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Research Article

Unique Adsorption Properties of Malachite Green on Interlayer Space of Cu-Al and Cu-Al-$SiW_{12}O_{40}$ Layered Double Hydroxides

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Abstract

Cu-Al layered double hydroxide (LDH) was intercalated with Keggin ion of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ to form Cu-Al-$SiW_{12}O_{40}$ LDH. The obtained materials were analyzed by X-ray Diffraction (XRD), Fourier Transform Infra Red (FTIR) spectroscopy, and Brunaur-Emmett-Teller (BET) surface area analysis. Furthermore, the materials were used as adsorbents of malachite green from aqueous solution. Some variables for adsorption, such as: effect of adsorption times, malachite green concentration, and also adsorption temperature, were explored. The results showed that diffraction at 11.72° on Cu-Al LDH has interlayer distance of 7.56 Å. The intercalation of that LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion resulted increasing interlayer distance to 12.10 Å. The surface area of material was also increased after intercalation from 46.2 m^2/g to 89.02 m^2/g. The adsorption of malachite green on Cu-Al and Cu-Al-$SiW_{12}O_{40}$ LDHs followed pseudo second order kinetic and isotherm Langmuir model with adsorption capacity of Cu-Al and Cu-Al-$SiW_{12}O_{40}$ LDHs was 55.866 mg/g and 149.253 mg/g, respectively. That adsorption capacity is equal with increasing interlayer space and surface area properties of material after intercalation. Thus, the adsorption of malachite green on Cu-Al and Cu-Al-$SiW_{12}O_{40}$ LDHs is unique and dominantly occurred on interlayer space of LDH as active site adsorption.

Keywords: layered double hydroxide; Cu-Al; intercalation; adsorption; malachite green

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1. Introduction

Dyes contamination from industrial activities, such as: textile [1], paint, plastic, rubber, leather, cosmetic [2], and drug, are the main environmental problem due to un degrade properties [3], stable under light and oxidation. Thus, removal of dyes from wastewater is vital [4]. Removal dyes from wastewater has been applied using numerous method such as biological treatment [2], adsorption [5], membrane filtration

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and light irradiation [6]. Among these ways, the popular simple method is adsorption due to fast way, easy process, low cost, and also high efficiency to remove dyes from aqueous solution [7]. The main problem for adsorption is to develop adsorbent which has selectivity and high efficiency [8−9]. Certain adsorbents were tested to remove dyes from aqueous phase, such as: zeolite [10], bentonite, montmorillonite, clay [1], chitosan [11], algae [12], cellulose [13], and also layered double hydroxide materials [14].

Layered double hydroxide (LDH) is inorganic layers material with consisted by divalent and trivalent metal cations. The LDH is well-known as hydrotalcite-like materials. The surface layer of materials was balanced with various anions depending on synthetic condition and can be replace and exchanged to obtain unique properties of layer. The general formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]+xA_{x}^{-n}mH_2O$, where M^{2+} is divalent metal ion, M^{3+} is trivalent metal ion, A_{x}^{-n} is anion with n valent state, and water of crystallization [15−16]. The common anion on interlayer LDH was found, such as: nitrate, carbonate, hydroxide, and also chloride [17−18]. The existence of these anions results in the small interlayer distance and space on LDH. On the other hand, due to the various applications of LDH as adsorbent of dyes, thus this space is important to create to be larger space to provide active site for adsorbate [19]. The anion should be exchanged with larger anion compound such as polyoxometalate [20]. Polyoxometalate is metal-oxygen inorganic clusters which have various structures, shapes, oxidation state, and also high charges compounds. Polyoxometalate can be used as an intercalant of LDH to increase interlayer distance on LDH [21].

Mg/Al LDH was intercalated with Keggin ion $[H_2W_{12}O_{40}]^{6-}$ to form pillared compound with various ratio of polyoxometalate [22]. Polyoxometalate $K_3[\alpha\text{-}PW_{12}O_{40}]$ has been intercalated on interlayer Zn/Al LDH and the space slightly increase than pure Zn/Al LDH [18]. Keggin type polyoxometalate of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was also used as intercalant of Ca-Al LDH to form Ca-Al-$[\alpha\text{-}SiW_{12}O_{40}]$ [23]. According to previous research, the intercalated material can be enhanced its adsorption ability of cationic dye such as malachite green [14]. The malachite green is representative triphenylmethane cationic dye which has seriously bad effect for environment due to covering water surface and high residual [24]. Similar reported by Lesbani *et al.* [14]. NiAl LDH was intercalated by polyoxometalate has good ability to remove malachite green and obtained 80% malachite green removal. In addition, Xu *et al*. [25] reported that polyoxometalate intercalating ZnAlFe LDH was applied as methylene blue adsorption and obtained adsorption capacity 67.47 mg/g. Polyoxometalate $[PW_{10}Mo_2O_{40}]^{5-}$ with high charges was used to intercalate Zn-Al LDH. The material used as removal agent of methylene blue from aqueous solution with adsorption capacity higher than pure Zn/Al LDH [20].

