



Removal of Nitrophenol from Water by Dodecyl Sulfate Modified Layered Double Hydroxides

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Removal of nitrophenols from aqueous solutions through the adsorption process by using dodecyl sulfate modified layered double hydroxides was investigated. It was found that dodecyl sulfate modified layered double hydroxides had a high adsorption capacity for removing nitrophenols, while adsorption reached equilibrium within 1 h. To ascertain the mechanisms of sorption, the experimental data were modeled by using the pseudo-first and pseudo-second order kinetic equations and the results indicated that the adsorption kinetics of nitrophenols on dodecyl sulfate modified layered double hydroxides well-matched with the pseudo-second order rate expression.

Keywords: Adsorption, Layered double hydroxides, Nitrophenols, Dodecyl sulfate, Pollutants.

INTRODUCTION

Aromatic pollutants were widely found in wastewater discharged from industries such as chemical cleaning agents, petroleum refining, resins and plastics¹⁻⁴. Because of their toxicity, poor biodegradability and accumulation potential in plant and animal tissues, some of them have been listed as priority toxic pollutants by U.S. Environmental Protection Agency. Therefore, removal of these pollutants from aquatic environments is a major focus of wastewater treatment. Various physicochemical processes sorption is regarded as a promising one for removal of phenol from wastewater⁵. However, some of them are relatively expensive and readily saturated and has less effectiveness to reduce the concentration of the organic pollutants in the presence of dissolved organic matter⁶⁻⁹. Therefore, great effort has been exerted to explore new sorbents with high sorption capacity and efficiency, low cost, for example, layered double hydroxides *etc.* taken into account.

Layered double hydroxides (LDHs) are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and solvation molecules^{10,11}. The cations occupy the centers of edge sharing octahedra, whose vertexes contain hydroxide ions that connect to form infinite 2D sheets. The most widely studied LDHs contain both divalent and trivalent metal cations, a generic formula for these LDHs may be written as; $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$, where M^{2+} may be Zn^{2+} , Mg^{2+} , or Ni^{2+} and M^{3+} may be Al^{3+} , Ga^{3+} or Fe^{3+} . A^{n-} is a non-framework charge compensating inorganic or organic anion, *e.g.*, CO_3^{2-} , Cl^- , SO_4^{2-} and x is normally between 0.2-0.4.

Layered double hydroxides may also contain M^+ and M^{4+} cations but these are limited to specific examples such as Li^+ and Ti^{4+} . Layered double hydroxides, therefore serve as a good template for the formation of functional composite materials by host-guest structural design and assembly. The species, composition and ordering of the metallic cations, stacking sequence of layers, size and orientation of the guest, as well as the interactions between the negatively charged guest and the positively charged LDH layers are all critical factors influencing the structure of LDHs and thus determining the specific applications of these materials¹²⁻¹⁵.

In the present work, dodecyl sulfate intercalated layered double hydroxides (DS-LDHs) were used as an adsorbent for the removal of nitrophenols from aqueous solutions through the batch experiments. In order to analysis of experimental data, pseudo-first and pseudo-second order kinetic equations were used based on which the adsorption characteristics and mechanisms of DS-LDHs were attempted to be ascertained. The research results in the laboratory could be applied in wastewater treatment plant for elimination of nitrophenols and other organic contaminants.

EXPERIMENTAL

All chemicals including $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, $NaNO_3$, sodium dodecyl sulfate, *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol were analytically pure reagents and used as received without purification. They were purchased from the Beijing Chemical Plant Limited. All the water used was deionized and decarbonated.

The precursor $Mg_{0.66}Al_{0.34}(OH)_2(NO_3)_{0.34}$ (LDHs) was synthesized by a procedure similar to that of described previously^{16,17}. Under nitrogen atmosphere through the conventional route, a solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.18 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.09 mol) in deionized water (300 mL) was added dropwise over 2 h to a solution of NaOH (0.40 mol) and $NaNO_3$ (0.32 mol) in water (100 mL). The mixture was held at 75 °C for 24 h. The precipitates were separated by centrifugation, washed with water and dried at 70 °C for 20 h.

