

C.1.c.3.3-Citrate-ZnAl Layered Double Hydroxide as Adsorbent of Congo Red from Aqueous Solution.pdf

By Risfidian Mohadi

Citrate-Zn/Al Layered Double Hydroxide as Adsorbent of Congo Red from Aqueous Solution

Nurlisa Hidayati ¹, Neza Rahayu Palapa ¹, Bakri Rio Rahayu ¹, Risfidian Mohadi ^{1,2}, Elfita ¹
and Aldes Lesbani ^{1,2,3,*}

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia

² Research Center of Inorganic Materials and Coordination Complexes, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia

³ Graduate School of Mathematics and Natural Sciences, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia

Abstract: Layered double hydroxide (LDH) of Zn/Al and citrate-Zn/Al was prepared and used as an adsorbent of Congo red from aqueous solution. LDH was characterized by X-ray, FTIR, and BET analysis. Adsorption of Congo red was studied through kinetic, isotherm, and thermodynamic analyses. Zn/Al LDH has diffraction at 10.29° (003) with interlayer distance 8.59 Å and citrate-Zn/Al LDHs have anomalous diffraction at 7.57° (003) with interlayer distance 11.68 Å. The surface area of citrate-Zn/Al (40.50 m² g⁻¹) has higher than pristine LDH (1.97 m² g⁻¹). Adsorption of Congo red was conducted at pH 6 for Zn/Al LDH and at pH 8 for citrate-Zn/Al LDH. Adsorption of Congo red on both LDHs follows the pseudo-second-order kinetic model. The isotherm parameter follows the Freundlich isotherm model with maximum adsorption capacity 166.67 mg g⁻¹ for Zn/Al and 249.99 mg g⁻¹ for citrate-Zn/Al LDH. Adsorption of Congo red on both LDHs was classified as physical adsorption with energy 4.085-4.148 kJ mol⁻¹.

Keywords: citric acid, layered double hydroxide, Zn/Al, adsorption, Congo red.

1. Introduction

The use of dyes in the industrial process such as painting, film, textile, plastic, pigment, and so on is sharply increased. It causes an environmental problem due to the undegradable properties of dyes. Various methods have been applied to remove stains from an aqueous solution such as adsorption ^{1,2}, precipitation ³, filtration ⁴, coagulation ⁵, membrane ⁶, ... Among these methods, adsorption is a suitable method to remove dyes due to the easy way, simple process, and also low-cost process ^{7,8}. The efficiency of the adsorption process depends on the properties of adsorbent.

Wide range organic and inorganic adsorbent has been used to reduce dyes from an aqueous solution such as chitin, chitosan ⁹, cellulose ¹⁰, bentonite ¹¹, kaolin ¹², clay ¹³, carbon nanotube ¹⁴, zeolite ¹⁵, and also layered double hydroxide (LDH) ¹⁶⁻¹⁸. LDH is inorganic layer material with the general formula [M²⁺/M³⁺(OH)₆]ⁿ⁺[Aⁿ⁻]ⁿ⁻·mH₂O where M²⁺/M³⁺ is divalent and trivalent metal ions, from stacking brucite-like layers metal oxide containing a positive charge due to partial substitution of divalent metal cation by trivalent metal cation ¹⁹. The negative charge is represented by

anions located in the interlamellar spaces. Interlamellar space is also known as interlayer, can exchange species Aⁿ⁻ to other anions ²⁰. The interlayer can be expanded to an adapted wide range of interlayer anion. Therefore, Aⁿ⁻ can be exchangeable with inorganic or organic anionic compounds, such as polyoxometalate ²¹⁻²², halide ²³, nitrate, phosphate, carbonate ²⁴, and also EDTA ²⁵.

The LDH showed the efficient material as adsorbent of anionic and cationic of dyes such as Congo red ²⁶, safranin ²⁷, indigo carmin ²⁸, crystal violet and malachite green ²⁹, and also methylene blue ³⁰. LDH M²⁺/M³⁺ (M²⁺ = Zn), M³⁺ = Al, ⁴, Cr) were used as adsorbent of direct violet follow pseudo-second-order kinetic adsorption model rather than pseudo-first-order model ³¹. Zn/Cr LDH was also used as an efficient adsorbent of Congo red and direct yellow dyes, which were an anionic dyes ³². Based on these results, the use of LDH as an efficient adsorbent of dyes is the priority. On the other hand, modification of LDH by intercalation with anion onto interlayer distance has been conducted to increase interlayer distance and surface area properties of LDH. Zn/Cr LDH has been intercalated with [α-SiW₁₂O₄₀]⁴⁻ to

*Corresponding author: Aldes Lesbani

Email address: aldeslesbani@pps.unsri.ac.id

DOI: <http://dx.doi.org/10.13171/mjc02003131281al>

Received December 23, 2019

Accepted January 2, 2020

Published December 13, 2020

form Zn/Cr-[α -SiW₁₂O₄₀] by substitution of Keggin type polyoxometalate to nitrate ion of Zn/Cr LDH resulted increasing the surface area from 31.638 m²/g to 128.871 m²/g after intercalation process³³. This material after intercalation was effective as inorganic adsorbent. Organic anions such as citrate and malate have been applied as intercalant of Mg/Al LDH and show efficient as an adsorbent for removal lead and copper³⁴.

In this research, Zn/Al LDH was intercalated with citrate ion to increase both interlayer distance and surface area properties of LDH. The material was used as an adsorbent for Congo red from water. The effect of various conditions, including pH, time, initial concentration, and temperature adsorption were investigated in batch adsorption apparatus. Kinetic, isotherm, and thermodynamic adsorption of Congo red on citrate-Zn/Al LDH was discussed in this article. The structure of Congo red was shown in Figure 1.

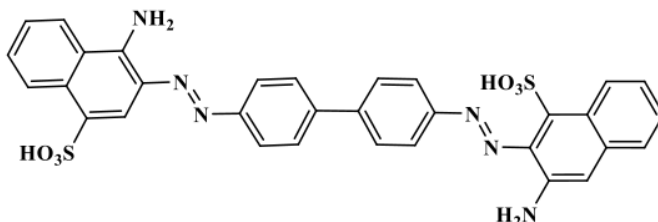


Figure 1. Structure of Congo Red

2. Experimental Section

2.1. Chemicals and Instrumentations

Chemicals were supplied from Merck and Sigma Aldrich, such as zinc nitrate, aluminum nitrate, sodium hydroxide, hydrochloric acid, sodium carbonate, citric acid, and Congo red. These reagents were used directly after purchased without further purification. Water was obtained from the water purification Purite® water purification system equipped with an ion-exchange system at Universitas Sriwijaya. X-ray analysis was conducted using XRD powder Rigaku Miniflex-6000. The sample was homogenized using a mortar and scanned at 3° min⁻¹. FTIR spectra were recorded using Shimadzu FTIR Prestige-21 by KBr method. The sample was examined at wavenumber 400-4000 cm⁻¹. Surface area analysis was measured using a Quantachrome instrument at 77K. Congo red dye was analyzed using spectrophotometer UV-Vis BioBase BK-UV 1800 PC at wavelength 497 nm.

