Studies on adsorption of phenol and 4-nitrophenol on MgAl-mixed oxide derived from MgAl-layered double hydroxide

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ABSTRACT

In this research, the removal of two phenols (4-nitrophenol and phenol) from aqueous solution was investigated using MgAl-mixed oxide. This oxide was prepared by calcining crystalline MgAl–CO₃-layered double hydroxide (LDH) at 500 °C for 4 h. We found that it takes 10–12 h for adsorption of 4-nitrophenol to reach the equilibrium at room temperature while the equilibrium time is 20–25 h for phenol adsorption. The kinetic process of 4-nitrophenol adsorption seemingly follows the first-order reaction but phenol is adsorbed in a pseudo-second-order model. We also noted that the maximum adsorption amount of 4-nitrophenol by fitted three-parameter Langmuir–Freundlich isotherm is 367.8 mg/g, much higher than that of phenol (46.9 mg/g). The differences in the adsorption kinetics and dynamics have been related to the adsorption mechanism and adsorbate–adsorbent interactions. The reconstruction of MgAl-mixed oxide in aqueous solution incorporates 4-nitrophenolate into the interlayer. However, it is difficult to intercalate phenolate due to its weaker affinity for LDH in comparison with OH[−]. In addition, adsorption of MgAl-mixed oxide for 4-nitrophenol and phenol is slightly affected by the initial pH, but considerably facilitated by increasing the adsorption temperature.

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1. Introduction

Removal of the organic pollutants from wastewater before its discharge is necessary in order to reduce their side effect on the environment and human health. Various organic pollutants, in particular phenolic derivatives, are the products of many industrial processes and found in industrial wastewater. Phenolic derivatives, such as a number of chloro- and nitrophenols, are toxic and carcinogenic. They can persist for many years in the environment because of their resistance to microbiological degradation. In the last decade, various methods have been proposed to remove phenols, including catalytic oxidation [1,2], photo-oxidation [3], electrochemical oxidation [4], biological degradation [5], ultrafiltration [6] and adsorption [7–15]. Since the other methods need special process requirements or special catalysts, adsorption seems to be a good choice in terms of the cost and operation for the removal of phenolic compounds from wastewater.

Various adsorbents were tested to adsorb the phenolic compounds in aqueous solution in the past years. For example, Roostaei and Tezel investigated phenol adsorption on silica gel, activated alumina, activated carbon and zeolites, the latter two materials show a higher capacity for the adsorption of phenol [12]. Rodriguez and co-workers found that activated carbons are good adsorbents for phenol and 2,4,5-trichlorophenol [9]. Some other materials, such as calcined layered double hydroxides [11,15], dried sewage sludge [14], crosslinked starch polymers from an agro alimentary by-product [8], sewage treatment plant biosolids [7], coir pith carbon [16], crosslinked starch gels containing tertiary amine groups [8] and mesoporous silicate [10] were tested to remove phenol and substituted phenols from aqueous solution. In particular, the calcined MgAl-LDHs, i.e. MgAl-oxides, show an effective adsorption for substituted phenols in aqueous solution because such an oxide can be readily reconstructed to LDH structure, during which anionic phenolates are intercalated (incorporated), which was reported by Hermosin et al. [11] and Ulibarri et al. [15].

LDHs are a class of lamellar hydroxides that consist of brucite-type mixed metal hydroxide layers and exchangeable interlayer anions, with a general formula of $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where $x=0.2-0.33$, M^{II} and M^{III} represent any divalent and trivalent metal cations and A^{n-} any anion [17,18]. One naturally