Herein, Keggin type polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was used as intercalator of Cu-Al LDH to form Cu-Al-$SiW_{12}O_{40}$ as adsorbent of malachite green. The materials were characterized by XRD powder analysis, identification of functional group by FTIR spectroscopy, and also measurement of surface area properties by nitrogen adsorption desorption analysis. The malachite green is toxic cationic dye which cannot be degraded by aquatic system [26]. The removal of malachite green from aqueous solution is carried out by batch system adsorption process. The factor that influencing adsorption process was studied such as effect of adsorption time, effect of initial concentration of malachite green, and also effect of adsorption temperature to obtain kinetic and thermodynamic adsorption properties. The unique adsorption properties on Cu-Al and Cu-Al-$SiW_{12}O_{40}$ LDHs is expected after intercalation process of Cu-Al LDH.

2. Materials and Methods

2.1 Chemical and Instrumentation

Chemicals, such as: copper (II) nitrate trihydrate (Merck, 99.1%), aluminum (III) nitrate nonahydrate (Merck, 98.5%), sodium tungstate dihydrate (Sigma Aldrich, 99.0%), sodium metasilicate pentahydrate (Sigma Aldrich, 97.0%), sodium hydroxide (Merck, 99.0%), sodium carbonate anhydrate (Merck, 99.9%), potassium chloride (Merck, 99.9%), and hydrochloric acid (Merck, 36%), were used as precursor. Water was demineralized using Purite® water purification apparatus equipped with resin ion exchange system. Characterization of materials were carried out using XRD Rigaku Miniflex-6000. Sample was grounded with mortar and analyzed using XRD at diffraction 5−60° with scan speed 1°/min. Analysis of functional group was performed using FTIR Shimadzu Prestige-21. Sample was mixed with KBr and was vacuumed to form KBr pellet. Sample was analyzed in the range of wavenumber 400−4000 cm^{-1}. Analysis of nitrogen adsorption desorption was conducted using Micrometric

ASAP Quantachrome apparatus. Sample was degassed several time prior analysis using liquid N_2. Analysis of malachite green was conducted using UV-Visible Spectrophotometer Bio-Base BK-UV 1800 PC. Malachite green was analyzed at wavelength 619 nm.

2.2 Synthesis of Cu-Al LDH

Synthesis of Cu-Al LDH was conducted using coprecipitation method at pH 10 as previous reported by Palapa *et al.* [27]. Copper (II) nitrate (0.75 M, 10 mL) was mixed with aluminum (III) nitrate (0.25 M, 10 mL). Reaction was gentle stirred for one hour until dissolution of all starting materials. Sodium hydroxide (4 M) was added to the mixture and pH of solution was adjusted to 10 with this solution. The reaction mixture was kept for 20 hours to form solid material. The solid material was filtered and washed with water several times and dried at 110 °C overnight.

2.3 Synthesis of Polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$

The synthesis of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was prepared with slightly modification from Lesbani and Co-workers [28]. Solution of hydrochloric acid (4 M, 165 mL) was added to solution of sodium tungstate (182 g in 300 mL water) with gentle stirring to remove solid precipitate of tungstic acid. Solution of sodium meta silicate (11 g in 100 mL water) was added to the reaction mixture following with addition of sodium tungstate (1 M, 80 mL). pH reaction was adjusted to 5 by addition of hydrochloric acid 4 M. The reaction was kept at 80 °C for 1 hour. Reaction was kept at room temperature with constant stirring. Potassium chloride was added to the reaction solution and stirred for 1 hour to form $K_4[\alpha\text{-}SiW_{12}O_{40}]$.

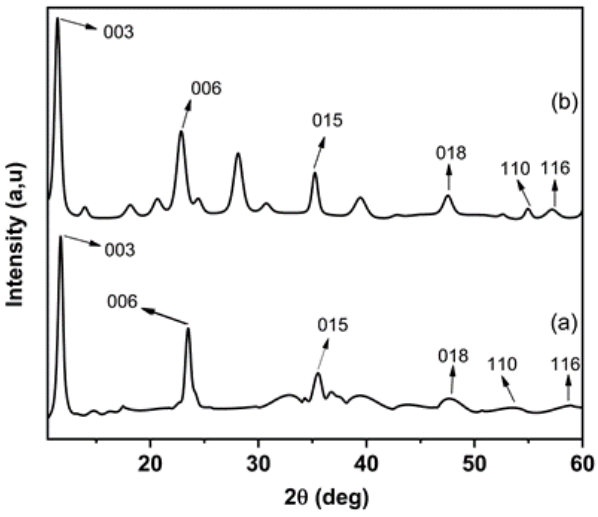

Figure 1. XRD of (a) Cu-Al LDH and (b) Cu-Al-$SiW_{12}O_{40}$.

