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## Removal of Malachite Green Dye using Keggin Polyoxometalate Intercalated ZnAl Layered Double Hydroxide

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### Abstract

The ZnAl Layered double hydroxides (LDHs) have been successfully synthesized by the coprecipitation method, followed by intercalation using Keggin ion of  $\alpha$ -dodecatungstosilicic acid [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> to form ZnAl- $[\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs. The prepared ZnAl- $[\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs were characterized by using X-Ray, FTIR, and BET surface area analyses, which were, then, used as adsorbents of malachite green dye from aqueous solution. The synthesized ZnAl LDH showed a typical diffraction peak of the layered compound at 11° (003) with an interlayer space of 8.59 Å. After intercalation, it was recorded that the interlayer space of ZnAl- $[\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDH increased to 10.65 Å. Moreover, the specific surface area of the intercalated LDH increased from 1.9685 to 14.0422 Å. The adsorption study revealed that the adsorption capacity of ZnAl- $[\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDH toward malachite green dye was higher (37.514 mg.g<sup>-1</sup>) than the pristine ZnAl LDH (32.845 mg.g<sup>-1</sup>). The adsorption kinetics study showed that malachite green adsorption onto both pristine and intercalate LDH followed the pseudo-2<sup>nd</sup>-order model. The adsorption thermodynamic investigation indicated that adsorption of malachite green onto ZnAl- $[\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDH was a spontaneous process and was classified as physical adsorption with activation energy ranging from 10.074 to 15.476 kJ.mol<sup>-1</sup>.

**Keywords:** Malachite green, Layered double hydroxides, Zn/Al, Keggin ion, X-Ray, Polyoxometalate

### Introduction

The use of various synthetic chemicals in many activities leads to their accumulation in the environment. Various hazardous substances, such as dyes from textiles, paintings, plastics, and pigments that are contaminated in the aquatic environment, lead to water quality degradation. Moreover, the contaminated chemical not only affecting human health but also other living creatures due to their toxicity and non-biodegradable properties. Consequently, the attempts to remove hazardous chemicals from wastewater are attracting widespread interest in recent decades to maintain environmental sustainability.

Various methods have been developed in this regard, including adsorption, precipitation, filtration, coagulation, and membrane separation [1-3]. Generally, adsorption is considered one of the most suitable methods since it is a simple process, low cost, easy to perform, and availability of abundant adsorbent material. However, the adsorption efficiency depends on the capability of the used adsorbent. Nowadays, numerous low-cost and eco-friendly adsorbents have been tested to remove dyes from wastewater, e.g., zeolite, natural clay, activated carbon, and layered double hydroxides [4-6].

Layer double hydroxides (LDHs), also well known as anionic clay, are a class of layered inorganic materials that exhibited interesting properties like ease of fabrication, high anion exchange capacity, swelling properties, as well as high thermal and chemical stability. The chemical formula of LDHs is  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot nH_2O$ , where  $M^{2+}$  is divalent,  $M^{3+}$  a trivalent metal ions and  $A^{n-}$  interlayer anions such as nitrate, sulfate, or carbonate, depending on their synthetic precursor [7,8]. LDHs have been widely used as a catalyst in various chemical reaction and adsorbents to remove numerous pollutants from industrial wastewater. ZnAl LDH has been reported as an efficient adsorbent to remove methylene blue and indigo carmine [9]. Calcined and uncalcined MgNiAl LDH has also been reported as an effective adsorbent to remove anionic methyl orange dye at high temperatures [10]. Furthermore, Palapa *et al.* (2018) have reported that Ni/Al and ZnAl LDHs with different interlayer distances can be employed as an efficient adsorbent for direct yellow dye removal from aqueous solution [11].

As a synthetic clay, the LDH structure can be tuned and modified in several ways. One of the conventional methods in LDH modification by changing the anion on the interlayer space of the layered structure. Anion in the interlayer space of LDHs can be replaced with another anion to increase their interlayer distance. The main advantage of this process is to increase interlayer space as well as the surface area of the material for application as an adsorbent or catalyst. Various anions with different sizes and characteristics have been intercalated into LDH. Chai, Xu, Lin, Evans, and Li [12] reported that intercalation of ZnAl LDH with 2,3-dihydroxy naphthalene-6-sulfonate anion could increase its interlayer distance from 0.90 to 1.59 nm and increased its thermostability.

