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By Risfidian Mohadi

A Comparative Study on Azo Dyes Removal Behavior to ZnAl and ZnCr LDHs

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Received 30 November 2019; Accepted 31 August 2020

ABSTRACT

The two synthetic anionic clay layered double hydroxides (LDH) consists of Zn²⁺ as M²⁺ cation with different M³⁺ cation, i.e., Al³⁺ and Cr³⁺ were used applied as removal congo red agent in aqueous solution. These materials were characterized and confirmed the successfully of synthesis. The effect of adsorption time, concentration of dye, and various temperature were examined in a batch technique in order to investigate the characteristic of Congo Red adsorption onto both adsorbents. The experimental data were assessed according to the adsorption study of kinetics, isotherm, and thermodynamics. The results of LDH characterization showed that the interlayer of Zn-Al LDH higher than Zn-Cr LDH, although Zn-Cr LDH has a higher surface area. The results of FT-IR spectrum indicated the interlayer space of both materials was dominated by CO₃²⁻ as the interlayer anion species. The adsorption kinetics study of Congo Red on both materials represented that the adsorption process follows PSO and the adsorption isotherm, the experimental data fit well with the Freundlich model. Moreover, based on the thermodynamic parameter, the adsorption process that occurred on both adsorbents was spontaneous with exothermic nature.

Keywords: adsorption, Congo Red, layered double hydroxide, adsorption, kinetic and thermodynamic study.

INTRODUCTION

Industrial effluent causes various kinds of environmental pollution that were considered as the ecological problem by producing a hazardous substance to the surrounding environment [1]. The textile industry is an industry that commonly used synthetic dye in a considerable amount. Annually, around 7 x 10⁵ tons of synthetic dyes produced to supply the industrial need where most of them used in the fabric. However, due to the deficiency of production capability, it was reported that approximately 10-15% of dyes released as effluent during the dyeing process [2]. Once discarded to the environment without appropriate handling, the dye effluent reduces the penetration of the day sunlight into the depleted dissolved oxygen zone and disrupt the life of the aquatic biota. Furthermore, the dyes molecule consists of a highly complex organic molecule that hardly degraded readily. Even though they can be degraded, they can produce a highly toxic substance as the degradation product.

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The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

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Many works have been done and reported in the case of hazardous substance treatment and removal [3]. Separation methods including flocculation, coagulation, oxidation, reverse osmosis, solvent extraction, microbial degradation, and adsorption, are the most studied method in dye removal [4]. Among them, adsorption is recognized as one of the most attractive methods due to its simple, low-cost, and operational ease [5]. Nowadays, various commercial adsorbents have been produced and developed such as zeolite, graphene, activated carbon, silica gel, alumina, chitosan, bentonite, etc. [6]. However, in order to increase the adsorption efficiency, researches continuously investigate and develop an alternative material that has high adsorption capacity.

Layered double hydroxide (LDH) are a well-known as anionic-synthetic clay material which has a layered structure [7]. Recently, LDH has gained significant attention and consideration owing to its high anion exchange property, composition flexibility, and high surface area. Moreover, LDH is relatively easy to be synthesized and has broad species composition [4]. Basically, LDH is a hydrotalcite-like mineral in which its structure comprises of brucite-like layer and exchangeable anions located in the basal spacing of layered material. The brucite-like layer of LDH has a positive charged due to the isomorphous substitution of the coexisting trivalent and divalent cation in the octahedral sheet. The general form of LDH is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]X^{n-}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are bivalent and trivalent metal cations, and A^{n-} is anion on basal spacing of n valence. The anion that commonly found in the interlayer space of LDH including CO_3^{2-} , NO_3^- , Cl^- , and SO_4^{2-} [8].

In this work, we have synthesized two kinds of layered double hydroxides that consist of Zn as M^{2+} metal cation and different M^{3+} cation, i.e., Al and Cr. Both Zn-Al and Zn-Cr LDH were prepared using the facile coprecipitation method. The effect of different M^{3+} metal cation to the properties of LDH was investigated through the X-ray diffraction analysis, FTIR and also surface area analysis. For further study, we employed both LDH for removal of Congo Red dye from aqueous solution. We compared the adsorption capacity of both material as the effect of the different M^{3+} metal cations.