2.4 Intercalation of Cu-Al LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$

Intercalation of Cu-Al LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ was conducted using ion exchange method. Cu-Al LDH was mixed with solution of 1 M sodium hydroxide (25 mL). Polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was dissolved with 50 mL water. Solution of polyoxometalate was mixed with solution of Cu-Al LDH with gentle stirring for 5 minutes. Reaction mixture was introduced with nitrogen with slow stirring and kept for 24 hours to form suspension. Suspension was filtered, washed with water several times and dried at 120 °C for 48 hours.

2.5 Adsorption Study

Adsorption of malachite green was performed using small batch reactor system equipped with stirring bar and temperature control. Adsorption process was studied by variation of adsorption time, variation of initial concentration of malachite green, and variation of adsorption temperature. Variation of adsorption time was studied in the range of 5-210 minutes. Variation of initial concentration of malachite was studied at 25, 50, 75, and 100 mg/L. Variation of adsorption temperature was studied at 303, 313, 318, and 323 K. Concentration of malachite green after adsorption was analyzed by UV-Visible Spectrophotometer at 619 nm.

3. Results and Discussions

Analysis of Cu-Al LDH and intercalated material using XRD powder analysis is shown in Figure 1. Several diffraction peaks were found on Cu-Al LDH at 11.72° (003), 23.51° (006), 35.59° (015), 47.83° (018), 58.70° (110), and 61.23° (116). Diffraction peaks at 11.72° (003) and 61.23° (116) are identified as well formation of layer structure of LDH of Cu-Al (JCPDS 37-630) [29]. The peak at 11.72° has interlayer distance of 7.56 Å. The anion of interlayer distance is nitrate due to synthetic starting materials. Cu-Al LDH was intercalated with Keggin type polyoxometalate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to increase interlayer distance of Cu-Al LDH. XRD powder analysis of Cu-Al after intercalation is shown in Figure 1b.

Diffraction peak of Cu-Al LDH after intercalation $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to form Cu-Al-$SiW_{12}O_{40}$ has diffraction similar with pristine material. The diffraction of 11.72° on Cu-Al LDH was shifted to lower diffraction at 11.34° due to insertion of Keggin ion. These diffractions have interlayer distance 12.10 Å. The increasing interlayer can be calculated as Equation (1):

$$d_{(003)}\ \text{increasing (Å)} = d_{(003)}\text{Cu-Al-SiW}_{12}\text{O}_{40} - d_{(003)}\text{Cu-Al} \quad (1)$$

Based on this calculation, intercalation of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ on interlayer distance of Cu-Al can increase the layer distance up to 4.54 Å. The other diffraction peaks after intercalation were identified at 22.88° (006), 35.13° (015), 48.18° (018), 54.92° (110), and 56.01° (116).

FTIR spectrum of Cu-Al LDH is shown in Figure 2a. The main vibration peaks of Cu-Al LDH were identified at wavenumber 3448 cm^{-1} (υ O–H stretching, water), 1635 cm^{-1} (υ O–H bending, water), and 1318 cm^{-1} (υ N–O nitrate), 817 cm^{-1} (υ Al–O), and 462 cm^{-1} (υ Cu–O). The intercalation of Cu-Al LDH with $[a\text{-}SiW_{12}O_{40}]^{4-}$ ion will replace the nitrate as anion. Thus our emphasis to identify FTIR spectrum after intercalation is vibration around 1300 cm^{-1}. The FTIR spectra of Cu-Al-$SiW_{12}O_{40}$ is shown in Figure 2b. The vibration peak of Cu-Al-$SiW_{12}O_{40}$ LDH did not found at area 1300 cm^{-1} thus intercalation of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion is conducted. On the other hand, vibration of Keggin ion of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ was sharply appeared at 1111 cm^{-1} (υ Si–O) and 974 cm^{-1} (υ W=O) [9].

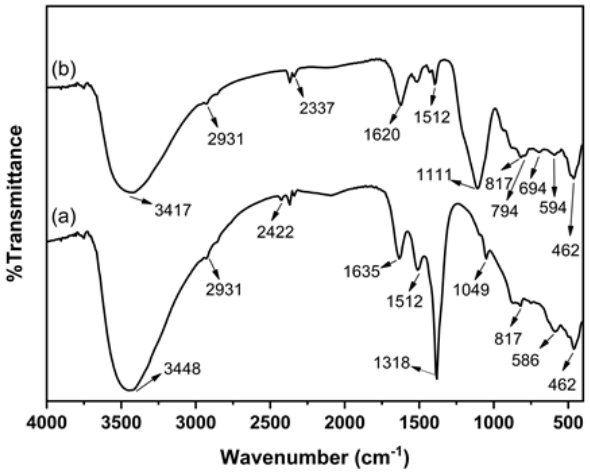

Figure 2. FTIR of (a) Cu-Al LDH and (b) Cu-Al-$SiW_{12}O_{40}$.

