

# Study on adsorption of glyphosate (*N*-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution

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## Abstract

MgAl-layered double hydroxides with different interlayer anions (nitrate, carbonate and chloride) were evaluated for their abilities to adsorb the organic pesticide glyphosate (*N*-phosphonomethyl glycine, Gly). The adsorption isotherms of Gly on layered double hydroxides (LDHs) nitrate were described by the Langmuir equation at lower equilibrium concentration of Gly ( $C_e < 1.0$  mmol/L), and the Gly adsorption capacity on LDHs increased with the layer charge density, i.e. the structural  $\text{Al}^{3+}/\text{Mg}^{2+}$  ratio. Gly adsorption on LDHs nitrate generally occurred through two processes, external surface adsorption and interlayer anion exchange. The adsorption amount on LDHs at  $C_e = 1.0$  mmol/L decreased in the order of interlayer anions:  $\text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$ .

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## 1. Introduction

Widespread use of pesticides for agriculture production has led to their accumulation in soil, surface and ground water, resulting in serious environmental problems [1,2]. However, there has been increasing interests in past decades to develop new adsorbents, such as cationic clays [3–10], which can remove pesticides efficiently from aqueous solutions.

Layered double hydroxides (LDHs), also known as hydrotalcite-like anionic clays materials, are rare in nature but can be synthesized readily [11]. The structure consists of brucite-like layers, where a fraction of the divalent cations is replaced by trivalent cations. The positively charged layers are separated by the charge-balancing anions and water

molecules [12–14]. LDHs have the general formula  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}, \text{Fe}, \text{Co}, \text{Cu}, \text{Ni}$  or  $\text{Zn}$ ) and  $\text{M}^{3+}$  ( $\text{Al}, \text{Cr}, \text{Ga}, \text{Mn}$  or  $\text{Fe}$ ) are di- and trivalent cations, respectively;  $x$  is equal to the molar ratio of  $\text{M}^{2+}/(\text{M}^{2+} + \text{M}^{3+})$  in the range 0.2–0.33 and  $\text{A}^{n-}$  is an anion. LDHs have relatively large surface areas (30–150  $\text{m}^2/\text{g}$ ), high charge density, which changes from 50  $\text{\AA}^2$  per charge (=equivalent area) for a  $\text{M}^{2+}/\text{M}^{3+}$  molar ratio of 4–25  $\text{\AA}^2$  per charge for a ratio of 2. The ion exchange capacities (2–5 mmol/g) are higher than the cationic clay minerals [11,15]. LDHs are, therefore, considered as potential adsorbents for the elimination of toxic or ecologically undesirable anionic species, such as  $\text{CrO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SeO}_3^{2-}$  as well as phenol, humic substances, anionic surfactants and pesticides [16–24].

Glyphosate (*N*-phosphonomethyl glycine),  $\text{HOCOCH}_2\text{NHCH}_2\text{PO}(\text{OH})_2$ , an organophosphorus pesticide, is widely used in agriculture and has been detected in surface and

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subsurface water. The glyphosate (Gly) molecule is amphoteric, ranging from univalent positive charge to trivalent negative charge, and exhibits the following aqueous dissociation constants:  $pK_1 < 2$ ,  $pK_2 = 2.6$ ,  $pK_3 = 5.6$  and  $pK_4 = 10.6$  [25]. Until now, only LDHs with interlayer carbonate and their calcined products have been tested as adsorbents for the removal of Gly from water [23,26]. Because LDHs generally have greater affinities for multivalent anions, in particular carbonate, than monovalent anions [27,28], the adsorption efficiency of LDHs should be considerably affected by the nature of the initial interlayer anions. In this paper, we prepared MgAl-LDHs with different  $Mg^{2+}/Al^{3+}$  molar ratios and interlayer anions, such as nitrate, carbonate and chloride. The retention of Gly on LDHs was studied by batch adsorption.

## 2. Experimental

### 2.1. Preparation of samples

Layered double hydroxides are designated as MgAlR-X, where R is the  $Mg^{2+}/Al^{3+}$  molar ratio in the synthesis mixture and X is the interlayer anion (nitrate, carbonate, chloride or Gly anion).

