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Synthesis of Ni/Al Layered Double Hydroxides (LDHs) for Adsorption of Malachite Green and Direct Yellow Dyes from Solutions: Kinetic and Thermodynamic

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Abstract. Ni/Al layered double hydroxides (LDHs) was synthesized by co-precipitation method at constant pH and characterized using XRD and FTIR analyses. Ni/Al LDHs was applied as adsorbent to removal malachite green and direct yellow in aqueous solution. The results show direct yellow more effective adsorbed than malachite green because LDHs has positive charges. Kinetics study showed that the adsorption process is more fits with PSO than PFO based on correlation coefficients. The adsorption process is describe by Freundlich isotherm models for all dyes. The value of enthalphy and entrophy shows that the adsorption process was endothermic and negative free energy value was indicated that the process was spontaneous.

INTRODUCTION

Most of the widely industries was use the synthetics dyes such as textile industries, paper printing and packaging the industrial stuff [1]. The synthetics dyes more preferable than natural dyes because the synthetic dyes has a brighter color and a longer color endurance [2]. One of dyes are malachite green and direct yellow. Those dyes were harmful and high toxicity[3-4]. Malachite green and direct yellow are cationic and anionic dyes, respectively. However, both has a high stability and hard to biodegradable [3-5], bad impact of colored wastewater containing the synthetics dyes for human (such as liver, dysfunction of kidneys, reproductive system and cancer)[6] and environment. Therefore, most important to minimize the impact of wastewater containing synthetic dyes before its disposal to the environment.

Many of researchers were studied for removal the synthetic dyes in wastewater such as biological treatment (aerobic and anaerobic) [7], electrochemical coagulation [8], membrane filtrate [9], oxidation [10], photodegradation[11] and adsorption[12]. Among all of the method, adsorption method has been prefer as the one of most efficient method because of its relatively flexibility, easy to operation, low cost, fast reaction and have no pollutant [13-14]. The adsorption process need the adsorbent to removal dyes from wastewater. the most adsorbent widely use such as carbon active [15], bentonite [6], zeolite [16] and layered double hydroxides [17]. Layered double hydroxides has been advantages of being easily synthesis and can be easily used in desired process compared to the naturals adsorbent [18].

Layered double hydroxides (LDHs) are known as synthetic anionic clays [19]. Layered double hydroxides has positively charged brucite-like layers and anions in interlayer galleries [20]. The interlayer galleries contain charge-balancing anion (such as OH^-, Cl^-, SO_4^{2-}, NO_3^- , and CO_3^{2-}) and water [12]. The general formula of layered double hydroxides is $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2](A^{n-})_{x/n}\bullet nH_2O$ with the identities of M^{2+} and M^{3+} are divalent and trivalent metal cation and A^n is interlayer anion as counter balancing the metals cations [21]. The anion can be taking up by layered

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double hydroxides uses three mechanism such as anion exchanges in interlayer, surface adsorption and reconstruction layered double hydroxides calcined by 'memory effect' [22]. Previous studies showed that layered double hydroxides Ni/Fe, Mg/Al, Mg/Fe, Zn/Al can be potentially be used as adsorbent to remove dyes in wastewater [4,23-24]. in this study, layered double hydroxides was prepared Ni/Al using co-precipitation method with the constant pH. Layered double hydroxides were characterization using X-ray diffraction, fourier transform infrared spectroscopy. Furthermore, LDHs were applied to remove dyes i.e. malachite green and direct yellow. The effect of various conditions such as pH solution, adsorption time, temperature and initial concentration. The investigation of kinetic, thermodynamic and isotherm adsorption were discussed.

EXPERIMENTAL SECTION

Chemicals and Instrumentation

Chemicals were analytical grade from Merck and Sigma Aldrich such as nickel nitrate, aluminum nitrate, sodium hydroxide, sodium carbonate. Water was supplied from Integrated Research Laboratory, Universitas Sriwijaya using water system Purite® ion exchange pH 7. FTIR spectrophotometer was conducted using Shimadzu FTIR Prestige-21 using KBr disk and scanning was performed at wavenumber 400-4000 cm^{-1}. XRD was conducted using Rigaku Miniflex-600 and scanned at 0.1 deg min^{-1}. Analysis of malachite green and direct yellow were used UV-Vis spectrophotometer double beam EMC-61PC.

