# Removal of 2-Chlorophenol from Aqueous Solution by Mg/Al Layered Double Hydroxide (LDH) and Modified LDH

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Sorption is a common treatment for removing pollutants from natural environments. Layered double hydroxides (LDHs), which consist of brucite-like positive layers and sodium dodecyl sulfate intercalated with LDH (SDS-LDH), are considered to be potential organic pollutant sorbents. The objectives of this study were (1) to evaluate the impact of removing 2-chlorophenol (2-CP) using Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH and SDS-LDH and (2) to investigate the removal efficiencies of these two compounds. All fitted sorption data reveal that the second-order model and the Langmuir model best describe the sorption kinetics and isotherms, respectively. By visual MinteqA2 (2000) calculation, the dissociation  $pK_a$  of 2-CP is 8.56. The experimental results indicate that a high concentration of 2-CP is sorbed by the hydrophilic-hydrophilic physical interaction of LDH when the pH is >8.56; however, the hydrophobic-hydrophobic partition interaction of SDS-LDH is more vital when the pH is <8.56. LDH and SDS-LDH can be removed not only in the ionic form, but also in the molecular form of 2-CP. The efficiencies of LDH and SDS-LDH, in regard to enhancing 2-CP sorption, are strongly dependent on the pH, 2-CP speciation, ionic strength, and metal dissolution. These results are of practical interest, with respect to the selection of sorbents, to optimize aquatic environment remediation technologies.

#### 1. Introduction

Recently, rapid industrial and commercial development has resulted in improved living conditions. However, because of insufficient management of land utilization, environmental considerations have lagged behind. Consequently, massive industrial pollutants have been discharged into the natural environment, creating serious soil and water pollution. Chlorophenols are aromatic compounds that contain chlorine, which have important roles in industry and medicine. However, because of improper manufacturing procedures and poorly controlled emissions, they have become common organic pollutants in the environment. Chlorophenols usually are found in the bottom sediment of lakes and rivers, in tannery waste and sewage sludge, in aerosols, and at hazardous waste sites, because of the wastewater that is discharged from the petroleum, steel, refinery, dye, timber, plastic, and pesticide industries. The discharge of these dechlorinated wastewaters through anaerobic treatments from factories increases the solubility of monochlorophenols, such as 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), and 4-chlorophenol (4-CP). Photolytic transformation has been proposed as one of the major pathways of 2-CP degradation in aquatic environments. A mechanism that involves the 2-CP excited-state nucleophilic displacement of chlorine by water is believed to account for catechol formation.<sup>2,3</sup> Even low levels of 2-CP are well-known to be carcinogenic, and exposure to air by inhalation, either through skin contact or ingestion, can cause headaches, coughing, impaired breathing, and gastrointestinal cramps. Because 2-CP has a severe impact on the human environment, the United States Environmental Protection Agency (USEPA) considers it to be a priority pollutant.<sup>3,4</sup> For example, the USEPA recommends that the drinking water that is consumed over the lifetime of an adult should have a 2-CP content of no more than 0.04 mg/L.<sup>5</sup>

Sorption is a common treatment for removing organic pollutants from natural environments.<sup>6–12</sup> Layered double hydroxides (LDHs), which first were reported in the mid-19th century, are mixed-metal hydroxides that consist of octahedral double hydroxyl layers with exposed positive surface charges and interlayer anions. 13–15 LDHs have biological, pharmaceutical, and environmental applications. <sup>16–18</sup> The general known formula of LDH is  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}A_{x/m}^{m-} \cdot nH_2O$ , where M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent cations, respectively, each with an ionic radius similar to that of Mg<sup>2+</sup>. <sup>13,19-21</sup> The application of LDHs has been shown to be successful for the binding of anionic contaminants from water.<sup>22</sup> However, they seem to be less effective at binding hydrophobic organic compounds (HOCs), such as pesticides or phenols, because of their strongly hydrophilic surface. Anionic surfactants, such as sodium dodecyl sulfate (SDS), are used in several industrial processes and are contained in most household detergents and other cleaning agents. They constitute one of the main modifying organic components of many clay minerals. Many studies have shown that modified clays can enhance their sorptive capacity for organic pollutants, such as trichloroethylene, tetrachloroethylene, and phenol compounds, and, to a lesser extent, for monochlorophenols. The objective of this study was (1) to utilize the large surface area and positive charge of LDH and SDSintercalated LDH (hydrophobic SDS-LDH) to sorb anionic and molecular types of 2-CP and (2) to investigate their resultant removal efficiencies.