MgAlR-X (X =  $NO_3$  or Cl) compounds with different  $Mg^{2+}/Al^{3+}$  molar ratios were prepared under nitrogen atmosphere (in order to minimize the contamination with atmospheric  $CO_2$ ) and vigorous magnetic stirring. Fifty microlitre of aqueous Mg and Al nitrate (or chloride) solution with the desired  $Mg^{2+}/Al^{3+}$  molar ratio to give a total cationic concentration of 1.2 M was added dropwise to a flask containing 200 mL of deionized water, and a solution of sodium hydroxide (1 M) was simultaneously added to fix the pH of coprecipitation at  $10.0 \pm 0.1$ . The addition of the salt solution was completed in 4 h. The precipitate was aged for 24 h at room temperature, and then washed by four dispersion and centrifugation cycles in deionized water, and finally air-dried.

MgAl<sub>2</sub>-CO<sub>3</sub> was prepared by coprecipitation method. Fifty microlitre of aqueous of 0.8 M  $Mg(NO_3)_2$  and 0.4 M  $Al(NO_3)_3$  solution was added dropwise to 200 mL of 0.4 M sodium carbonate solution. The pH of mixture was held constant at  $10.0 \pm 0.1$  by simultaneous addition of 1 M sodium hydroxide solution. The addition of the salt solution was completed in 4 h. The precipitate was aged for 24 h at room temperature, and then washed by four dispersion and centrifugation cycles in deionized water, and finally air-dried.

MgAl<sub>2</sub>-Gly was prepared through an anion exchange route. Under nitrogen atmosphere and vigorous magnetic stirring, 150 mL of 0.02 M Gly aqueous solution was added into 200 mL of 0.3 g of MgAl<sub>2</sub>-NO<sub>3</sub> dispersion. The pH of mixture was held constant at  $7.0 \pm 0.1$  by simultaneous addition of 1 M sodium hydroxide solution. The exchange process was kept at room temperature for 24 h. The precipitate was washed by four dispersion and centrifugation cycles in water, and finally air-dried.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns for the samples were recorded using a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu K $\alpha$  ( $\lambda = 0.154$  nm). The samples were scanned in steps of  $0.04^\circ$  ( $2\theta$ ) with a count time of 10 s/step. The observed basal spacings were corrected using elemental Si as an internal standard [ $d(111) = 0.31355$  nm; JCPDS 27-1402].

Elemental analysis for metals in LDHs was performed using an inductively coupled plasma emission spectroscopy (Ultima ICPS-7500). Samples were dried at  $100^\circ C$  for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute hydrochloric acid (1:1). The C, H and N content were determined by elemental microanalysis (Elementar Vario analyzer). The chloride content was determined using Mohr method.

Fourier transform infrared (FT-IR) spectra (KBr pellets, 1 mg in 100 mg of KBr) were recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  with  $2\text{ cm}^{-1}$  resolution on a Bruker Vector-22 Fourier transform spectrometer.

Analysis of the amount of Gly in solution [29] Gly was nitrosated by nitrite in the presence of KBr and sulfuric acid. The nitrosated product was determined by Shimadzu UV-2501PC spectrometer at 243 nm.

### 2.3. Adsorption experiments

The adsorption isotherms were measured at  $25^\circ C$  using the batch equilibrium method in open bottles. Each experiment was repeated at least three times. The suspensions were kept in a vessel with continuous shaking. To get a homogeneous dispersion, the samples were dispersed in 25 mL of deionized/decarbonated water and stirred for 24 h before the Gly was added. The pH value was adjusted by hydrochloric acid (0.1 M) or NaOH (0.1 M). Different experiments by varying the pH value of dispersion and the initial Gly concentration with a final volume of 50 mL were carried out. Hundred microgram of the LDHs mass was used for different batch equilibrium experiments. After a contact time of 24 h, the suspensions were centrifuged. The amount of Gly adsorbed by the LDH ( $Q_e$ ) was determined from the difference between the initial ( $C_i$ ) and the final equilibrium concentration ( $C_e$ ) per gram of adsorbent. The initial concentrations and those of supernatants were analyzed by UV-vis spectroscopy, and the absorbance was measured around 243 nm.

