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Research Paper

Kinetic Adsorption of Direct Yellow Onto Zn/Al and Zn/Fe Layered Double Hydroxides

Neza Rahayu Palapa[1], Bakri Rio Rahayu[1], Tarmizi Taher[2], Risfidian Mohadi[1], Aldes Lesbani[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Jl. Palembang-Prabumulih, Km. 32, Ogan Ilir, South Sumatra, Indonesia*
[2]*Department of Enviromental Science, Graduate School, Sriwijaya University, Jl. Padang Selasa No. 524 Ilir Barat 1, Palembang-South Sumatra, Indonesia*
*__Corresponding author__: aldeslesbani@pps.unsri.ac.id

Abstract
Zn/Al and Zn/Fe layered double hydroxides has successfully synthesized by co-precipitation methods with molar ration 3:1. The samples were characterized using X-Ray Diffraction, Fourier Transform Infrared Spectroscopy and Surface Area using BET method. In this study, Zn/Al and Zn/Fe layered double hydroxides were used to remove direct yellow dye in aqueous solution. The experiments were carried out time variations with the aim of observing the kinetic studies. The results showed that the adsorption of direct yellow onto Zn/Al and Zn/Fe layered double hydroxides based on co-efficient correlation kinetic models more fit using pseudo-second-order than pseudo-first-order.

Keywords
Adsorption, Dye, Layered double hydroxides, Kinetic Study, co-precipitation

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1. INTRODUCTION

Layered double hydroxides as known as anionic clays with a positive charge excess in their brucite like layers and anion species in interlayer as counter balancing (Gong et al., 2013). In general, layered double hydroxides has formula $[M^{2+}_{(1-x)}M^{3+}x(OH)_2](An^-)x/nH_2O$ where, M^{2+} is divalent metal cation and M^{3+} is trivalent metal cation (Kefif et al., 2019; Palapa et al., 2019). Layered double hydroxides is one of most considered attention in recent years with their ability to remediation wastewater were contains dye, toxic metals and organic pollutant in aqueous solution (Meng et al., 2019). Layered double hydroxides were widely used to adsorbent caused their ability. The benefits of layered double hydroxides are easy to synthesized, high flexibility structure and easy to modified (Gonçalves et al., 2019).

Dyes effluent contained with wastewater can be bad impact to environment. The remediation technique of wastewater has been studied. The different physical or chemical methods has advantages and disadvantages. The examples of chemical technique such as photocatalysis (Hidayati et al., 2019), and physicochemical methods such as ion exchange, coagulation, adsorption and membrane filtration (Kazeem et al., 2019). Many of them are expensive, hard to use and has limitation of dye separation efficiency (Daud et al., 2019; Hidayati et al., 2019). However, the adsorption method has more advantages which is this method are more useful, low cost, easy to used and have no pollutant (dos Santos et al., 2017; Milagres et al., 2017).

In this study, Zn/Al-LDH and Zn/Fe-LDH was applied to removal direct yellow dye in wastewater. As known, synthetics dye has bad impact to bodies and environment. According to Kausar et al. (2018) direct dyes are usually used for leather industries, cotton and rayon dyeing and paper industries. The main classes of direct dyes include poly azo and oxazine compounds Palapa et al. (2018a). These dyes have a high affinity of dyeing process on cellulosic fiber in aqueous solution. In Palembang, these dyes are most popular used for Jumputan home industries. Many of craftsmen assumed that direct dyes have effect brighter than other synthetic dyes. In other hand, direct dye was reported that the effect health to body is bladder cancer carcinogen Sun et al. (2010); Zhang et al. (2018); Palapa et al. (2018b). This research was removal direct yellow using layered double hydroxides (LDH) by adsorption method. The amount of absorbed were calculated and studied by kinetic models. Kinetic models were fitted are pseudo-first-order and pseudo-second-order.

2. EXPERIMENTAL SECTION

2.1 Materials

The chemicals all purchased by Merck such as aluminum nitrate nonahydrate, iron nitrate nonahydrate, zinc nitrate hexahydrate, and sodium hydroxide. Nitrogen gas were pro-analytic and The solution was prepared by deionized purity water. Then characterized by XRD Diffractometer Rigaku Miniflex-600 and

Spectrophotometer FT-IR Shimadzu FT-IR Prestige-21.

