

## ZnAl-Humic Acid Composite as Adsorbent of Cadmium(II) From Aqueous Solution

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### Abstract

The modified ZnAl composites with humic acid (HA/ZnAl composite) were a coprecipitation method used as an adsorbent to remove cadmium(II) in an aqueous solution. The synthesized material was characterized using SEM-EDX, FTIR, and XRD. From the analysis using XRD, there is a widening peak at an angle of  $2\theta$  ( $24^\circ$ ), FTIR analysis there is a new peak at  $1000\text{ cm}^{-1}$  and  $1220\text{ cm}^{-1}$  and SEM analysis show that there is a change in surface morphology due to more aggregated particles. The experimental results on HA/ZnAl composite followed the PSO model, where the cadmium(II) removal process was chemical adsorption. The adsorption isotherm follows the Langmuir model where adsorption occurs in a monolayer and maximum adsorption capacity was obtained  $38.76\text{ mg/g}$  higher than pristine. Thermodynamics of the adsorption process of cadmium(II) in an aqueous solution occurred spontaneously where  $G < 0$  at all temperatures and endothermic properties were tested. The performance of the HA/ZnAl composite showed that strong potential as an adsorbent of low cost, high efficiency, easy operation, and good reusability. The cadmium(II) was absorbed on the surface of HA/ZnAl composite by surface complexation and chelating interactions, and surface complexation was the main route of cadmium(II) removal. In addition, HA/ZnAl composite has excellent treatment efficiency in actual aqueous solution.

### Keywords

LDH, Humic Acid, Composite, Cadmium(II), Adsorption Performance, Regeneration

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## 1. INTRODUCTION

Heavy metal accumulation is a threatening contaminant in water pollution because of its high toxicity. One of pollution is one of the most severe water pollution issues worldwide because of the high toxicity and easy accumulation of heavy metals. Cadmium(II) (Cd(II)) is one of the heavy metals that has received widespread attention today because of its high activity and is widely used in typical heavy metal elements (Li et al., 2019). There are many ways to remove Cd(II) from aqueous solutions, including adsorption, ion exchange, chemical precipitation, membrane filtration, electrochemical treatment, plant and microbial methods (Zhu et al., 2019). However, those methods have limitations. For example, chemical precipitation, such as chemical precipitation, is generally expensive and environmentally unfriendly because of the amounts of chemical reagents for regulating the pH (Su et al., 2019).

Adsorption is popular because it has the advantages of easy operation, high efficiency, and reusability (Siregar et al., 2021). In addition, the adsorbent has a high potential for water treatment. Activated carbon, zeolite, and silica gel are the adsor-

bents widely used in removing Cd through the adsorption process. However, these materials have several disadvantages, are challenging to modify, and their structure tends to be rigid (Gu et al., 2019). On the other hand, synthetic materials are easier to modify and flexible. This uniqueness makes them interesting to study (Yao et al., 2019).

LDH is a material that can be easily modified (Tichit et al., 2019). LDH is a synthetic anionic clay mineral having the general formula  $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$  where  $M^{2+}$  and  $M^{3+}$  represent divalent metal cations and trivalent metal cations, respectively (Bukhtiyarova, 2019). LDH is a stack of positive layers separated by interlamellar spaces consisting of anions and water molecules (Mishra et al., 2018). Whereas space within the anions has the role of counterbalancing and exchanging species symbolized by  $A^{n-}$ , including nitrate, carbonate, sulfate, organic acid anions, and inorganic anions (Sun et al., 2019). Furthermore, LDH has a large surface area, good ion exchange capacity, layered structure, easy modification, high flexibility, and acid-base properties (Mostafa and Bakr, 2019). However, LDH has several disadvantages,

including peeling off during application and not reusing (Ruan et al., 2016). So it is necessary to improve the structure of LDH in adsorbent applications by using supporting materials that can increase the layer integrity of LDH (Qu et al., 2019). Many researchers have modified LDHs as heavy metal adsorbents in aqueous environments and exhibited great adsorption performance. Adsorbent  $\text{Fe}_3\text{O}_4/\text{MgAl-LDH}$  showed a large adsorption capacity as adsorbent of Pb and Cd metals in an aqueous solution (Sun et al., 2019). Lyu et al. (2019) reported that  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  adsorption using chitosan/MgAl composite produced a maximum adsorption capacity of 33.3 mg/g and 140.8 mg/g in an aqueous solution. Dye adsorption using CuAl/biochar composite, with a maximum capacity of 470.96 mg/g (Palapa et al., 2020).