## 3. Results and discussion

### 3.1. Synthesis of MgAlR-X compounds

We note that in the cases of MgAl<sub>2</sub>-NO<sub>3</sub> and MgAl<sub>4</sub>-NO<sub>3</sub>, the analytical data (Table 1) indicate a slightly partial occupation by carbonates, which are commonly observed in the synthesis of LDHs, even when the synthesis is carried out

Table 1  
Analytical and structural data for the synthesized LDHs

Samples	Formula	Al <sup>3+</sup> /Mg <sup>2+</sup> molar ratio	Lattice parameter <i>a</i> (nm)
MgAl <sub>2</sub> -NO <sub>3</sub>	Mg <sub>0.66</sub> Al <sub>0.34</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>0.26</sub> (CO <sub>3</sub> ) <sub>0.04</sub> ·0.68H <sub>2</sub> O	0.52	0.304
MgAl <sub>3</sub> -NO <sub>3</sub>	Mg <sub>0.755</sub> Al <sub>0.245</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>0.245</sub> ·0.65H <sub>2</sub> O	0.32	0.307
MgAl <sub>4</sub> -NO <sub>3</sub>	Mg <sub>0.81</sub> Al <sub>0.19</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>0.13</sub> (CO <sub>3</sub> ) <sub>0.03</sub> ·0.70H <sub>2</sub> O	0.23	0.308
MgAl <sub>2</sub> -Cl	Mg <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> Cl <sub>0.33</sub> ·0.61H <sub>2</sub> O	0.49	0.304
MgAl <sub>2</sub> -CO <sub>3</sub>	Mg <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.165</sub> ·0.73H <sub>2</sub> O	0.49	0.304

under nitrogen. The Al<sup>3+</sup>/Mg<sup>2+</sup> molar ratios in the final products are similar to those in the initial synthesis mixtures. The XRD patterns of all LDHs exhibit the characteristic diffractions of well-crystallized hydrotalcite-like layered double hydroxides (JCPDS 38-0487) [13] (Fig. 1) and no other crystalline phases are present. The XRD patterns give a series of (00*l*) peaks indexed as (003), (006) and/or (009), appearing as symmetric lines at low 2θ angle, corresponding to the basal spacing. LDH is hexagonal, where the lattice parameter *a* is a function of the average distance of metal ions within the layers and reflects the density of metal ions stacking in 003 crystal plane. Assuming a 3R stacking of the layers, the lattice parameter *a* is calculated [13]. By  $a = 2d_{110}$ , it increases with increasing magnesium content on the brucite-like layers, as the ionic radius for Mg<sup>2+</sup> (0.065 nm) is larger than that of Al<sup>3+</sup> (0.050 nm).

### 3.2. Adsorption properties of LDH materials

#### 3.2.1. Gly adsorption on MgAl<sub>2</sub>-NO<sub>3</sub>

After a contact time of 150 min Gly adsorption on LDH reaches equilibrium state (Fig. 2). Removal of Gly from aqueous solutions is slightly slower than of 4-chloro-2-methylphenoxyacetic acid (MCPA) on LDHs, which required