# 2. Experimental Section

**2.1. Preparation and Identification of LDH.** A layered double hydroxide (Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH) was synthesized using a procedure that was modified from that previously reported.  $^{22-24}$ 

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Table 1. Properties of the Synthesized Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH and SDS-LDH

	Value			
property	Mg <sub>3</sub> -Al-(NO <sub>3</sub> ) LDH	SDS-LDH		
Mg <sup>2+</sup> /Al <sup>3+</sup> molar ratio	$2.82 \pm 0.02$	$2.82 \pm 0.02$		
nitrogen content (%)	3.4	0.11		
carbon content (%)	0.28	21.95		
sulfur content (%)	none detected	4.5		
hydrogen content (%)	3.75	6.6		
$AEC^a$	290.31 cmol/kg	$72.9\%^{b}$		
structural formula Mg3-Al-(NO3) LDH	$[Mg^{2+}_{0.74}Al^{3+}_{0.26}(OH)_2]^{0.26-}(NO_3)^{-}_{0.24}(CO_3)^{2-}_{0.01} \cdot 0.85H_2O$			
SDS-LDH	$[Mg^{2+}_{0.74}Al^{3+}_{0.26}(OH)_2]^{0.26-}(CH_3(CH_2)_{11}OSO_3)^{-}_{0.24}(NO_3)^{-}_{0.013} \cdot 1.7H_2O$			

<sup>&</sup>lt;sup>a</sup> AEC is a theoretical calculation. The molecular weight is 89.56. AEC =  $(q/\text{Mw}) \times 10^5$  (cmol/kg), where q is the value of the layer charge for an octahedral unit and Mw is the weight of the chemical formula for each octahedral unit.<sup>29b</sup> Percentage relative to AEC.<sup>30</sup>

It was prepared by simultaneously adding, dropwise, a mixed aqueous solution of 0.3 mol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.1 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O salts and an aqueous solution of 2 M NaOH (Merck, Darmstadt, Germany) into a Teflon bottle that contained 80 mL of double-distilled water (DDW). The two solutions were exposed to constant stirring by means of a magnetic stirrer and were purged with N<sub>2</sub> gas, and the suspension pH was maintained at pH 10. To avoid CO2 contamination, the double-distilled solution was preheated to 100 °C, free of CO<sub>2</sub>, to prepare Mg, Al, and NaOH solutions. The suspension was stirred continuously and maintained at 74 °C for 36 h, after which time it was allowed to settle at a constant temperature of 74 °C for 24 h. At the end of 24 h, the suspension was centrifuged at  $12400 \times$ g (Hitachi, model 18PR-52) for 10 min. The excess salt in the collected precipitates was removed by washing them five times with DDW, after which the remaining solids of LDH (Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH) were freeze-dried and stored prior to further use.

To prepare SDS-LDH, an LDH sample was heated to 550 °C for 5 h.<sup>25</sup> The calcined LDH sample (1 g) was treated with sodium dodecyl sulfate (SDS) solution (i.e., 80 mL of a solution that represented 300% of the anionic exchange capacity (AEC) of LDH) to equilibrate within 2 d. The SDS-LDH suspension then was centrifuged, washed five times with DDW, and freezedried

The SDS and 2-chlorophenol (2-CP) used in the experiment were supplied by Merck Co. (Darmstadt, Germany) without further purification. The molecular formula, molecular mass, density, solubility, solubility in water, melting and boiling points, and log  $K_{\rm ow}$  of the liquid phase 2-CP were C<sub>6</sub>H<sub>5</sub>ClO, 128.56 g/mol, 1.262 g/cm<sup>3</sup>, 22 g/L of water (at 20–25 °C), 8 °C, 173–175 °C, and 2.15, respectively.

2.2. Laboratory Analyses. Layered double hydroxide (Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH) and SDS-LDH precipitates were identified by X-ray diffraction (XRD) analysis on a Rigaku Geigerflex X-ray diffractometer from  $3^{\circ}$  to  $50^{\circ}$  (2 $\theta$ ) at a scanning rate of  $1^{\circ}$  (2 $\theta$ ) per min. The Cu Ka radiation used in the XRD study was operated at 35 kV and 15 mA. The particle morphology of LDH was observed by scanning electron microscopy (SEM, LEO Model 1530), with an acceleration voltage of 15 kV. The sample for SEM analysis was spread over carbon tape and placed on a silicon wafer substrate, with a slight platinum sputter coating (SPEC, 208 HR) on the particle surface, to prevent any electron charge on the sample surface. The Fourier infrared (FT-IR) spectrum was obtained using a Nexus FTIR 470 (Thermo Nicolet) scanner at 400–4000 cm<sup>-1</sup>. The resolution was set at 4 cm<sup>-1</sup>. One mg of LDH was mixed well with 200 mg of ovendried KBr and pressed to form a pellet 13 mm in diameter. The specific surface area of the LDH was measured by the eightpoint BET equation with a Micromeritics model ASAP 2010 instrument and was examined from a 57-point N<sub>2</sub> sorption isotherm at 77 K. Particle size analysis of the LDH was