EXPERIMENT

Chemicals and instrumentation

Chemicals were used after purchased from Merck such as zinc nitrate, chromium nitrate, aluminum nitrate and from Sigma Aldrich such as sodium hydroxide. X-ray powder analysis was performed using X-ray Diffractometer Lab-X type 6000 with $Cu-K\alpha$ radiation and 1 deg. min^{-1} scanning speed from 0° to 80° . IR spectrum was conducted using FTIR Shimadzu Prestige-21 by KBr disk, and the spectrum was recorded at $400-4000 \text{ cm}^{-1}$. BET analysis was performed using nitrogen adsorption-desorption on the Micromeritic apparatus system. The sample was degassed at 77 K for 12 hours following with automatic measurement. Analysis of Congo Red was conducted using the UV-Vis spectrophotometer EMC-61PC series.

Preparation of layered material

Zn/Al and Zn/Cr LDH were prepared using nitrate salt of metals by the precipitation treatment by adjusting pH 10. The solution of M^{2+} and M^{3+} (3:1) ratio molar was mixed and stirred slowly. A solution of 10 mL sodium hydroxide 2 M was added slowly during the stirring process to form a stable suspension. The pH of mixtures was adjusted to 10 by adding sodium hydroxide 0.1 M. Reaction was stirred in 24 hours then wash and dried. LDH was characterization using X-Ray analysis, FTIR spectroscopy, and BET analysis.

Study of dye removal

Adsorption of CR was investigated through variation of adsorption time, concentration of dye, and various temperature. Adsorption time of CR on LDH was adjusted at 10-100 minutes on 25 mg/L of CR. The initial concentration of CR was studied using 5-30 mg/L of CR at 90 minutes adsorption time. Investigation of adsorption temperature was conducted at 30-70 °C. Analysis of dye adsorption was conducted using a UV-Vis spectrophotometer. The amount of dye uptake at various time (q_t); at equilibrium state (q_e) was calculated by:

$$q_t = \frac{(C_o - C_t)}{w} \cdot V \quad (1)$$

$$q_e = \frac{(C_o - C_e)}{w} \cdot V \quad (2)$$

Where C_o is CR concentration (mg/L), C_t is the final dye concentration after t adsorption (mg/L), C_e is the remaining dye concentration at equilibrium state (mg/L), w is the amount of adsorbent (g), and V is the volume of dye solution (L).

RESULT AND DISCUSSION

Zn-Al and Zn-Cr LDH have been synthesized and the products were characterized using XRD with Co-K α radiation. The XRD pattern of Zn-Al and Zn-Cr LDH are presented in Figure 1. As can be seen in Figure 1(A), the sharp and symmetrical peak of Zn-Al LDH indicated that the synthesized material has good crystallinity. The typical characteristic of LDH material as (003) and (006) basal reflection were recorded at the low 2θ angel [9]. Moreover, the other characteristic reflection peaks of LDH, (110) and (113), were appeared at 2θ angel around 60° to 65°. All these typical characteristic peaks of LDH also recorded on the XRD pattern of the Zn-Cr LDH as presented in Figure 1(B). According to these findings, it can be deduced that the synthesized materials have the basic structure and framework of layered double hydroxide material.