2.2. Preparation of Zn/Al and Intercalated Citric Acid Zn/Al Layered Double Hydroxides

Zn/Al LDH was synthesized using the coprecipitation method at pH 10³⁵. The solution of zinc nitrate (0.3 M, 100 mL) and aluminum nitrate (0.1 M, 100 mL) was mixed under constant stirring. The mixture of sodium hydroxide (1 M, 50 mL) and sodium carbonate (1 M, 50 mL) was added into the mixture, and the pH of the solution mixture was adjusted to 10 by adding sodium hydroxide. The reaction was performed overnight to form a white solid material. The solid material was washed with water and dried at 110°C for 24 hours.

Citric acid-Zn/Al LDH was prepared using the gel method under nitrogen conditions. A citric acid

solution (4 g in 250 mL water) was added to a gel form of Zn/Al LDH. The reaction mixture was stirred at 60°C for 1 hour, pH was adjusted to 10 by adding sodium hydroxide solution then the reaction was kept with constant stirring for 24 hours to form citrate-Zn/Al LDH.

2.3. pH pzc determination³⁶

The pH at the point zero charge of materials was conducted using 0.05 g adsorbents added into 50 mL the solution of sodium chloride 0.1 M under various pH conditions using hydrochloric acid or sodium hydroxide solution. The solution of sodium chloride 0.1 M was adjusted to pH in the range 1-10 by addition hydrochloric acid 0.1 M of sodium hydroxide 0.1 M solutions. The material of Zn/Al and citric acid-Zn/Al LDH was added into the series of pH solution, and then the solution mixtures were stirred continuously for 24 hours. The solutions were filtered, and pH of the filtrate was determined by pH meter. The graph of pH pzc was obtained by comparison initial and final pH solution.

2.4. Study Mixture adsorption

Adsorption of dye using Zn/Al and citrate-Zn/Al LDHs was firstly investigated through mixtures dyes adsorption. Congo red, methyl orange and malachite green were mixed to determine the adsorption competition of dyes. The dyes mixtures were conducted at the acid and base condition. Congo red and methyl orange were anionic dyes, whereas malachite green was cationic dye. The time of adsorption was varied from 5 to 120 minutes. The filtrate was scanned using UV-Vis spectrophotometer in the range 400-700 nm.

2.5. Adsorption of Congo Red

Adsorption of Congo red with Zn/Al and citrate-Zn/Al LDHs was carried out using a batch small reactor system. Adsorption was studied through the effect of adsorption time, the effect of Congo red concentration, and adsorption temperature. Effect of adsorption time was investigated at various adsorption time i.e. 5, 10, 15, 20, 30, 50, 70, 90, 120,

150, 180 minutes. The effect of Congo red concentration was varied at 40, 60, 80 mg L⁻¹ and at temperature 303, 313, 323, 333 K. Concentration of Congo red after adsorption process was analyzed using UV-vis spectrophotometer at 497 nm.

3. Results and Discussion

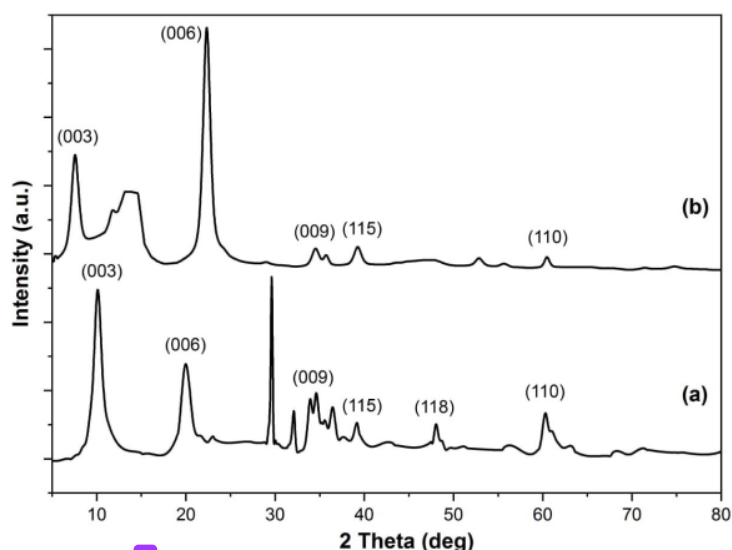


Figure 2. XRD powder patterns of Zn/Al (a) and citrate-Zn/Al (b) LDHs

The XRD powder patterns of Zn/Al and citrate-Zn/Al LDHs are shown in Figure 2. Zn/Al LDH has diffraction peak at 10.29°(003), 20.07°(006), 31.50°(009), 39.60°(115), 48.95°(118), and 60.20°(110). The diffraction peak at 31.50° indicates the formation of carbonate on the interlayer distance of Zn/Al LDH. The formation of a well-ordered layer structure was identified at 10.29° and 60.20° with an interlayer distance of 8.59 Å at diffraction 10.29° (003). The intercalation of Zn/Al LDH with citric acid has slightly changed the

diffraction peaks. The crystallinity of material after the intercalation process was decreased, as indicated by the formation of a diffraction peak at 15°. The diffraction of (003) was shifted to 7.56° with interlayer distance 11.68 Å. Other peaks were detected at 24.35°(006), 34.50°(009), 39.89°(115), 60.42°(110). The interlayer distance of Zn/Al LDH was expanded because of the insertion of citrate ion. The citric acid size is approximately 7.2 Å thus citrate ion was inserted as slanted orientation as illustrated in Figure 3.

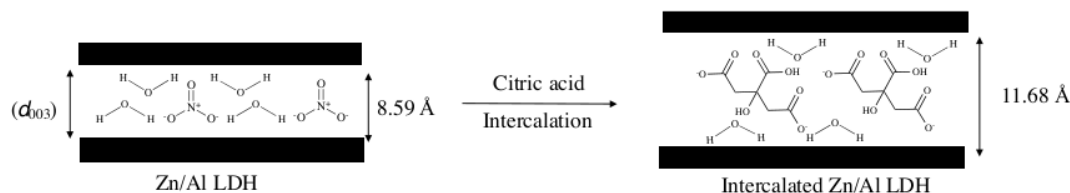


Figure 3. Structure of LDH and intercalated with citrate ion.