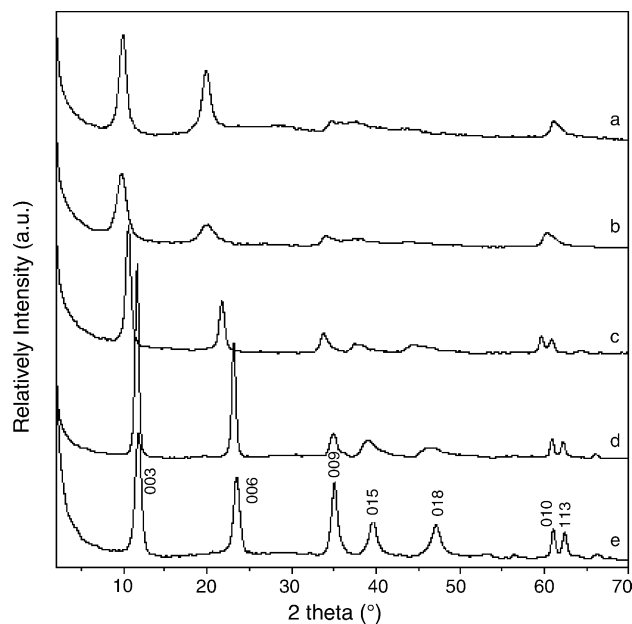


Fig. 1. XRD patterns for (a) MgAl<sub>2</sub>-NO<sub>3</sub>, (b) MgAl<sub>3</sub>-NO<sub>3</sub>, (c) MgAl<sub>4</sub>-NO<sub>3</sub>, (d) MgAl<sub>2</sub>-Cl and (e) MgAl<sub>2</sub>-CO<sub>3</sub>.

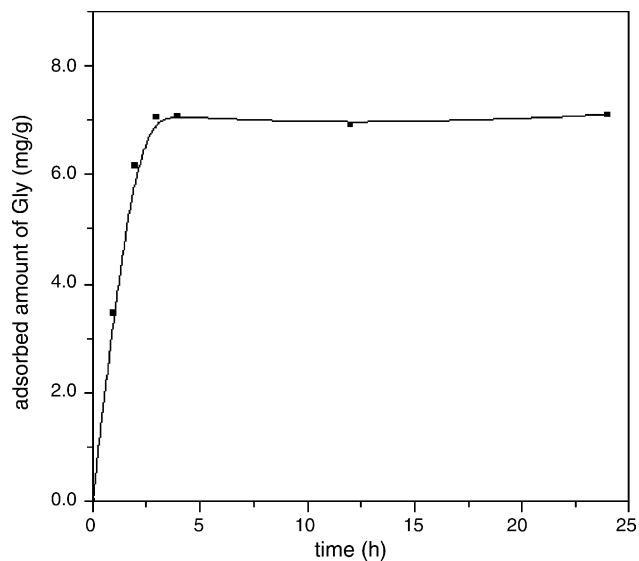


Fig. 2. Time dependence for Gly adsorption on 100 mg of MgAl<sub>2</sub>-NO<sub>3</sub> at 25 °C (*C*<sub>i</sub> = 0.15 mmol/L Gly solution).

~45–60 min equilibration time [30]. The pH value of dispersions by the addition of Gly changed in a characteristic way before and after adsorption (Table 2), due to the basic properties of LDHs. The effect of pH of the dispersion on adsorption is illustrated in Fig. 3. Gly is in the anionic form in the tested pH range [25]. Adsorption shows an adsorption plateau in the range of pH from 5.6 to 11.5. The decrease above pH 11.5 is more likely ascribed to the competition adsorption of OH<sup>-</sup> on LDH as consequence of increasing solution pH. Therefore, the adsorption experiments with a Gly-LDH contact time of 24 h were carried out at pH of 7.0, which generally corresponds to that of surface and subsurface water.

The adsorption isotherms of MgAl<sub>2</sub>-NO<sub>3</sub> and MgAl<sub>4</sub>-NO<sub>3</sub> reach a plateau at intermediate equilibrium

Table 2

Change of the pH values of dispersions by the addition of Gly before and after adsorption

Initial pH value	Final pH value
5.6	6.2
7.0	9.7
8.1	9.8
10.6	10.8
11.5	11.7
12.3	12.2
13.1	13.1

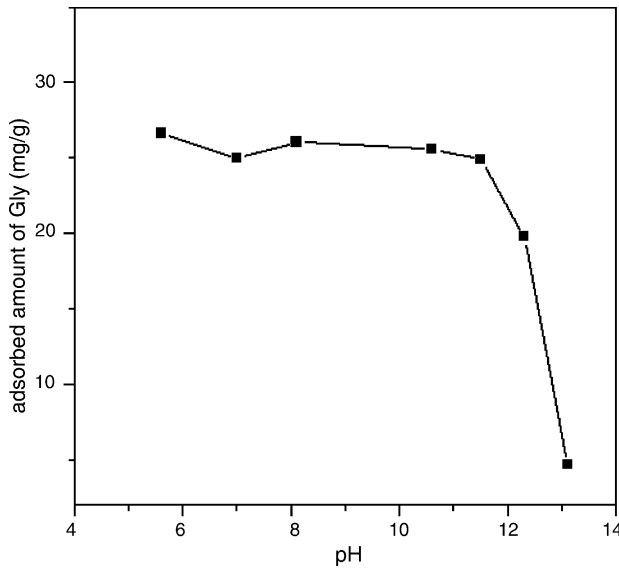


Fig. 3. Influence of the initial pH value of solution on Gly adsorption on 100 mg of  $\text{MgAl}_2\text{-NO}_3$  at 25 °C ( $C_i = 0.37$  mmol/L Gly solution).