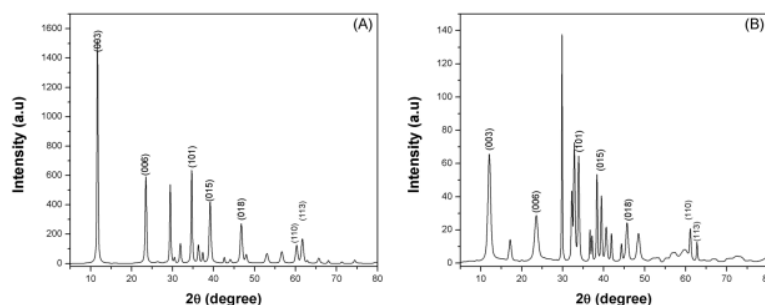


Figure 1. X-ray diffraction pattern of (A) Zn-Al LDH and (B) Zn-Cr LDH

The lattice parameters of a and c rhombohedral can be determined from the results of LDH diffractogram. Where a is the gap between the adjacent cation within the brucite-like layer, in which the value could be calculated as $2d(110)$. In addition, the c value can be calculated as $3d(003) = 3c'$, where c' is the thickness of the brucite and interlayer. For the brucite-like sheet, the distance between the two adjacent oxygen atoms is 2Å [9]. Hence, the interlayer space of the LDH structure can be calculated as the value of c' minus 2Å . The lattice parameters of LDH are summarized in Table 1. According to the basal spacing, the

larger of basal spacing denotes that Zn-Al LDH has larger interlayer spacing rather than Zn-Cr LDH. Moreover, the obtained value of the lattice parameter a and c indicated that CO_3^{2-} is the main constituent of the interlayer anion [10].

The slightly different of a value between Zn-Al and Zn-Cr LDH can be contributed to the trivalent metal radii from LDH, in which Cr^{3+} (0.61 nm) has ionic radii larger than Al^{3+} (0.51 nm). Consequently, the distance between Zn^{2+} and Cr^{3+} is larger than the distance between Zn^{2+} and Al^{3+} , and Zn-Cr has higher a value than Zn-Al.

Table 1. XRD indexing of Zn-Al and Zn-Cr LDH

Materials	Parameter (Å)			a	c	Interlayer spacing
	$d(003)$	$d(006)$	$d(110)$			
Zn-Al LDH	7.589	3.792	1.505	3.010	22.768	5.589
Zn-Cr LDH	7.336	3.781	1.517	3.034	22.009	5.336

FT-IR and surface area analyses

FT-IR spectrum of Zn-Al and Zn-Cr LDH are presented in Figure 2. The spectra of both LDHs showed several absorption bands in the fingerprint region under 1000 cm^{-1} , in which these bands were assigned as the M-O vibration band. Although with different intensity, both Zn-Al and Zn-Cr LDHs have the same vibration band properties at 1381 cm^{-1} and shoulder at 1450 cm^{-1} . According to Hirata, et al. [11], and Mohapatra and Parida [1], the presence of a vibration band around 1381 cm^{-1} can be assigned as the ν_3 band of CO_3^{2-} anion. This finding agrees with the result of XRD analysis that the interlayer space of the synthesized LDHs is mainly contained by CO_3^{2-} anion. The broad vibration band recorded at 3448 cm^{-1} for both LDHs spectra correspond to the $\nu_3\text{ O-H}_{\text{sym}}$ stretching band of M-OH located in layer or lamellae structure and structural water molecule in the interlayer space [12].

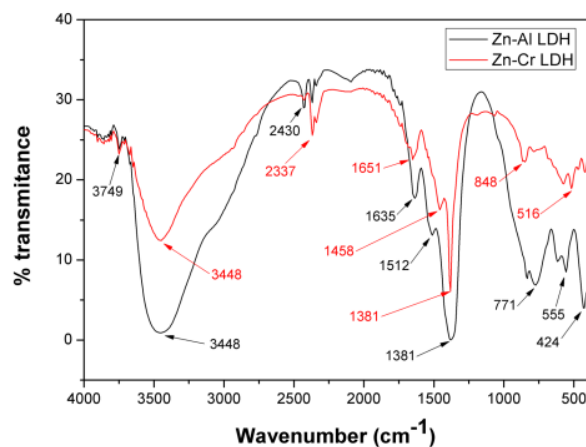


Figure 2. FT-IR spectra of synthesized Zn-Al and Zn-Cr LDH

Surface area analysis

N_2 adsorption-desorption isotherm were calculated to obtained the surface area and pore size distribution of materials. The surface area and pore properties of these materials are

presented in Table 2. The obtained data showed that Zn-Cr LDH has a higher value of the surface area. Moreover, the Zn-Al LDH has a larger pore size compared to the Zn-Cr LDH. This finding indicated the result of the XRD analysis in which Zn-Al LDH has higher interlayer space distance. As reported by [13], the adsorption behavior of hydrotalcite material cannot only attributed to its surface active sites but also its memory effect properties.