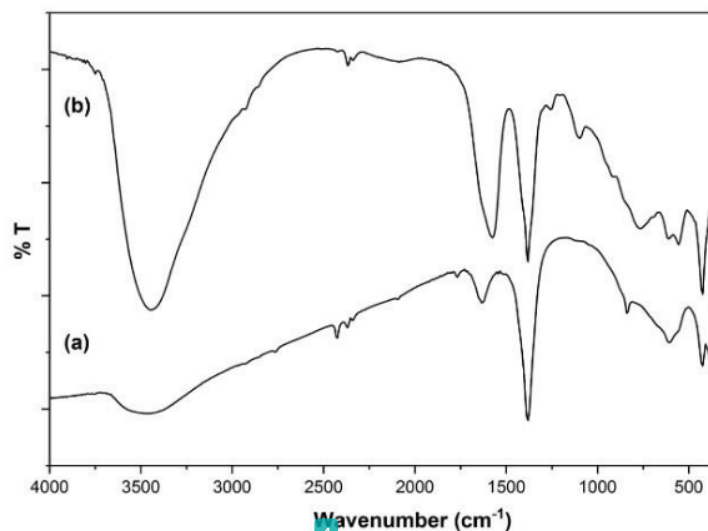


Figure 4. FTIR spectra of Zn/Al (a) and citrate-Zn/Al (b) LDHs

The FTIR spectra of Zn/Al and intercalated Zn/Al LDHs with citric acid are shown in Figure 4. As shown in Figure 4a, the broad peak at 3400 cm^{-1} was assigned as the -O-H stretching vibration. These vibrations are coming from the water on interlayer distance, water on the hydroxide layer, and also adsorbed water from the air. Water also has to bend vibration at 1610 cm^{-1} as small vibration in Figure 4a. The sharp peak vibration at 1370 cm^{-1} is attributed

to carbonate vibration. Intercalation of Zn/Al with citrate ion resulted in sharp vibration of citrate ion at 1600 cm^{-1} as vibration C=O . The vibration of carbonate has still remained. The $\text{-CH}_2\text{-}$ the vibration of citrate ion was detected at 2900 cm^{-1} with a small vibration peak. The vibration of water molecule appeared extremely broad at 3400 cm^{-1} , similar to pristine LDH³⁸.

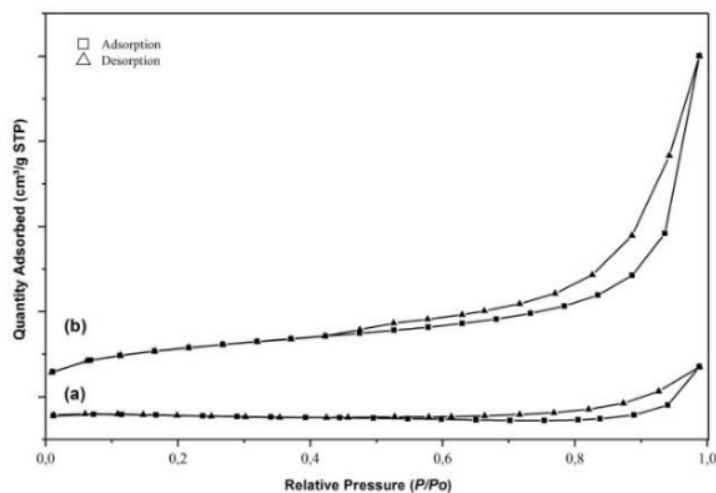


Figure 5. Nitrogen adsorption-desorption profile of Zn/Al (a) and citric acid-Zn/Al (b) LDHs

The surface area of Zn/Al LDH and intercalated Zn/Al-citrate LDH were determined by nitrogen adsorption-desorption. The adsorption-desorption isotherm of materials is shown in Figure 5. There is a

hysteresis loop with H3 type on both Zn/Al and intercalated materials³⁹. The materials are classifying as mesoporous. The BET analysis is shown in Table 1 and shows that pore diameter was slightly decreased

er intercalation, but the significant increase of surface area and pore volume after intercalation with

citric acid. The morphologies of Zn/Al and Zn/Al-citrate LDH were represented in Figure 6.

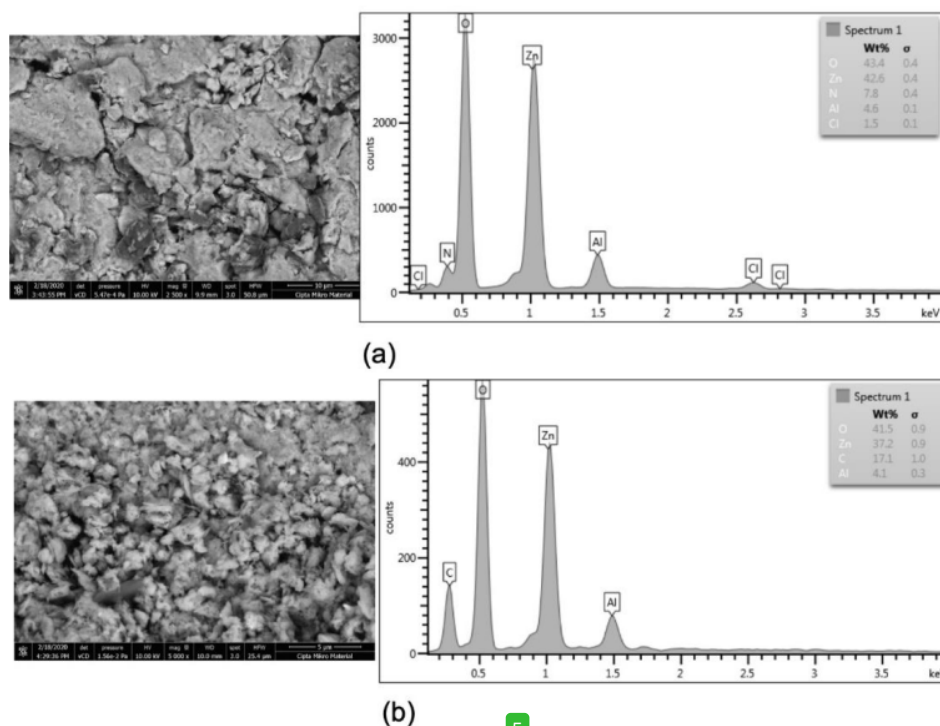


Figure 6. SEM images and composition of Zn/Al LDH (a) and Zn/Al-citrate (b)

Figure 6.a shows the morphology of Zn/Al before citrate intercalation. The morphology of Zn/Al shows the agglomeration of materials caused the pH setting 2nd temperature due to the synthesis process. Similar reported by Palapa *et al.* (2020), that the agglomeration of LDH indicated the heterogeneity in surface area and active site become low⁴⁰. According to EDX composition Figure 6.a. shows the dominant component is oxygen from water and anion; Zn forms divalent metal of LDH; N from nitrate and also Al

from trivalent metal cation of LDH structure. Figure 6.b indicated the intercalation process was successfully conducted and EDX composition of the material was presented. The morphology of Zn/Al-citrate also shows the agglomeration of materials. The white particle indicated the morphology of citrate. According to Rahmanian *et al.* (2018), the LDH intercalated citrate anion has homogeneity plates-like shape with nano-size particles⁴¹.

Table 1. BET Analysis.

Properties	LDHs	
	Zn/Al	Citrate-Zn/Al
BET surface area ($\text{m}^2 \text{g}^{-1}$)	1.968	40.502
Pore volume ($\text{cm}^3 \text{g}^{-1}$), BJH	0.006	0.116
Pore diameter (nm), BJH	27.687	16.350

The surface charges of material were determined using pH pzc (point zero charges), as shown in Figure 7. The intersection point of Zn/Al LDH was at pH 6, whereas intercalated material at pH 8. At that point,

the surface charges of materials were zero. The point of under pH pzc indicated that the materials' surface is positively charge and vice versa. Thus the application of adsorption was conducted at pH pzc.

