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By Risfidian Mohadi

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B. R. Rahayu, N. R. Palapa, T. Taher, et al.

Adsorption of Direct Violet Dye by Zn/Cr and Zn/Al Layered Double Hydroxides: Thermodynamic Study

B. R. Rahayu[1], N. R. Palapa[1], T. Taher[2], R. Mohadi[1] and A. Lesbani[1, a)]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Sriwijaya University, Palembang 30662, South Sumatra, Indonesia*
[2]*Department of Environmental Sciences, Graduate School, Sriwijaya University, Palembang 30139, South Sumatra, Indonesia*

[a)]Corresponding author: aldeslesbani@pps.unsri.ac.id

Abstract. In this study, Zn/Cr and Zn/Al layered double hydroxides have been prepared as adsorbent. The adsorbent was characterized using X-Ray Diffraction and the surface area was analyzed by BET method. The adsorption effect and influencing factors were studied. The value of dye absorbed was calculated and suggested of high efficiency to remove direct violet (DV) dye in aqueous solution. The isotherm models were examined using Freundlich and Langmuir. The results showed the Freundlich isotherm models are fitted and indicating multilayers adsorption mode. The higher adsorption capacity of Zn/Cr and Zn/Al reached at 323 K at the amount of 45.06 mg $g^{-1}$and 30.23 mg g^{-1}, respectively. The thermodynamic study showed that the adsorption processes were spontaneous. The negative value of ΔG and endothermic found the cost of LDH positively.

Keywords: Zn/Cr layered double hydroxide, Zn/Al layered double hydroxide, direct violet dye, thermodynamic study

INTRODUCTION

The layered double hydroxides have widely applied as adsorbent caused by their ability and unique structure [1]. Layered double hydroxide is a classification of anionic synthesis clay. Layered double hydroxide has hexagonal structure form of trivalent and divalent metal cations, and is considered to have positively charge excess in the brucite layer [2]. Layered double hydroxide has general formula of $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} A_{x/n}^{n-} .yH_2O$, where M^{2+} and M^{3+} denoted divalent, and trivalent metal cations (Ni,Zn,Mg,Fe,Cu and Fe,Cr,Al), interlayer anions such as nitrate anions, carbonate anions, and sulfate anion denoted A^{n-}[3, 4]. The one of layered double hydroxides' ability is interlayer anion can be easily exchangeable with other anions [5]. Since the layered double hydroxides can be anion exchangeable, the characteristic of layered double hydroxides is special so that layered double hydroxides are useful for many applications [6].

Nowadays, synthetic dyes are widely used in industrial applications [7] (paper, pulp, textile, etc.). Most of dye wastewater contained in water disposal, canal, and sometimes watercourse. Many industries, e.g., home industries ignore the harmful of dyes wastewater [8]. As we know, synthetic dyes usually made up of some mercury, lead, chromium, copper, and benzene [9, 10]. Exposure of too large doses of dye synthetic can be toxic and can have a severe effect to human bodies [11]. That is why many types of research recently use all ways to solve this problem, such as the use of adsorbent to remove the synthetic dyes wastewater. However, the adsorption method is the most popular way to remove sewage because this method is useful for dye removal, cheaper, and easy to prepare [12, 13]. In this research, layered double hydroxides have been successfully prepared as an adsorbent to remove the synthetic dye wastewater. Layered double hydroxides was determined by XRD and BET analyses. The adsorption of dye onto

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layered double hydroxides was calculated by kinetic model adsorption, isotherm models and thermodynamic parameters.

EXPERIMENTAL

Materials and Instrumentation

Chemicals applied in the study, namely zinc nitrate aluminum nitrate and chromium nitrate were obtained from Merck and used as received without further purification. Direct violet (DV) (IUPAC name 7-anilino-3-[[4-[(2,4-dimethyl-6-sulfophenyl)diazenyl]-2,5-dimethylphenyl]diazenyl]-4-hydroxynaphthalene-2-sulfonic acid) dye was employed as the model of wastewater received from the local textile industry. As solvent, the de-ionized water utilized for the study of adsorption was obtained from the Purite instrument.