Humic acid (HA) is a natural and multifunctional macromolecular organic compound consisting of a carbon skeleton with a high aromatic character and having a functional group containing mostly oxygen atoms. The humic acid functional groups have different abilities as ligands in the formation of complexes with metal cations. Extensive sources and low price of HA consider and has been considered as an adsorbent for heavy metals. Recently, HA was included as a support material to increase the surface area of the material (Shi et al., 2020). Moreover, it has a large adsorption capacity and surface area (Yang et al., 2019). Advanced utilization of humic acid (HA) in a structural improvement of materials was reported in LDH composites. This material is used in removing water contaminants through the adsorption method. The materials that can be used for LDH modification are carbon-based, metal oxides, and synthetic polymer materials that can increase the integrity of the adsorbent to a certain extent and limit applications in wastewater treatment (Zhang et al., 2020; Normah et al., 2021). While other materials such as natural polymer materials have various sources, wide varieties, and low cost. Therefore, the modified LDH material as a metal ion adsorbent has a much greater potential than other supporting materials. As promising adsorbent (Basu et al., 2019). Shi et al. (2020) wrote that humic acid/Mg-Al LDH composites as  $\text{Cd}^{2+}$  metal adsorbent resulted in an adsorption capacity of 155.28 mg/g.

ZnAl-LDH was used as a raw material in this paper due to the ability of anionic species to intercalate and there is a large interlayer space (high porosity), the ability of anions to be exchanged between the positively charged layers, and the structural water resistance. However, ZnAl-LDH has a weakness so that it needs to be modified to increase its integrity as an adsorbent (Palapa et al., 2021). This paper will modify LDH by being composited with a carbon-based material, namely humic acid. This paper, synthesize HA/ZnAl composite, was proposed and researched. Considering the wide range of raw material sources and the sample preparation method, it may be a promising adsorbent with broad application prospects for Cd(II) adsorption.

This research aimed to synthesize HA/ZnAl composite explore its adsorption performance. First, I observed the surface properties of HA/ZnAl composite with a series of characteri-

zation methods. Then, the adsorption capacity of HA/ZnAl composite was studied by batch Cd(II) adsorption experiments. In this paper, to see the performance of HA/ZnAl composite adsorbent in absorbing metal Cd(II) in aqueous solution, it will be discussed and investigated in batch adsorption equipment, by covering various conditions such as the effect of pH, time, concentration, adsorption temperature, regeneration and effectiveness of the adsorbent so that it can be reused.

## 2. EXPERIMENTAL SECTION

### 2.1 Material and Instrumentation

The synthesis of materials in this study used HCl (by Merck),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (by Merck) humic acid (by Merck), NaOH (by Sigma Aldrich),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (by Merck),  $\text{CdCl}_2$  (by Merck), 1,10-phenanthroline monohydrate (by Merck), acetate buffer (by Merck), ethanol (by Merck), and acetone (by Merck). In this paper, characterization material using XRD the Rigaku Miniflex-6000 diffractometer, the FTIR analysis using Shimadzu FTIR Prestige-21, and the SEM analysis using SEM Quanta-650 Oxford instrument. Spectrophotometer UV-Visible Biobase BK-UV 1800PC was used to measure the concentration of the solution.

### 2.2 Preparation of ZnAl-LDH and HA/ZnAl Composite

The preparation HA/ZnAl composite was made by developing previous research using the coprecipitation method (Shi et al., 2020). The preparation of ZnAl-LDH was carried out by Karami et al. (2019). The materials used in this synthesis included 10 mL of 0.75 M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 10 mL of 0.25 M  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (3:1) mixed with vigorous stirring for one hour until homogeneous. Then the resulting mixture was added with 1 g of humic acid and then stirred continuously until the solution was homogeneous. Then the mixture was adjusted to pH 10 using a 2 M NaOH solution slowly until a precipitate was formed in the solution. Then the mixture was stored at 65°C for three days. Finally, the composite was washed and dried at 40°C.

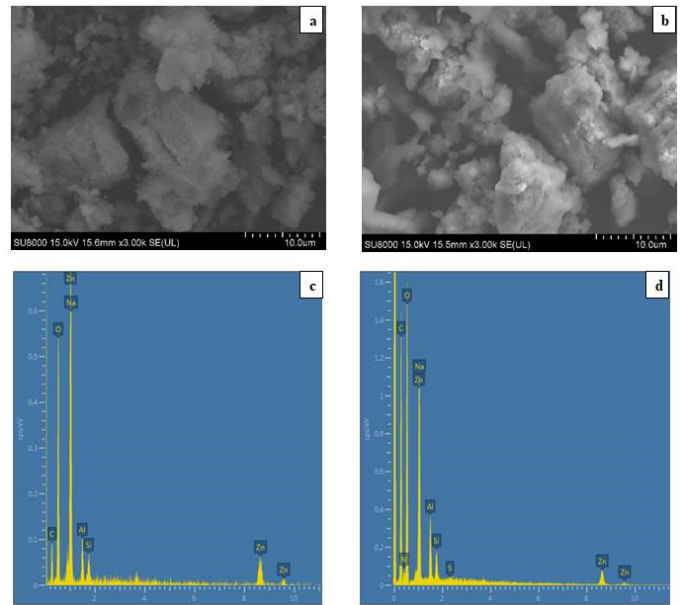
### 2.3 Batch adsorption experiments and Regeneration Study