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Nomenclature

b	adsorption constant (L/mg)
c_0	initial concentration of phenols (mg/L)
c_e	equilibrium concentration of phenols (mg/L)
k	Freundlich constant ((mg/g)(L/mg) ^{1/n})
k_{ad}	adsorption rate constant (L/h)
LDH	layered double hydroxide
m	mass of MgAl-mixed oxide (g)
NO ₂ PhOH	4-nitrophenol
NO ₂ PhO [−]	deprotonated 4-nitrophenol
PhOH	phenol
PhO [−]	deprotonated phenol
q_e	adsorption amount of phenols at the equilibrium (mg/g)
q_t	adsorption amount of phenols at any time t (mg/g)
Q	maximum adsorption amount of phenols (mg/g)
t	time (h)
V	solution volume (L)

existing example is hydrotalcite (Mg₃Al(OH)₈(CO₃)_{1/2}·2H₂O). LDHs and the related materials find a number of applications [17,18], such as ion exchangers [19], basic catalysts for organic synthesis [17,18] and carriers for efficient cellular delivery [20,21]. In particular, after calcination at moderate temperatures (450–650 °C), MgAl-CO₃-LDH can be converted to a mixed metal oxide with a specific surface area of ~200 m²/g and homogeneous dispersion of metal cations. The mixed metal oxide can be reconstructed in aqueous solution to regain the layered structure with different anions intercalated in the interlayer, and thus the MgAl-mixed oxide is a promising adsorbent to eliminate ecologically undesirable inorganic or organic anions [17,18].

This research reports the adsorption behaviors of phenol (PhOH) and 4-nitrophenol (NO₂PhOH) on MgAl-mixed oxide. We note that the derived MgAl-mixed oxide is a potential adsorbent for some phenols in terms of the adsorption capacity.

2. Materials and methods

2.1. Materials preparation

Precursor MgAl-CO₃-LDHs were prepared by co-precipitation. Typically, a salt mixture solution (200 mL) containing 0.10 mol of AlCl₃ and 0.20 mol of MgCl₂ was added to an alkaline solution (200 mL) containing 0.60 mol of NaOH and 0.055 mol of NaCO₃ under vigorous stirring. After further stirring for 10 min, the slurry was collected and washed once with distilled water via centrifugation. The slurry was then dispersed in 400 mL distilled water, and then hydrothermally treated at 100 °C for 4 h. The MgAl-CO₃-LDH material was collected via high-speed centrifugation and dried at 50 °C overnight. As-prepared LDH material was then calcined in a muffle furnace at 500 °C for 4 h to derive MgAl-mixed oxide used as the adsorbent for the adsorption of PhOH and NO₂PhOH.

2.2. Materials characterization

X-ray diffraction (XRD) patterns of the LDH and the derived mixed oxide were collected on a powder X-ray diffractometer (XRD, Rigaku Miniflex with a variable slit width) with Co K α radiation (λ = 0.1790 nm) at a scanning rate of 2°/min from 2θ = 5° to 2θ = 80°. Infrared spectra were collected using KBr discs on a Perkin-Elmer 2000 FTIR after 40 scans within 4000–400 cm^{−1} at a resolution of 2 cm^{−1}. The electron microscopic images were obtained on a JEOL JSM-6400F field emission scanning electron microscope (SEM)

at an acceleration voltage of 10 kV. Mg/Al ratio was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Varian Vista Pro. Thermogravimetric analysis (Shimatsu, TG50H) was carried out using air as the carrier gas at a flow rate of 100 mL/min. During the measurement, 10–20 mg of LDH sample was heated at a rate of 10 °C/min over a temperature range of 30–800 °C.

2.3. Adsorption of phenols

Prior to adsorption, the MgAl-mixed oxide was pressed and crushed to the mesh size of 40–60. The isothermal adsorption experiments were carried out in batch under constant shaking. For the adsorption kinetics, MgAl-mixed oxide (0.10 g) was used to adsorb phenols at a concentration of 100 mg/L (20 mL) at pH 10 or 5 in a series of reaction tubes. The reaction tubes were immersed in a shaker and kept at room temperature (22 ± 2 °C) or at 55 ± 2 °C under shaking. At a desired time point from 0 to 30 h, 1.0 mL of the supernatant was taken from the suspension. After filtration with a 0.22- μ m filter and high-speed centrifugation, the phenol concentration in the supernatant was determined with the UV absorption on a JASCO V-550 UV/vis spectrophotometer, and thus the adsorbed amount of phenols was calculated.