Polyoxometalate (POM) is a class of advanced materials that consists of metal oxide clusters from an early transition metal, including W, Mo, and V [13]. POM has been widely engineered and employed as an efficient catalyst in different chemical reactions. Yun and Pinnavaia [14] have long studied and demonstrated that the introduction of POMs anion into LDHs structure through intercalation can produce enough interlayer space as well as a unique interlayer environment that can be used as the host for conducting both catalytic and adsorption activity. Recently, Liu, Xu, Yao, Miras, and Song [15] have prepared Tris-LDH-CO<sub>3</sub> intercalated by polyoxometalate of X<sub>4</sub>(PW<sub>9</sub>)<sub>2</sub> and reported that the obtained material exhibited high efficiency as a bifunctional material for cascade reaction. Although the application of POM intercalated LDH as catalysts have widely been investigated, their utilization as an adsorbent is still limited.

Recently, a heteropoly compound containing molybdenum, which substituted the addenda atom of Keggin type, was used as an intercalant for ZnAl LDH to form ZnAl-PW<sub>10</sub>Mo<sub>2</sub>. This material was reported to be an efficient adsorbent of methylene blue cationic dye [19]. The use of Polyoxometalates of Keggin and Dawson types [CoW<sub>12</sub>]<sub>5</sub> and [P<sub>2</sub>W<sub>17</sub>]<sup>10-</sup> as intercalant of ZnAlFe LDH resulted in materials with not only high adsorption capacity for methylene blue but also showed photocatalytic properties to degrade methylene blue [16].

In this study, ZnAl LDHs were intercalated with Keggin ion [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> and used as an adsorbent for malachite green dye removal from aqueous solution. The physicochemical properties of these materials were examined through X-ray powder diffraction analysis, FTIR spectroscopy, nitrogen adsorption-desorption, and determination of pH<sub>pzc</sub> of material. The adsorption process was studied through the effect of pH, adsorption time, malachite green concentration, and temperature. Also, kinetic and thermodynamic adsorption properties were further discussed.

## Materials and methods

### Chemicals and instrumentations

All the used chemicals were purchased and used as received without further purification.  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and NaOH were purchased from Sigma Aldrich. Malachite green dye and HCl were purchased from Merck.

The material was examined using X-Ray powder diffractometer Rigaku Miniflex-600, and the sample was scanned at a speed scan  $0.1 \text{ deg min}^{-1}$ . Other characterizations were conducted using the Shimadzu FTIR Prestige-21 spectrophotometer. FTIR spectra were recorded at wavenumber  $400 - 4,000 \text{ cm}^{-1}$  with KBr pellet while the surface area analysis was determined through nitrogen gas adsorption-desorption isotherms using the Quantachrome instrument at 77 K. Besides, the concentration of malachite green was determined using UV-Vis BioBase BK-UV 1800 PC spectrophotometer. Keggin ion of  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  was synthesized as described in our previous report [17]. In brief, a solution of 50 mmol metasilicate and 0.55 mol of sodium tungstate was added then 4 M of HCl solution was added drop by drop under vigorous stirring. The solution is kept at  $100 \text{ }^\circ\text{C}$  for 1 h. After cooling to room temperature, the solution is filtered then the pH is adjusted to 2 with aqueous KOH followed by the addition of KCl. The potassium salt is removed by filtration then dried in the air.

### Synthesis of ZnAl and its intercalation with Keggin ion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$

ZnAl LDH was synthesized by the coprecipitation method with adjusted final pH 10. In brief,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with a molar ratio of 3:1 were dissolved into distilled water under vigorous stirring for 30 min followed by dropwise addition of 2M NaOH until a constant pH 10 was reached. The mixture was kept for 24 h then the produced white solid precipitate was separated by vacuum filtration, washed with distilled water several times to remove the remaining salt, then dried in the oven at  $60 \text{ }^\circ\text{C}$  for 24 h.