In this paper, to determine the adsorption performance of ZnAl-LDH and HA/ZnAl composites various experiments need to be carried out. These included making a solution of 1.634 g  $\text{CdCl}_2$  with 1000 mL of water to obtain 1000 mg/L as a Cd(II) stock solution. Standard solutions are prepared by diluting the Cd(II) stock solution. Measurement of the standard curve was carried out by measuring each solution that had been complexed with a 1,10-phenanthroline solution and then measured using a UV-Vis spectrophotometer at the maximum wavelength obtained. A batch system carried out the Cd(II) adsorption in aqueous solutions. The Cd(II) adsorption process was carried out by varying the pH of the initial solution from 2 to 9, contact time from 10 to 200 minutes, initial Cd(II) concentrations of 5 mg/L and 10 mg/L. The thermodynamic parameters are determined by concentration variation of (9, 12, 15, and 20) mg/L, 0.02 g of adsorbent, 20

mL of Cd(II), and temperature variations at 30-60°C. After that, the mixture was centrifuged at a constant stirring speed of 400 rpm then the mixture is filtered. The resulting supernatant was then measured to determine Cd(II) concentration using a UV-Visible spectrophotometer after complexing with 1,10-phenanthroline. The process of regenerating uses the adsorption-desorption process repeatedly in 5 cycles. First, as much as 0.02 g of adsorbent was added 20 mL of Cd(II) with a concentration of 10 mg/L, stirred for 2 hours. The adsorbate residue was measured using a UV-Vis spectrophotometer, and the adsorbent was dried for desorption using water, sodium hydroxide, hydrochloric acid, acetone, and ethanol. Finally, a desorption process was carried out with several solvents to obtain a suitable solvent. In this paper, to determine the adsorption performance of ZnAl-LDH and HA/ZnAl composites various experiments need to be carried out. These included making a solution of 1.634 g CdCl<sub>2</sub> with 1000 mL of water to obtain 1000 mg/L as a Cd(II) stock solution. Standard solutions are prepared by diluting the Cd(II) stock solution. Measurement of the standard curve was carried out by measuring each solution that had been complexed with a 1,10-phenanthroline solution and then measured using a UV-Vis spectrophotometer at the maximum wavelength obtained. A batch system carried out the Cd(II) adsorption in aqueous solutions. The Cd(II) adsorption process was carried out by varying the pH of the initial solution from 2 to 9, contact time from 10 to 200 minutes, initial Cd(II) concentrations of 5 mg/L and 10 mg/L. The thermodynamic parameters are determined by concentration variation of (9, 12, 15, and 20) mg/L, 0.02 g of adsorbent, 20 mL of Cd(II), and temperature variations at 30-60°C. After that, the mixture was centrifuged at a constant stirring speed of 400 rpm then the mixture is filtered. The resulting supernatant was then measured to determine Cd(II) concentration using a UV-Visible spectrophotometer after complexing with 1,10-phenanthroline. The process of regenerating uses the adsorption-desorption process repeatedly in 5 cycles. First, as much as 0.02 g of adsorbent was added 20 mL of Cd(II) with a concentration of 10 mg/L, stirred for 2 hours. The adsorbate residue was measured using a UV-Vis spectrophotometer, and the adsorbent was dried for desorption using water, sodium hydroxide, hydrochloric acid, acetone, and ethanol. Finally, a desorption process was carried out with several solvents to obtain a suitable solvent.