To test the phenol adsorption capability, MgAl-mixed oxide (0.10 g) was placed in a series of reaction tubes containing various concentrations (10–2000 mg/L) of PhOH or NO₂PhOH (20 mL). The suspensions were shaken at 22 ± 2 °C for 30 h to reach the adsorption equilibrium, and then the supernatants were treated by filtering through a 0.22- μ m filter and high-speed centrifugation, followed by the UV measurement to determine the equilibrium concentration (c_e in mg/L) of the phenol that was not adsorbed. Therefore, the amount of phenols (q_e in mg/g) adsorbed on MgAl-mixed oxide was calculated using Eq. (1):

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where V is the volume of solution (L), c_0 (mg/L) and c_e (mg/L) the initial and equilibrium concentration of PhOH or NO₂PhOH, respectively, and m the mass of adsorbent (g).

3. Results and discussion

3.1. Structural properties

As shown in Fig. 1, the complete transformation of crystalline MgAl-CO₃-LDH to MgAl-mixed oxide is reflected by the XRD patterns. MgAl-CO₃-LDH shows a series of the basal reflections from the (0 0 3), (0 0 6) planes, etc. and from plane (1 1 0) (Fig. 1A), with an interlayer spacing of 0.762 nm and unit cell parameter a of 0.306 nm [17,18]. After calcination at 500 °C, the crystalline LDH phase changes to MgO phase (JCPDS 43-1022) that is indicated by the two broad peaks at 52° [plane (2 0 0)] and 75° [plane (2 2 0)] (Fig. 1B). This transformation has been also confirmed by the FTIR spectra (see Supplementary Fig. S1).

Also shown in Fig. 2 are the SEM morphological images of the original LDH and the derived oxide. As-prepared LDH particles are featured in shape with the usual hexagonal platelets, with the lateral dimension being 100–200 nm and the thickness 20–30 nm [17]. After calcination, some big particles (in 1 μ m scale) are formed with certain shape, probably attributed to the aggregation during the calcination, while most oxide particles are much smaller and shapeless.

The elemental analysis from ICP-AES indicates that the Mg/Al atomic ratio is 2.02. The approximate formula of as-prepared LDH is Mg_{2.02}Al(OH)_{6.04}(CO₃)_{0.5}·1.17H₂O, giving a total weight loss of 42.6% when converted to the mixed oxide (Mg_{2.02}AlO_{3.52}), in good

Fig. 1. XRD patterns of (A) MgAl-CO₃-LDH and (B) MgAl-mixed oxide. The diffraction peaks marked with (#) are attributed to the aluminum holder.

agreement with the weight loss (42.5%) at 700 °C measured by TGA (see Supplementary Fig. S2). The TGA data further indicate that calcination at 500 °C for 4 h has completely converted as-prepared MgAl-CO₃-LDH to the mixed oxide since after 500 °C there is no obvious weight loss step.

3.2. Adsorption kinetics

The adsorption of phenols from the liquid to solid phase was first investigated with the adsorption time. As shown in Fig. 3A, the adsorption of NO₂PhOH continues to 10–12 h, and then keeps almost unchanged to 30 h at pH of both 5 and 10. The adsorption behavior indicates that the adsorption on the MgAl-mixed oxide is not affected by the initial pH and reaches the equilibrium at 12 h. The adsorbed amount of NO₂PhOH at 12 h is 16–17 mg/g, indicating that 80–85% of initial NO₂PhOH is removed by MgAl-oxide under the current conditions. In contrast, MgAl-oxide continues to adsorb PhOH till 20–25 h. Although the initial pH does not affect PhOH adsorption behavior, the adsorbed amount of PhOH on the same mixed oxide is much smaller, 1.4–1.5 mg/g at 15 h, corresponding to 7–7.5% of the initial PhOH in the solution.