The intercalation of Keggin ion  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  into the ZnAl LDH interlayer was conducted using a simple ion-exchange method. Typically, 1 g of synthesized ZnAl LDH was dissolved in 50 mL of NaOH solution containing 8 g of tungstosilicate polyoxometalate. The mixture was vigorously stirred for 36 h at room temperature, then the solid was filtered using vacuum filtration, washed with distilled water, then dried in the oven at  $80 \text{ }^\circ\text{C}$  for 8 h. The obtained product was, then, labeled as ZnAl- $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  LDH.

### Determination of pH Point Zero Charge

The pH point zero charges (pHpzc) of the synthesized materials were determined by the salt addition method [18]. 0.1 g of the synthesized materials were added to a solution of 0.1 M sodium chloride. The initial pH (pHi) was adjusted with 0.1M sodium hydroxide or 0.1M hydrogen chloride to the desired value in the range of 1 to 10. Then, the solution was stirred for 24 h. After filtration, the final pH (pHf) of the filtrate was measured with a pHmeter. The pHpzc was determined from the graph pHf-pHi vs. pHi.

### Adsorption experiments

Malachite green stock solution 1,000 mg/L was prepared by dissolving 1 g malachite green into 1,000 mL of distilled water. The standard solution was obtained from the dilution of the malachite green stock solution. Adsorption of cationic malachite green was conducted in a small-batch adsorption system. Adsorption was carried out at various times from 5 to 120 min, the various concentration of cationic malachite green dye from 40 to 150 mg/L, and different temperatures from 30 to  $60 \text{ }^\circ\text{C}$ . The pH was adjusted to ten by the addition of 0.1 M sodium hydroxide. The concentration of the adsorbed malachite green was determined by using a UV-Vis spectrophotometer at 617 nm. Adsorption kinetic parameter was obtained by calculating data of variation of adsorption time using the 2 most used adsorption kinetics models, namely pseudo-1<sup>st</sup>-order and pseudo-2<sup>nd</sup>-order kinetic models as follows [19,20].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

where  $q_e$  is adsorption capacity at equilibrium ( $\text{mg.g}^{-1}$ );  $q_t$  is adsorption capacity at  $t$  ( $\text{mg.g}^{-1}$ );  $t$  is adsorption time (min), and  $k_1$  is adsorption kinetic rate at pseudo-1<sup>st</sup>-order ( $\text{min}^{-1}$ ).

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where  $q_e$  is adsorption capacity at equilibrium ( $\text{mg.g}^{-1}$ );  $q_t$  is adsorption capacity at  $t$  ( $\text{mg.g}^{-1}$ );  $t$  is adsorption time (min); and  $k_2$  is adsorption kinetic rate at pseudo-2<sup>nd</sup>-order ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ).

Adsorption capacity as a thermodynamic parameter was obtained from Langmuir and Freundlich equations [21,22]. Langmuir used chemical adsorption as an assumption for adsorption, while Freundlich used multilayer adsorption as physical adsorption. The Langmuir equation was used as follow:

$$\frac{C}{m} = \frac{1}{bK_{ML}} + \frac{C}{b} \quad (3)$$

Where  $C$  is a saturated concentration of adsorbate;  $m$  is the amount of adsorbate;  $b$  is the maximum adsorption capacity ( $\text{mg.g}^{-1}$ ), and  $K_{ML}$  is the Langmuir constant ( $\text{L.mg}^{-1}$ ). The Freundlich isotherm model was determined by the following equation:

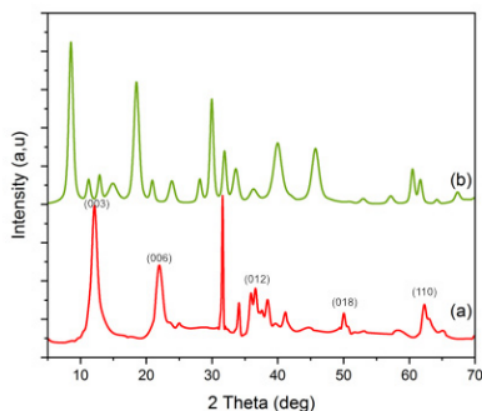
$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where  $q_e$  is adsorption capacity at equilibrium ( $\text{mg.g}^{-1}$ );  $C_e$  is a concentration of adsorbate at equilibrium ( $\text{mg.L}^{-1}$ ), and  $K_f$  is Freundlich constant.