Synthesis of dodecyl sulfate intercalated layered double hydroxides: The dodecyl sulfate intercalated layered double hydroxides (DS-LDHs) was obtained by the method of ion exchange. A 100 mL solution of 3 g of sodium dodecyl sulfate (SDS) was added to a suspension of LDHs (10 g) in water and the solution pH was kept 7. The mixture was heated at 60 °C under a nitrogen atmosphere for 48 h. The product was washed extensively with deionized water, centrifuged and dried at 70 °C for 20 h.

Sorption experiments: Nitrophenols sorption experiments were carried out using a batch method. Both the effects of contact time and nitrophenol concentration on the adsorption were investigated, the effect of contact time was used to determine kinetic model of nitrophenol sorption and equilibrium time. 3.8 g of DS-LDHs and 30 mL of nitrophenols solutions were added to 100 mL Erlenmeyer stopper flasks. After capped and vigorously shaken by hand, the flasks were placed in a water bath at certain temperature (*e.g.* 30 °C) and gently shaken for specific time period or until adsorption equilibrium. The suspensions were filtered and the nitrophenol concentrations were determined using UV-vis spectrophotometer (*p*-nitrophenol at $\lambda = 317$ nm, *m*-nitrophenol at 330 nm and *o*-nitrophenol at 350 nm). The amount of nitrophenols adsorbed by the DS-LDHs was calculated by the difference between the initial ($C_{a,0}$) and equilibrium concentrations ($C_{a,e}$), per kilogram of LDHs adsorbent: $Q_e = (C_{a,0} - C_{a,e}) \times V/m$.

RESULTS AND DISCUSSION

Isotherms for the adsorption of nitrophenols in aqueous solutions by DS-LDHs are presented in Fig. 1. It was found that DS-LDHs had high retention capacities for nitrophenols. Within the concentration range studied, all adsorption isotherms

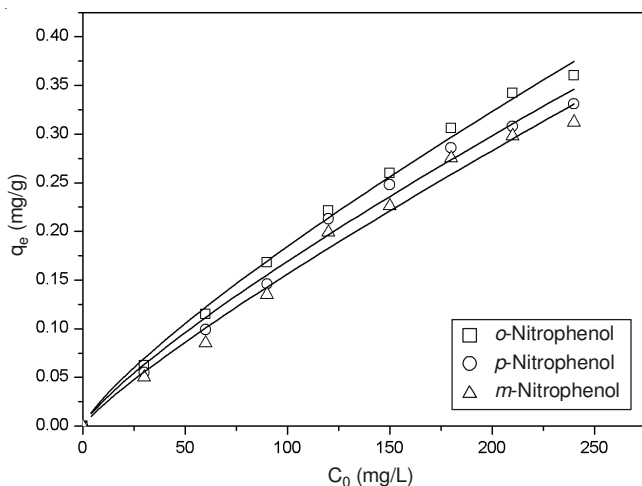


Fig. 1. Adsorption isotherms of nitrophenols by DS-LDHs

were characterized by relatively high linearity. As for the adsorption of nitrophenols by DS-LDHs, two models were used to fit the experimental data: (1) Langmuir model (equation (1))^{18,19}; (2) Freundlich model (equation (2))²⁰

$$\frac{q_e}{q_m} = \frac{K_L C_{a,e}}{1 + K_L C_{a,e}} \quad (1)$$

$$q_e = K C_{a,e}^{1/n} \quad (2)$$

where $C_{a,e}$ is the equilibrium concentration of nitrophenols in the solution (mol/m^3); q_e is the adsorption capacity at equilibrium (mol/kg); q_m and K_L are the Langmuir constants related to the capacity and energy of adsorption, respectively; K and n are Freundlich temperature-dependent constants. Table-1 lists the Freundlich constants for the adsorption. The experimental q_e values agree well with the calculated ones obtained from Freundlich model, indicating that adsorption isotherms can best be represented by the Freundlich model.