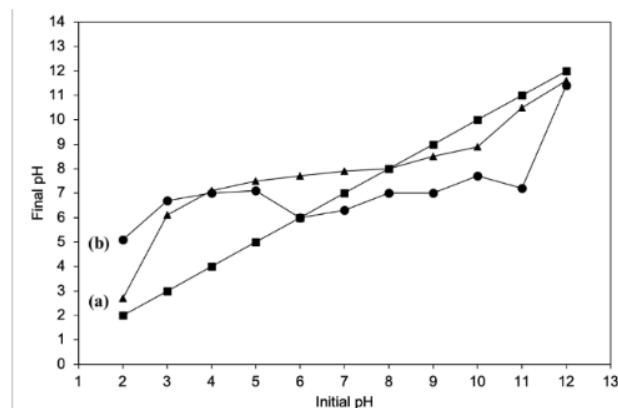


Figure 7. pH pzc graph of initial pH (a), Zn/Al (b) and citrate-Zn/Al

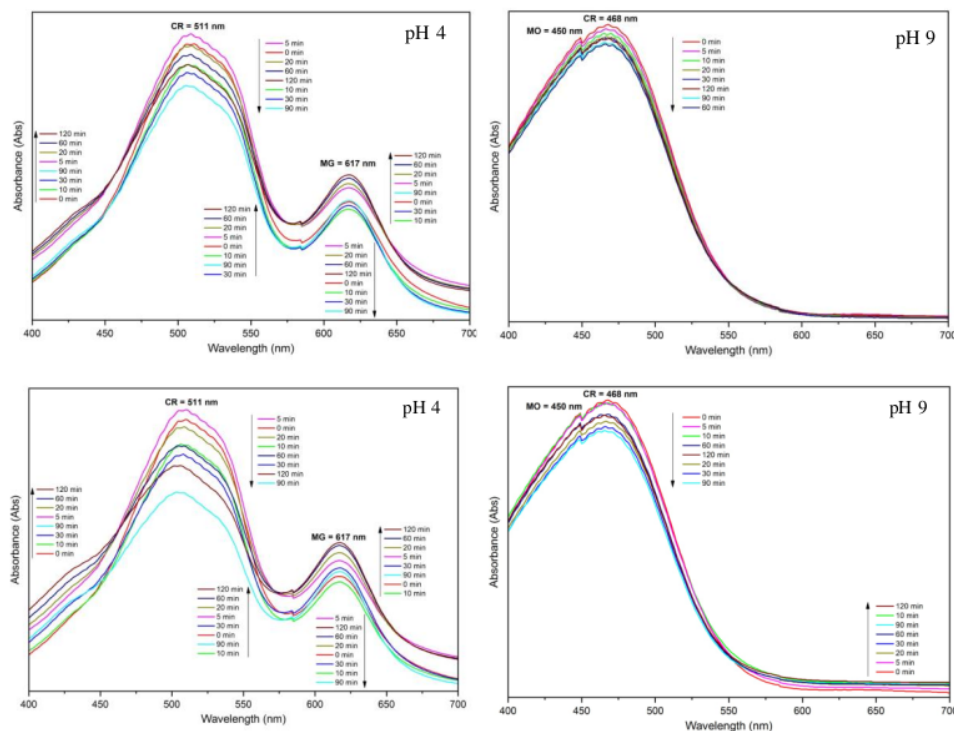


Figure 8. UV-visible spectra of a mixture of dyes (congo red, methyl orange, malachite green) with pH 4 (above) and pH 9 (below) after treating with Zn/Al and citric acid-Zn/Al LDHs

Figure 8 shows the adsorption of mixture dyes using Zn/Al and citrate-Zn/Al LDHs. The dyes were Congo red and methyl orange as anionic dyes and malachite green as a cationic dye. The adsorption was conducted at pH acid and base. All dyes were detected at acid condition, but malachite green was not detected at base condition due to anionic dyes reacted with a hydroxyl group. At acid condition, the absorbance of Congo red was slightly decreased by increasing adsorption time.

On the other hand, the absorbance of methyl orange and malachite green was almost stable. The amount of Congo red was adsorbed dominantly than methyl orange or malachite green on both Zn/Al and intercalated materials. Thus, the adsorption of Congo red was further investigated through the effect of adsorption time, the concentration of Congo red, and temperature adsorption.

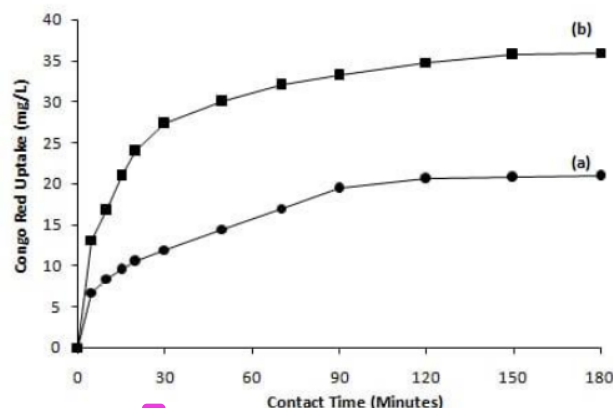


Figure 9. Effect of adsorption time on Zn/Al (a) and citrate-Zn/Al (b) LDHs

The effect of adsorption time of Congo red on Zn/Al and intercalated Zn/Al LDHs material was shown in Figure 9. The adsorbed Congo red was gradually increased by increasing adsorption time and reach equilibrium at 120 minutes. Adsorption of Congo red on intercalated LDH material is higher than pristine Zn/Al LDH. The data in Figure 8 was used to obtain adsorption rate k_1 and k_2 using pseudo-first-order and pseudo-second-order kinetic model as follows ⁴²:

Pseudo first-order kinetic model:

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

where: q_e is adsorption capacity at equilibrium (mg.g^{-1}); q_t is adsorption capacity at t (mg.g^{-1}); t is adsorption time (minute); and k_1 is adsorption kinetic rate at pseudo first-order (minute^{-1}).

Pseudo-second-order kinetic model:

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

where q_e is adsorption capacity at equilibrium (mg.g^{-1}); q_t is adsorption capacity at t (mg.g^{-1}); t is adsorption time (minute); and k_2 is adsorption kinetic rate at pseudo second-order ($\text{g.mg}^{-1}.\text{minute}^{-1}$). The data of kinetic adsorption is shown in Table 2.

Table 2. Kinetic model of congo red adsorption on LDH.

Kinetic Adsorption Model	Kinetic Parameter	LDH	
		Zn/Al	Citrate-Zn/Al
Pseudo First-Order	Q_e (mg.g^{-1})	25.704	33.037
	Q_e experiment (mg.g^{-1})	29.208	44.958
	R^2	0.972	0.971
	k_1 (min^{-1})	0.0299	0.0276
Pseudo Second-Order	Q_e (mg.g^{-1})	30.303	50.001
	Q_e experiment (mg.g^{-1})	29.208	44.958
	R^2	0.991	0.999
	k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	0.0014	0.0016

The pseudo second-order kinetic model is appropriate for both adsorbents due to R value close to one. The k_2 value for intercalated material is slightly larger than Zn/Al without intercalation. The reactivity of intercalated material is probably due to the opening of interlayer distance after intercalation. According to

Sepehr *et al* (2012), the kinetic models determined by coefficient correlation and the value of q_e experiment are close to q_e calculation ⁴³. In Table 2, the q_e experiment use pseudo-second order, both LDH close with q_e calculation.