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Table 2. Surface area properties of Zn/Al and Zn/Cr LDH

LDH	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Zn-Al	9.41	0.045	19.274
Zn-Cr	118.95	0.112	3.771

Congo Red Adsorption Study Adsorption isotherm

The adsorption isotherm model can be investigated from the obtained experimental data obtained at the equilibrium state with different adsorption capacity (q_e) and concentration (C_e) [14]. In this case, the experimental data were obtained from studying the effect of dye concentration toward the LDH's adsorption capacity. Recently, the two most investigated the isotherm model, i.e., Langmuir and Freundlich model, in order to illustrate and presents the data. Whether both models are appropriate to the adsorption equilibrium data was judged from the value of the correlation coefficients (R^2) of their linear equation. The equation of the Langmuir is written as [15].

$$\frac{C_e}{q_e} = \frac{1}{q_L \cdot K_L} + \left(\frac{1}{q_L}\right) \cdot C_e \quad (3)$$

Where q_L is the maximum uptake of CR, according to Langmuir model (mg/g) and K_L is constant of the Langmuir model (l/mg).

The Freundlich was studied according to its well-known logarithmic form as follows [16].

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \cdot \ln C_e \quad (4)$$

Where both K_f and $\frac{1}{n}$ is the constant of the Freundlich model, in which K_f refers to the amount of adsorbed and $\frac{1}{n}$ related to how far the adsorption process was favorable. If the $1/n$ value in 0-1 indicated the heterogeneity of the surface and the more it closer to zero, the more its heterogeneity.

The adsorption isotherm data extracted from the plot of both the isotherm models are listed in Table 3. From the obtained data, it can be seen that the adsorption of CR on both adsorbent more fit to the Freundlich rather than the Langmuir. This opinion refers to R^2 value of each model. Freundlich model gave higher R^2 value in all the adsorbent than the Langmuir model. The value of $1/n$ can be concluded that the Zn-Cr LDH has better surface homogeneity since its value is closer to unity than Zn-Al LDH.

Table 3. Isotherm parameter results of CR adsorption LDH

Adsorbent	Langmuir	Freundlich
Zn-Cr LDH	q_m (mg/g)	36.900
	kL (L/mg)	0.118
	R^2	0.793
Zn-Al LDH	q_m (mg/g)	48.978
	kL (L/mg)	0.053
	R^2	0.184

Adsorption kinetics

The influence of adsorption time toward the adsorption capacity of CR on both Zn-Al and Zn-Cr LDH was examined. The experiments of adsorption were set in different contact time ranging from 0 to 100 min, and the result is presented in Figure 3. The data explained in the figure, the adsorption rapidly occurred in the first 30 min and then slower after than until it reached equilibrium for around 100 min. This phenomenon occurred due to at the beginning, the availability of free active sites of the adsorbent is high. By the adsorption time increased, the active site of the adsorbent gradually occupied and the adsorption rate decreased [17].

The adsorption kinetics was studied in order to explain the uptake of dye by varying contact time and to investigate the required time to reach the adsorption equilibrium. By studying the adsorption kinetics, the potential rate-controlling steps involved during the adsorption process can be identified. In this work, we employed two well-known adsorption kinetics model, pseudo-first-order (PFO) and pseudo-second-order (PSO), to the obtained experimental data. Both adsorption kinetics model can be written as their linear form as follow, respectively.

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (6)$$

Where K_1 adsorption rate constant of the PFO model (1/min) and K_2 is the adsorption rate constant related to the PSO model (g/mg min).

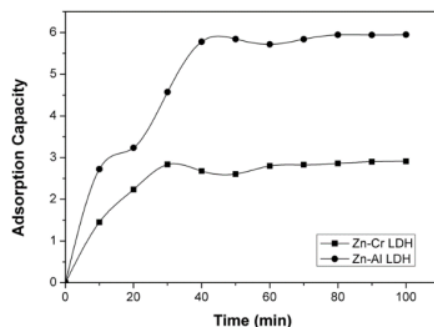


Figure 3. Effect of adsorption time toward the adsorption capacity of CR on Zn-Al and Zn-Cr LDH.