2.2 Synthesis of Layered Double Hydroxides

Zn/Al-LDH was synthesized using a co-precipitation method. A mixed-metal nitrate solution (0.25 M Zn^{2+} and 0.08 M Al^{3+}) was adjusted to the solution pH of 9–10 by adding the required amount of 2 M NaOH. The mixture was flowed nitrogen system and heated to 80 °C for 18 h. The white precipitate was formed. Subsequently, it was filtered and rinsed with deionized water. After drying at 85 °C, the obtained material was ground gently into a fine powder. Zn/Fe-LDH was synthesis by $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ salt solution were mixed in a desired Zn (II)/Fe (III) 3:1 molar ratio and titrated slowly with the basic solution of 2M NaOH until the pH reached 10.0 at room temperature maintaining a nitrogen atmosphere. The brown precipitate was formed then the mixed solution was filtered and rinse with deionized water, drying at 80 °C to obtain powdery LDH.

2.3 Effect of Contact Time Adsorption Direct Yellow by Zn/Al-LDH and Zn/Fe-LDH

The adsorption of direct yellow onto Zn/Al-LDH and Zn/Fe-LDH was performed taking 50 mL from sample solution 100 mg/L. 0.05 g of Zn/Al-LDH and Zn/Fe-LDH were contact to 50 mL direct yellow 100 mg/L. The mixing solution were shake in horizontal shaker 250 rpm by varying times (between 5-180 min). The solution was centrifuged and the filtrate was analyses using UV-Vis Spectrophotometer at 403 nm. Before analyses, five point of standard curve has been examined and coefficient correlation was linear amount 0.99. The amount of adsorbed were calculated from initial concentration and equilibrium concentration in supernatant after centrifugation. After that, the data were tested using kinetic models. The kinetic model was used pseudo-first-order and pseudo-second-order. The kinetic parameters are calculated using the pseudo-first-order:

$$log(qe - qt) = log qe - k_1/(2.303)t \quad (1)$$

and pseudo-second-order equations as follows:

$$t/qt = (1/k_2 qe^2) + (1/qe)t \quad (2)$$

where qt is the amount of adsorbate adsorbed at time t ($mg.g^{-1}$), qe is the adsorption capacity in the equilibrium (mg g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}), k2 is the pseudo-second-order rate (g $mg^{-1}min^{-1}$) and t is the contact time (min) [6,13].

3. RESULTS AND DISCUSSION

3.1 Characterization of Layered Double Hydroxides

Zn/Al-LDH and Zn/Fe LDH has been successfully prepared and characterized using XRD and FTIR. In Fig. 1. Shows the XRD pattern of Zn/Al-LDH and Zn/Fe-LDH. The booth of diffractograms were shows high crystallinity and specific diffraction of LDH was shows at amount 11° about interlayer distance (Taher et al., 2019). The distance of interlayer Zn/Al-LDH and Zn/Fe-LDH is 7.57 Å and 5.80 Å, respectively.

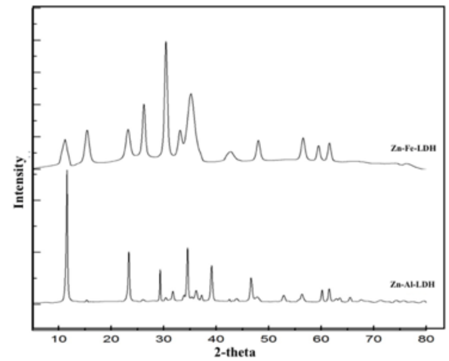

Figure 1. XRD pattern of Zn/Al-LDH and Zn/Fe-LDH

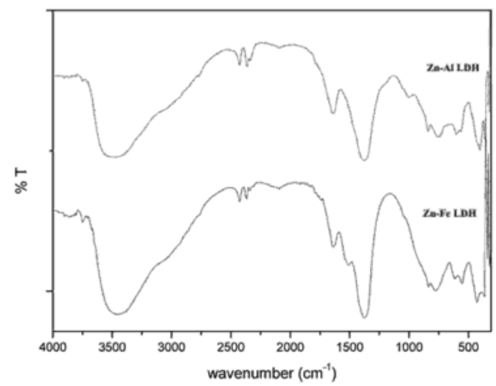

Figure 2. FTIR spectra of Zn/Al-LDH and Zn/Fe-LDH

Fig. 2. shows the spectra of both layered double hydroxides. both spectra have similar spectra. The presence of vibrations at wavenumber about 3400 cm^{-1} which is OH vibration from hydroxyl group and about 1635 cm^{-1} a identified the presence of water molecules in interlayer. The sharp peaks at 1381 cm^{-1} were indicated the vibration of nitrate. The vibration of metal-oxide are shows at 700-900 cm^{-1}.