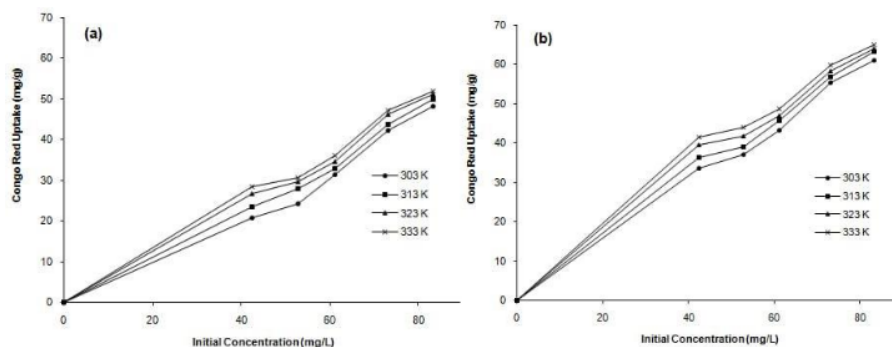


Figure 10. Effect of concentration of congo red and temperature adsorption on Zn/Al (a) and citrate-Zn/Al (b) LDHs

Figure 10 shows the effect of initial concentration and temperature adsorption of congo red on Zn/Al and citrate-Zn/Al adsorbents. The amount of congo red adsorbed increased by increasing temperature adsorption. The adsorption profile shows that physical adsorption has occurred in this research. The data of isotherm adsorption was obtained using Langmuir and Freundlich isotherms equation as follows ⁴⁴:

Langmuir equation:

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

where C is a saturated concentration of adsorbate; m is the amount of adsorbate; b is the maximum adsorption capacity (mg g^{-1}), and K_{ML} is the Langmuir constant (L mg^{-1}).

Freundlich equation:

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

Where q_e is adsorption capacity at equilibrium (mg g^{-1}); C_e is a concentration of adsorbate at equilibrium (mg L^{-1}), and K_F is Freundlich constant. The data of isotherm adsorption of congo red on LDHs are shown in Table 3.

Table 3. Isotherm adsorption of congo red.

	Isotherm	Isotherm Parameter	Temperature (K)			
			303	313	323	333
Zn/Al	Langmuir	q_{\max} (mg g^{-1})	47.619	111.112	166.666	112.045
		K_{ML} (L mg^{-1})	0.011	0.007	0.001	0.003
		R^2	0.580	0.433	0.429	0.449
	Freundlich	k_F ($\text{mg g}^{-1}(\text{L mg})^{1/n}$)	0.091	2.716	1.315	2.051
		n	0.608	0.774	1.040	1.175
		R^2	0.890	0.922	0.834	0.814
Citrate-Zn/Al	Langmuir	q_{\max} (mg g^{-1})	249.990	166.667	111.111	90.909
		K_{ML} (L mg^{-1})	0.009	0.018	0.082	0.070
		R^2	0.171	0.426	0.707	0.832
	Freundlich	k_F ($\text{mg g}^{-1}(\text{L mg})^{1/n}$)	3.811	6.561	12.882	17.458
		n	1.302	1.592	2.283	2.778
		R^2	0.818	0.803	0.749	0.769

Table 3 showed that adsorption capacity for citrate-Zn/Al is higher than pristine Zn/Al LDH. The adsorption capacity is up to 249.99 mg g^{-1} for citrate-Zn/Al LDH and 166.67 mg g^{-1} for Zn/Al LDH without intercalation. The adsorption capacities are related to the increased surface area properties after

intercalation. The decreasing of adsorption capacity of intercalated material by increasing temperature is probably due to decreasing pore diameter of intercalated material, as shown in Table 1. The compared materials as adsorbent of congo red were shown in Table 4.

Table 4. Compared materials as an adsorbent for Congo red dye.

Adsorbent	Adsorption Capacity (mg/g)	Ref
Ni/Co LDH	909.2	45
Mg/Fe-CO ₃	104.6	46
Fe ₃ O ₄ -MgAl LDH	813	47
CNT-MgAl-O LDH	1250	48
sodium dodecyl sulfate SDS-LDH	714	49
Borates-Mg/Al LDH	138.6	50
Ni/Al-S ₁ LDH	120.5	51
MgO-GO microspheres	227.7	52
NiFe LDH	80.2	53
Mg/Fe-NO ₃ LDH	58.54	53
Zn/Al LDH	112.04	This work
Zn/Al-citrate	249.9	This work

The thermodynamic properties of Congo red adsorption on Zn/Al and intercalated Zn/Al LDHs is shown in Table 5 and was calculated according to the equation as follows ⁵⁴:

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

$$\Delta G^{\circ} = -RT \ln K_{ML} \quad (6)$$

Where T is the temperature (K); R is the gas constant (8.314 J mol⁻¹ K⁻¹), and K_{ML} is the modified Langmuir constant.

Table 5. Thermodynamic parameter of Congo red adsorption on LDHs.

	ΔG° (kJ mol ⁻¹)				ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
	303 K	313 K	323 K	333 K		
Zn/Al	-0.213	-0.355	-0.497	-0.638	4.085	0.014
Citrate-Zn/Al	-1.487	-1.673	-1.859	-2.045	4.148	0.019

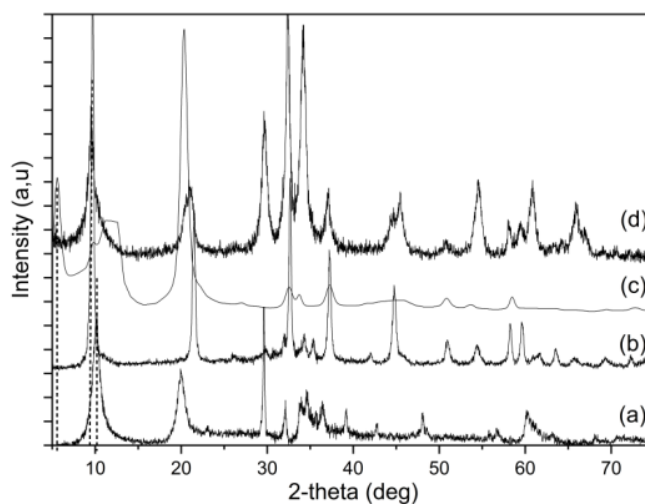


Figure 11. XRD pattern of (a) Zn/Al, (b) Zn/Al after adsorption, (c) Zn/Al-Citrate and (d) Zn/Al-Citrate after adsorption Congo red

The data in Table 5 showed the value of Gibbs energy, enthalpy, and entropy of Congo red adsorption on LDHs. All adsorption of methyl orange on LDHs was spontaneously occurred due to the negative value of Gibbs energy. Adsorption of Congo red on LDHs was classified as physical adsorption with energy in the range 4.085–4.148 kJ mol⁻¹ and also there was increasing randomness of adsorption system on both LDHs as adsorbent. The adsorption of Congo red into Zn/Al-Cit LDH was more efficient than Zn/Al LDH. The study of a LDH structure after the adsorption process was conducted using XRD analysis. The pattern of XRD before and after adsorption of Congo red was shown in Figure 11.