concentration ( $C_e$ ) (Figs. 4 and 6). At higher  $C_e$ ,  $Q_e$  continues to increase again. But a plateau is not observed for  $\text{MgAl}_3\text{-NO}_3$  (Fig. 5). The isotherms for  $\text{MgAl}_2\text{-NO}_3$  and  $\text{MgAl}_4\text{-NO}_3$  tend to become S-type for  $C_e > 1.0$  mmol/L while that for  $\text{MgAl}_3\text{-NO}_3$  tends to become C-type for  $C_e > 1.0$  mmol/L [31]. This is suggested that the adsorption process is composed of the different mechanisms. At first, Gly can be adsorbed onto the external surface of LDHs through electrostatic attraction and hydrogen bonds. Initial adsorbed Gly molecular may modify the surface properties of LDHs from hydrophilic to hydrophobic characteristics. Sequentially, the hydrophobic interactions or hydrogen bonds between Gly molecules may increase the Gly adsorption for  $C_e > 1.0$  mmol/L. In addition, an interlayer anion exchange process with Gly anions on LDHs also may occur at higher  $C_e$  (*vide infra*).

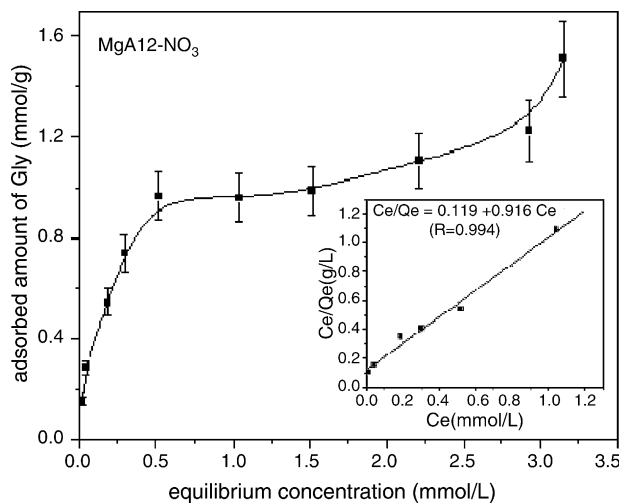


Fig. 4. Gly adsorption isotherms on  $\text{MgAl}_2\text{-NO}_3$ .

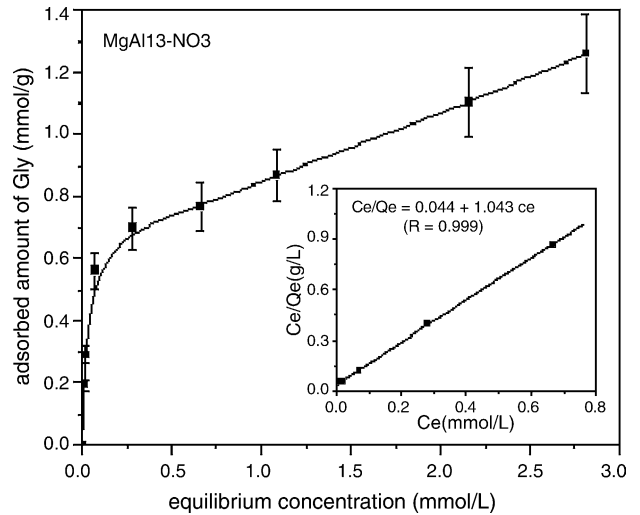


Fig. 5. Gly adsorption isotherms on  $\text{MgAl}_3\text{-NO}_3$ .

