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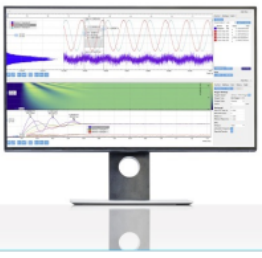

Thermodynamic Study of Direct Dye Adsorption Process onto Zn-Al-NO_3 and Zn-Fe-NO_3 Layered Double Hydroxides

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Abstract. The adsorption of direct yellow onto Zn-Al and Zn-Fe layered batch system experiments have prepared double hydroxides. Zn-Al and Zn-Fe layered double hydroxides were successfully synthesized by the co-precipitation method with adjusting to pH 10 and characterized using XRD and surface area analyses by BET method. The value of Zn-Al and Zn-Fe surface area-specific were obtained 9.41 $m^2.g^{-1}$ and 2.88 $m^2.g^{-1}$, respectively. Freundlich isotherm models described the high efficiency of adsorption direct yellow onto layered double hydroxides. The maximum adsorption capacity uptake were 98.006 $mg.g^{-1}$ and 76.078 $mg.g^{-1}$. The parameters of thermodynamic study were examined by ranging temperature (303–323 K) and obtained the adsorption process was spontaneous, endothermic, and physisorption. This work was indicating that Zn-Al and Zn-Fe layered double hydroxides have high efficiency in in adsorbing direct yellow in wastewater.

Keywords: Layered double hydroxides, dyes removal, direct dye, adsorption, Freundlich isotherm

INTRODUCTION

The contamination of fresh water is the most critical environmental problem in Indonesia. Among the contamination source, synthetic dyes could induce a serious health issue to the aquatic ecosystem and humans [1]. The synthetics dyestuff wastewater are usually anionic dyes or toxic metal cations (i.e., Cr, Cd, Pb, Cu) [2-4]. The most significant contributor of dye wastewater is the industries (textile, paper, and pulp) since the synthetics dyes have many advantages such as brighter color, long-lasting, and cheap [5, 6]. Many industries are ignoring the harmful effect of wastewater, and synthetic dyes are hard to be biodegraded [7] and hazardous to environmental [1]. The brighter color in wastewater is not only comes from aesthetic pollutants, but the color may also interfere with light penetration affecting the aquatic ecosystem [8]. On the other hand, exposure of a lot of synthetic dyes wastewater can cause skin cancer, carcinogenic or mutagenic to human life [8]. Recently, researchers worldwide are looking for the way of how to reduce the damage and effectively recover pollutants in wastewater. The methods of pollutant removal in wastewater include ion exchange [9, 10], membrane filtration, chemical precipitation, adsorption and photocatalytic [7, 11-14]. Among all these methods, adsorption method is the most popular because this method is cheap, easy to use and have no pollutant [15, 16].

Since the treatment of wastewater became an important problem to the environment, many researchers studied the effectiveness of adsorbent. For examples, hydrotalcite [17], activating carbon [1], and metal-organic framework [18].

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However, activating carbon and metal-organic framework have disadvantages because their methods are expensive and hard to re-use. Hence, hydrotalcite becomes popular as adsorbent since its ability can be effectively and easily synthesized, modified and also low-cost synthetic sorbents [19]. Hydrotalcite also called as layered double hydroxides which have brucite layers substitutions of M^{2+} and M^{3+} and anion as counterbalancing in interlayer [18, 20]. The layered double hydroxides have a positive charge and require ion-exchanged of others anions. According to Zubair et al. layered double hydroxides can remove the anionic dye by ion exchanged method and has been reported to have a high affinity to adsorb pollutants [21].

In this work, layered double hydroxides have been synthesized using the method of co-precipitation by adjusting at pH constant. After obtained the products, the layered double hydroxides were applied as sorbents to reduce the direct yellow in aqueous solution. The adsorption of direct yellow onto layered double hydroxides was studied by thermodynamic parameter and isotherm model adsorption. Sorbents were characterized using surface area analyses BET method and X-Ray diffraction analyses.