Table 2. Langmuir Parameters for Sorption of 2-CP on Mg\_3-Al-(NO $_3$ ) LDH and SDS-LDH

adsorbent	pН	$K_{\rm L}$ (L/mg)	$\beta \; (\text{mg/g})$	R
Mg <sub>3</sub> -Al-(NO <sub>3</sub> ) LDH	10	0.172	21.45	0.962
	9	0.114	14.38	0.981
	8	0.188	6.13	0.994
	7	0.045	4.81	0.987
	6	0.026	4.23	0.931
SDS-LDH	9	0.075	3.57	0.986
	8	0.041	7.65	0.931
	7	0.171	18.08	0.997
	6	0.198	8.48	0.990
	5	0.127	6.60	0.992

performed using the Raser beam scattering method (Coulter Multisizer II Coulter Counter). The LDH samples were digested by aqua regia solution. The Mg and Al contents were determined by inductively coupled plasma—atomic emission spectrometry (ICP—AES, Perkin—Elmer, model Optima 2000DV). The amounts of Mg and Al were calculated using the chemical formula of LDH with the general formula of  $[M(II)_{1-x}M(III)_{x-1}(OH)_2]A_{x/n}$  ·  $mH_2O$ , where M(II) and M(III) are divalent and trivalent cations, respectively, and A is an anion.

The elemental composition (C, H, N, and S) of SDS-LDH was determined using an elemental analyzer (EA), which applied the dry combustion method (Heraeus VarioEL-III), with acetanilide as the standard.

**2.3. Sorption Isotherms.** For 2-chlorophenol (2-CP) sorption, the concentration of 2-CP was set as 5, 10, 15, 20, and 25 mg/L, and the final concentration of LDH and SDS-LDH was 0.5 g/L at pH 5, 6, 7, 8, 9, and 10. All aqueous solutions for 2-CP sorption contained 0.005 M NaNO3, to maintain a constant ionic strength. The suspensions were adjusted to the desired pHs using an HNO<sub>3</sub> or NaOH solution and monitored by pHstat (Radiometer, TIM865). Suspensions then were reacted at 150 rpm on a rotary shaker. After 12 h, the suspensions were sampled with a syringe and filtered through a 0.22-µm Millipore filter membrane. To measure the effect of ionic strength, 0.005, 0.05, and 0.1 M of NaNO<sub>3</sub> were subjected to sorption isotherm studies (i.e., for LDH sorption suspensions, pH maintained at pH 10; for SDS-LDH, at pH 7). The total 2-CP concentration of the filtrates was determined using an ultraviolet-visible light (UV-vis) spectrometer (Cintra 6 3247, GBC, Australia), while scanning at wavelengths of 292 and 274 nm, with respect to the ionic and molecular types of 2-CP.<sup>26</sup> The data shown later in Table 2 are mean values of the experiments performed in triplicate.

The sorption isotherms for 2-CP sorption by LDH and 2-CP sorption by SDS-LDH were modeled using the Langmuir and Freundlich equations. The Langmuir equation is

$$q_{\rm e} = \frac{\beta K_{\rm L} C_{\rm e}}{(1 + K_{\rm L} C_{\rm e})} \tag{1}$$

Table 3. Kinetic Parameters for the Sorption of 2-CP on Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH

wigs-Ai-(110)	5) LD11						
		reaction		R			
model	pН	$k^{a}$ (mM/h)				p	SE (mM)
zero-order	10	0.006	0.0065			0.0002	0.0096
	9 8 7 6		0.0040 0.0017 0.0007			< 0.0001	0.0045 0.0019 0.0012
						< 0.0001	
						0.0006	
			0.0004		1 .	< 0.0001	0.0005
	5	0.000	0.55	0.550 0.1234		0.0004	
		reaction	rate,				
	pН	$k^{\rm a}$ (h	1)	R		p	SE (mM)
first-order	10	0 0.0982			0	0.0003	0.0911
	9	0.052	.0	0.940 < 0.0001			0.0332
	8 0.0199			0.93	8 .	< 0.0001	0.0171
	7	0.007			0.0009	0.0170	
	6	0.0036			< 0.0001	0.0171	
	5	0.0062		0.50	5	0.1331	0.0164
		reactio					
	pН	ka (mM	$^{-1} h^{-1}$ )	I	?	p	SE (mM)
second-order	10	3.930	3.9307		82	< 0.0001	0.0056
	9	1.47	1.4716		90	< 0.0001	0.0018
	8	0.479	99	0.9	90	< 0.0001	0.0006
	7	0.180	06	0.9	30	< 0.0001	0.0008
	6	0.083		0.9	56	< 0.0001	0.0003
	5	6 ×	$10^{-5}$	0.5	51	0.0981	13.6640
	рΗ α	. (mg/h) β	((mg/g)	<sup>-1</sup> )	R	p	SE (mM)
Elovich	10	14.51	0.31	(	0.882	0.0003	6.9580
equations	9	8.49	0.54	0.869		0.0004	3.5430
	8	4.30	1.27	(	0.876	0.0004	1.0085
	7	2.71	2.65	(	0.969	< 0.0001	0.2119
	6	1.85	5.81	(	0.965	< 0.0001	0.5124
	5	8.05	14.9	(	0.892	0.0012	0.7960

where  $q_e$  equals the amount of sorption (in units of mg/g LDH),  $C_{\rm e}$  is the equilibrium solute concentration (in units of mg/L),  $\beta$ is the maximum capacity of sorption (in units of mg/g), and the parameter  $K_{\rm L}$  relates to bonding strength (expressed in terms

2.4. Kinetics of the pH Envelope of 2-CP Sorption. The kinetic experiments for 2-CP sorbed by LDH and SDS-LDH were conducted as the dose concentration was 0.5 g/L at pH 5, 6, 7, 8, 9, and 10 and with the 2-CP concentration at 10 mg/L. At the end of each reaction period of 0.083, 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, 6.0, 9.0, 12.0, 18.0 and 24.0 h, 10 mL of the thoroughly mixed suspensions were sampled with a syringe and filtered through a 0.22- $\mu$ m membrane. The 2-CP concentrations of the filtrates were determined using a UV-vis spectrometer. The data reported in later in Figure 4 and Tables 3 and 4 represent the mean value of kinetic experiments that were performed in triplicate. Sorption data were fitted with zero-, first-, and secondorder kinetic models and the Elovich kinetic equations.<sup>27</sup>

The mathematical expressions of the zero-, first-, and secondorder models, and the Elovich kinetic models are

Zero-order equation: 
$$C_A = C_{A0} - kt$$
 (2)

First-order equation: 
$$\ln C_A = \ln C_{A0} + kt$$
 (3)

Second-order equation: 
$$\frac{1}{C_{\Lambda}} = \frac{1}{C_{\Lambda 0}} + kt$$
 (4)

Elovich equation: 
$$q_e = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$$
 (5)

where  $C_A$  is the concentration of 2-CP in the solution at time t;  $C_{\rm A0}$  is the initial concentration (at t=0) of 2-CP in the solution; k is the rate constant;  $\alpha$  and  $\beta$  are empirical constants in the

Table 4. Kinetic Parameters for the Sorption of 2-CP on SDS-LDH

model	рН	reaction k <sup>a</sup> (ml		R			SE (mM
model	рп	K (IIII	V1/11)	Λ	p		SE (IIIVI
zero-order	10	0.00	0.0004		0.00	03	0.0006
	9	0.0007		0.915	< 0.00	01	0.0009
	8	0.00	09	0.948	< 0.00	01	0.0010
	7	0.00	49	0.909	0.00	01	0.0068
	6	0.00		0.931	< 0.00		0.0033
	5	0.00	25	0.946	< 0.00	01	0.0027
		reaction					
	pН	k <sup>a</sup> (h	<sup>-1</sup> )	R	p		SE (mM
first-order	10	0.00	36	0.894	0.00	03	0.0171
	9	0.00	70	0.918	< 0.00	01	0.0187
	8	0.01	01	0.950	< 0.00	01	0.0170
	7	0.06	77	0.913	0.00	01	0.0173
	6	0.03	28	0.934	< 0.00	01	0.0170
	5	0.03	02	0.943	< 0.00	01	0.0172
			on rate,				
	pН	ka (mN	$I^{-1} h^{-1}$	R	p		SE (mM
second-order	r 10	0.0	0848	0.941	< 0.0	001	0.0005
	9	0.1	.687	0.976	< 0.0	001	0.0004
	8	0.2	2478	0.992	< 0.0	001	0.0003
	7	2.3	3235	0.977	< 0.0	001	0.0028
	6	0.8	8810	0.994	< 0.0		0.0007
	5	0.7	430	0.988	< 0.0	001	0.0010
	рΗ α	(mg/h)	3 ((mg/g)	$^{-1}$ ) $R$		p	SE (mN
Elovich	10	2.08	5.47	0.97	76 < 0.	0001	0.4681
equations	9	2.48	3.00	0.95	59 < 0.	0001	0.1119
	8	3.09	2.41	0.89	9 0.	0002	0.1224
	7	14.25	0.42	0.88		0003	5.3719
	6	7.84	0.76	0.92	27 < 0.	0001	2.4550
	5	4.80	0.89	0.85	51 0.	0007	1.9638