TABLE-1
FREUNDLICH CONSTANTS FOR THE ADSORPTION
OF NITROPHENOLS BY DS-LDHs

	Adsorption		
	K	n	R ²
<i>o</i> -Nitrophenol	4.45×10^{-3}	0.809	0.990
<i>p</i> -Nitrophenol	3.93×10^{-3}	0.817	0.987
<i>m</i> -Nitrophenol	3.01×10^{-3}	0.857	0.989

Effect of contact time: The experimental data dealing with the relation between nitrophenols concentration and contact time are shown in Fig. 2. It shows the plot of sorption of nitrophenols against contact time at the initial nitrophenols concentration of 90 mg/L. It could be found that the nitrophenols concentrations decreased swiftly with the contact time. The minimum amount of nitrophenols was sequestered from the solution within 1 h. However, the further increase of contact time did not make obvious change of nitrophenols concentrations. At the same experimental conditions, the decreases of nitrophenols compounds concentration were follow the order as: *o*-nitrophenol > *p*-nitrophenol > *m*-nitrophenol. The

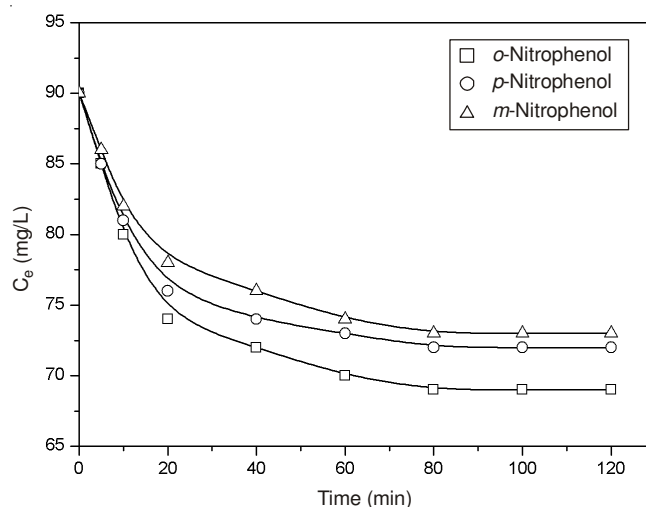


Fig. 2. Relationship between nitrophenols concentrations in solution and contact time

results might be explained that the difference of adsorbed amount might be controlled by the structure and the dipole moment at the same size.

Kinetic models: Kinetic studies of nitrophenols by adsorption on DS-LDHs were concerned with obtaining essential information for the application of adsorbent used in treatment systems. Adsorption kinetics is mainly controlled by various steps including four steps which can be enumerated and applied for removal of nitrophenols:

(1) Nitrophenols transfer from the bulk solution to the boundary film bordering the DS-LDHs surface.

(2) Nitrophenols transport from the boundary film to the surface of the adsorbent.

(3) Nitrophenols transfer from the surface to the intraparticle active sites.

(4) Uptake of nitrophenols on the active sites, with reaction occurring in the interlayer of LDHs.

Step-1 relates to the batch agitation and the homogeneity of the solution. The agitation provided to the solution in these experiments is sufficient to ignore this step as a controlling process. Adsorption is an exothermic phenomenon so the transfer of the heat of reaction has to be considered. Step-2 describes external mass transfer resistance. Step-3 relates to the intraparticle diffusion model. Step-4 relates to chemisorption and the rate of adsorption is generally controlled by the kinetic of bond formation. The objective of this study is to determine the main limiting step in the overall uptake mechanism. Pseudo-first-order kinetics model and a pseudo-second-order kinetic model are used to fit the experimental data.

As the adsorption efficiency are dominated by adsorption kinetics, the kinetic models, such as pseudo-first order²¹⁻²³ and the pseudo-second order^{24,25} models, are commonly used for analysis of reaction process and mechanisms. In comparison between these two models, the mechanism of adsorption and potential rate controlling procedures could be determined.

Pseudo-first-order kinetic model: This model was suggested by Lagergren for the sorption of solid/liquid systems. It has been used by many authors, where k_1 (min^{-1}) is the pseudo-first-order rate constant of removal of dodecyl sulfate, q_e (mg/L) is the amount adsorbed at equilibrium and q_t (mg/L) is the amount adsorbed at time t . This equation can be expressed in linear form: By plotting $\ln(q_e - q_t)$ against t , a straight line is obtained and the value of the rate constant k_1 can be calculated.

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order kinetic model: The pseudo second-order kinetic model is expressed by the equation where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant of adsorption. This model is based on the assumption that the rate-limiting step involves chemisorption of the sorbate on the sorbent. The following integrated form can be obtained where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second order adsorption. Plotting t/q_t against t , a line is obtained and the rate constant k_2 as well as q_e can be calculated.