## Results and discussion

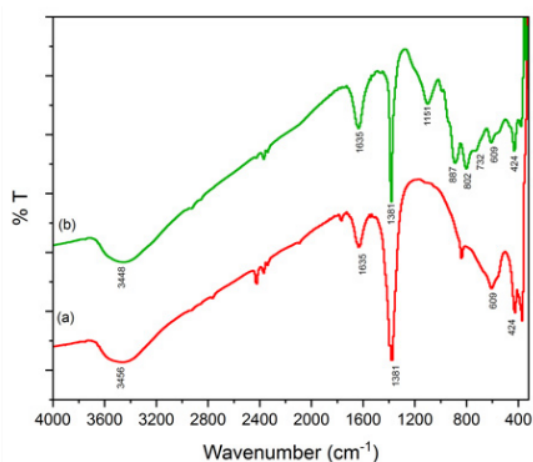
The synthesized materials were characterized by XRD, where the result is shown in **Figure 1**. The synthesized ZnAl LDH showed several diffraction peaks at  $11^\circ$ ,  $23^\circ$ ,  $32^\circ - 40^\circ$ ,  $50^\circ$ , and  $63^\circ$  where the main diffraction for ZnAl LDH was  $11^\circ$  (003),  $23^\circ$  (006), and  $63^\circ$  (110) [23]. The formation of the layer was identified at  $11^\circ$  (003) with a basal spacing of 8.59 Å. These interlayer galleries are common for all types of LDH with various divalent and trivalent ions and should be expanded to be used as adsorbents. Intercalation is frequently used as a common method to increase the interlayer distance of LDH using a large anion. This research uses Keggin ion of  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  as intercalant to increase the interlayer distance of ZnAl LDH. X-ray powder diffraction of intercalated ZnAl- $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  LDH is shown in **Figure 1b**. Diffraction at (003) shifted to a lower angle to  $9^\circ$  due to the insertion of a large anion on interlayer space. The interlayer distance was 10.65 Å, with an increase of about 2.06 Å falling in the range of 2 - 5 Å as expected. Therefore, it can be assumed that the intercalation of  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$  on interlayer ZnAl LDH was successfully conducted.



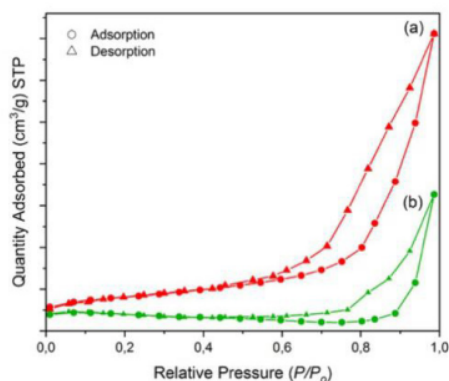


**Figure 1** XRD powder pattern of ZnAl LDH (a) and ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs (b).

IR spectra of ZnAl LDH and intercalated ZnAl LDHs are shown in **Figure 2**. There are 3 parts of important vibration bands for both ZnAl and intercalated ZnAl LDHs, including 3,440 - 3,450, 1,381, and 400 - 800  $\text{cm}^{-1}$  [24]. The broad vibration at 3,340 - 3,450  $\text{cm}^{-1}$  for both LDHs was attributed to the stretching of the hydroxyl group. The sharp vibration at 1,381  $\text{cm}^{-1}$  was assigned to the nitrate group. There were several peaks at 400 - 800  $\text{cm}^{-1}$  after intercalation showed the characteristic of Keggin structure at 887, 802, and 732  $\text{cm}^{-1}$  for  $\nu(\text{Si-O})$ ,  $\nu(\text{W=O})$ , and  $\nu(\text{W-O-W})$ . Moreover, a new band observed at 1,151  $\text{cm}^{-1}$  was correspond to the presence of O-Si-O bonding. These results suggested that the Keggin ion [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> was successfully intercalated onto ZnAl LDH.