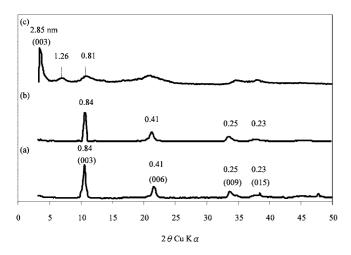
Elovich equation; and  $1/\beta$  and  $(1/\beta) \ln(\alpha/\beta)$  are the slope and intercept, respectively.

2.5. Statistical Analysis. The linear form of kinetic and isotherm equations were applied to the sorption data. The correlation coefficient (R), the level of significance (p-value), and the standard error (SE) were used to identify the best-fit sorption model.

#### 3. Results and Discussion

3.1. Characterization of LDH and SDS-LDH Solids. The surface area and mean particle sizes of LDH were measured to be 40 m<sup>2</sup>/g and 2-6  $\mu$ m, respectively. The SEM micrographs of LDH revealed a hexagonal morphology with a mean size of  $0.3-0.5 \mu m$ .<sup>28</sup> The particle size distribution, measured using a Coulter counter and SEM analysis, seemed to be caused by dispersion of the wet method and aggregation during sample drying.

The chemical properties, such as the molar ratio of Mg<sup>2+</sup> to Al3+, the nitrogen, carbon, sulfur, and hydrogen content, and the structural formulas of the synthesized Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH and SDS-LDH are shown in Table 1. Approximately 72.9% of SDS was intercalated into the LDH interlayer, with respect to the AEC of LDH. The d-spacings of the X-ray diffractograms of LDH, calcined LDH<sup>31</sup> rehydrated in the NaNO<sub>3</sub> solution, and SDS-LDH are depicted in Figure 1, which coincides with JCPDS File Card No. 22-700 of the rhombohedral HT. 13,32 The chain length of the SDS molecules was measured to be 2.08 nm.<sup>30</sup> The interlayered d-spacing before and after SDS intercalation was 2.01 nm with distortion. Thus, the intercalation angle of SDS into the LDH interlayer, calculated using trigonometry, was 75°, which is almost perpendicular to the basal plane of the LDH. 7,30



**Figure 1.** X-ray diffractograms of (a) Mg<sub>3</sub>-Al-(NO<sub>3</sub>) LDH, (b) calcined LDH (rehydrate), and (c) SDS-LDH.

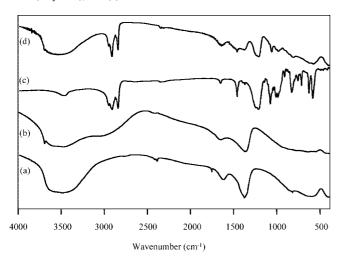
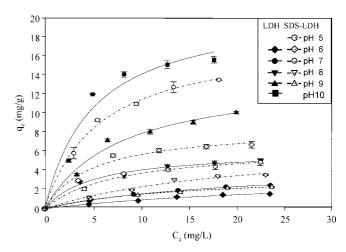


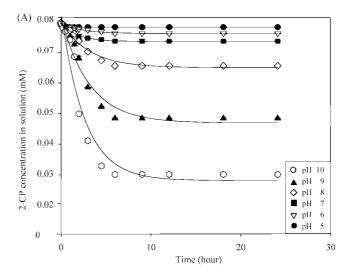
Figure 2. FT-IR spectra of (a) LDH, (b) calcined LDH (rehydrate), (c) SDS, and (d) SDS-LDH.