Figure 11.b. shows the LDH pattern after adsorption of Congo red was shifted to lower 2 theta from 10.29

with interlayer distance 8.59 Å to 9.725 with interlayer distance 8.54 Å. The interlayer was decreased after adsorption, but the structure of LDH has no change. However, intercalated LDH shows the adsorption capacity higher than pristine LDH. This phenomenon related that the decrease interlayer after adsorption Congo red and 2 theta shifted to a higher degree. Figure 11. c and d show the shifted with decrease the interlayer distance from 11.68 Å to 8.65 Å indicated that the Congo red was coated and piled up the active site so that the XRD confirm that the interlayer decreased slightly. The effectivity of adsorbent was determined by reusability. Desorption study was conducted before the regenerator process, desorption was conducted using several reagents to determine the suitable solvent, and the results were shown in Figure 12.

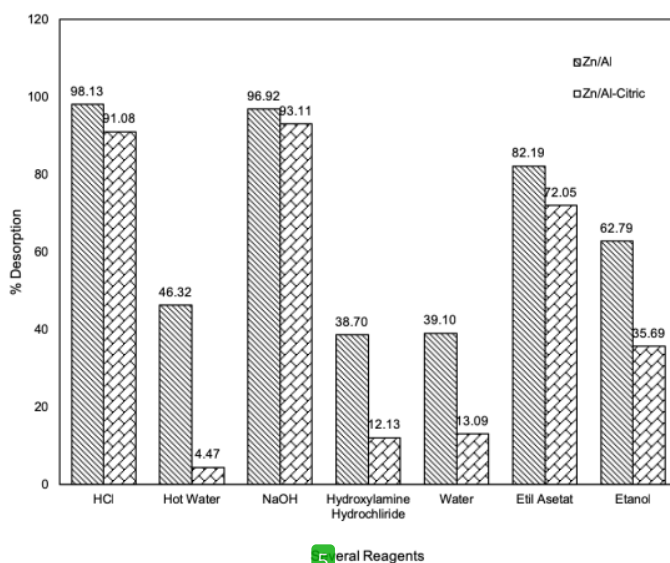


Figure 12. Desorption Zn/Al LDH and Zn/Al-Citrate LDH

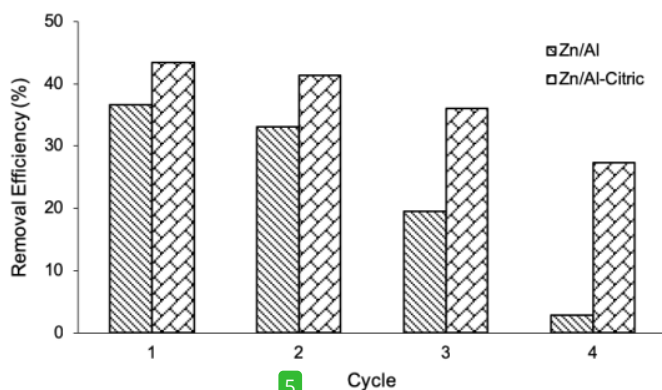


Figure 13. Reusability Zn/Al LDH and Zn/Al-Citrate LDH

Figure 12 shows the desorption of Zn/Al and Zn/Al-Citrate LDHs were conducted using HCl, hot water, NaOH, hydroxylamine hydrochloride, water, ethyl acetate, and ethanol. Before desorption, both adsorbents were adsorbed the 150 mg/L of Congo red and adsorbed capacity was 96 mg/g and 132 mg/g at room temperature. The adsorbed materials were shaken with each reagent. The result obtained that the LDH pristine using HCl uptake 98.13 % and Zn/Al intercalated citrate using NaOH with 93.11 % desorption. Subsequently, Zn/Al and Zn/Al-citrate after desorption used to Congo red adsorption. The removal efficiency of these materials showed in Figure 13.

The removal efficiency of both materials slightly decreased. The Zn/Al LDH was decreased dramatically after a four-cycle process. According to Palapa *et al.* (2020), the LDH can be exfoliated in acid solution, and LDH has reduced reusability activity. Nevertheless, Zn/Al-citrate has more effectivity to reuse as adsorbent ⁴⁰. The removal efficiency of Zn/Al-citrate is quietly decreased until the fourth cycle. The Zn/Al after intercalating citrate anion has more efficient as an adsorbent to remove Congo red in water solution.

4. Conclusion

Citrate-Zn/Al LDH and pristine LDHs were successfully synthesized and used as adsorbent of Congo red from aqueous solution. The adsorption of Congo red on LDHs follows the pseudo-second-order kinetic model. The adsorption capacity is up to 249.99 mg g⁻¹ for citric acid-Zn/Al LDH and 166.67 mg g⁻¹ for pristine LDH. The adsorption process was categorized as physical adsorption with energy adsorption 4.085-4.148 kJ mol⁻¹. The reusability study shows the Zn/Al after intercalated citrate anion is efficient and effective use as an adsorbent.

Acknowledgement

The authors express their gratitude to Ministry of Research Technology and Higher Education (Kemenristekdikti) Republik Indonesia through "Hibah Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT)" in 2019-2020 fiscal year with contract no. 0060.05/UN9/SB3.LP2M.PT/2019.

References

- 1- M. K. Dahri, M. R. R. Kooh, L. B. L. Lim, Water remediation using a low-cost adsorbent walnut shell for removal of malachite green: equilibrium, kinetics, thermodynamics and regeneration studies, *Journal of Environmental Chemical Engineering*, **2019**, 2, 1434-1444.
- 2- M. R. Samarghandi, M. Zarrabi, M. N. Sepehr, R. Panahi, M. Foroghi, Removal of Acid Red 14 by Pumice Stone as a Low-cost Adsorbent: Kinetic and Equilibrium Study, *Iranian Journal of Chemistry and Chemical Engineering*, **2012**, 31, 19-27.
- 3- C. Shen, Y. Pan, D. Wu, Y. Liu, C. Ma, F. Li, H. Ma, Y. Zhang, A crosslinking-induced precipitation process for the simultaneous removal of poly(vinyl alcohol) and reactive dye: the importance of covalent bond forming and magnesium coagulation, *Chemical Engineering Journal*, **2019**, 374, 904-913.
- 4- P. J. Ong, S. W. Tay, L. Hong, Removal of water-soluble dyes by conjugated organic skeletons through drain flow-diffusion filtration, *Journal of Environmental Chemical Engineering*, **2018**, 6, 4612-4622.
- 5- M. Alizadeh, E. Ghahramani, M. Zarrabi, M. N. Sepehr, Efficient de-colorization of methylene blue by the electro-coagulation method: Comparison of iron and aluminum electrode, *Iranian Journal of Chemistry and Chemical Engineering*, **2015**, 34, 39-47.
- 6- X. L. Cao, Y. N. Yan, F. Y. Zhou, S. P. Sun, Tailoring nanofiltration membranes for effective removing dye intermediates in complex dye-wastewater, *Journal of Membrane Science*, **2020**, 595, 117476.
- 7- M. R. Samarghandi, M. Zarrabi, A. Amrane, M. M. Soori, M. N. Sepehr, Removal of acid black dye by pumice stone as a low-cost adsorbent: kinetic, thermodynamic and equilibrium studies, *Environmental Engineering and Management Journal*, **2013**, 12, 2137-2147.
- 8- Y. Yang, L. Yan, J. Li, J. Li, T. Yan, M. Sun, Z. Pei, Synergistic adsorption and photocatalytic reduction of Cr(VI) using Zn-Al-layered double hydroxide and TiO₂ composite, *Applied Surface Science*, **2019**, 492, 487-496.
- 9- N. Parshi, D. Pan, V. Dhavle, B. Jana, S. Maity, J. Ganguly, fabrication of lightweight and reusable salicylaldehyde functionalized chitosan as an adsorbent for dye removal and its mechanism, *International Journal of Biological Macromolecules*, **2019**, 141, 626-635.
- 10- Y. Song, J. Y. Seo, H. Kim, K. Y. Beak, Structural control of cellulose nanofibrous composite membrane with metal-organic framework (ZIF-8) for highly selective removal of cationic dye, *Carbohydrate Polymers*, **2019**, 222, 115018.
- 11- T. Taher, D. Rohendi, R. Mohadi, A. Lesbani, Thermal and acid activation (TAA) of bentonite as an adsorbent for removal methylene blue: a kinetics and thermodynamic study, *Chiang Mai Journal of Science*, **2018**, 45, 1770-1781.
- 12- T. A. Aragaw, F. T. Angerasa, Adsorption of basic yellow dye dataset using Ethiopian kaolin as an adsorbent, *Data in Brief*, **2019**, 26, 104504.
- 13- H. Quaddari, A. Karim, B. Achiou, S. Saja, A. Aaddane, J. Bennazha, I. E. A. E. Hassani, M. Ouammou, A. Albizane, Now low-cost ultrafiltration membrane made from purified