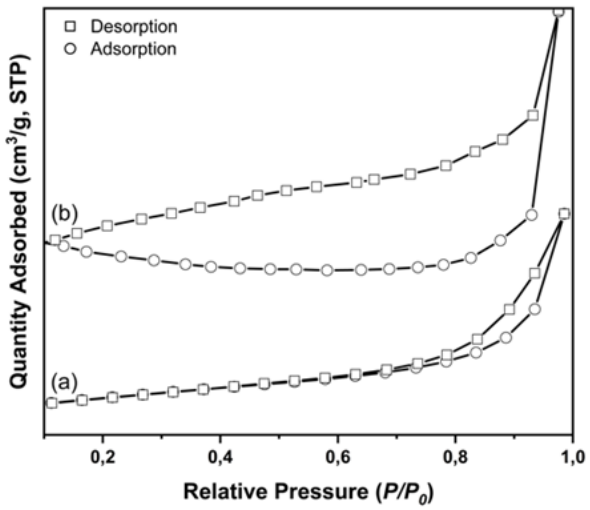

Figure 3. BET of (a) CuAl LDH and b) CuAl-$SiW_{12}O_{40}$.

Analysis of adsorption desorption nitrogen on Cu-Al and Cu-Al-$SiW_{12}O_{40}$ is shown in Figure 3. There is a different adsorption desorption lane for both materials, which was indicated that these materials have hysteresis loop. The profile also showed that type IV isotherm model for Cu-Al LDH. Another hand, the different space between adsorption and desorption of intercalated material is too large, thus this material is not classifying as type I-VI adsorption desorption isotherm model [30]. The BET analysis was obtained from data in Figure 3 as shown in Table 1.

The surface area properties of Cu-Al-$SiW_{12}O_{40}$ is higher almost two folds than pristine material. On the other hand, opposite results were obtained for d_{pore} and d_{pore} of Cu-Al-$SiW_{12}O$ LDH. The d_{pore} and V_{pore} of Cu-Al-$SiW_{12}O_{40}$ LDH was smaller than Cu-Al LDH. Due to opening interlayer distance of intercalated Cu/Al LDH, the d_{pore} and V_{pore} of Cu-Al-$SiW_{12}O_{40}$ LDH to be smaller and covered with the large size of anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$.

The adsorption of malachite green on Cu-Al and Cu-Al-$SiW_{12}O_{40}$ was firstly investigated by effect of adsorption time. Figure 4 shows the kinetic adsorption model of malachite green on both LDH adsorbents. The kinetic model was calculated using pseudo-first order (P-FO) kinetic model and pseudo-second order (P-SO) kinetic model by equation below [31].

Table 1. BET analysis parameter of Cu-Al and Cu-Al-$SiW_{12}O_{40}$ LDHs.

Materials	Surface area (m^2/g)	d_{Pore} (nm)	V_{Pore} (cm^3/g)
CuAl-$SiW_{12}O_{40}$	89.02	1.908	0.0975
CuAl	46.2	10.39	0.116

PFO kinetic model:

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (2)$$

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_1 is adsorption kinetic rate at pseudo first-order (minute^{-1}).

PSO kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

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 (g.mg^{-1}.minute^{-1}). The kinetic adsorption parameter of PFO and PSO of malachite green on Cu-Al and Cu-Al-SiW$_{12}$O$_{40}$ LDH is shown in Table 2.

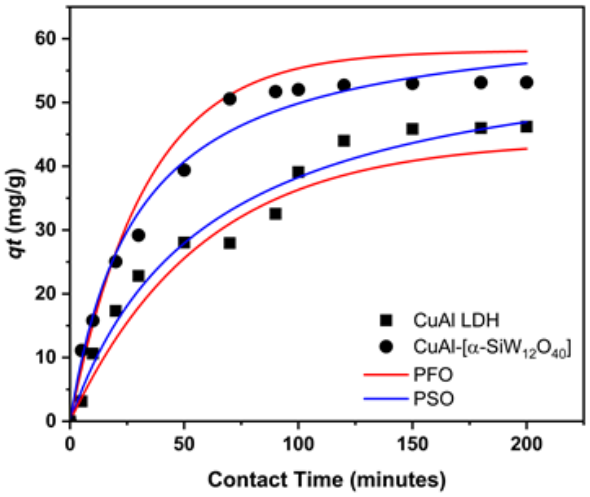

Figure 4. Effect of adsorption time and kinetic adosption calculation of malachite green on Cu-Al and Cu-Al-SiW$_{12}$O$_{40}$ LDHs.

The kinetic parameter data in Table 2 showed that adsorption of malachite green on Cu-Al and Cu-Al-SiW$_{12}$O$_{40}$ LDH was follow PSO kinetic model with R^2 value close to one. The k_2 is adsorption rate constant for the adsorption and k_2 of Cu-Al LDH is smaller than Cu-Al- SiW$_{12}$O$_{40}$ LDH. Thus, of Cu-Al-SiW$_{12}$O$_{40}$ LDH is slightly reactive than starting material without intercalation. The second adsorption study is effect of various malachite green concentration and temperature effect as shown in Figures 5a and b.