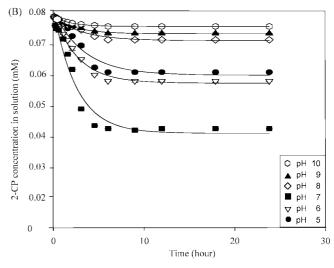
FT-IR spectra of LDH, calcined LDH rehydrated in the NaNO<sub>3</sub> solution, SDS, and SDS-LDH are shown in Figure 2. The wavenumbers of the 3600–3300 broad absorption of water molecules were assigned as OH stretching in the brucite-like layer, and the 2950–2850 cm<sup>-1</sup> wavenumbers were assigned as the CH<sub>2</sub> stretching mode. The wavenumbers 1700–1610 cm<sup>-1</sup> and 1469 cm<sup>-1</sup> denote the O-H of water-bending mode and the C-H absorption bend, respectively. On the other hand, the wavenumber value of 1383 cm<sup>-1</sup> was assigned as the nitrate IR absorption band. The wavenumbers 1219 and 1066 cm<sup>-1</sup> (1240–1210 cm<sup>-1</sup>) can be assigned to the OSO<sub>3</sub><sup>-</sup> asymmetric and symmetric stretching mode, and 700–500 cm<sup>-1</sup> can be assigned to the metal-oxygen bonding vibration. As, 34,35

**3.2. Sorption Isotherms.** The amounts of 2-CP sorbed by LDH and SDS-LDH after selected reaction periods at different pHs in suspension are given in Table 2 and Figure 3. All fitted sorption isotherms reveal that the Langmuir model fits the sorption data better than the Freundlich model. The sorption maximum capacity values of  $\beta$  for 2-CP by LDH (21.45 to 4.23 mg 2-CP/g LDH) exhibit a high correlation coefficient (R > 0.931) at pHs ranging from 10 to 6. However, the maximum sorption capacity of the SDS-LDH ranges from 18.08 to 3.57 mg 2-CP/g LDH at pH 5-9 (Table 2). The R value of the SDS-LDH sample fittings are greater than 0.931. The bonding strength ( $K_L$ ) ranged from 0.188 to 0.026 L/mg for LDH, and from 0.198 to 0.041 L/mg for SDS-LDH.



**Figure 3.** Sorption isotherms of 2-CP on LDH and SDS-LDH at various pH levels. Data represent the mean  $\pm$  1SD (n=3). ([2-CP] = 10 mg/L, [LDH] and [SDS-LDH] = 0.5 g/L, T=25 °C).





**Figure 4.** Time variation of 2-CP sorption on (A) LDH and (B) SDS-LDH at various pH levels. ([2-CP] = 10 mg/L, [LDH] and [SDS-LDH] = 0.5 g/L,  $T = 25 \,^{\circ}\text{C}$ ).

All sorption isotherm curves of the 2-CP-LDH and 2-CP-SDS-LDH systems were L-type (Figure 3). However, the hydrophobic-hydrophobic interactions of the 2-CP and SDS-LDH suspensions were not a constant partition (CP) and did not exhibit C-type curves, because of the low log  $K_{\rm ow}$  values

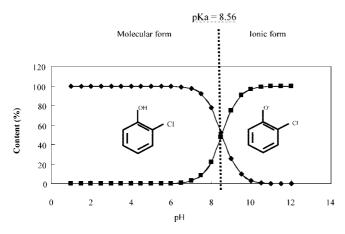


Figure 5. Speciation of 2-CP at various pH.

for 2-CP (i.e., 2.15). 13,30 In terms of the slope of the initial sorption of the curves, the shapes of the isotherms corresponding to 2-CP sorbed by LDH and SDS-LDH were classified as L-type classification system proposed by Giles et al.36,37 This type of isotherm was similar to those of hexadecyltrimethylammonium (HDTMA) organoclays sorbed by 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-DDT), 1,1-dichloro-2,2bis(p-chlorophenyl) ethylene (p,p'-DDE), and 2,4-dichlorophenozy propionic acid.8 The curves tended toward a constant value of  $q_{\rm e}$ , indicating the formation of a complete monolayer of DDT and DDE molecules covering the surface of the sorbents.<sup>10</sup>