Several models were developed to describe adsorption phenomena. Here, the adsorption data were in good accord with Langmuir equation at lower  $C_e$  ( $< 1.0$  mmol/L):  $C_e/Q_e = C_e/Q_m + 1/(Q_m K_e)$ , where  $Q_e$  is the amount of pesticide per unit weight of the LDH,  $C_e$  the equilibrium concentration of the adsorbate,  $Q_m$  the maximum amount of adsorbate that can be adsorbed in a monolayer (adsorption capacity, mmol/g), while  $K_e$  is the Langmuir constant related to the energy of adsorption. The three fits based on the Langmuir adsorption model are displayed in the insets of Figs. 4–6, respectively. It suggests a surface adsorption process at lower  $C_e$ . Note that the adsorption capacity increases with the layer charge density of the material, i.e.  $\text{MgAl}_2\text{-NO}_3 > \text{MgAl}_3\text{-NO}_3 > \text{MgAl}_4\text{-NO}_3$ .

To further determine the interaction mechanism, the XRD patterns of  $\text{MgAl}_2\text{-NO}_3$  after adsorption of Gly at  $C_e = 2.9$  mmol/L was measured (Fig. 7). A smaller degree displacement of (003) diffraction line is shifted slightly, indicating an increase of the basal spacing from 0.89 to

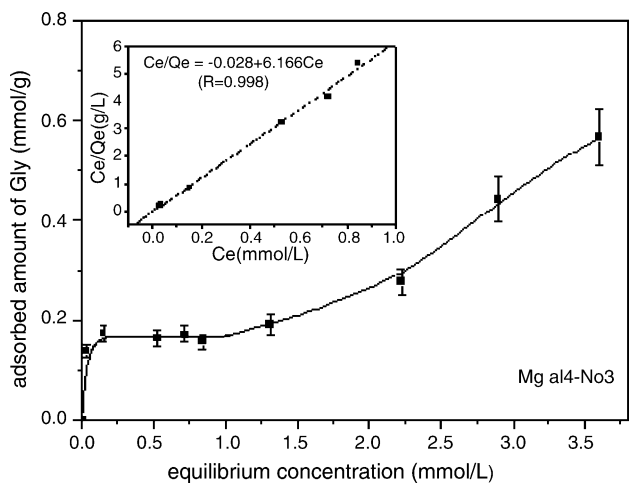


Fig. 6. Gly adsorption isotherms on  $\text{MgAl}_4\text{-NO}_3$ .

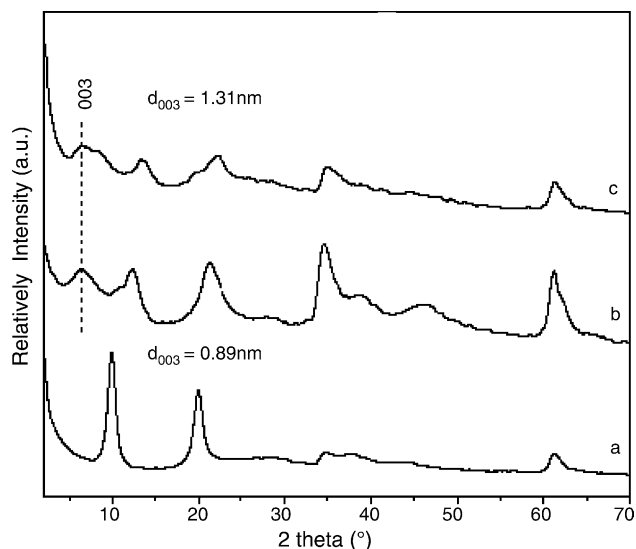


Fig. 7. XRD patterns for (a)  $\text{MgAl}_2\text{-NO}_3$ , (b)  $\text{MgAl}_2\text{-Gly}$  and (c)  $\text{MgAl}_2\text{-NO}_3$  adsorbed by Gly at  $C_e = 2.9$  mmol/L.