**Figure 2** FTIR spectra of ZnAl LDH (a) and ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs (b).



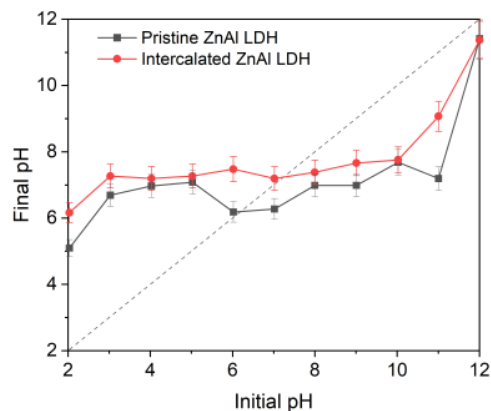
**Figure 3** Nitrogen sorption-desorption on ZnAl (a) and ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs (b).

**Figure 3** shows nitrogen adsorption-desorption isotherm at 77 K on ZnAl and intercalated ZnAl LDHs. Adsorption-desorption of nitrogen on ZnAl and intercalated ZnAl LDHs show type III isotherm adsorption-desorption [25]. There is hysteresis in type III due to slit-shaped pores, and the distribution of pores is not uniform on ZnAl and intercalated ZnAl LDHs. Calculation of these results using the Brunauer-Emmett-Teller (BET) analysis resulted in surface area, pore-volume, and pore diameter of ZnAl and intercalated ZnAl LDHs, as shown in **Table 1**.

**Table 1** Textural Properties of LDHs.

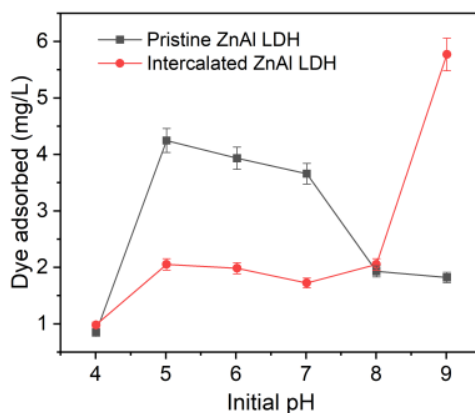
Properties	LDH	
	ZnAl	ZnAl-[ $\alpha$ -SiW <sub>12</sub> O <sub>40</sub> ]
BET Surface Area (m <sup>2</sup> .g <sup>-1</sup> )	1.9685	14.0422
Brunsmuir Surface Area (m <sup>2</sup> .g <sup>-1</sup> )	3.2060	136.5698
BJH Surface Area (m <sup>2</sup> .g <sup>-1</sup> )	0.828	12.321
Total Pore Volume (cm <sup>3</sup> .g <sup>-1</sup> )	0.006651	0.055023
Micropore Volume (cm <sup>3</sup> .g <sup>-1</sup> )	0.002015	0.001713
Average Pore Width (nm)	13.51462	15.67372
BJH Pore Diameter (nm)	27.6876	17.4590

The BET surface area of ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] was increased 7-fold than ZnAl LDHs. The total pore volume of ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] was also increased in 8-fold than ZnAl LDHs. There was an increase in textural properties of ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] after the intercalation process since water and nitrate ions on interlayer space were changed to Keggin ion. Interlayer space increased from 8.59 to 10.65 Å. The opening of interlayer space affects to adsorption capacity expected in this research.