EXPERIMENTAL

Preparation of Zn-Al-NO_3 and Zn-Fe-NO_3 layered double hydroxides

According to Palapa et al. Zn-Al-NO_3 and Zn-Fe-NO_3 were synthesized using the method of co-precipitation at a constant pH. The process of LDHs synthesis applied with molar ratio of 3:1 was performed in zinc nitrate $Zn(NO_3)_2{\cdot}6H_2O$ (100 mL, 0.3 M) and a trivalent metal cation such as aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$, iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$ (100 mL, 0.1 M), respectively. The mixture was labelled as Solution A. Next, the solution A was stirred for 1 h. Solution B was synthesized with 10 mL of sodium carbonate 1 M and 10 mL of NaOH 3 M. Further, the solution B was slowly inserted into solution A accompanied with an intense stirring for 2 h and the pH was adjusted to 10 by adding the NaOH, while the temperature was maintained at 60 °C for 24 h to acquire the layered double hydroxides. Then, the layered double hydroxides were rinsed and maintained at room temperature [17].

Adsorption

Adsorption of disodium;5-[(4-hydroxyphenyl)diazenyl]-2-[(*E*)-2-[4-[(4-hydroxyphenyl)diazenyl]-2-sulfonatophenyl]ethenyl]benzenesulfonate (direct yellow) onto layered double hydroxides was performed by the batch method. The effect of concentration and temperature was investigated. As much as 0.05 g of layered double hydroxide added into 50 mL dye solution were shaken at 240 rpm for a specific time. The suspension was filtered and determined after sorption concentration using Spectrophotometer FT-IR Shimadzu FT-IR Prestige-21 at $\lambda = 510$ nm.

RESULTS AND DISCUSSION

Characterization of Zn-Al-NO_3 and Zn-Fe-NO_3 Layered Double Hydroxides

Layered double hydroxides has been successfully prepared and the characterization used the X-ray diffraction and surface area analyses. The XRD patterns of layered double hydroxides is shown in Fig. 1a. The booth of diffractograms showed a high crystallinity and specific diffraction of LDH was shows at amount 11° about interlayer distance. The basal spacing of interlayer Zn-Al-NO_3 and Zn-Fe-NO_3 is 7.57 Å and 5.80 Å, respectively. The basal spacing (d) of the layered materials could be determined using the basal reflection by applying the Bragg's equation $\lambda = 2d\sin\theta$. Then, both layered double hydroxides were characterized using surface area analyses. The morphology difference might impact the surface area in specific, size of the pore, thereupon the adsorption capacities and extraction efficiencies of the sorbents. It is interesting, that even though the similar process was applied for the layered double hydroxides synthesis, the different morphologies were observed in all of the LDHs, which was ascertained with the results of XRD reflections. The surface area analyses results is shown in Fig. 1b. The characteristic of nitrogen adsorption-desorption isotherms and the related pore size distribution. All of the curves show typical IV isotherms indicating mesoporous for both layered double hydroxides. Table 1 shows list the data of the surface area and porous

size. Based on the results, Zn-Al-NO_3 has a more significant surface area than Zn-Fe-NO_3, amount 9.41 m^2/g and 2.88 m^2/g, respectively.

Isotherm Adsorption and Thermodynamic Parameters

Adsorption of direct yellow by Zn-Al-NO_3 and Zn-Fe-NO_3 layered double hydroxides are shown in Fig. 2. It showed the adsorption capacity of Zn-Al-NO_3 is much larger than Zn-Fe-NO_3. The data in Fig. 2, related to the surface area and interlayer space of these materials, which is Zn-Al-NO_3 has a greater surface area and interlayer space. The result shows the higher adsorption in 200 ppm at 323 K is the largest, its uptake is 98.006 $mg.g^{-1}$ for Zn-Al-NO_3 layered double hydroxides and 76.078 $mg.g^{-1}$. The results have shown that Zn-Al-NO_3 was better to remove direct yellow than Zn-Fe-NO_3 in a relatively high concentration. The isotherm model for direct yellow adsorption onto Zn-Al-NO_3 and Zn-Fe-NO_3 layered double hydroxides were modeled by isotherm of Freundlich 1 and Langmuir 2, the equation can be express as:

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

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

where q_e (mg/g) is the adsorbate amount at equilibrium, qm (mg/g) the theoretical maximum monolayer sorption capacity, C_e (mg/L) the equilibrium concentration of adsorbate solution, and K_F, n and K_L are empirical constants. The measured Langmuir and Freundlich isotherm constants are shown in Table 2. The adsorption data of direct yellow onto layered double hydroxides were followed the Freundlich isotherm model than Langmuir isotherm model based on coefficient correlation. This phenomenon was identified from the distribution of sorbate adsorbed on the surface and interlayer of materials.

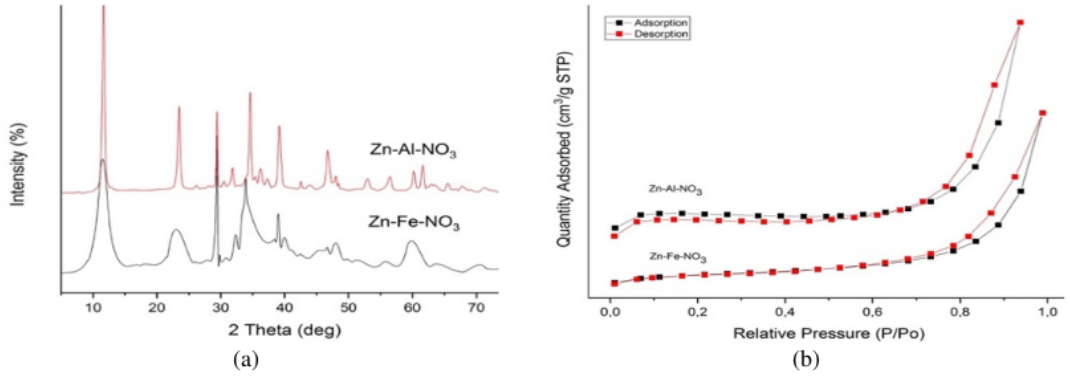

FIGURE 1. (a) XRD Characterization and (b) surface area analyses of Zn-Al-NO_3 and Zn-Fe-NO_3 layered double hydroxides.

TABLE 1. Data of surface area analyses by BET methods.

Adsorbent	S_{BET} (m^2/g)	Pore volume (BJH, cm^3/g)	Pore size (ø, nm)
Zn-Al-NO_3	9.4128	0.045351	19.2743
Zn-Fe-NO_3	2.8834	0.010334	14.6964

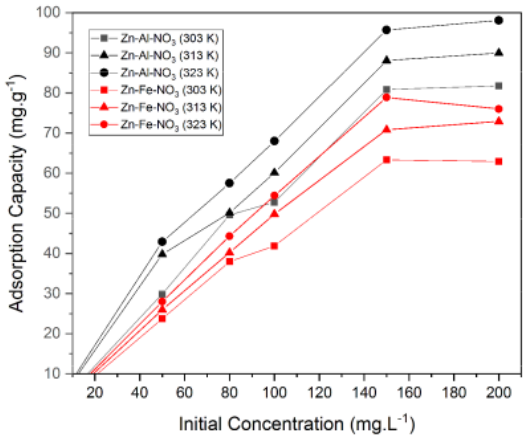

FIGURE 2. Effect of initial concentration of direct yellow by Zn-Al-NO_3 and Zn-Fe-NO_3 at various temperature.

TABLE 2. Langmuir and Freundlich isotherm models for adsorption of direct yellow onto layered double hydroxides.