- natural clays for direct red 80 dye removal, *Journal of Environmental Chemical Engineering*, **2019**, 7, 103268.
- 14- Q. Huang, M. Liu, J. Chen, Q. Wan, J. Tian, L. Huang, R. Jiang, Y. Wen, X. Zhang, Y. Wei, Facile preparation of MoS₂ based polymer composites via mussel inspired chemistry and their high efficiency for removal of organic dyes, **2017**, 419, 35-44.
 - 15- G. V. Brião, S. L. Jahn, E. L. Foletto, G. L. Dotto, Highly efficient and reusable mesoporous zeolite synthesized from a biopolymer for cationic dyes adsorption, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2018**, 556, 43-50.
 - 16- N. R. Palapa, T. Taher, R. Mohadi, A. Lesbani, Removal of anionic direct dye using Zn/Al, Zn/Fe, and Zn/Cr layered double hydroxides toward the interlayer distance, *Science and Technology Indonesia*, **2019**, 4, 70-76.
 - 17- L. M. Ahmed, M. S. Gasser, Adsorption study of anionic reactive dye from aqueous solution to Mg-Fe-CO₃ layered double hydroxide (LDH), *Applied Surface Science*, **2012**, 259, 650-656.
 - 18- N. R. Palapa, R. Mohadi, A. Lesbani, Adsorption of direct yellow dye from aqueous solution by Ni/Al and Zn/Al layered double hydroxides, *AIP Conference Proceeding*, **2018**, 2026, 020018.
 - 19- N. R. Palapa, T. Taher, R. Mohadi, M. Said, A. Lesbani, Synthesis of Ni/Al layered double hydroxides (LDHs) for adsorption of malachite green and direct yellow dyes from solution: kinetic and thermodynamic, *AIP Conference Proceeding*, **2018**, 2026, 020033.
 - 20- G. Huang, L. Jiang, D. Wang, J. Chen, Z. Li, S. Ma, Intercalation of thiacalix[4]arene anion via calcined/restored reaction into LDH and efficient heavy metal capture, *Journal of Molecular Liquids*, **2016**, 220, 346-353.
 - 21- T. Taher, Y. Irianty, R. Mohadi, M. Said, R. Andreas, A. Lesbani, Adsorption of cadmium(II) using Ca/Al layered double hydroxides intercalated with Keggin ion, *Indonesian Journal of Chemistry*, **2019**, 19, 873-881.
 - 22- T. Taher, M. M. Christina, M. Said, N. Hidayati, Ferlinahayati, A. Lesbani, Removal of iron(II) using intercalated Ca/Al layered double hydroxides with $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$, *Bulletin of Chemical Reaction Engineering and Catalysis*, **2019**, 14, 260-267.
 - 23- M. Szabados, G. Varga, Z. Kónya, Á. Kukovecz, S. Carlson, P. Sipos, I. Pálkó, Ultrasonically-enhanced preparation, characterization of CaFe-layered double hydroxides with various interlayer halide, azide and oxo anions (CO₃²⁻, NO₃⁻, ClO₄⁻), *Ultrasonic Sonochemistry*, **2018**, 40, 853-860.
 - 24- M. Shafigh, M. Hamidpour, G. Furrer, Zinc release from Zn-Mg-Fe(III)-LDH intercalated with nitrate, phosphate and carbonate: the effects of low molecular weight organic acids, *Applied Clay Science*, **2019**, 170, 135-142.
 - 25- H. Chen, J. Lin, N. Zhang, L. Chen, S. Zhong, Y. Wang, W. Zhang, Q. Ling, Preparation of MgAl-EDTA-LDH based electrospun nanofiber membrane and its adsorption properties of copper(II) from wastewater, *Journal of Hazardous Materials*, **2018**, 345, 1-9.
 - 26- R. Lafi, K. Charradi, M. A. Djebbi, A. B. H. Amara, A. Hafiane, Adsorption study of Congo red from aqueous solution to Mg-Al-layered double hydroxide, *Advanced Powder Technology*, **2016**, 27, 232-237.
 - 27- F. Mohamed, M. R. Abukhadra, M. Shaban, removal of safranin dye from water using polypyrrole nanofiber/Zn-Fe layered double hydroxide nanocomposite (PpyNF/Zn-Fe LDH) of enhanced adsorption and photocatalytic properties, *Science of the Total Environment*, **2018**, 640-641, 352-363.
 - 28- M. A. Ahmed, A. A. Brick, A. A. Mohamed, An efficient adsorption of indigo carmine dye from aqueous solution on mesoporous Mg/Fe layered double hydroxide nanoparticles prepared by controlled sol-gel route, *Chemosphere*, **2017**, 174, 280-288.
 - 29- G. George, M. P. Saravanakumar, Facile synthesis of carbon-coated layered double hydroxide and its comparative characterization with Zn-Al LDH: application on crystal violet and malachite green dye adsorption-isotherm, kinetics and Box-Behnken design, *Environment Science and Pollution Research*, **2018**, 25, 30236-30254.
 - 30- B. Bi, B. Xu, X. Liu, Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media, *Applied Clay Science*, **2011**, 54, 242-247.
 - 31- N. R. Palapa, T. Taher, R. Mohadi, A. Lesbani, Kinetic aspect of direct violet adsorption on M²⁺/M³⁺ (M²⁺ = Zn, M³⁺ = Al, Fe, Cr) layered double hydroxide, *AIP Conference Proceeding*, **2019**, 2194, 020079.
 - 32- B. R. Rahayu, T. Taher, P. L. Hariani, A. Lesbani, Congo red and direct yellow dye removal from aqueous solution by Zn/Cr layered double hydroxides, *AIP Conference Proceeding*, **2018**, 2026, 020023.
 - 33- M. Oktiriyanti, N. R. Palapa, R. Mohadi, A. Lesbani, Modification of Zn-Cr layered double hydroxide with Keggin ion [SiW₁₂O₄₀] as Cr(VI) adsorbent, *Indonesian Journal of Environmental Management and Sustainability*, **2019**, 3, 93-99.
 - 34- H. N. Tran, C. C. Lin, S. H. Woo, H. P. Chao, Efficient removal of copper and lead by Mg/Al layered double hydroxides intercalated with organic acid anions: adsorption kinetics,