3.3. Kinetic Models of 2-CP Sorption by LDH and **SDS**-**LDH.** The time functions of the sorption of 2-CP by LDH and SDS-LDH are shown in Figure 4A and 4B. The results of kinetic sorption on the two sorbents show that, after 6 h, the reaction reaches equilibrium. In addition, the reaction rates (k and  $\alpha$ ) of the four kinetic models to 2-CP sorption on LDH at pH 8–10 through the hydrophilic – hydrophilic interactions, and on SDS-LDH at pH 5-7 through hydrophobic-hydrophobic interactions, decrease and  $\beta$  values increase with decreasing pH values. The values of these parameters (i.e., R, p, and SE) obtained by applying different models to the kinetic data in the reactions of 2-CP sorption for LDH and SDS-LDH are given in Tables 3 and 4. All four rate equations fit the 2-CP sorption data well. Among the four models tested, for 2-CP sorbed by LDH and SDS-LDH, the R value of the second-order kinetic model generates the highest values.  $^{30}$  Generally, the p values of all suspensions demonstrate significant differences ( $p \le 1 \times 1$  $10^{-4}$ –1.2 ×  $10^{-3}$ ), except for the pH 5 system, because of the dissolution of Mg from LDH. Furthermore, the standard error (SE) values of the second-order kinetic model at 2-CP vs LDH, and of the 2-CP vs SDS-LDH suspensions are lower than for the other kinetic models (i.e., zero-order, first-order, and Elovich equations), except for pH 5 with its high dissolution of Mg from LDH (see Tables 3 and 4). Statistically, the second-order kinetic model is the best fit for the kinetic data.

3.4. Sorption Mechanisms of 2-CP onto LDH and SDS-LDH. 3.4.1. pH Effect. The pH affects 2-CP speciation (Figure 5) and metal dissolution from sorbents (Figure 6); hence, it has a significant impact on the sorption of LDH and of SDS-LDH to 2-CP (Figures 3 and 4). Using a visual MinteqA2 calculation (Figure 5),  $^{38}$  the dissociation (p $K_a$ ) of 2-CP is seen to be 8.56, so that 2-CP can be presented as a phenolate when the pH is >8.56, and as molecular when the pH is <8.56. Almost 75% was the anionic type of 2-CP at pH 9, and a similar percentage was molecular type at pH 8. This percentage can be 95% or more anionic when the pH is > 10 and  $\geq$  95% molecular when the pH is <7. The pH also affects Mg and Al dissolution

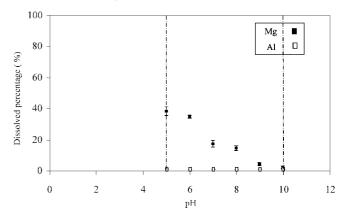


Figure 6. Mg and Al on LDH and SDS-LDH dissolved percentage at various pH.

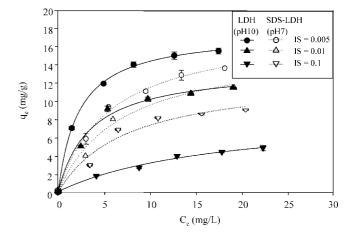


Figure 7. Sorption isotherms of 2-CP on LDH (pH 10) and SDS-LDH (pH 7) at various ionic strength. Data represent mean  $\pm$  1SD (n=3). ([2-CP] = 10 mg/L, [LDH] and [SDS-LDH] = 0.5 g/L, T = 25 °C).

from LDH and SDS-LDH (Figure 6). Because of the pH dependence of Mg and Al solubility, Mg dissolves at pH < 10 and Al at pH <4 and >10.39 Thus, in the LDH and SDS-LDH systems, the percentage of Mg that dissolves increases as pH decreases, whereas Al is only slightly dissolved within the pH range of 5-10. Consequently, because Mg dissolves at a low pH, the LDH and SDS-LDH structure can be destroyed, and the resultant positive position and SDS-intercalated LDH contents can diminish.

3.4.2. 2-CP Speciation and the Metal Dissolution from **Sorbents Effect.** In the LDH-2-CP system (Figure 4A), 2-CP can be present as a phenolate when pH > 8.56. Consequently, the Coulombic forces of the physical adsorption mechanism between positive LDH and dissociation of 2-CP can be a hydrophilic-hydrophilic interaction. The sorption quantity becomes higher when pH is increased, so that 75% and 95% of 2-CP is ionic type at pH 9 and pH 10, respectively. Therefore, the sorption capacity increases when the pH is higher. In addition, 2-CP can be present as molecular type when the pH is <8.56 (Figure 5). Thus, the interaction between hydrophilic LDH and hydrophobic 2-CP is not as good as before (Figures 3 and 4A). On the other hand, the reason that there still is an adsorption quantity at pH 7 and 8 is that LDH can sorb 25% of the anionic type and 75% of the slightly polar molecular type of 2-CP (i.e.,  $\log K_{ow}$  is 2.15) at pH 8, and 95% of the molecular type of 2-CP at pH 7 by electrostatic and ion-dipole interactions. In addition, the LDH structure is destroyed, because of dissolution of Mg at pH <10 (Figure 6). Thus, the adsorption

quantity of molecular 2-CP on LDH is lower than anionic 2-CP, because a lower pH is associated with a lower sorption quantity.