Malachite green adsorption onto CuAl LDH and CuAl-SiW$_{12}$O$_{40}$ was sharply increased by increasing malachite green concentration at 20 mg/L. The optimum adsorption was achieved at malachite green concentration start at 75 mg/L. The adsorption patterns also showed that similar style profile for both Cu-Al LDH and Cu-Al-SiW$_{12}$O$_{40}$ LDH. Thus, adsorption type of these adsorbent is similar. The isotherm adsorption of Freundlich and Langmuir was calculated based on data in Figure 5c using equation as below [32]. Langmuir equation:

$$\frac{C}{m} = \frac{1}{bK_{ML}} + \frac{C}{b} \quad (4)$$

where C is a saturated concentration of adsorbate; m is the amount of adsorbate; b is the

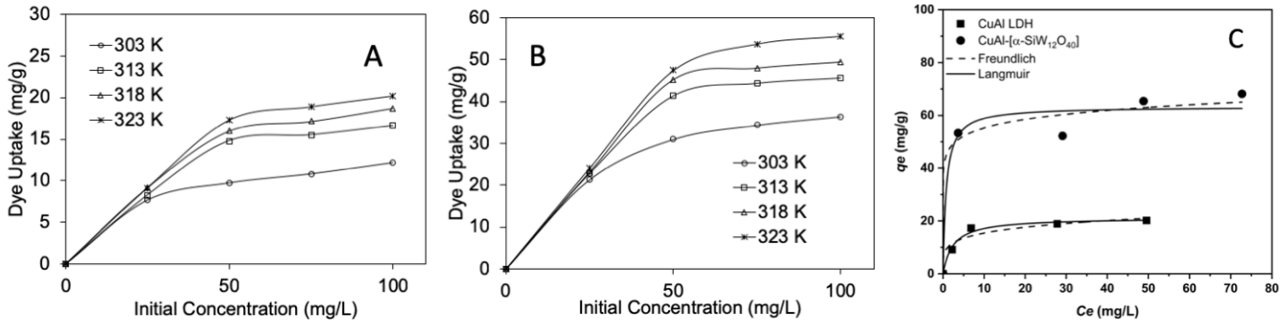

Figure 5. Effect of temperature and various malachite green concentration onto (a) CuAl LDH and (b) CuAl-SiW$_{12}$O$_{40}$ and (c) isotherm adsorption.

Table 2. Kinetic adsorption parameter.

Adsorbent	Qe$_{exp}$ (mg/g)	P-FO			P-SO		
		Qe$_{Calc}$ (mg/g)	R^2	k_1	Qe$_{Calc}$ (mg/g)	R^2	k_2
CuAl LDH	46.225	65.501	0.905	0.028	57.653	0.913	0.0003
CuAl-[α-SiW$_{12}$O$_{40}$]	57.256	73.856	0.981	0.043	64.117	0.985	0.0007

maximum adsorption capacity (mg.g^{-1}), and K_{ML} is the Langmuir constant (L.mg^{-1}). Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where q_e is adsorption capacity at equilibrium (mg.g^{-1}); C_e is the concentration of adsorbate at equilibrium (mg.L^{-1}), and K_F is Freundlich constant.

Isotherm Langmuir is appropriate for adsorption of malachite green on both Cu-Al LDH and Cu-Al-$SiW_{12}O_{40}$ LDH as adsorbents, which was obtained from Table 3. The value of R^2 is closed to one for isotherm Langmuir rather than isotherm Freundlich. The Q_{max} of Cu-Al-$SiW_{12}O_{40}$ LDH is higher almost three-fold than Cu-Al LDH. The adsorption capacity of Cu-Al-$SiW_{12}O_{40}$ is higher than without intercalation can be easily explained due to opening of interlayer distance and also surface area properties of CuAl-$SiW_{12}O_{40}$. The adsorption capacity is increased by increasing temperature. The adsorption capacity of Cu-Al and CuAl-$SiW_{12}O_{40}$ LDHs is up to 55.866 mg/g and 149.253 mg/g, respectively. This increasing adsorption capacity is equal with increasing surface area properties. Thus, adsorption of malachite green on Cu-Al and CuAl-$SiW_{12}O_{40}$ is occurred dominantly on interlayer space of LDH. The several adsorbents for malachite green adsorption were reported by others listed in Table 4. Table 4 showed the adsorption capacity on this work has good adsorbed ability and exhibited good performance to remove malachite green in aqueous solution.

The thermodynamic adsorption parameter was also obtained based on data in Figure 5a and b using equation as follow.

$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

Table 3. Isotherm of adsorption.

LDH	Isotherm Models	Adsorption Constant	T (K)			
			303	313	318	323
CuAl LDH	Langmuir	Q_{max}	16.444	20.609	19.597	55.866
		k_L	0.040	0.073	0.360	0.038
		R^2	0.999	0.991	0.997	0.993
	Freundlich	n	2.761	2.324	4.568	4.133
		k_F	2.628	3.125	8.308	8.632
		R^2	0.996	0.896	0.905	0.819
CuAl-[α-$SiW_{12}O_{40}$]	Langmuir	Q_{max}	70.777	127.602	134.223	149.253
		k_L	0.219	0.314	0.440	0.691
		R^2	0.982	0.997	0.996	0.999
	Freundlich	n	3.354	4.056	3.479	4.870
		k_F	19.528	49.028	17.676	72.168
		R^2	0.909	0.821	0.581	0.693

Table 4. Comparison of malachite green adsorbed onto several adsorbents reported.