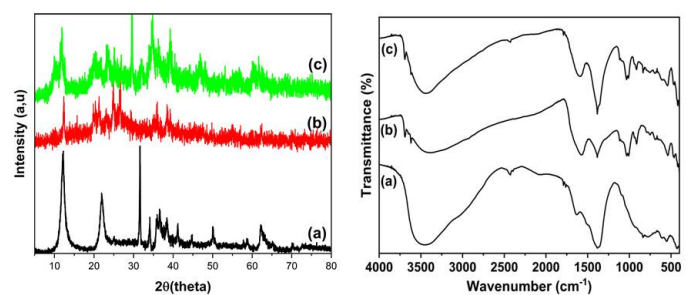
### 3. RESULTS AND DISCUSSION

The structural morphologies of ZnAl-LDH and HA/ZnAl composite were investigated using SEM with a particle size of about 10.00 μm, which had been successfully prepared (Figure 1a and 1b) HA/ZnAl composite Figure had a rougher surface than ZnAl-LDH, Overall, and the composite presented a stacked layered structure with a large amount of debris, and this is due to the presence of humic acid. EDX image (Figure 1c and 1d) of HA/ZnAl composite and the elemental mapping presented shows that the HA/ZnAl composite contains zinc, aluminum, oxygen, carbon, and nitrogen of 13.3%, 6.6%,



**Figure 1.** Morphologies and Compositions of ZnAl-LDH (a,c) and HA/ZnAl Composite (b,d)

46.9%, 24.6%, and 5.8% for ZnAl-LDH pristine the content of zinc, aluminum, oxygen, and carbon were 48.3%, 38.2%, 4.9%, and 4.2% respectively. The mapping images show that oxygen, zing, and aluminum have an excellent correlation due to using the same raw material. The carbon distribution is heterogeneous, with more in the upper left and right sides and less in the middle. According to [Koesnarpadi et al. \(2015\)](#) the effect of foreign carbon may cause this. Nitrogen has a homogeneous distribution and good correlation with other elements, but the overall content was lower. The rough surface and debris may both create new adsorption sites, which increase the adsorption of Cd(II).



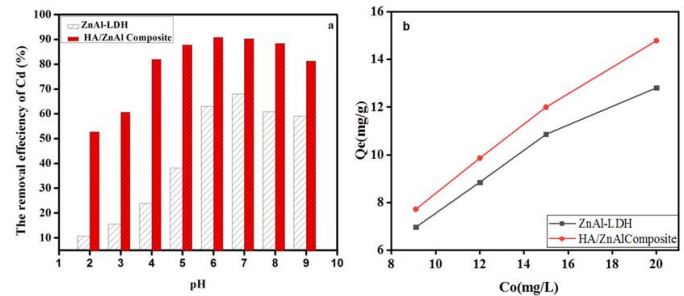
**Figure 2.** XRD Patterns and FTIR Spectra of ZnAl-LDH (a) Humic Acid (b) and HA/ZnAl Composite (c)

The XRD and FTIR characterization of ZnAl-LDH, humic acid, and HA/ZnAl composite was shown in Figure 2. Figure 2a ZnAl-LDH pristine has diffraction peaks at 10.29°, 20.07°, 29.59°, 32.12°, 34.02°, 48.06° and 60.16° that can be indexed to the (003), (006), (101), (012), (015), (107) and

(110) based on the diffraction peaks the formation of the ZnAl material structure is following JCPDS 48-1023 file. Figure 2b shows that the diffraction peaks at  $12.36^\circ$  (001),  $20.01^\circ$  (110),  $24.88^\circ$  (002), and  $26.64^\circ$  (111) are typical peaks of humic acids. According to Abate and Masini (2005) the diffraction peak at  $20-26^\circ$  indicates that the humic acid contains a lot of carbon and oxygen. Figure 2c for HA/ZnAl composite all the diffraction peaks matched well with those of ZnAl-LDH pristine, in Figure 2c the diffraction peak around  $24^\circ$  is the characteristic peak of the HA/ZnAl composite material which has an amorphous diffraction pattern (Shi et al., 2020). This may be related to the addition of modified humic acid. The results of material analysis using FT-IR spectrum are shown in Figure 2. The characteristic peaks of humic acid in the composite were detected around the peaks at  $1000\text{ cm}^{-1}$  and  $1220\text{ cm}^{-1}$  indicating C-O and -COOH groups. According to Shi et al. (2019) the characteristics of humic acids are characterized by the presence of a carboxyl group (-COOH). The band at  $3448.72\text{ cm}^{-1}$  indicated the O-H region extends from the material layer and water molecules between layers. The peak at  $1703\text{ cm}^{-1}$  indicates a COO-carbonyl group, the peak at  $1000\text{ cm}^{-1}$  indicated the C-C group. The characteristic band of the -OH group in the layer and peak of the  $\text{H}_2\text{O}$  bending vibration is  $1637.7\text{ cm}^{-1}$  (Deng et al., 2015). The peak at  $1500-1800\text{ cm}^{-1}$  indicates the COO- group. The peak at  $2088.8\text{ cm}^{-1}$  is the C-O vibration (Sun et al., 2019). The peak of  $1250\text{ cm}^{-1}$  indicated the C-OH group. The peak at  $1117.8\text{ cm}^{-1}$  corresponds to the -COO- vibration and the C-O strain vibration, respectively (Shi et al., 2019). In addition, the bands at  $671.3\text{ cm}^{-1}$  and  $558.8\text{ cm}^{-1}$ , located in the  $450\text{ cm}^{-1}-750\text{ cm}^{-1}$  region, all represent Al-O and Zn-O vibrations. Overall this confirms that humic acid has been successfully loaded into LDH.