Adsorbent	Isoterm	Parameters	T (K) 303	313	323
Zn-Al-NO_3	Langmuir	q_{max} ($mg.g^{-1}$)	100.7060	118.7815	121.3768
		k_L (Lmg^{-1})	0.0090	0.0328	0.0515
		R^2	0.6023	0.7954	0.905
	Freundlich	k_F ($mg.g^{-1}$)(Lmg^{-1})$^{1/n}$	3.5136	13.5060	19.5108
		n	1.3646	2.3814	2.6625
		R^2	0.9025	0.9045	0.9363
Zn-Fe-NO_3	Langmuir	q_{max} ($mg.g^{-1}$)	86.4756	91.1563	104.3262
		k_L (Lmg^{-1})	0.0052	0.0041	0.0033
		R^2	0.6999	0.992	0.9855
	Freundlich	k_F ($mg.g^{-1}$)(Lmg^{-1})$^{1/n}$	1.8634	1.788	1.8525
		n	1.2733	1.183	1.1330
		R^2	0.9734	0.998	0.9986

The curved of fitted isotherm data are shown in Fig. 3, The straight blue square line indicate the adsorption isotherm model of Freundlich, whereas the square symbol with red line reflects the adsorption isotherm model of Langmuir and the black symbol indicates the experiment data of absorption. The equilibrium isotherm was investigated at 303, 313 and 323 K. The adsorption capacity increased with temperature indicating that the adsorption mechanism is an endothermic process. The thermodynamic parameter is shown in Table 3. The Gibbs free energy (ΔG) was calculated and found to be negative at all temperatures confirming the spontaneity of the adsorption process. The ΔH positive value confirms the endothermic characteristic of direct yellow sorption whereas the ΔS positive value shows an increased randomness at the solid/solution interface.

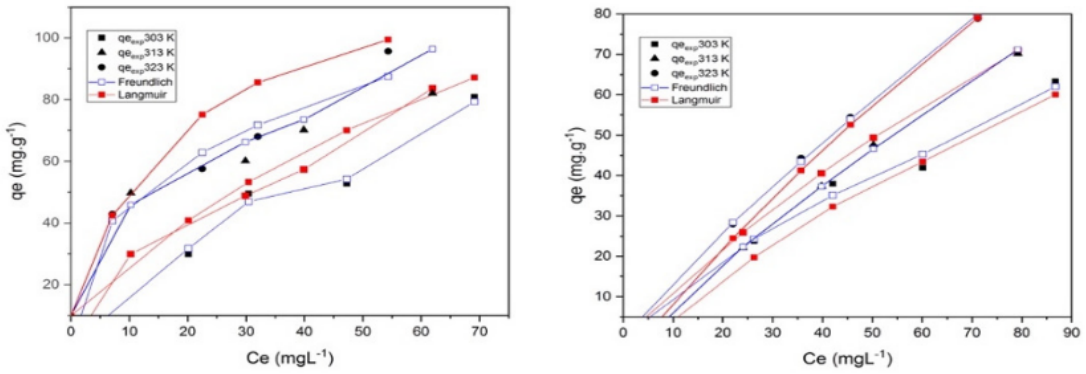

FIGURE 3. Langmuir and Freundlich isotherm models (a) Zn-Al-NO_3 and (b) Zn-Fe-NO_3.

TABLE 3. Data of thermodynamic parameters of Zn-Al-NO_3 and Zn-Fe-NO_3.

T (K)	C (mg.L^{-1})	Zn-Al-NO_3 LDHs			Zn-Fe-NO_3 LDHs		
		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	150	-0.378	30.336	8.814	-0.838	11.06	1.96
313		-0.984			-1.379		
323		-1.591			-1.920		

CONCLUSION

In this work, the adsorption of direct yellow onto Zn-Al-NO_3 and Zn-Fe-NO_3 has been studied and calculated by the thermodynamic parameters. Isotherm adsorption of both layered double hydroxides followed the Freundlich isotherm model and adsorption capacity shows a higher adsorption in 200 ppm at 323 K is the largest, its uptake is 98.006 mg.g^{-1} for Zn-Al-NO_3 layered double hydroxides and 76.078 mg.g^{-1}. Based on the thermodynamics parameters, both layered double hydroxides have spontaneity and endothermic adsorption process.

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