Synthesis of Ni/Al Layered Double Hydroxides

Ni/Al layered double hydroxides were synthesized by co-precipitation method at constant pH[25-26]. Nickel nitrate (100mL, 0.3 M) and alumunium nitrate (100 mL, 0.1 M) with the molar ratio 3:1 were stirring for a hour. Then, 100 mL of sodium carbonate solution 0.3 M at 353 ^{o}K was added slowly. The solution was added with 25 mL of sodium hydroxides 2 M and the mixtures was slowly stirring at 353 ^{o}K for 17 hours. The solution kept at pH 10 to form blue solid bulky material. After that, the blue material was washed with water and kept overnight at 335 ^{o}K to obtain Ni/Al layered double hydroxides. Characterization of Ni/Al layered double hydroxides was performed using XRD powder analysis and IR spectroscopy.

Adsorption Experiment

Preparing malachite green and direct yellow solution by 1 g of solid malachite green and direct yellow powder with 1000 mL of water to obtain 1000 mg/L as dye stock solution. The standard solution prepared by diluting dye stock solution. To obtain a standard curve of the dyes solution, dyes were measured of each standard solution using spectrophotometer UV-Vis at maximum wavelength, respectively. The adsorption of dyes were conducted in batch system. An amount of adsorbent was added into 50 mL of dyes solution then mixture using horizontal shaker at 240 rpm at constant temperature for any predeterminate time. The solution was filtered and measuring using UV-Vis spechtrophotometer.

In order to study of the effect of time adsorption, the experiment set up as follow. 0.05 g of adsorbent was added to 50 mL of dyes solution then shake at variying time with temperature 303 ^{o}K and the concentration of dyes solution was 100 mg/L. The thermodynamic parameters investigated based on two kinetic parameter models, pseudo-first-order and pseudo-second-order. The thermodynamics studied by variying initial concentration, the experiment set up as follow. 0.05 g of adsorbent added to 50 mL of variying concentration dyes solution. Then shake in variying temperature 303-343 ^{o}K.

RESULT AND DISCUSSION

Adsorbent Characterization

The XRD pattern of Ni/Al layered double hydroxides (LDHs) was showed in Fig. 1. The XRD pattern of Ni/Al LDHs have sharp and symmetrical peaks with some asymmetrical peaks at high angle indicated high crystallinity[25]. The basal spacing of Ni/Al layered double hydroxides was showed at 2 theta 11^{o} is 7.65 Å. The

FTIR spectra of Ni/Al layered double hydroxides are shown in Fig. 2. The intensity at wavenumber 3448 cm^{-1} is assigned to the OH stretching vibration. Wavenumber at 1635 cm^{-1} is assigned as OH bending in the interlayer water molecule. Also, the intent band at 1380 cm^{-1} is shown as stretching of nitrate anion in the interlayer. Bands in the range at 600-700 $cm^{-1}$are attributed to Ni-O-Al[27].