Adsorbents	Adsorbed capacity (mg/g)	Ref
NiFe-POM	8.81	[14]
Magnetic nanocomposite Bacterial/GO	270.27	[34]
Apricot Activated Carbon	17.60	[35]
Superabsorbent Hydrogel	56.95	[36]
ZnAl LDH	111	[37]
Lime Peel Activated Carbon	47.0	[38]
CuAl Biochar LDH composite	470.96	[27]
CuAl-$SiW_{12}O_{40}$	149.253	This Work
CuAl LDH	55.866	This Work

where T is temperature (K); R is the gas constant (8.314 J.mol^{-1}.K^{-1}), and K_{eq} is the reaction on change temperature.

Table 5 showed that adsorption of malachite green on all adsorbents were spontaneous occurred in which the negative value of ΔG. The enthalpy is in ten range 7.621-8.916 kJ/mol. These values showed that adsorption of malachite green on both adsorbents is categorized as physical adsorption. The value of ΔS is increased after intercalation means that increasing randomness adsorption process on malachite green on material after intercalation. Thus, opposite in previous results of the isotherm adsorption belong to Langmuir which indicated the adsorption occurs on monolayer surface although the high adsorption capacity might suggest the formation of multiple layers. However, this theory as similar reported by Ribeiro *et al*. [33] that the Langmuir assumption of dye adsorption is infinite dilution and saturation monolayer occur to gases system, which has a small adsorbed molecule, homogeneous active sites and has very low interaction.

4. Conclusion

Cu-Al LDH was successfully intercalated with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to form Cu-Al-$SiW_{12}O_{40}$ with increasing interlayer distance from 7.56 Å to 12.10 Å. The surface area properties of material were also increased after intercalation from 46.2 m^2/g to 89.02 m^2/g. Adsorption of malachite green on Cu-Al and CuAl-$SiW_{12}O_{40}$ LDH has adsorption capacity 55.866 mg/g and 149.253 mg/g, respectively. The increasing adsorption capacity is almost three-fold than before intercalation, which was equal with increasing the surface area properties. Thus, adsorption of malachite green in this research was occurred dominantly on interlayer space of LDH and the adsorption process were physisorption due to this adsorption process has low energies from thermodynamics calculated parameters.

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References

[1] Kausar, A., Iqbal, M., Javed, A., Aftab, K., Nazli, Z.i.H., Bhatti, H.N., Nouren, S. (2018). Dyes adsorption using clay and modified clay: A review. *Journal of Molecular Liquids*, 256, 395-407. DOI: 10.1016/j.molliq.2018.02.034

[2] Panswad, T., Luangdilok, W. (2000). Decolorization of reactive dyes with different molecular structures under different environmental conditions. *Water Research*, 34, 4177–4184. DOI: 10.1016/S0043-1354(00)00200-1

[3] Palapa, N.R., Taher, T., Mohadi, R., Lesbani, A. (2019). Kinetic aspect of direct violet adsorption on M^{2+}/M^{3+} (M^{2+}: Zn; M^{3+}: Al, Fe, Cr) layered double hydroxides. *AIP Conference Proceedings*, 2194, 020079. DOI: 10.1063/1.5139811

[4] Darmograi, G., Prelot, B., Geneste, A., Martin-Gassin, A., Salles, F., Zajac, J. (2016). How does competition between anionic pollutants affect adsorption onto Mg-Al layered double hydroxide? Three competition schemes. *Journal of Physical Chemistry C*, 120, 10410–10418. DOI: 10.1021/acs.jpcc.6b01888

Table 5. Thermodynamic adsorption parameter.

LDH	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)
CuAl	303	52.357	8.916	30.070	-0.194
	313	53.516			-0.495
	318	56.807			-0.646
	323	57.434			-0.796
CuAl-[α-$SiW_{12}O_{40}$]	303	75.421	7.621	34.569	-2.853
	313	77.678			-3.199
	318	78.382			-3.372
	323	78.606			-3.544

[5] Boulaiche, W., Hamdi, B., Trari, M. (2019). Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamic studies. *Applied Water Science*, 9, 1–10. DOI: 10.1007/s13201-019-0926-8

[6] Haile, H.L., Abi, T., Tesfahun, K. (2015). Synthesis, characterization and photocatalytic activity of MnO2/Al2O3/Fe2O3 nanocomposite for degradation of malachite green. *African Journal of Pure and Applied Chemistry*, 9, 211–22. DOI: 10.5897/ajpac2015.0656

[7] Shan, R.R., Yan, L.G., Yang, Y.M., Yang, K., Yu, S.J., Yu, H.Q., Zhu, B.C., Du, B. (2015). Highly efficient removal of three red dyes by adsorption onto Mg–Al-layered double hydroxide. *Journal of Industrial and Engineering Chemistry*, 21, 561-568. DOI: 10.1016/j.jiec.2014.03.019