Zn/Al and Zn/Cr layered double hydroxide was determined by X-ray diffraction and surface area was analyzed by BET method. XRD analysis was carried out using a Rigaku Miniflex 600 XRD instrument with CuKa radiation at 30 kV and 10 mA and scanned at 2 theta range from 5° to 80°. The surface area analyses was carried out using BET (ASAP Micromeritics 2020).

Preparation of Zn/Al LDH

Zn/Al layered double hydroxides was synthesized using co-precipitation method at pH 10. Zinc nitrate (10 mL, 0.75 M) and aluminum nitrate (10 mL, 0.25 M) were called A solution. A solution was added dropwise 10 mL of solution sodium hydroxides 2 M to form a white gel at 80 °C for 4 h. Then, the white solid was washed with water. The powder obtained were characterized using XRD and BET.

Preparation of Zn/Cr LDH

The synthesis of Zn/Cr LDH has been studied by Rahayu et al. [13] As much as 13.072 g of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 100 mL volumetric flask. Into another container, $Cr(NO_3)_3{\cdot}9H_2O$ as much as 10.004 grams were weighed and dissolved with 100 mL deionized water. Both solutions $Zn(NO_3)_2{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ were then mixed at 2:1 ratio. The mixture was then added with 10 mL of Na_2CO_3 2.5 M and 25 mL of NaOH 3M with intense stirring for 2 h. The solution's pH was kept at 10 by adding NaOH solution and the mixture's temperature was maintained at 60 °C for 24 h. Upon completion, the produced Zn/Cr LDH was then sieved and washed couple of times with de-ionized water and finally dried at 60 °C for 24 h. The solid product was then stored in a closed container and can be applied as an adsorbent for the next experiment.

Adsorption Study

DV solution was prepared with 1 g of powdery dye with 1L of water to produce 1000 mg/L as dye solution stock. The curve standard was obtained by measuring each standard at the lambda maximum, respectively. The adsorption of dyes was conducted in a batch system. An amount of adsorbent was added into 50 mL of dyes solution then mixed using horizontal shaker at 250 rpm in a varied temperature and concentration.

RESULTS AND DISCUSSION

Material Characterization

Figure 1 shows the XRD pattern of the layered double hydroxides. The pattern in Fig. 1a indicates a unique layered structure of layered double hydroxides Zn/Al 1164°, 23.42°, 31.88° and 60.19° (split peaks), then layered double hydroxides Zn/Cr assigned at 11.05°, 21.71°, 32.65° and 61.00° (split peaks), respectively. However, both layered double hydroxides had a sharp diffraction peak at 2θ value of 11°. This diffraction has denoted the presence of anions lied between interlayer by creating an area between layers with distance about 7.57 Å and 7.32 Å, Zn/Al and Zn/Cr LDH, respectively. After that, both layered double hydroxides had been characterized using surface area analyses by BET method. Figure 1b shows the graphics isotherm of adsorption-desorption Zn/Al and Zn/Cr layered double hydroxides. The isotherm adsorption-desorption type as shown in Fig. 1b indicated that Zn/Al and Zn/Cr layered double hydroxides have a mesoporous variety, with pore size between 2–50 nm. According to IUPAC, the diameter of pore has many typical pores. The typical pores are micropore <2 nm, mesopore 2–50 nm, and macropore >50 nm. Based on the result of surface area analyses by BET method, Zn/Al and Zn/Cr layered double hydroxides has BET surface area 9.41 m^2/g and 11.8 m^2/g.

Adsorption Isotherm and Thermodynamic Study

Zn/Al and Zn/Cr layered double hydroxides were used as an adsorbent for DV removal, each 0.5 g of both adsorbents was inserted into 50 mL dye solution with various concentrations, respectively. After shaken for 30 min (at 240 rpm), the mixture was centrifugated and analyzed using UV-Vis spectrophotometer. The adsorption capacity of DV onto Zn/Al and Zn/Cr layered double hydroxides was calculated according to [14]:

$$q_e = \frac{(C_o - C_e)}{m} \cdot V \quad (1)$$

Adsorption experiment was applied for adsorption thermodynamic parameters investigation with various adsorption temperatures, i.e. 303 K, 313 K and 323 K and initial concentration of dye (i.e. 60, 70, 80 and 100 mg/L). The data was obtained by:
Isotherm model of Langmuir:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2)$$