3.2 Effect of Adsorption Time Direct Yellow by Zn/Al LDH and Zn/Fe-LDH

The comparison of Zn/Al-LDH and Zn/Fe-LDH was showed in Fig. 3. The adsorption efficiency was increased rapidly at 100 min for Zn/Al-LDH with amount of dye adsorbed is reach 71.93% from 100 mg/L and Zn/Fe-LDH about 51.24% for adsorb direct yellow from 100 mg/L. Layered double hydroxides both are increasing rapidly thereafter becomes slow until reach equilibrium. Is caused layered double hydroxides has available active site before equilibrium, so that layered double hydroxides can adsorb rapidly. Dyes sorption of Zn/Al-LDH higher than Zn/Fe-LDH. The difference of equilibrium times and efficiency adsorbed may cause the Zn/Fe-LDH has smaller interlayer than Zn/Al-LDH.

According to Ulibarri and Hermosin (2006) that the adsorption of anionic contaminant can be adsorb into surface active site and sometimes exchanges mechanism can be happen in interlayer (Kausar et al., 2018; Palapa et al., 2018b). The schematics of direct yellow adsorption onto layered double hydroxides was shows in Fig. 4.

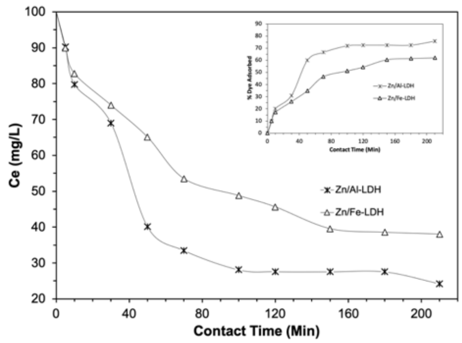

Figure 3. Comparison of the adsorption efficiency direct yellow by Zn/Al-LDH and Zn/Fe-LDH

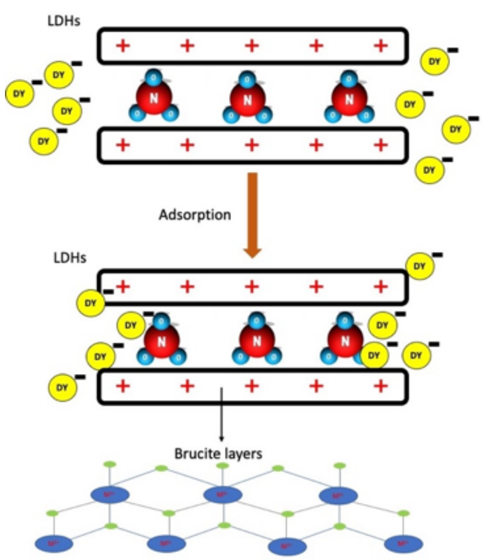

Figure 4. The schematic adsorption process of direct yellow onto layered double hydroxides

Kinetic modeling of the adsorption process provides a prediction of adsorption rates, and allows the determination of fitting rate expressions characteristic for possible reaction mechanisms. In this study, pseudo-first-order and pseudo-second-order has been examined. The parameters of pseudo-first-order and pseudo-second-order was estimated with the aid of the non-linear regression. the obtained value and coefficient correlation were showed in Table 1. Based on coefficient correlation both layered double hydroxides are higher for pseudo-second-order than pseudo-first-order. The result indicated that the adsorption process is chemisorption (Kazeem et al., 2019; Hidayati et al., 2019).

Table 1. kinetic parameters of adsorption direct yellow onto layered double hydroxides

Kinetic models	Parameters	Layered double hydroxides	
		Zn-Al-NO_3	Zn-Fe-NO_3
Pseudo-first order	k_1	0.0597	0.0339
	R^2	0.9127	0.891
Pseudo-second order	k_2	0.0064	0.0072
	R^2	0.9544	0.9176
	qe	80.791	54.965

4. CONCLUSIONS

In this study, adsorption experiment for removal direct yellow by Zn/Al-LDH and Zn/Fe-LDH. The synthesis of Zn/Al-LDH and Zn/Fe-LDH using co-precipitation method with molar ratio and obtained white and brown powder. Zn/Al-LDH and Zn/Fe-LDH were characterized using XRD and FTIR and applied as adsorbent to removal direct yellow dye in aqueous solution. The adsorption was carried out by varying time and fitted to kinetic models. The result was shows both layered double hydroxides more fitted using pseudo-second-order than pseudo-first-order.