[8] Giscard, D., Kamgaing, T., Temgoua, R.C.T., Ymele, E., Tchieno, F.M.M., Tonlé, I.K. (2016). Intercalation of oxalate ions in the interlayer space of a layered double hydroxide for nickel ions adsorption. *International Journal of Basic and Applied Sciences*, 5, 144. DOI: 10.14419/ijbas.v5i2.5672

[9] Ma, J., Yang, M., Chen, Q., Zhang, S., Cheng, H., Wang, S., Liu, L., Zhang, C., Tong, Z., Chen, Z. (2017). Comparative study of Keggin-type polyoxometalate pillared layered double hydroxides via two synthetic routes: Characterization and catalytic behavior in green epoxidation of cyclohexene. *Applied Clay Science*, 150, 210–216. DOI: 10.1016/j.clay.2017.09.030

[10] Abdelrahman, E.A. (2018). Synthesis of zeolite nanostructures from waste aluminum cans for efficient removal of malachite green dye from aqueous media. *Journal of Molecular Liquids*, 253, 72–82. DOI: 10.1016/j.molliq.2018.01.038

[11] Yan, H., Li, H., Yang, H., Li, A., Cheng, R. (2013). Removal of various cationic dyes from aqueous solutions using a kind of fully biodegradable magnetic composite microsphere. *Chemical Engineering Journal*, 223, 402–411. DOI: 10.1016/j.cej.2013.02.113

[12] Foroutan, R., Mohammadi, R., Razeghi, J., Ramavandi, B. (2019). Performance of algal activated carbon/Fe3O4 magnetic composite for cationic dyes removal from aqueous solutions. *Algal Research*, 40, 101509. DOI: 10.1016/j.algal.2019.101509

[13] Shenvi, S.S., Isloor, A.M., Ismail, A.F., Shilton, S.J., Al Ahmed, A. (2015). Humic Acid Based Biopolymeric Membrane for Effective Removal of Methylene Blue and Rhodamine B. *Industrial & Engineering Chemistry Research*, 54, 4965–4975. DOI: 10.1021/acs.iecr.5b00761

[14] Lesbani, A., Taher, T., Neza, N., Palapa, R., Mohadi, R., Rachmat, A., Mardiyanto, M. (2020). Preparation and utilization of Keggin-type polyoxometalate intercalated Ni-Fe layered double hydroxides for enhanced adsorptive removal of cationic dye. *SN Applied Sciences*, 2, 470. DOI: 10.1007/s42452-020-2300-8

[15] Mishra, G., Dash, B., Pandey, S. (2018). Applied Clay Science Layered double hydroxides : A brief review from fundamentals to application as evolving biomaterials. *Applied Clay Science*, 153, 172–186. DOI: 10.1016/j.clay.2017.12.021

[16] Gholami, P., Khataee, A., Soltani, R.D.C., Dinpazhoh, L., Bhatnagar, A. (2020). Photocatalytic degradation of gemifloxacin antibiotic using Zn-Co-LDH@biochar nanocomposite. *Journal of Hazardous Materials*, 382, 121070. DOI: 10.1016/j.jhazmat.2019.121070

[17] Parida, K.M., Mohapatra, L. (2012). Carbonate intercalated Zn/Fe layered double hydroxide: A novel photocatalyst for the enhanced photo degradation of azo dyes. *Chemical Engineering Journal*, 179, 131–139. DOI: 10.1016/j.cej.2011.10.070

[18] Lesbani, A., Hensen, H., Taher, T., Hidayati, N., Mohadi, R., Andreas, R. (2018). Intercalation of Zn/Al layered double hydroxides with Keggin ion as adsorbent of cadmium(II). *AIP Conference Proceedings*, 2026, 020011. DOI: 10.1063/1.5064971

[19] Yanming, S., Dongbin, L., Shifeng, L., Lihui, F., Shuai, C., Haque, M.A. (2017). Removal of lead from aqueous solution on glutamate intercalated layered double hydroxide. *Arabian Journal of Chemistry*, 10, S2295–2301. DOI: 10.1016/j.arabjc.2013.08.005

[20] Bi, B., Xu, L., Xu, B., Liu, X. (2011). Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media. *Applied Clay Science*, 54, 242–247. DOI: 10.1016/j.clay.2011.09.003

[21] Carriazo, D., Lima, S., Martín, C., Pillinger, M., Valente, A.A., Rives, V. (2007). Metatungstate and tungstoniobate-containing LDHs: Preparation, characterisation and activity in epoxidation of cyclooctene. *Journal of Physics and Chemistry of Solids*, 68, 1872–1880. DOI: 10.1016/j.jpcs.2007.05.012

[22] Nijs, H., Bock, M.D.E., Vansant, E.F. (1999). Comparative Study of the Synthesis and Properties of Polyoxometalate Pillared Layered Double Hydroxides (POM-LDHs). *Journal of Porous Materials*, 110, 101–110.