### 3.1 Effect of Solution pH and Effect of Initial Concentration

The adsorption process in this paper controls the pH of the solution as the main parameter. Because it can affect the surface charge of the adsorbent and the ionization behavior of the solution. The Cd(II) solution with a concentration of  $5\text{ mg/L}$  for ZnAl-LDH and  $10\text{ mg/L}$  for HA/ZnAl composite where the pH was adjusted with HCl (0.1N) and NaOH (0.1N). In Figure 3a Cd(II) removal increased significantly with increasing pH of the initial solution, Highest adsorption capacity at pH 6.5 for LDH pristine and pH 6 for composites the removal efficiencies can reach up to 68.01% and 90.77% respectively. This may be due to the deprotonation of functional groups in the HA/ZnAl composite through the formation of hydrogen bonds or water bridges, electrostatic interactions or ion exchange, coordination bonds, and chelate ring structures. At low pH, the adsorbed Cd(II) is very small, and a Cd(II)-HA/ZnAl composite complex is formed. This is due to a large number of Cd(II)  $\text{H}^+$  ions in the system causing the composite to tend to be protonated, which results in strong hydrogen bonds between functional groups in protonated composites, both intermolecular (Terdkiatburana et al., 2008). Prevent the adsorption of metal ions on



**Figure 3.** pH Amount of ZnAl and HA/ZnAl Composite (a) Initial Cd(II) Concentration (b)

the composite surface due to electrostatic repulsion between equal charges.

In this paper, the initial concentration of metal ions plays an important role in adsorbent absorption. The effect of initial concentrations of Cd(II) (9, 12, 15, and 20 mg/L) was tested using ZnAl-LDH and HA/ZnAl composite at pH 6.5 and pH 6. Figure 3b The resulting adsorption capacity increased at low concentrations. While the adsorption capacity gradually decreased with increasing Cd(II) concentration. This process indicates that the vacant active sites on both adsorbents are filled at critical concentrations. However, the equilibrium adsorption capacity continued to increase as the Cd(II) concentration increased. the maximum absorption of Cd(II) using ZnAl pristine is  $19.92\text{ mg/g}$  while HA/ZnAl composite is  $21.882\text{ mg/g}$ .

### 3.2 Adsorption Kinetics and Isotherms

The effect of adsorption time on Cd(II) adsorption in aqueous solution using ZnAl-LDH and HA/ZnAl composite was through variations in the contact time of the adsorbate with the adsorbent. A total of  $0.02\text{ g}$  of the sample was added to an erlenmeyer containing  $20\text{ mL}$  of Cd(II) with a concentration of  $5\text{ mg/L}$  for ZnAl-LDH and  $10\text{ mg/L}$  for HA/ZnAl composite whose pH value had been adjusted according to the provisions, with time variation 10-200 minutes. The adsorption ability of all concentrations increased with increasing time from 0 to 120 minutes for the HA/ZnAl composite occurred rapidly in the first stage. while the second stage is slower and tends to equilibrium, this tendency in the early stages, This process occurs because the higher accessibility of the carboxyl group results in many vacant sites for adsorption on the surface of the adsorbent. The optimal equilibrium time was 120 minutes for ZnAl-LDH and 90 minutes for HA/ZnAl composite.

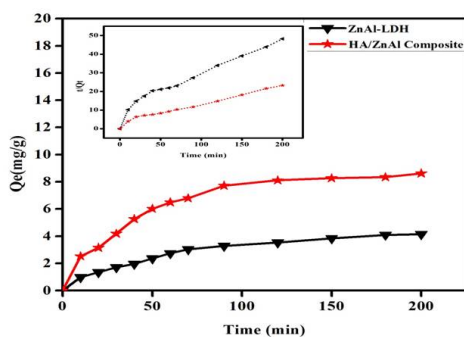
Adsorption kinetics of Cd(II) onto ZnAl-LDH and HA/ZnAl composite was investigated using pseudo-first-order and pseudo-second-order, shown in equations (1) and (2)

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{Q_t} = \left( \frac{1}{k_2 Q_e^2} \right) + \frac{1}{Q_e} t \quad (2)$$