- isotherms, and thermodynamics, *Applied Clay Science*, **2018**, 154, 17-27.
- 35- M. L-Sánchez, G. N-Maléndez, G. Luna, V. S. Pérez, J. A. Rivera, G. Fetter, ZnAl layered double hydroxides impregnated with eucalyptus oil as efficient hybrid materials against multi-resistant bacteria, *Applied Clay Science*, **2018**, 153, 61-69.
 - 36- H. N. Umh, Y. Kim, Sensitivity of nanoparticles' stability at the point of zero charge (PZC), *Journal of Industrial and Engineering Chemistry*, **2014**, 20, 3175-3178.
 - 37- Y. Wang, Y. Zhang, B. Zhou, C. Li, F. Gao, X. Wang, D. Liang, Y. Wei, In-situ observation of the growth behavior of ZnAl layered double hydroxide film using EQCM, *Materials and Design*, **2019**, 180, 107952.
 - 38- M. Dinari, A. Haghighi, P. Asadi, Facile synthesis of ZnAl-EDTA layered double hydroxide/poly(vinyl alcohol) nanocomposites as an efficient adsorbent of Cd(II) ions from the aqueous solution, *Applied Clay Science*, **2019**, 170, 21-28.
 - 39- S. Yudarkal, C. Garlisi, L. Özcan, M. Bellardita, G. Palmisano, Photocatalyst characterization techniques: adsorption isotherms and BET, SEM, FTIR, UV-Vis, photoluminescence, and electrochemical characterizations, *Heterogeneous Photocatalysis*, Elsevier, **2019**, 87-152.
 - 40- N. R. Palapa, R. Mohadi, A. Rachmat, A. Lesbani, Adsorption Study of Malachite Green Removal from Aqueous Solution Using Cu/M³⁺ (M³⁺=Al, Cr) Layered Double Hydroxide, *Mediterranean Journal of Chemistry*, **2020**, 10, 33-45.
 - 41- O. Rahmanian, S. Amini, M. Dinari, Preparation of zinc/iron layered double hydroxide intercalated by citrate anion for capturing Lead (II) from aqueous solution, *Journal of Molecular Liquids*, **2018**, 256, 9-15.
 - 42- T. Taher, R. Mohadi, A. Lesbani, Effect of Ti⁴⁺/clay ratio on the properties of titanium pillared bentonite and its application for Cr(VI) removal, *Rasayan Journal of Chemistry*, **2018**, 11, 1244-1254.
 - 43- M. N. Sepehr, S. Nasseri, M. Zarrabi. Removal of Cr (III) from tanning effluent by *Aspergillus niger* in airlift bioreactor, *Separation and Purification Technology*, **2012**, 96, 256-262.
 - 44- T. Taher, R. Mohadi, D. Rohendi, A. Lesbani, Congo red removal from aqueous solution by acid-activated bentonite from Sorolangun: kinetic, equilibrium, and thermodynamic studies, *Arab Journal of Basic and Applied Sciences*, **2019**, 26, 125-136.
 - 45- H. Hu, J. Liu, Z. Xu, L. Zhang, B. Cheng, W. Ho, Hierarchical porous Ni/Co-LDH hollow dodecahedron with excellent adsorption property for Congo red and Cr (VI) ions, *Applied Surface Science*, **2019**, 478, 981-990.
 - 46- I. M. Ahmed, M. S. Gasser, Adsorption study of anionic reactive dye from aqueous solution to Mg-Fe-CO₃ layered double hydroxide (LDH), *Applied surface science*, **2012**, 259, 650-656.
 - 47- L. Lu, J. Li, D. H. Ng, P. Yang, P. Song, M. Zuo, Synthesis of novel hierarchically porous Fe₃O₄@MgAl-LDH magnetic microspheres and its superb adsorption properties of dye from water, *Journal of Industrial and Engineering Chemistry*, **2017**, 46, 315-323.
 - 48- S. Yang, L. Wang, X. Zhang, W. Yang, G. Song, Enhanced adsorption of Congo red dye by functionalized carbon nanotube/mixed metal oxides nanocomposites derived from layered double hydroxide precursor, *Chemical Engineering Journal*, **2015**, 275, 315-321.
 - 49- L. Deng, H. Zeng, Z. Shi, W. Zhang, J. Luo, Sodium dodecyl sulfate intercalated and acrylamide anchored layered double hydroxides: A multifunctional adsorbent for highly efficient removal of Congo red, *Journal of colloid and interface science*, **2018**, 521, 172-182.
 - 50- Y. H. Jia, Z. H. Liu, Preparation of borate anions intercalated MgAl-LDHs microsphere and its calcinated product with superior adsorption performance for Congo red, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2019**, 575, 373-381.
 - 51- D. Bharali, R. C. Deka, Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide, *Journal of environmental chemical engineering*, **2017**, 5, 2056-2067.
 - 52- J. Xu, D. Xu, B. Zhu, B. Cheng, C. Jiang, Adsorptive removal of an anionic dye Congo red by flower-like hierarchical magnesium oxide (MgO)-graphene oxide composite microspheres, *Applied Surface Science*, **2018**, 435, 1136-1142.
 - 53- N. Hidayati, D. R. Apriliani, T. Taher, R. Mohadi, A. Lesbani, Adsorption of congo red using Mg/Fe and Ni/Fe layered double hydroxides, In *Journal of Physics: Conference Series IOP Publishing*, **2019**, 1282, 012075.
 - 54- S. Agarwal, I. Tyagi, V. K. Gupta, S. Mashhadi, M. Ghasemi, Kinetic and thermodynamics of malachite green dye removal from aqueous phase using iron nanoparticles loaded on ash, *Journal of Molecular Liquids*, **2016**, 223, 1340-1347.

C.1.c.3.3-Citrate-ZnAl Layered Double Hydroxide as Adsorbent of Congo Red from Aqueous Solution.pdf

ORIGINALITY REPORT

11%

SIMILARITY INDEX

PRIMARY SOURCES

1	pdfs.semanticscholar.org Internet	118 words — 3%
2	arpnjournals.org Internet	108 words — 2%
3	www.jeeng.net Internet	48 words — 1%
4	worldwidescience.org Internet	45 words — 1%
5	www.ncbi.nlm.nih.gov Internet	40 words — 1%
6	journal.gnest.org Internet	34 words — 1%
7	www.jett.dormaj.com Internet	31 words — 1%
8	doaj.org Internet	25 words — 1%
9	idoc.pub Internet	25 words — 1%

EXCLUDE QUOTES OFF
EXCLUDE BIBLIOGRAPHY ON

EXCLUDE MATCHES < 1%