**Figure 4** pH pzc graph (A = intersection; B = ZnAl LDH; C = intercalated ZnAl LDH).

The stability ZnAl and ZnAl intercalated with Keggin ion were identified by determining the pH point 0 charges (pzc), as shown in **Figure 4**. In case ZnAl and intercalated LDHs are used as adsorbents of malachite green, then a charge of material should be identified. **Figure 4** showed that the intersection point was determined at pH 6 for ZnAl LDH and pH 7 for intercalated ZnAl LDH. There are no charges of materials at that intersection points. The materials have positive charges below the intersection point of pH pzc but negative charges above pH pzc point. The effect of pH medium of adsorption malachite green on LDHs was investigated in the range acid, base, and pH pzc, shown in **Figure 5**.



**Figure 5** Effect initial pH on the adsorption of malachite green.

The effect of various pH adsorption of malachite green at the range of pHpzc of ZnAl LDH was decreased slowly to pH 7. The adsorption of malachite green at pH 8 was sharply reduced. Also, the effect of pH malachite green adsorption on intercalated ZnAl LDH was relatively stable around pH 5 - 7



and increased dramatically at base conditions due to the hydroxyl ion. The pHPzc of ZnAl and intercalated ZnAl LDH in stable pH effect and electrostatic force in the range of 5 - 7 had a balance between positive and negative charges. That condition is appropriate for the investigation adsorption process of malachite green of intercalated ZnAl LDH.

Adsorption of malachite green dye on ZnAl LDH and intercalated ZnAl was conducted at pH pzc, expecting that there is no effect of charges on the adsorption. Adsorption of malachite green dye on ZnAl and intercalated ZnAl LDHs was investigated first through the influence of adsorption time, as shown in Figure 6.

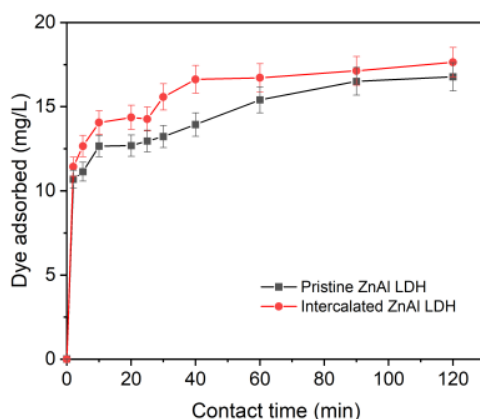


Figure 6 Effect of contact time on the adsorption of malachite green.

Figure 6 showed that the adsorption of malachite green on ZnAl LDH and intercalated ZnAl LDH is quite similar. Adsorption of malachite green on both ZnAl and intercalated ZnAl showed the reactivity of adsorbent on the malachite green. The amount of malachite green adsorbed onto intercalated ZnAl LDH was slightly higher than ZnAl before intercalation. The obtained data were then fitted to the 2 most used kinetic models, namely the pseudo-1<sup>st</sup>-order and pseudo-2<sup>nd</sup>-order model, as displayed in equations 1 and 2. Data in Figure 6 was calculated using pseudo-1<sup>st</sup>-order and 2<sup>nd</sup>-order kinetic model equations to obtain the adsorption parameter, as shown in Table 2.

Table 2 Kinetic adsorption of malachite green on ZnAl and intercalated ZnAl LDH.

Kinetic Adsorption Model	Kinetic Parameter	LDH	
		ZnAl-NO <sub>3</sub>	ZnAl-[ $\alpha$ -SiW <sub>12</sub> O <sub>40</sub> ]
Pseudo 1 <sup>st</sup> Order	Qe <sub>Exp</sub> (mg/g)	16.823	17.853
	Qe <sub>Calc</sub> (mg/g)	7.906	5.403
	R <sup>2</sup>	<b>0.917</b>	<b>0.913</b>
Pseudo 2 <sup>nd</sup> Order	Qe <sub>Exp</sub> (mg/g)	16.823	17.853
	Qe <sub>Calc</sub> (mg/g)	17.321	18.113
	R <sup>2</sup>	<b>0.994</b>	<b>0.998</b>

The kinetic adsorption model for both LDHs is appropriate with pseudo-2<sup>nd</sup>-order kinetic than the 1<sup>st</sup>-order model since the correlation coefficient ( $R^2$ ) for the pseudo-2<sup>nd</sup>-order kinetic adsorption model higher than the pseudo-1<sup>st</sup>-order model. Also, the data shows that intercalated ZnAl LDH has higher reactivity than ZnAl LDH from  $Q_{e_{Exp}}$  values. The main reasons are the opening of the interlayer distance of ZnAl LDH after intercalation with Keggin ion [ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>.