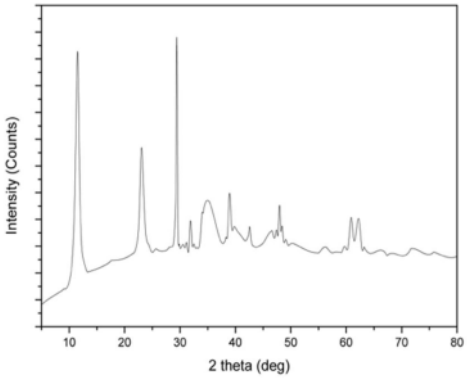


FIGURE 1. XRD pattern of Ni/Al layered double hydroxides

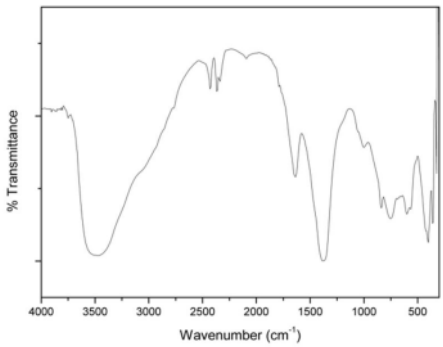


FIGURE 2. FTIR spectra of Ni/Al layered double hydroxides

Effect of Contact Time and Kinetic Parameters

Effect of adsorption time of dyes by Ni/Al LDHs shown in Fig. 3. The adsorption of malachite green and direct yellow on Ni/Al LDHs were shows the adsorption of direct yellow more faster than malachite green. The maximum of adsorption time on direct yellow by Ni/Al LDHs at 60 min with maximum uptake 79.02 mg/g whereas the maximum adsorption on malachite green by Ni/Al LDHs at 120 min with maximum uptake 73.38 mg/g. According to this research, LDHs has been widely investigated has positive charges on layers, therefore LDHs is a better to removal the anionic dyes[2]. In order to identify the kinetics parameter adsorption process, two kinetic models i.e, Pseudo-first-order and pseudo-second-order are applied. The kinetics parameters is calculated using the pseudo-first-order and pseudo-second-order equations as follows:

$$\log (Qe-Qt) = \log Qe - k_1/(2.303)\, t \qquad (1)$$

$$t/Q_t = (1/k_2 Q_e^2) + (1/Q_e)\, t \qquad (2)$$

Where qe and qt are capacities of adsorbed (mg/g) at equilibrium and t is contact time (min), k_1 is the rate constant of Pseudo-First-Orde. Then, k_2 is the rate constant of pseudo-second-order. The calculated kinetics parameters for malachite green and direct yellow by Ni/Al LDHs are given in Table 1. It shows that, of the two models kinetic equations, the PSO model is more fit than PFO based on the correction coefficient R^2.

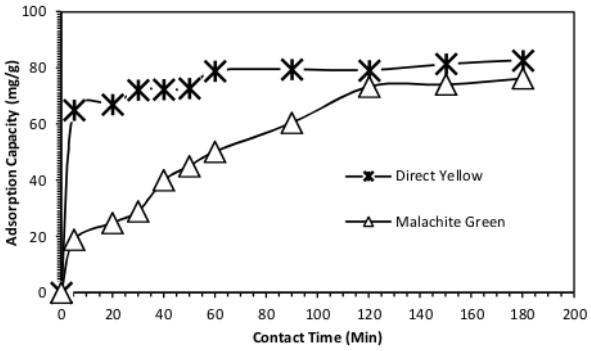


FIGURE 3. Time adsorption of dyes by Ni/Al LDHs

TABLE 1. Kinetics Parameters Adsorption of Dyes by Ni/Al LDHs

Kinetics Models	Parameters	Dye	
		Direct Yellow	Malachite Green
Pseudo-First-Order	Qe_{Exp} (mg/g)	82.782	76.328
	Qe_{Calc} (mg/g)	18.677	92.299
	K_1 (min^{-1})	0.017	0.024
	R^2	0.895	0.946
Pseudo-Seconds-Order	Qe_{Exp} (mg/g)	82.782	76.328
	Qe_{Calc} (mg/g)	84.041	99.176
	K_2 (min^{-1})	0.0024	0.0001
	R^2	0.999	0.948