**Table 1.** Parameters Kinetic for Cd(II) Adsorption onto ZnAl-LDH and HA/ZnAl Composite

Kinetics Models	Parameters	Adsorbent	
		ZnAl-LDH	HA/ZnAl Composite
PFO	$Q_{eExp}$ (mg/g)	4.148	8.61
	$Q_{eCalc}$ (mg/g)	4.797	7.509
	$K_1$ ( $min^{-1}$ )	0.021	0.02
	$R^2$	0.928	0.979
PSO	$Q_{eExp}$ (mg/g)	4.148	8.61
	$Q_{eCalc}$ (mg/g)	5.359	10.267
	$K_2$ ( $min^{-1}$ )	0.003	0.002
	$R^2$	0.99	0.994

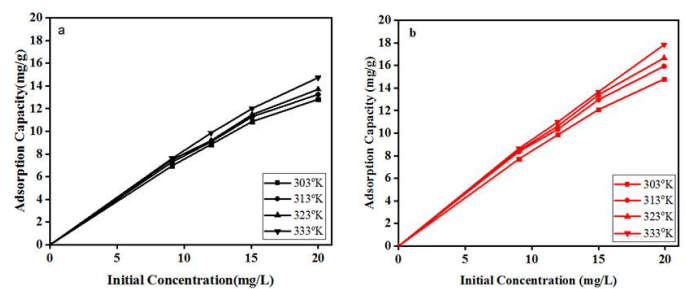


**Figure 4.** Time Adsorption of Cd(II) by ZnAl-LDH and HA/ZnAl Composite

where  $Q_e$  (mg/g) and  $Q_t$  (mg/g) are the adsorption capacity of ZnAl-LDH and HA/ZnAl composite for Cd(II) at equilibrium and time  $t$  (min), respectively;  $k_1$  (1/min) and  $k_2$  (g/mg.min) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

The results of the two-parameter kinetic model are shown in Table 1. both adsorbents provide a larger correlation coefficient ( $R^2$ ) in the pseudo-second-order model compared to the pseudo-first-order model. From the results obtained, the pseudo second order kinetics model is more suitable to describe the adsorption of Cd(II) on ZnAl-LDH and HA/ZnAl-LDH composite. According to Niu et al. (2011) this proves that the rate-limiting step for ZnAl-LDH and HA/ZnAl composite adsorption of Cd(II) is most likely chemical adsorption. In addition, the resulting  $Q_e$  value for the LDH pristine adsorbent is smaller than the  $Q_e$  value for the composite adsorbent, the adsorption process can involve a series of functional groups on the surface of the composite, including hydroxyl groups, carboxyl groups, etc. These results indicate that composite material exhibits a large adsorbent potential compared to LDH pristine.

The isotherm data analysis has shown that the isotherm parameters were calculated using the Langmuir isotherm model, formulated in Equations (3). The hypothesis of the Langmuir



**Figure 5.** Adsorption Isotherm of Cd(II) by using ZnAl-LDH (a) and HA/ZnAl Composite (b)

adsorption model, the adsorbent has several properties, including uniform adsorption sites, monolayer adsorbent surface, and no lateral interactions between the adsorbed molecules.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{3}$$

The equilibrium concentration of Cd(II) and equilibrium adsorption capacity of ZnAl-LDH and HA/ZnAl composite materials are respectively  $C_e$  (mg/L) and  $Q_e$  (mg/g). The maximum adsorption of the Langmuir model is  $Q_m$  (mg/g). Langmuir's constant is  $K_L$  (L/mg). The isotherm fittings parameters are shown in Figure 5 and Table 2. The maximum adsorption capacity of the HA/ZnAl composite increased significantly up to 38.76 mg/g at 60°C. The maximum adsorption capacity of HA/ZnAl composite is higher than LDH pristine. Thus, the HA/ZnAl composite showed high effectiveness in adsorption. This finding confirms that the composite material improves the absorption performance of heavy metals related to the synergistic effect of humic acid which contains many functional groups such as carboxyl and ZnAl-LDH in the composite because of the surface area of the HA/ZnAl composite is higher than LDH pristine.

**Table 2.** Parameters and Coefficient of Langmuir Isotherms Models of Cd(II) Adsorption onto ZnAl-LDH and HA/ZnAl Composite

Adsorbent	Adsorption Isotherm	T (°K)	Adsorption Constant		
			Q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>
ZnAl-LDH	Langmuir	303	19.920	0.259	0.989
		313	19.305	0.344	0.985
		323	19.802	0.353	0.977
		333	22.727	0.349	0.997
HA/ZnAl Composite	Langmuir	303	21.882	0.609	0.998
		313	20.325	0.842	0.969
		323	21.834	0.929	0.964
		333	38.760	0.408	1.000

