from Figure 6 that adsorption efficiency is approaching maximum at this dosage. Increased dosages had the effect of

providing more surfaces and adsorption site; hence increased adsorbent enhances adsorption to a maximum with eventual equilibrium stage.

### Effect of particle size

Figure 7 shows the effect of particle size on adsorption efficiency is represented by adsorption profile of 100 mg/L initial concentration by three particle sizes in 6 h. It can be seen that decrease in particle size from 600 μm 425 μm and 212 μm, had resulted in the increase in percentage of dye removal due to the increase in surface area and available sites allowing more dye molecules to be bound to the adsorbent. The removal of dye was 89 % in the case of 212 μm particle size compared to 72 % for 600 μm.

### Effect of temperature

Increase of temperature had increased the adsorption efficiency of AB adsorption (Figure 8). The result demonstrates that with higher kinetic energy, dye molecules were able to overcome the energy barrier, restricting the bonding between AB and ZnAlCO<sub>3</sub>-LDH. The adsorption of 100 mg/L AB carried out at 25 °C, 30 °C and 35 °C had resulted in 99% adsorption at 30 °C. Further increase in temperature to 35 °C had little effect on further adsorption.

### Adsorption isotherms

The adsorption data were applied to both the linearized form of Freundlich and the Langmuir equations (Figure 9). Table 2 illustrates the correlation coefficients of determinant, R<sup>2</sup> for both isotherm models. The values of R<sup>2</sup>, 0.934 for Langmuir and 0.958 for Freundlich suggest that both homogenous monolayer and heterogenous mechanism in adsorption process are at play. The adequacy of both models to explain the adsorption process is further supported by the positive values of Langmuir and Freundlich isotherm constants [28] as shown in Table 2. The Freundlich constant n has a value which lies between 1 and 10, which indicate the sorption process by heterogenous binding is favourable [22]. In addition, the values of Langmuir dimensionless separation factor R<sub>L</sub> as shown in Figure 10 has values 0 < R<sub>L</sub> < 1; hence the sorption system may be considered favourable by Langmuir model (Table 1).

From this table; it was observed that the values of R<sub>L</sub> computed are observed to be in the range of 1-10, indicating that the sorption process is favourable for this adsorbent [9]. The R<sub>L</sub> values decrease with increasing concentrations suggesting that the dye uptake process is more favourable with higher concentration of dye [29].

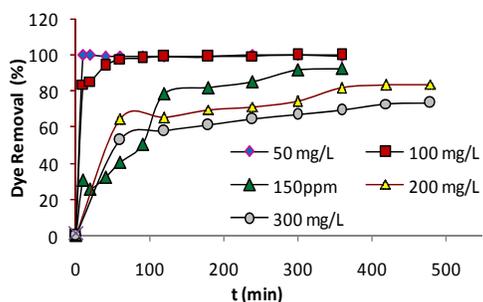


Figure 3: Effect of contact time on dye removal at different initial concentration