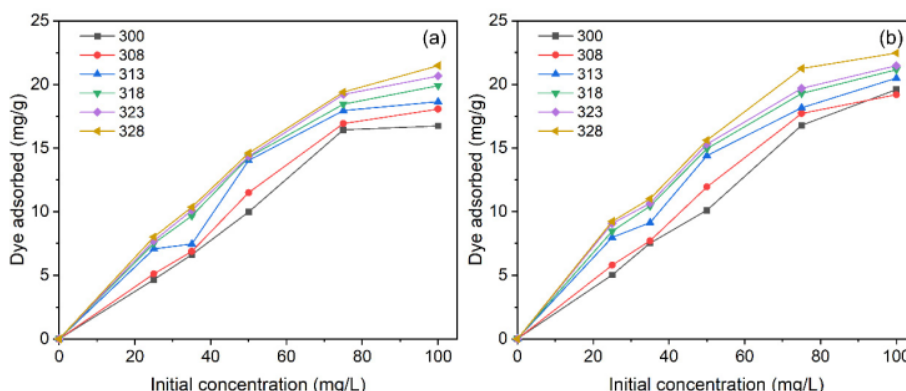


Figure 7 Effect of concentration of dye and temperature.

Data on the effect of malachite green concentration and temperatures are shown in Figure 7. Evidently, raising the concentration and temperature increases the amount of malachite green adsorbed on both ZnAl and intercalated ZnAl LDH. There is an anomaly at concentration malachite green at 30 mg.L<sup>-1</sup>, probably due to physical adsorption of malachite and adsorbate comes to both surface and the interlayer distance of LDH. Isotherm adsorption of malachite green on ZnAl and ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs was obtained from data in Figure 7 using Langmuir and Freundlich equations. Isotherm adsorption of malachite green on LDHs, as shown in Table 3.

Table 3 Isotherm adsorption of malachite green on ZnAl and ZnAl-[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>] LDHs.

	Isotherm	Isotherm parameter	Temperature (K)			
			303	308	313	318
ZnAl LDHs	Langmuir	$q_{max}$ (mg.g <sup>-1</sup> )	30.354	39.654	39.206	32.845
		$k_{ML}$ (L.mg <sup>-1</sup> )	0.010	0.034	0.023	0.044
		$R^2$	0.800	0.608	0.890	0.979
	Freundlich	$k_F$ (mg.g <sup>-1</sup> )(L.mg) <sup>1/n</sup>	0.405	0.192	1.776	2.452
		$n$	1.036	0.774	1.564	1.649
		$R^2$	0.980	0.970	0.908	0.985
ZnAl-[ $\alpha$ -SiW <sub>12</sub> O <sub>40</sub> ] LDHs	Langmuir	$q_{max}$ (mg.g <sup>-1</sup> )	26.254	23.371	27.159	37.514
		$K_{ML}$ (L.mg <sup>-1</sup> )	0.098	0.168	0.134	0.024
		$R^2$	0.985	0.950	0.921	0.984
	Freundlich	$k_F$ (mg.g <sup>-1</sup> ) (L.mg) <sup>1/n</sup>	4.590	6.955	2.712	4.640
		$n$	2.305	3.353	6.266	2.285
		$R^2$	0.986	0.952	0.982	0.987

The data in Table 3 showed that the  $R^2$  value of isotherm Freundlich is better than isotherm Langmuir for all temperature conditions. Multilayer malachite green adsorption phenomena probably occurred on LDHs rather than the monolayer adsorption process. This assertion is in line with data in Figure 7 as the adsorbate at concentration 30 mg. L<sup>-1</sup> starts to adsorb on surface and interlayer distance.