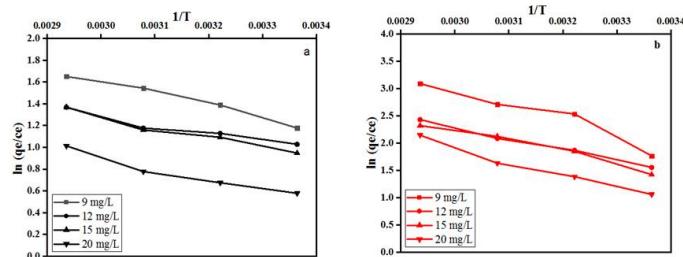
**Table 3.** Thermodynamic Parameters for the Adsorption of Cd(II) onto ZnAl-LDH and HA/ZnAl Composite

T (°K)	Concentration (mg/L)	ΔH(J/mol)	ZnAl-LDH		HA/ZnAl Composite		
			ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH(J/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)
303	20	11.724	0.043	-1.377	29.329	0.105	-2.568
313				-1.81			-3.621
323				-2.242			-4.674
333				-2.675			-5.726

**3.3 Thermodynamic Parameter Adsorption**

Calculation of thermodynamic parameters using the following Van't Hoff equation (4) and (5). The value of enthalpy (ΔH) and entropy (ΔS) can be calculated as the slope and intercept value of 1/T concerning ln Q<sub>e</sub>/C<sub>e</sub> as shown in equation (4).

$$\ln \frac{Q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$



**Figure 6.** Van't Hoff Linearity Equation for the Adsorption of Cd(II) onto ZnAl-LDH (a) and HA/ZnAl Composite (b)

The value of the Gibbs free energy change (ΔG) is calculated from the enthalpy value (ΔH) and entropy (ΔS) is presented in equation (5).

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

Table 3 describes the adsorption process that occurs endothermically, where the adsorption process occurs followed by the capture of heat from the environment to the system, this is indicated by the enthalpy value (ΔH) which is positive. According to Rakić et al. (2015) endothermic process, the adsorbate species displaces more than one water molecule to be adsorbed. The value of ΔH also describes the type of adsorption. The low enthalpy (ΔH) shows that Cd(II) is adsorbed through a physical interaction process (Juleanti et al., 2021). ΔS positive value indicates an increase in randomness on the surface of the adsorbent with the solution during the adsorption process, this is because of the physical bond between the Cd(II) molecule and the active site of the ZnAl-LDH and HA/ZnAl composite decreases with increasing temperature. ΔG negative value indicates that the adsorption process occurs spontaneously by the ZnAl-LDH and HA/ZnAl composite. Overall it can be concluded that the adsorption of Cd(II) is affected by changes in the temperature of the solution.

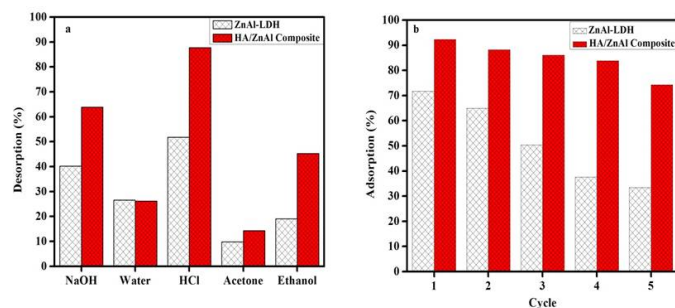
**3.4 Adsorbents Performance**

The most important indicator to evaluating the performance of adsorbent is by carrying out the desorption and reusability process. The adsorbent desorption process was carried out using several eluents for Cd(II) desorption from the ZnAl-LDH and HA/ZnAl composite as shown in Figure 7a. The results obtained that the percentage of desorption in acid solution was as high as possible according to the LDH charge to be positive. However, the electrostatic attraction of the Cd(II)-adsorbent molecules and H-bonds weakened. Based on Pearson's clas-