We used the first-order Lagergren equation (Eq. (2)) and the pseudo-second-order equation (Eq. (3)) [13,22] to treat the adsorption of phenols over the MgAl-mixed oxide in aqueous solution:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (2)$$

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

where q_e and q_t are amounts of phenols adsorbed by the adsorbent (mg/g) at the equilibrium time and time t , respectively, and k_{ad} the adsorption rate constant. Adsorption data were fitted by both equations, and we found that the first-order Lagergren model is more suitable for the adsorption of NO₂PhOH while the pseudo-second-order model is better for PhOH adsorption. As shown in Fig. 4A, the first-order Lagergren kinetic model gives a straight line in the plots of q_t vs. t at pH 5 and 10 for NO₂PhOH adsorption. On the other hand, the linearity of the plots of t/q_t vs. t shows a better agreement with the pseudo-second-order model for the PhOH adsorption (Fig. 4B). The fitting parameters are listed in Table 1. We note again that the initial pH has little effect on these parameters and that the equi-

Fig. 2. SEM images of (A) MgAl-CO₃-LDH and (B) derived MgAl-mixed oxide.

librium adsorption amount for NO₂PhOH is 5–10 times as that for PhOH.

3.3. Adsorption capability for phenols

To examine the adsorption capability of MgAl-mixed oxide for phenols in aqueous solution, we carried out a series of equilibrium adsorption tests (30 h at room temperature) by varying phenol concentration from 10 to 2000 ppm. The adsorption data are shown in Fig. 5. We employed three isotherm models to treat the adsorption data [12]. The three models are:

$$\text{Langmuir isotherm: } q_e = \frac{Qbc_e}{1 + bc_e} \quad (4)$$

where Q (mg/g) and b (L/mg) are the Langmuir constants related to the loading and energy of adsorption.

$$\text{Freundlich isotherm: } q_e = kc^{1/n} \quad (5)$$

Table 1
Fitting parameters for the adsorption kinetic models.

Adsorbate	Model	Initial pH	q_e (mg/g)	k_{ad} (L/h)	R^2
4-Nitrophenol	Lagergren first-order	5	17	0.175	0.972
		10	16.6	0.125	0.972
Phenol	Pseudo-second-order	5	2.74	0.351	0.996
		10	1.51	0.154	0.978

where k [(mg/g)(L/mg) $^{1/n}$] and n are the Freundlich temperature-dependent constants.

Three-parameter Langmuir–Freundlich isotherm :

$$q_e = Q \frac{(bc_e)^{1/n}}{1 + (bc_e)^{1/n}} \quad (6)$$

where Q (mg/g) is the maximum adsorption amount, b (L/mg) and $1/n$ are constants related to the adsorption strength. In addition, c_e is the equilibrium concentration of phenols (mg/L), and q_e (mg/g) the adsorption amount on MgAl-mixed oxide at the equilibrium.

As shown in Fig. 5, the adsorption data of both phenols are better fitted with three-parameter Langmuir–Freundlich isotherm (solid line), which is also reflected by the higher regression coefficient in Table 2. In addition, Freundlich isotherm seems good for PhOH adsorption while Langmuir is better for NO₂PhOH. Further note that the maximum adsorption capability of the mixed oxide for NO₂PhOH is 367.8 mg/g from three-parameter Langmuir–Freundlich isotherm, quite close to the real experimental adsorption capacity (360–380 mg/g) at the concentration range of 500–1700 mg/L. This amount is much bigger than that for PhOH (46.9 mg/g) that is almost double the real adsorption capacity at the concentration of ca. 700 mg/L. We also note that other param-

eters are quite different for two phenols (Table 2). The differences in the fitting parameters as well as in the adsorption behaviors presented previously suggest that these two phenols are adsorbed by two different mechanisms, as addressed shortly.