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

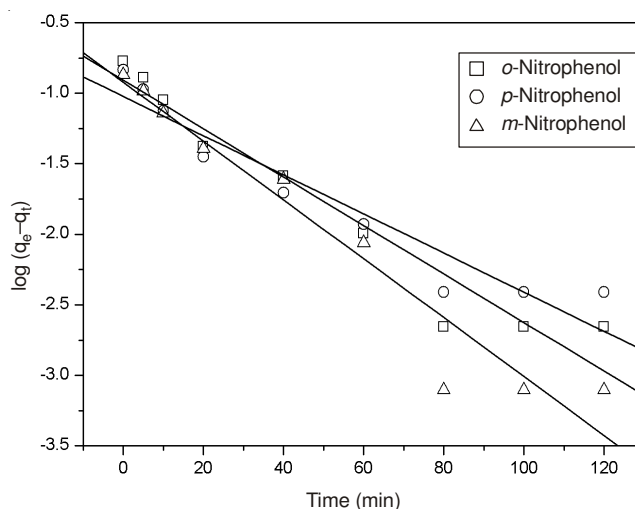


Fig. 3. Pseudo-first-order adsorption kinetics of nitrophenols by DS-LDHs

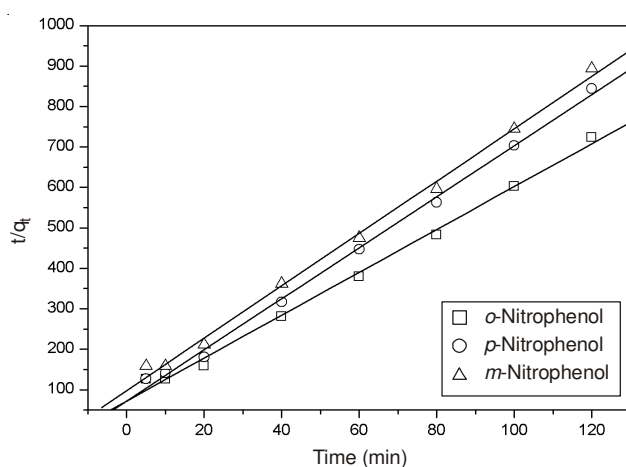


Fig. 4. Pseudo-second-order adsorption kinetics of nitrophenols by DS-LDHs

TABLE-2
KINETIC PARAMETERS AND CORRELATION
COEFFICIENTS FOR ADSORPTION OF ITROPHENOLS

Adso-rbate	Pseudo-first-order				Pseudo-second-order		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1	R^2	$q_{e,cal}$ (mg/g)	k_2	R^2
<i>o</i> -NP	0.168	0.123	0.0396	0.969	0.189	0.387	0.997
<i>p</i> -NP	0.146	0.0947	0.0319	0.960	0.159	0.549	0.998
<i>m</i> -NP	0.135	0.119	0.0480	0.970	0.154	0.427	0.998

The curve-fitting plots of the pseudo-first-order and pseudo-second order models on DS-LDHs are shown in Figs. 3 and 4, respectively. The kinetics parameters are listed in Table-2. It can be seen that the straight lines with extremely high correlation coefficients ($R^2 > 0.995$) for the pseudo-second order model in comparison with those for the pseudo-first order model for the adsorption of nitrophenols onto DS-LDHs. It was strongly suggested that the adsorption systems were a pseudo-second order model based on the assumption that the rate-limiting step may be chemical sorption. Furthermore, the calculated values of q_e by the pseudo-second order model were also agreed very well with the experimental values. It could also be assumed that the adsorption of nitrophenols onto DS-LDHs took place *via* hydrogen bonding and hydrophobic interactions.

Conclusion

Modification of the layered double hydroxides with dodecyl sulfate was prepared to remove nitrophenols from aqueous solutions. The sorptions of DS-LDHs were investigated regarding with contact time, initial nitrophenols concentration and sorption isotherms. It was evident that the increase of initial nitrophenols concentration was favorable to increase sorption although the contact time. Compared sorption isotherms of three sorbents and values of *p*-nitrophenol and *m*-nitrophenol, the results indicated that *m*-nitrophenol can be mostly adsorbed by DS-LDHs and the sorption isotherms of nitrophenols on DS-LDHs followed the known Freundlich model. It was suggested that DS-LDHs would be used in special water treatment process for removal of organic pollutants.

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