**Table 4.** Comparison of Cd(II) Adsorption using Several Types of Adsorbents

Adsorbent	Experimental Condition	t/min	Adsorption Capacity (mg/g)	Ref
HA/MgAl-LDH	pH = 5.5	80	155.28	(Shi et al., 2020)
Fe <sub>3</sub> O <sub>4</sub> /Mg-Al-CO	pH = 9.0	300	45.6–54.7	(Shan et al., 2015)
Mg/AlCO <sub>3</sub> -LDH	pH = 4.0	60	61.4–70.2	(Shan et al., 2015)
CQDs/ZnAl-LDH	pH = 6.0	20	12.6	(Rahman et al., 2018)
FeMnMg-LDH	pH = 6.5	250	59.99	(Zhou et al., 2018)
MGO/MgAl-LDH	pH = 6.5	240	45.05	(Huang et al., 2018)
Kiwi Biochar/MgFe-LDH	pH = 6.5	120	25.8	(Tan et al., 2019)
Humic Acid (HA)	pH = 5.0	60	8,8	(Abate and Masini, 2005)
Biochar W/HA	pH = 7.5	30	167.3	(Park et al., 2017)
MRSA/ZnFe-LDH	pH = 8.5	240	70.99	(Moaty et al., 2017)
Chitosan/TiFe-LDH	pH = 8.5	60	98	(Mahmoud et al., 2017)
Co-Fe LDH Nanoparticle	pH = 8.0	360	65-94	(Moaty et al., 2017)
HA/Fe-Mn-OLB	pH = 6.0	720	67.11	(Guo et al., 2019)
ZnAl-LDH	pH = 7.0	120	22.72	This Study
HA/ZnAl Composite	pH = 6.0	90	38.76	This Study

sification of hard-soft electrophile, Cd(II) is categorized as a soft electrophile. Therefore, increasing the number of deprotonated carboxylic groups with increasing pH, which is a weak nucleophile, will lower adsorption power (Liu et al., 2008). In the base condition, the desorption process on the material is also higher due to hydrophobic interactions, and the OH<sup>-</sup> ions formed so that they have a higher affinity for anion exchange to occur.

**Figure 7.** Desorption of Adsorbent (a) and Regeneration of Adsorbent (b)

The results of the regeneration of each adsorbent on the Cd(II) can be seen in Figure 7b. As a similar result of increasing surface area properties after the formation of HA/ZnAl composite, thus adsorption of Cd(II) was higher than starting materials. The effect of the number of additives in this experiment follows the general trend, the greater the number of additives, the higher the adsorption efficiency. Nevertheless, humic acid has a good adsorption effect. This is because humic acid contains many hydrophilic functional groups, such as hydroxyl and carboxylic groups. The presence of this functional group can increase the solubility of humic acid, which increases

the ability of humic acid to adsorb. Therefore, HA/ZnAl composite has good adsorption efficiency due to its large specific surface area. This may be due to the addition of humic acid to create new adsorption sites. According to Rosset et al. (2020) the decrease in adsorption capacity in the regeneration process after repeated cycles, is due to the progressive loss of solid crystallinity during the reconstruction process in layered materials and is caused by the incorporation of residual organic species.

Based on several types of adsorbents that have recently been found to remove Cd(II) in aqueous solutions in recent years and will compare the adsorption capacity with the adsorbents produced in this paper. In Table 4 the adsorption capacity of most of the adsorbents for Cd(II) is between 0 and 150 mg/g. The maximum adsorption capacity of pure ZnAl-LDH was 22.72 mg/g, while the maximum adsorption capacity of HA/ZnAl composite was 38.76 mg/g. Overall, HA/ZnAl composite materials are very promising to be used as heavy metal removal adsorbents in aqueous solutions.

#### 4. CONCLUSIONS

Modification of ZnAl-LDH using humic acid as a support material to improve structural stability and adsorption performance has been successfully carried out using a simple coprecipitation method to remove Cd(II) in an aqueous solution. The characterization results suggest that HA/ZnAl composite by SEM-EDX, XRD, and FTIR has a stacked layered structure, a large specific surface area, and many carbon-containing functional groups and the morphology of HA/ZnAl composite showed heterogeneity with some aggregates of LDH. The surface area characterization of HA/ZnAl composite increased the surface area increase greater than LDH pristine. From the results obtained, highest adsorption capacity at pH 6.5 for LDH pristine and pH 6 for composite the removal efficiencies

can reach up to 68.01% and 90.77% respectively. The kinetic parameters corresponding to PSO dynamics proved that the adsorption process of Cd(II) on HA/ZnAl composite was most likely chemical adsorption. The equilibrium of Cd(II) adsorption using ZnAl pristine was reached at 120 minutes and the equilibrium of the HA/ZnAl composite was reached at 90 minutes. The adsorption isotherm follows the Langmuir model where adsorption occurs in a monolayer and maximum adsorption capacity was obtained 38.76 mg/g higher than pristine. Thermodynamic analysis showed that the adsorption of Cd(II) on ZnAl-LDH and HA/ZnAl composite was a spontaneous and endothermic process. Additionally, Cd(II) was absorbed on the surface of HA/ZnAl composite by surface complexation and chelating interactions, and surface complexation was the main route for Cd(II) removal. The HA/ZnAl composite was high structural stability on the Cd(II) readsorption process until five cycles process. All results illustrated that the prepared HA/ZnAl composite has an excellent adsorption performance and is promising for a potential application.

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