[23] Taher, T., Christina, M.M., Said, M., Hidayati, N., Ferlinahayati, F., Lesbani, A. (2019). Removal of iron(II) using intercalated Ca/Al layered double hydroxides with [-

$SiW_{12}O_{40}]^{4-}$. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14, 260–267. DOI: 10.9767/bcrec.14.2.2880.260-267

[24] Gao, M., Wang, Z., Yang, C., Ning, J., Zhou, Z., Li, G. (2019). Novel magnetic graphene oxide decorated with persimmon tannins for efficient adsorption of malachite green from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 566, 48–57. DOI: 10.1016/j.colsurfa.2019.01.016.

[25] Xu, M., Bi, B., Xu, B., Sun, Z., Xu, L. (2018). Polyoxometalate-intercalated ZnAlFe-layered double hydroxides for adsorbing removal and photocatalytic degradation of cationic dye. *Applied Clay Science*, 157, 86–91. DOI: 10.1016/j.clay.2018.02.023

[26] Alderman, D.J. (1985). Malachite green: a review. *Journal of Fish Diseases*, 8, 289–298. DOI: 10.1111/j.1365-2761.1985.tb00945.x

[27] Palapa, N.R., Taher, T., Rahayu, B.R., Mohadi, R., Rachmat, A., Lesbani, A. (2020). CuAl LDH/Rice Husk Biochar Composite for Enhanced Adsorptive Removal of Cationic Dye from Aqueous Solution. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15, 525–537. DOI: 10.9767/bcrec.15.2.7828.525-537

[28] Lesbani, A., Fitriliana, F., Mohadi, R. (2015). Conversion of cyclohexanone to adipic acid catalyzed by heteropoly compounds. *Indonesian Journal of Chemistry*, 15, 64–69. DOI: 10.22146/ijc.21225

[29] Palapa, N.R., Mohadi, R., Rachmat, A., Lesbani, A. (2020). Adsorption Study of Malachite Green Removal from Aqueous Solution Using Cu/M^{3+} (M^{3+} = Al, Cr) Layered Double Hydroxide. *Mediterranean Journal of Chemistry*, 10, 33–45.

[30] Shaji, A., Zachariah, A.K., (2017). Chapter 9 - Surface Area Analysis of Nanomaterials, In *Micro and Nano Technologies, Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*, Editor(s): S. Thomas, R. Thomas, A.K. Zachariah, R.K. Mishra, Elsevier, 197-231, DOI: 10.1016/B978-0-323-46139-9.00009-8

[31] Xia, Y., Yang, T., Zhu, N., Li, D., Chen, Z., Lang, Q., Liu, Z., Jiao, W. (2019). Enhanced adsorption of Pb(II) onto modified hydrochar: Modeling and mechanism analysis. *Bioresource Technology*, 288, 1–8. DOI: 10.1016/j.biortech.2019.121593

[32] Elkhattabi, E.H., Lakraimi, M., Berraho, M., Legrouri, A., Hammal, R., El Gaini, L. (2018). Acid Green 1 removal from wastewater by layered double hydroxides. *Applied Water Science*, 8, 1–11. DOI: 10.1007/s13201-018-0658-1

[33] Ribeiro, C., Scheufele, F.B., Espinoza-Quiñones, F.R., Módenes, A.N., da Silva, M.G.C., Vieira, M.G.A., Borba, C.E. (2015). Characterization of Oreochromis niloticus fish scales and assessment of their potential on the adsorption of reactive blue 5G dye. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 482, 693–701. DOI: 10.1016/j.colsurfa.2015.05.057

[34] Arabkhani, P., Asfaram, A. (2020). Development of a novel three-dimensional magnetic polymer aerogel as an efficient adsorbent for malachite green removal. *Journal of Hazardous Materials*, 384, 121394. DOI: 10.1016/j.jhazmat.2019.121394

[35] Abbas, M. (2020). Experimental investigation of activated carbon prepared from apricot stones material (ASM) adsorbent for removal of malachite green (MG) from aqueous solution. *Adsorption Science and Technology*, 38, 24–45. DOI: 10.1177/0263617420904476

[36] Al-Aidy, H., Amdeha, E. (2020). Green adsorbents based on polyacrylic acid-acrylamide grafted starch hydrogels: the new approach for enhanced adsorption of malachite green dye from aqueous solution. *International Journal of Environmental Analytical Chemistry*, 100, 1–21. DOI: 10.1080/03067319.2020.1711896

[37] Hidayati, N., Mohadi, R., Elfita, E., Lesbani, A. (2020). Malachite Green Removal by Zn/Al-citrate LDHs in Aqueous Solution. *Science and Technology Indonesia*, 5, 59. DOI: 10.26554/sti.2020.5.2.59-61

[38] Ahmad, M.A., Afandi, N.S., Bello, O.S. (2017). Optimization of process variables by response surface methodology for malachite green dye removal using lime peel activated carbon. *Applied Water Science*, 7, 717–727. DOI: 10.1007/s13201-015-0284-0