In comparison, LDH-derived MgAl-mixed oxide seems to be a very good adsorbent for some phenolic compounds. Ulibarri et al. showed that MgAl-mixed oxide can effectively adsorb 2,4,6-trinitrophenol, with the adsorbed amount up to 2.25 mmol/g (ca. 550 mg/g) [11,15]. The current research finds that MgAl-mixed oxide can take up ca. 370 mg/g NO₂PhOH (ca. 2.3 mmol/g). Such an adsorption capability is higher than most common adsorbents [8], except for some activated carbons [9]. However, the adsorption for PhOH is not so effective, in comparison with other adsorbents [9,12,13].

The adsorption of two phenols on MgAl-mixed oxide is influenced to a large extent by the adsorption temperature. Our experimental tests show that the adsorption amount of MgAl-mixed oxide for both phenols at 55 °C for 0.5 h is remarkably increased, by ca. 10 times of that at 22 °C. The higher temperature speeds the phenol adsorption rate and probably the adsorption capacity, as discussed in the following section.

Fig. 3. Adsorption amount of (A) NO₂PhOH and (B) PhOH on MgAl-oxide at pH 10 (■) and pH 5 (Δ) as a function of adsorption time.

Fig. 4. (A) Lagergren first-order rate equation for adsorption of 4-nitrophenol and (B) pseudo-second-order rate equation for adsorption of phenol at pH 10 (■) and pH 5 (Δ).

Table 2
Fitting parameters from different equilibrium models.

Adsorbate	Three-parameter Langmuir–Freundlich				Langmuir			Freundlich		
	Q (mg/g)	b (L/mg)	1/n	R ²	Q (mg/g)	b (L/mg)	R ²	k ((mg/g)(L/mg) ^{1/n})	1/n	R ²
4-Nitrophenol	367.8	0.0179	4.667	0.998	439.7	0.00549	0.974	16.5	0.435	0.874
Phenol	46.9	0.00166	2.225	0.999	134.1	0.00030	0.911	0.0016	1.497	0.993

3.4. Adsorption mechanism

It is well known that the MgAl-mixed oxide derived by calcining its LDH precursor at mild temperatures can be readily reconstructed to regain the similar LDH structure in aqueous or basic solution [17,18,23,24]. As shown in Fig. 6A, the MgAl-mixed oxide starts to show the layered feature after shaking in basic solution (pH 10) for 4 h at room temperature, and the mixed oxide phase disappears after 16 h immersing. As for the adsorption of NO₂PhOH on the MgAl-mixed oxide, two reactions presumably take place simultaneously:

Fig. 5. Adsorption isotherms of (A) 4-nitrophenol and (B) phenol on Mg-Al-mixed oxide.

At pH 10 most NO₂PhOH (pK_a = 7.2) dissociates into the anionic form, and some can be intercalated into the interlayer space in the reconstructed LDH. The intercalation of NO₂PhO[−] is evidenced by the FTIR spectrum in Fig. 7A. The bands at 1592 and 1311 cm^{−1} indicate the presence of conjugated NO₂ group, and the band at 1171 cm^{−1} is due to an N⁺–O[−] vibration of the NO₂ group. As suggested by Ragavan et al. [25], the intercalation of NO₂PhOH into LDH is facilitated by the electrostatic interaction between –NO₂ group and the hydroxide layer. As presented previously, the maximum adsorption amount of NO₂PhOH on MgAl-mixed oxide is ca. 367.8 mg/g (Table 2), representing ca. 35% intercalation degree in the reconstructed LDH. This suggests that the affinity of NO₂PhO[−] is similar to OH[−] since at the end of adsorption the concentrations of NO₂PhO[−] and OH[−] are all in the range of 3–8 mM (suppose initial NO₂PhOH is 1000 mg/L).

As for the PhOH adsorption, we found that its maximum adsorption amount is ca. 46.9 mg/g from the three-parameter model, while the real amount is 25.5 mg/g (Fig. 5B). The latter amount is only corresponding to 3.6% intercalation degree in the reconstructed LDH if any. In the FTIR spectrum of the oxide after adsorption (Fig. 7B), we cannot observe any characteristic vibration bands of PhOH, but a peak at 1365 cm^{−1} which is exclusively attributed to the CO₃^{2−}

Fig. 6. XRD patterns of MgAl-mixed oxide as a function of the immersing time in water at pH 10 at 22 °C (A) and at 55 °C (B).