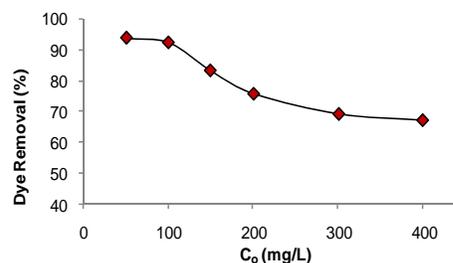


Figure 4: Effect of different initial concentrations on dye removal

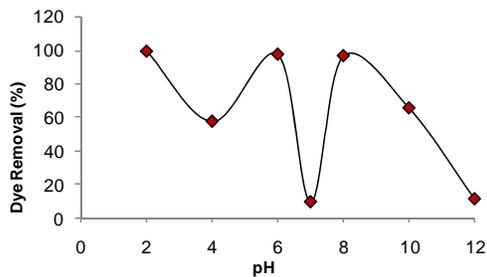


Figure 5: Effect of pH on AB removal

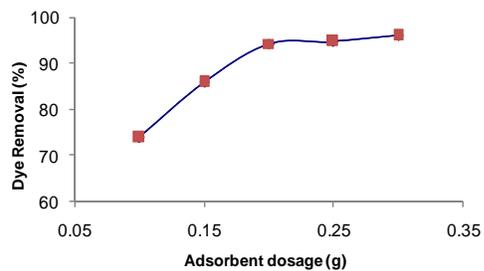


Figure 6: Effect of particle size on AB removal

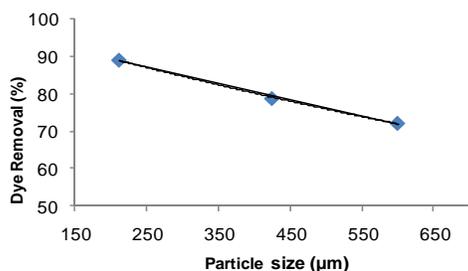


Figure 7: Effect of particle size on AB removal

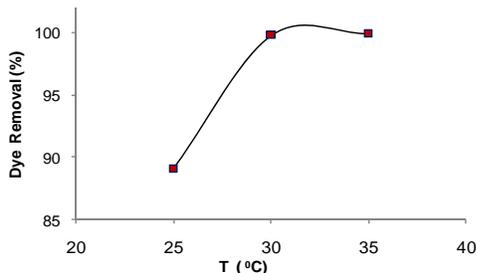
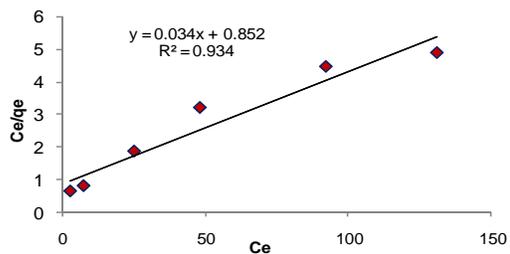
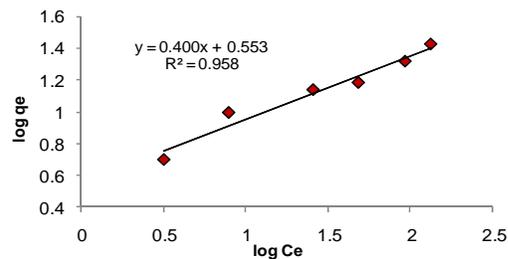


Figure 8: Effect of temperature on AB removal



(a)



(b)

Figure 9 : Langmuir (a) and Freundlich (b) adsorption isotherms model for AB adsorption by ZnAlCO<sub>3</sub>-LDH

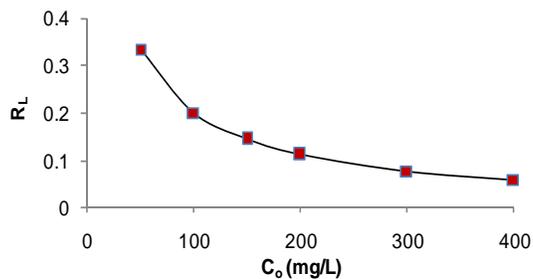


Figure 10: The dimensionless separation factor,  $R_L$  at different initial concentrations for AB adsorption by ZnAlCO<sub>3</sub>-LDH

Table 2: Summary of the Langmuir and Freundlich isotherm constants and correlation coefficients for AB adsorption by ZnAlCO<sub>3</sub>-LDH

Langmuir				Freundlich			
Equation	Q <sub>o</sub> (mg/g)	b (L/mg)	R <sup>2</sup>	Equation	n	K <sub>F</sub>	R <sup>2</sup>
y = 0.034x + 0.852	28.8	0.040	0.934	y = 0.400x + 1.274	2.5	3.58	0.959

### Conclusion

The present study shows that ZnAlCO<sub>3</sub>-LDH with a particle size of 212 µm is suitable adsorbents for the removal of Amido Black dye, which is an anionic dye from an aqueous solutions. The removal of AB was shown to be dependent on contact time, initial concentration, dosage and temperature. The experimental data give good fit for both Langmuir and Freundlich models, but Freundlich model fits better (R<sup>2</sup>>0.95). The results also suggest that adsorption capacity of ZnAlCO<sub>3</sub>-LDH was found to be 28.8 mg/g at 25 °C using linearized Langmuir isotherm model. The mechanism of adsorption seems to obey a heterogenous model better than monolayer isotherm model. The favorability of the adsorption process is reflected by the Langmuir dimensionless separation factor R<sub>L</sub> and also the n value of the Freundlich equation.

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