In the SDS-LDH-2-CP system (Figure 4B), there is low sorption capacity between hydrophilic 2-CP and hydrophobic SDS-LDH, when pH > 8.56. When the pH is < 8.56, SDS-LDH can sorb molecular type 2-CP by partition in the free intermolecular space. 22,30 Thus, the sorption capacity of 2-CP by the SDS-LDH system increases with decreasing suspension pH, theoretically due to the molecular type of 2-CP content at different pH values (Figure 5). The sorption capacity of 2-CP by the SDS-LDH system at various pHs did not follow the order pH 8 < pH 7 < pH 6 < pH 5. Instead, the SDS-LDH system sorption capacity of 2-CP followed the order pH 8 < pH 5 < pH 6 < pH 7, caused by the dissolution of Mg at low pH. Furthermore, the lowest sorption capacity was at pH 8, because there still was 25% anionic type 2-CP that could interfere with the sorption of the slightly polar molecular type of 2-CP on the SDS-LDH. Consequently, LDH exhibits its best adsorption capacity for the anionic type of 2-CP at pH 10, and SDS-LDH its best sorption capacity for molecular type 2-CP at pH 7. We observed that the bonding strengths and  $\beta$ values for 2-CP sorbed by LDH (i.e., pH 10) were similar to those of the SDS-LDH suspension (i.e., pH 7).

**3.4.3. Ionic Strength Effect.** The adsorption experiments to evaluate the ionic strength effect were conducted at three ionic strengths: 0.005, 0.05, and 0.1 M of NaNO<sub>3</sub> (Figure 7). The LDH-2-CP and SDS-LDH-2-CP systems were tested at pH 10 and 7, respectively, to reveal the greatest sorption capacity in the sorption isotherm experiments. Results demonstrated that the 2-CP sorption isotherm of the LDH suspension affected by ionic strength (IS) is greater than that of the SDS-LDH system. In the LDH-2-CP system, when the suspension pH is maintained at 10, the high concentration of NO<sub>3</sub><sup>-</sup> electrolytes compete with ionic-type 2-CP at the positive site of LDH. However, when the pH of the SDS-LDH system is 7, NO<sub>3</sub> decreases 2-CP sorption. There are only NO<sub>3</sub><sup>-</sup> can rather slightly decrease 2-CP sorption on SDS-LDH system than that increasing 2-CP sorption by salting-out effect. The interpretation of ionic strength increased with decreasing sorption capacity is list as follows. Table 1 shows that the percentage of SDS, relative to AEC, was 72.9%; thus, there was still <28.1% positive charge on the SDS-LDH, which can sorb more NO<sub>3</sub><sup>-</sup> when there are higher NO<sub>3</sub> concentrations via the concentration gradient effect. We conjectured that higher NO<sub>3</sub><sup>-</sup> concentrations can be attributed to decreased 2-CP sorption on the SDS-LDH, which might account for the dimensional shielding effect. Consequently, the bonding strengths and maximum capacity of LDH-2-CP ( $K_L = 0.284-0.057$  L/mg,  $\beta = 21.45-8.59$  mg/ g) and SDS-LDH-2-CP ( $K_L = 0.171-0.109$  L/mg,  $\beta =$ 13.58-18.08 mg/g) systems both decrease when the ionic strength increases.

### 4. Summary and Conclusions

Layered double hydroxides (LDHs) and sodium dodecyl sulfate-intercalated layered double hydroxide (SDS-LDH) have been regarded as potential organic pollutant sorbents for removing 2-CP. The sorption behavior of 2-CP on LDH and SDS-LDH better fit a Langmuir sorption isotherm than a Freundlich equation. The sorption curves of 2-CP in the LDH and SDS-LDH systems demonstrate an L-type isotherm, rather than a constant partition curve at low pH, which is caused by the low log  $K_{\rm ow}$  value of 2-CP (i.e., 2.15), relative to hydrophobic—hydrophobic interactions. Statistically, the second-order kinetic model fits the data better than the zero-order kinetic

model, first-order kinetic model, or Elovich kinetic equations. Based on its 2-CP speciation, metal dissolution, and ionic strength at different pHs, the best sorption capacity of anionic-type 2-CP is caused by the Coulombic forces of physical adsorption at pH 10, low ionic strength, and low metal dissolution of LDH, whereas, for molecular-type 2-CP, the best sorption capacity is caused by organic partition interactions at pH 7, low ionic strength, and 20% Mg dissolution of SDS—LDH.

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