The results of the kinetics parameter and the regression (R^2) according to the PFO and PSO model are calculated in Table 4. It can be shown that the R^2 value for the PSO model is higher than the PFO model at both Zn-Al and Zn-Cr LDH. Moreover, the value of the q_e calculation value for the PSO was in good agreement and closer with q_e experimental value. By this finding, it can be showed that the PSO model is preferable for describing the experimental data of Congo Red adsorption on both Zn-Al and Zn-Cr LDH.

Table 4. Adsorption kinetics parameter of Congo Red on Zn-Cr and Zn-Al LDH

Kinetics Model	Parameter	Zn/Cr	Zn/Al
Pseudo First Order	q_e experiment (mg/g)	2.912	5.946
	q_e calculation (mg/g)	1.402	10.472
	K_1 (min ⁻¹)	0.045	0.825
	R^2	0.757	0.871
Pseudo Second Order	q_e experiment (mg/g)	2.912	5.946
	q_e calculation (mg/g)	3.169	7.299
	K_2 (min ⁻¹)	0.037	0.008
	R^2	0.995	0.977

Adsorption thermodynamic

The adsorption thermodynamics is essential in order to investigate the changes of the energy as the results of the dye adsorption onto the adsorbent surface. The three most-common thermodynamic parameters, i.e., the changed of Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), have been employed to investigate the effect of temperature on the adsorption process. The change of free energy followed the adsorption process is related to the constant of the Langmuir (K_L), as shown in the following equation. Where R is the gas constant, and T is absolute temperature (K).

$$\Delta G^0 = -RT \ln K_L \quad (7)$$

$$K_L = \frac{\theta_e}{(1-\theta_e)C_e}, \theta_e = \frac{q_e}{q_{\max}} \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

The thermodynamic parameter of ΔH^0 and ΔS^0 were calculated as the a and b value of the Van'Hoff linear equation. The thermodynamic parameters of ΔG^0 , ΔH^0 , and ΔS^0 involved in this work are listed in Table 5. The obtained data showed that the adsorption of CR on both Zn-Al LDH and Zn-Cr LDH has exothermic nature since the values of ΔH^0 were negative. Moreover, the parameter of ΔS^0 of both adsorbents were positive. This finding denoted that due to process of adsorption, the randomness at the interaction of sorbate-sorbent was increasing [18]. For the changes of the Gibbs free energy, from Table 5 can be seen that the values of ΔG^0 were negative in all temperature range. This result revealed that the adsorption of Congo Red on the both adsorbents was a spontaneous process. Moreover, the negative

value of ΔG° increase by increasing the adsorption temperature, in which it denoted that the adsorption process is more agreement conducted in high temperature.

Table 5. Thermodynamic parameter for adsorption of Congo Red on Zn-Al and Zn-Cr LDH

Materials	ΔG° (J/mol)			ΔH°	ΔS°	R^2
	303 K	313 K	323 K			
Zn-Al LDH	-82187.66	-83492.56	-84797.46	-42649.30	130.48	
Zn-Cr LDH	-14542.86	-14710.27	-14877.69	-9470.34	16.74	

CONCLUSION

We have synthesized Zn based layered double hydroxides (LDH) with different M^{3+} cation, i.e., Al and Cr. The characterization result showed that the different sizes of M^{3+} cation influencing the distance of the interlayer space of the LDH product. In this work, we found that Zn-Al LDH has higher basal spacing distance rather than Zn-Cr LDH since the Al^{3+} has higher ionic radii than the Cr^{3+} . Although it has a higher surface area, Zn-Cr LDH has less adsorption capacity toward Congo Red dye in aqueous solution. In this case, we assumed that the adsorption process is highly influenced by the ion exchange since LDH has a unique characteristic of memory effect.

CONFLICT OF INTERESTS

Authors declare that there is no competing interest.

ACKNOWLEDGMENT

The authors profound acknowledge RISTEK DIKTI through Hibah PDUPT (fiscal year 2019) to A.L under contract no. 0060.05/UN9/SB3.LP2M.PT/2019 for financially supporting this research

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