The adsorption capacity of malachite green on both LDHs was evaluated through  $q_{max}$  (mg.g<sup>-1</sup>) value. ZnAl and intercalated ZnAl LDHs have  $q_{max}$  32.845 mg.g<sup>-1</sup> (318K) and 37.514 mg.g<sup>-1</sup> (318K), respectively. These results were higher adsorption capacity than many organic adsorbents, though lower than inorganic adsorbents such as bentonite, as shown in Table 4. The slight increase in adsorption capacity from ZnAl to intercalated ZnAl LDH was equal to the rising surface area properties of these materials.

**Table 4** Adsorption capacities of several adsorbents.

Adsorbent	$q_{max}$ (mg.g <sup>-1</sup> )	Temperature (K)	Ref
Bentonite	178.6	298	[26]
Annona squamosal seed	25.9	300	[27]
Carbon from Arundo donax root	8.69	303	[28]
Modified rice husk	15.49	303	[29]
Marine alga Caulerpa racemose var.cylindracea	19.88	298	[30]
Hen feathers	26.1	303	[31]
ZnAl-NO <sub>3</sub> - ZnAl-[ $\alpha$ -SiW <sub>12</sub> O <sub>40</sub> ]	32.845 - 37.514	318	This work

Then dynamic adsorption was determined to estimate the malachite green adsorption properties on LDHs. Thermodynamic parameters such as Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were calculated according to the following equations [32]. The thermodynamic parameter of malachite green adsorption on LDHs was reported in Table 5.

$$\ln K_{ML} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

$$\Delta G^\circ = -RT \ln K_{ML} \tag{6}$$

where T is the temperature (K); R is the gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>), and  $K_{ML}$  is the modified Langmuir constant. The modified Langmuir constant was obtained, as shown in Table 3.

**Table 5** Thermodynamic parameters for adsorption of malachite green on ZnAl and intercalated ZnAl LDHs.

LDHs	$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )				$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
	303 K	308 K	313 K	318 K		
ZnAl	-3.099	-2.895	-2.691	-2.487	15.476	40.847
ZnAl-[ $\alpha$ -SiW <sub>12</sub> O <sub>40</sub> ]	-2.530	-2.401	-2.281	-2.157	10.074	24.895

Adsorption of malachite green dye on ZnAl and intercalated ZnAl LDHs has  $\Delta H^\circ$  less than 100  $\text{kJ}\cdot\text{mol}^{-1}$ , which reflected its physical adsorption properties on LDHs. The value of  $\Delta H^\circ$  was 15.476  $\text{kJ}\cdot\text{mol}^{-1}$  for ZnAl and 10.074  $\text{kJ}\cdot\text{mol}^{-1}$  for ZnAl- $[\alpha\text{-SiW}_{12}\text{O}_{40}]$ , indicating an endothermic process. Adsorption of malachite green on various adsorbents such as activated carbon, clay materials, and graphene oxide also showed physical adsorption properties similar to previous studies [33,34]. The negative value of  $\Delta G^\circ$  showed that the adsorption process was spontaneous at all temperature conditions. Similarly, the negative value of  $\Delta S^\circ$  showed increased randomness of the adsorption process between malachite green and LDHs.

### Conclusions

Intercalated ZnAl LDHs with  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^+$  were easily prepared using the ion exchange method. ZnAl- $[\alpha\text{-SiW}_{12}\text{O}_{40}]$  LDHs with higher surface area properties showed efficient adsorbent to remove cationic malachite green from aqueous solution up to 32.845  $\text{mg}\cdot\text{g}^{-1}$  (ZnAl LDHs) and 37.514  $\text{mg}\cdot\text{g}^{-1}$  (intercalated ZnAl LDHs). Adsorption of malachite green on both ZnAl and ZnAl- $[\alpha\text{-SiW}_{12}\text{O}_{40}]$  LDHs were classified as physical adsorption with  $\Delta H^\circ$  value in the range 10.074 - 15.476  $\text{kJ}\cdot\text{mol}^{-1}$ . This material is prospective for selective adsorbent of cationic dyes.

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