Adsorption Isotherm and Thermodynamic Study

Fig. 4 were shows initial concentration vs concentration adsorbed with variying temperature of dyes adsorption by Ni/Al LDHs. In Fig. 4. Dyes adsorbed are higher at high temperature (343 ^oK) its means the interaction of adsorbate-adsorbent is much stronger than solvent-adsorbent at adsorption sites. Therefore, the adsorption isotherms for direct yellow dye using Ni/Al LDHs at varying temperature 303 ^oK, 323 ^oK and 343 ^oK were shown in Figure 5. The isotherms models Langmuir and Freundlich are used for this data. The Langmuir assumed that adsorbate was occupied into monolayer. Its used equation as follows:

$$C_e/Q_e = 1/(K_L Q_{max}) + (1/Q_{max})\, C_e \qquad (3)$$

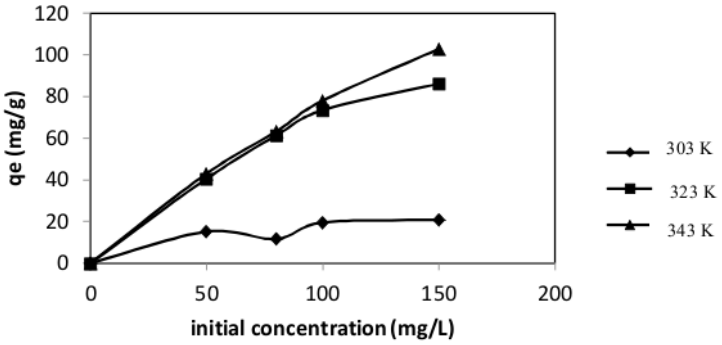
Where q_e is the equilibrium adsorption, C_e is equilibrium concentration, q_{max} is the maximum adsorption and k_L is the equilibrium adsorption constant. Then, the essential features of Langmuir isotherm namely R_L (equilibrium parameters). Value R_L has indicated the models of isotherm. If irreversible, the R_L calculated zero ($R_L = 0$), liniear when $R_L = 1$, and favorable when $0 > R_L > 1$ [28].

The Freundlich isotherm model identified the heterogenous adsorbent surface. The equation is following:

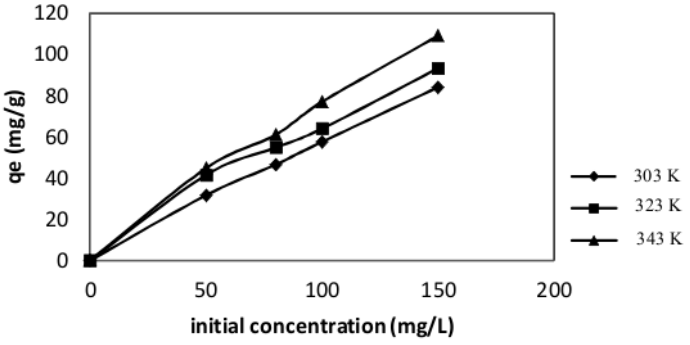
$$Log\ q_e = Log\ k_F + n\ Log\ C_e \quad (4)$$

Where k_F is adsorption capacity when equilibrium, the value of n gives information of favorability of adsorption process, if n=1 linear, n<1 is chemisorption and n>1 is favorable[29]. Table 2. Were present the parameter value of the Freundlich and Langmuir. It can be seen that the Freundlich model more fis of the experimental data with the correlative coefficient is 0.9 than Langmuir isotherm model. This phenom was reported indicated that the adsorbate interacted each other on surface sites of Ni/Al LDHs (physisorption)[30].

Table 3. showed the thermodynamic parameters values. The value of enthalphy and entrophy shows that the adsorption process is endothermic. Negative free energy value was indicated that the process is spontaneous and the desreases of free energy value with the increases of temperature indicated that the adsorption more favorable at low temperature (room temperature).