Isotherm model of Freundlich:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

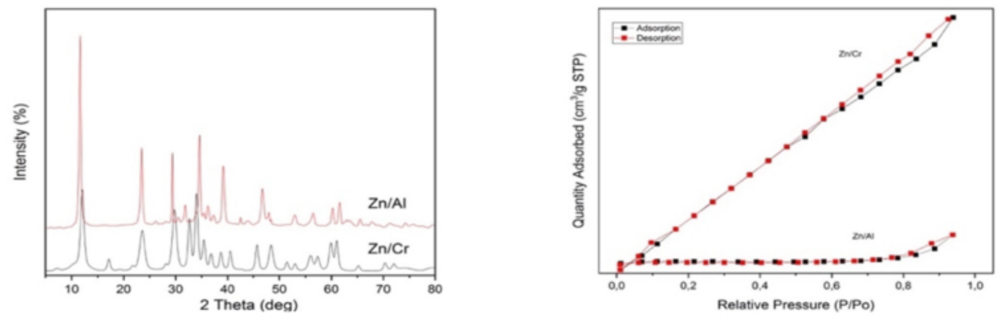
Thermodynamic adsorption parameters were then measured based on below formulation:

$$\ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

where: Co is the initial concentration of dye (mg/L), qe is the equilibrium capacity (mg/g), m is the mass of adsorbent (g), V is the volume of dye (L), Ce is the final concentration after adsorption (mg/L), qm is the equilibrium adsorption capacity maximum (mg/g), kF is constant of Freundlich, and kL is constant of Langmuir.

Based on Equation 1, the adsorption of DV onto layered double hydroxides were calculated and obtained the adsorption capacity. The adsorption capacity of both adsorbents has different values. The adsorption capacity of DV onto Zn/Al is higher than Zn/Cr layered double hydroxides (based on Fig. 2). The amount at 323 K is 100 mg/L DV solution uptake 45.06 mg/g and 30.23 mg/g, respectively.

The adsorption process of DV onto Zn/Cr and Zn/Al LDH was studied according to Langmuir and Freundlich adsorption isotherm model. The adsorption isotherm data was determined at various temperature i.e., 303 K, 323 K, and 343 K) for both adsorbents Zn/Cr and Zn/Al layered double hydroxides. The adsorption isotherm models are presented in Fig. 3a and Fig. 3b, respectively. The straight blue square line denotes the Freundlich adsorption isotherm model. The square symbol with red line represents the Langmuir adsorption isotherm model, and the black symbol represents the adsorption experiment data. The values for the adsorption parameters according to both models were presented in Table 1. Based on the coefficient correlation, the adsorption of DV onto Zn/Al and Zn/Cr layered double hydroxides followed the Freundlich Isotherm model. The value of coefficient correlation of Freundlich is up (>0.9) than Langmuir Isotherm model. This adsorption process indicated that the adsorption process occurred at heterogeneous surface properties, and the adsorption process was in a multilayer. Table 2 shows the thermodynamic



(a) (b)

FIGURE 1. The characterized of both layered double hydroxides, (a) XRD pattern and (b) Isotherm graphic of adsorption-desorption.

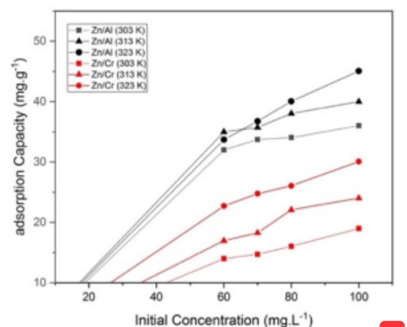
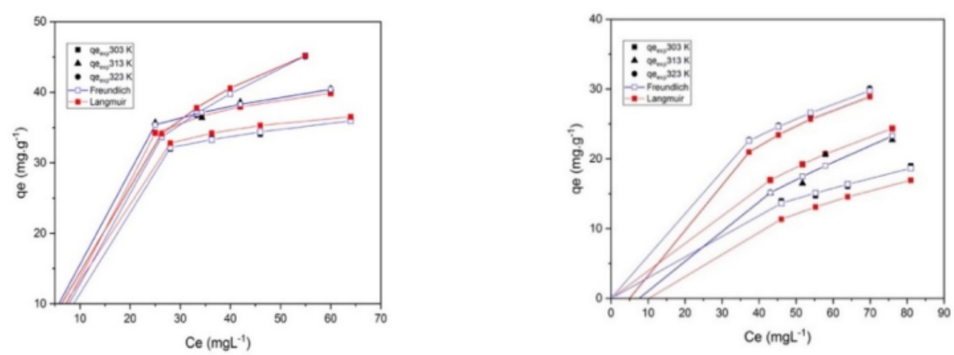