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REFERENCES

Daud, M., A. Hai, F. Banat, M. B. Wazir, M. Habib, G. Bharath, and M. A. Al-Harthi (2019). A review on the recent advances, challenges and future aspect of layered double hydroxides (LDH)–Containing hybrids as promising adsorbents for dyes removal. *Journal of Molecular Liquids*; 110989

dos Santos, R. M. M., R. G. L. Gonçalves, V. R. L. Constantino, C. V. Santilli, P. D. Borges, J. Tronto, and F. G. Pinto (2017). Adsorption of Acid Yellow 42 dye on calcined layered double hydroxide: Effect of time, concentration, pH and temperature. *Applied Clay Science*, **140**; 132–139

Gonçalves, R. G. L., P. A. Lopes, J. A. Resende, F. G. Pinto, J. Tronto, M. C. Guerreiro, L. C. A. de Oliveira, W. de Castro Nunes, and J. L. Neto (2019). Performance of magnetite/layered double hydroxide composite for dye removal via adsorption, Fenton and photo-Fenton processes. *Applied Clay Science*, **179**; 105152

Gong, M., Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, and H. Dai (2013). An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation. *Journal of the American Chemical Society*, **135**(23); 8452–8455

Hidayati, N., D. R. Apriliani, Helda, T. Taher, R. Mohadi, Elfita, and A. Lesbani (2019). Adsorption of congo red using Mg/Fe and Ni/Fe layered double hydroxides. *Journal of Physics: Conference Series*, **1282**; 012075

Kausar, A., M. Iqbal, A. Javed, K. Aftab, H. N. Bhatti, S. Nouren, et al. (2018). Dyes adsorption using clay and modified clay: a review. *Journal of Molecular Liquids*, **256**; 395–407

Kazeem, T. S., M. Zubair, M. Daud, N. D. Mu'azu, and M. A. Al-Harthi (2019). Graphene/ternary layered double hydroxide composites: Efficient removal of anionic dye from aqueous phase. *Korean Journal of Chemical Engineering*, **36**(7); 1057–1068

Kefif, F., K. Ezziane, A. Bahmani, N. Bettahar, and S. Mayouf (2019). Evans Blue dye removal from contaminated water on calcined and uncalcined Cu-Al-CO3 layered double hydroxide materials prepared by coprecipitation. *Bulletin of Materials Science*, **42**(1); 14

Meng, Z., M. Wu, S. Zhao, R. Jing, S. Li, Y. Shao, X. Liu, F. Lv, A. Liu, and Q. Zhang (2019). Removing anionic dyes from wastewater based on in-situ formation of Fe3O4@ Zn-Al layered double hydroxides by self-assembly. *Applied Clay Science*, **170**; 41–45

Milagres, J. L., C. R. Bellato, R. S. Vieira, S. O. Ferreira, and C. Reis (2017). Preparation and evaluation of the Ca-Al layered double hydroxide for removal of copper (II), nickel (II), zinc (II), chromium (VI) and phosphate from aqueous solutions. *Journal of environmental chemical engineering*, **5**(6); 5469–5480

Palapa, N. R., R. Mohadi, and A. Lesbani (2018a). Adsorption of direct yellow dye from aqueous solution by Ni/Al and Zn/Al layered double hydroxides. In *AIP Conference Proceedings*, volume 2026. AIP Publishing, page 020018

Palapa, N. R., T. Taher, R. Mohadi, and A. Lesbani (2019). Removal of Anionic Direct Dye Using Zn/Al, Zn/Fe and Zn/Cr Layered Double Hydroxides Toward Interlayer Distance. *Science and Technology Indonesia*, **4**(3); 70–76

Palapa, N. R., T. Taher, R. Mohadi, M. Said, and A. Lesbani (2018b). Synthesis of Ni/Al layered double hydroxides (LDHs) for adsorption of malachite green and direct yellow dyes from solutions: Kinetic and thermodynamic. In *AIP Conference Proceedings*, volume 2026. AIP Publishing, page 020033

Sun, Z., L. Jin, W. Shi, M. Wei, and X. Duan (2010). Preparation of an anion dye intercalated into layered double hydroxides and its controllable luminescence properties. *Chemical Engineering Journal*, **161**(1-2); 293–300

Taher, T., M. M. Christina, M. Said, N. Hidayati, F. Ferlinahayati, and A. Lesbani (2019). Removal of Iron(II) Using Intercalated Ca/Al Layered Double Hydroxides with [α-SiW12O40]4-. *Bulletin of Chemical Reaction Engineering & Catalysis*, **14**(2); 260

Zhang, H., H. Chen, S. Azat, Z. A. Mansurov, X. Liu, J. Wang, X. Su, and R. Wu (2018). Super adsorption capability of rhombic dodecahedral Ca-Al layered double oxides for Congo red removal. *Journal of Alloys and Compounds*, **768**; 572–581