(a)



(b)

FIGURE 4. Adsorption isotherm of malachite green (a) and direct yellow (b) by Ni/Al LDHs at several temperatures

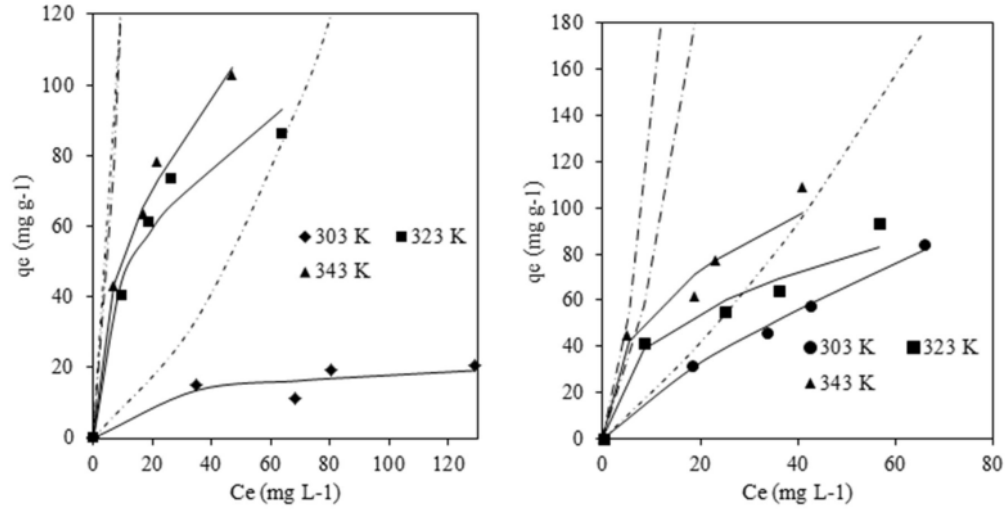


FIGURE 5. Adsorption isotherm, Langmuir and Freundlich models malachite green (a) and direct yellow (b) by Ni/Al LDHs. The solid line represents the model fitting Freundlich, the dash line represent the model fitting Langmuir, and the symbol represents experimental data.

TABLE 2. Langmuir and Freundlich Isotherm Models

Correlation Parameter	T= 303 K		T= 323 K		T= 343 K	
Langmuir	DY	MG	DY	MG	DY	MG
Q_{max}	255.1028	27.3290	121.8437	105.3400	145.3543	140.2492
K_L	0.0071	0.0200	0.0409	0.0730	0.0553	0.0560
R_L	0.00026-0.00078	0.0002-0.0007	0.000054-0.00016	0.00006-0.0001	0.000045-0.00013	0.00004-0.0001
R^2	0.817	0.623	0.847	0.996	0.829	0.9869
Freundlich	DY	MG	DY	MG	DY	MG
K_f	3.286	5.265	16.593	18.440	21.301	17.601
n	1.303	3.762	2.507	2.566	2.431	2.156
R^2	0.992	0.9702	0.906	0.9108	0.905	0.9884

TABLE 3. Values of Thermodynamic Parameters for The Adsorption of Dyes by Ni/Al LDHs

T (^{o}K)	Concentration (mg/L)	DY d G (kJ/mol)	DY d S (J/mol.K)	DY d H (kJ/mol)	MG d G (kJ/mol)	MG d S (J/mol.K)	MG d H (kJ/mol)
303		-1.506			-0.237		
323	50	-3.906	120.004	34.855	-2.975	136.934	41.253
343		-6.306			-5.714		
303		-0.831			-0.009		
323	80	-2.075	62.181	18.010	-2.180	108.559	32.884
343		-3.318			-4.351		
303		-0.066			-0.227		
323	100	-1.758	54.704	15.911	-2.101	93.695	28.161
343		-2.852			-3.975		
303		-0.501			-0.012		
323	150	-1.579	53.563	15.722	-1.050	51.863	15.701
343		-2.650			-2.087		

CONCLUSION

In this study, NiAl LDHs can be used effectively for removal dyes, both anionic dye or cationic dyes, malachite green and direct yellow respectively from aqueous solutions. The anionic dye is more effective adsorbed than cationic dye because LDHs has positive surface site. Kinetics study showed that the adsorption process is more fits with PSO than PFO based correlation coefficients. Th adsorption process is describe by Freundlich isotherm models for all dyes. The value of enthalphy and entrophy shows that the adsorption process is endothermic and negative free energy value was indicated that the process is spontaneous.

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