FIGURE 2. Curve of effect adsorption capacity vs initial concentration of DV onto Zn/Al and Zn/Cr layered double hydroxides in various temperatures.



(a) (b)

FIGURE 3. Langmuir and Freundlich isotherm models fitted adsorption of DV onto (a) Zn/Al, and (b) Zn/Cr layered double hydroxides.

parameters. Thermodynamic parameters were studied with Equation 4. The thermodynamic results show the adsorption process is spontaneous, based on ΔG for both adsorbents was negative. The enthalpy obtained indicates the endothermic condition, then the entropy shows the randomness surface of adsorbent [15].

TABLE 1. Isotherm model adsorption of DV onto Zn/Al and Zn/Cr layered double hydroxides.

Adsorbent	Isotherm	Parameters	T (K) 303	313	323
Zn/Al	Langmuir	q_{max} (mg.g^{-1})	39.654	45.2025	66.093
		k_L (Lmg^{-1})	0.1472	0.1246	0.0387
		R^2	0.9808	0.9473	0.998
	Freundlich	k_F	20.5059	20.6027	9.1501
		n	7.4144	6.189	2.5095
		R^2	0.9902	0.9942	0.998
Zn/Cr	Langmuir	q_{max} (mg.g^{-1})	37.6209	56.7362	47.5136
		k_L (Lmg^{-1})	0.0122	0.0099	0.0239
		R^2	0.9202	0.7694	0.9839
	Freundlich	k_F	1.6529	1.5044	4.6399
		n	1.8141	1.544	2.2851
		R^2	0.9621	0.902	0.987

TABLE 2. Thermodynamic parameters of DV onto Zn/Al and Zn/Cr layered double hydroxides

T (K)	C (mg.L^{-1})	Zn/Al LDH			Zn/Cr LDH		
		ΔG (kJ.mol^{-1})	ΔS (J.mol^{-1}K^{-1})	ΔH (kJ. mol^{-1})	ΔG (kJ. mol^{-1})	ΔS (J.mol^{-1}K^{-1})	ΔH (kJ mol^{-1})
303		-0.108			-3.083		
313	60	-0.764	32.76	9.819	-2.303	39.00	14.901
323		-1.419			-1.523		
303		-0.465			-3.413		
313	70	-0.840	18.774	5.223	-2.618	39.75	15.457
323		-1.216			-1.823		
303		-0.099			-3.427		
313	80	-0.743	32.18	9.650	-2.715	35.59	14.214
323		-1.387			-2.003		
303		-0.317			-3.749		
313	90	-0.952	31.77	9.311	-2.799	47.50	18.142
323		-1.588			-1.849		
303		-0.479			-3.689		
313	100	-1.084	30.29	8.699	-3.009	34.01	13.997
323		-1.690			-2.328		

CONCLUSION

Zn/Al and Zn/Cr layered double hydroxides has been successfully synthesized and determined by XRD and BET analyses. Then, both layered double hydroxides were utilized as an adsorbent to remove DV in aqueous solution. The adsorption capacity of DV onto Zn/Al is higher than Zn/Cr layered double hydroxides, the amount at 323 K are 100 mg/L DV solution uptake 45.06 mg/g and 30.23 mg/g, respectively. The isotherm model followed the Freundlich model. Thermodynamic analysis revealed that the adsorption process was an endothermic and spontaneous process.

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