Fig. 7. FTIR spectra of MgAl-oxide after adsorption of (A) 4-nitrophenol and (B) phenol for 30 h.

[17]. During the adsorption of PhOH, CO_2 contamination cannot be avoided, in particular under the basic condition (pH 10–11). The preference for CO_3^{2-} by LDH thus reduces the possibility for intercalation of both phenols. Unlike NO_2PhOH , the bulky hydrophobic phenyl ring in PhOH cannot provide any electrostatic interaction with the hydroxide layer, so phenolate has a very weaker affinity for LDH and its intercalation is more difficult than NO_2PhOH . Therefore, the affinity of phenolate for LDH is believed to be much weaker than OH^- . Although more than 60% of PhOH can dissociate to phenolate anion at pH 10–11 ($\text{pK}_a = 9.8$), the phenolate intercalation degree if any (3.6%) is much smaller than the NO_2PhO^- (35%), and most phenolates stay in the aqueous phase. In this connection, the adsorbed PhOH is possibly situated only on the surface, not intercalated into the interlayers, which involves an adsorption mechanism different from NO_2PhOH , as suggested by their adsorption behaviors (Fig. 4), the equilibrium adsorption profiles (Fig. 5) and the fitted parameters (Tables 1 and 2).

The LDH reconstruction is also dependent on the temperature. As shown in Fig. 6B, the LDH structure is well established after 1 h shaking in the basic water (pH 10) at 55 °C, and the mixed oxide phase is gone after 2 h reaction. The temperature facilitation of LDH structure regeneration from the mixed oxide has also been observed by Millange et al. through a time-resolved in situ XRD investigation [24]. The quick regeneration of LDH structure thus speeds up the phenol adsorption and probably increases the adsorption capacity by reducing the adsorption time and capturing less CO_2 from air.

We observed that the initial pH has a negligible effect on the adsorption for both phenols. This is because the initial pH (5.0) is quickly increased to 9–10 (see Supplementary Fig. S3). When the initial pH is 5.0, the pH sharply jumps to 9.9 after 1 h reconstruction and then gradually increases to 11.4 after 30 h. If the initial pH is 10, the pH is slightly increased to 11.5 during the reconstruction [15]. After 2 h reconstruction, the pH difference in these two cases becomes very limited, and this is the main reason why the adsorption of MgAl-mixed oxide for two phenols is less affected by the initial pH.

4. Conclusions

The present study shows that MgAl-mixed oxide, derived from its LDH precursor, is a potential adsorbent for the removal of

NO_2PhOH as well as PhOH from aqueous solution. The adsorption capacity of MgAl-mixed oxide can be as high as 367.8 mg/g for NO_2PhOH and 25.5 mg/g for PhOH at room temperature. Much more NO_2PhOH molecules are adsorbed due to the strong electrostatic interaction between the NO_2 group and the hydroxide layer of reconstructed MgAl-LDH. These two phenols show different adsorption kinetics on MgAl-oxide, with NO_2PhOH adsorbed according to the Lagergren first-order model while PhOH best fits the pseudo-second-order model. The Langmuir model well fits the equilibrium isotherm of NO_2PhOH whereas the Freundlich model fits the PhOH adsorption, and furthermore both phenols follow the three-parameter Langmuir–Freundlich isotherm. We find that it takes 10–20 h for the phenol adsorption to reach equilibrium at room temperature, but heating to 50–60 °C can shorten the equilibrium time to a few hours. The adsorption mechanism involves the reconstruction of MgAl-mixed oxide, during which NO_2PhO^- is intercalated into the interlayer while PhO^- is mainly adsorbed on the surface.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.seppur.2009.03.016.

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