1.31 nm. The XRD is similar to that of LDH prepared by anion exchange with Gly at pH of 7.0. Gly anionic species exist predominantly as  $(\text{OCOCH}_2\text{NHCH}_2\text{PO}_3)^{2-}$  and/or  $(\text{OCOCH}_2\text{NH}_2\text{CH}_2\text{PO}_3)^-$  at the pH of the LDHs suspension, and thus the Gly anions can be intercalated by anion exchange at higher  $C_e$ . The basal spacing is mainly determined by the orientation of the anions in the interlayer space. The value of the interlayer distance is the difference between the basal spacing and thickness of layers. As the thickness of the brucite-like layer is approximately 0.48 nm [13], the interlayer distance is close to 0.83 nm including the hydrogen domains on both sides of the layers. As the most stable conformers of Gly molecule show pinched conformations on the basis of an ab initio MO study [32], the length of this conformer is approximately 0.45 nm, near to the value of 0.43 nm reported by Maifin et al. [26]. Such a value may be associated with the formation of vertical interdigitated monolayer of Gly anions in the interlayer space with the phosphonate and carboxylate groups attached to the hydroxyl layers through strong hydrogen bonds and electrostatic attraction. Due to a small amount of interlayer carbonate ions in  $\text{MgAl}_2\text{-NO}_3$  and  $\text{MgAl}_4\text{-NO}_3$ , the interlayer anion exchange with Gly for the two samples is more difficult than that for  $\text{MgAl}_3\text{-NO}_3$ , resulting in two different types (S-type and C-type) adsorption isotherms.

The infrared spectra of free Gly molecule and the adsorbed samples between 400 and  $4000\text{ cm}^{-1}$  (Fig. 8) show the strong and broad band around  $3600\text{--}3200\text{ cm}^{-1}$ , centered at  $3465\text{ cm}^{-1}$ , which corresponds to the O–H stretching vibration of surface and interlayer water molecules [13]. They are found at lower frequencies in LDHs compared with the O–H stretching vibration in free water at  $3600\text{ cm}^{-1}$  [33]. This is related to the formation of hydrogen bonding of interlayer water with the interlayer anions as well as with hydroxide groups of the layers. The absorption at

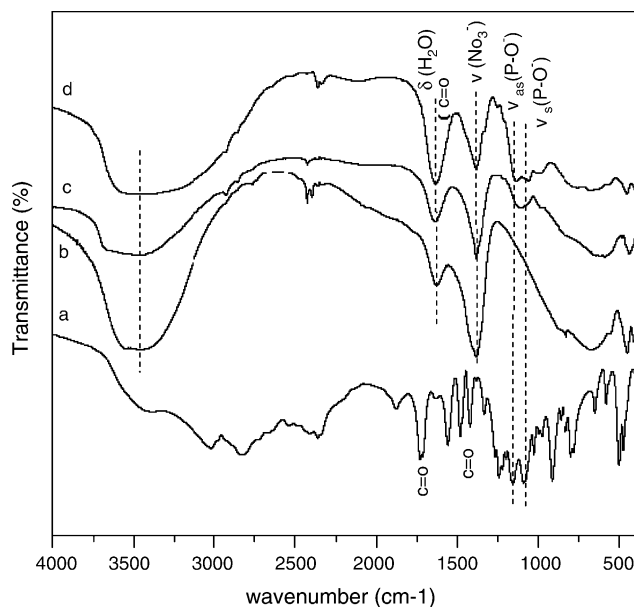


Fig. 8. FT-IR spectra for samples (a) Gly, (b) as-synthesized  $\text{MgAl}_2\text{-NO}_3$ , (c)  $\text{MgAl}_2\text{-NO}_3$  adsorbed by Gly at  $C_e = 0.5$  mmol/L and (d)  $\text{MgAl}_2\text{-NO}_3$  adsorbed by Gly at  $C_e = 1.0$  mmol/L.

$1630\text{ cm}^{-1}$  is assigned to the bending vibration of water. The bands observed in the low-frequency region of the spectrum are interpreted as the lattice vibration modes and can be attributed to M–O from  $850$  to  $600\text{ cm}^{-1}$  and O–M–O near  $440\text{ cm}^{-1}$  vibrations [34]. The absorption at  $1384\text{ cm}^{-1}$  is associated with the symmetric vibration of the interlayer nitrate anion. For free Gly, the frequencies of the symmetric and anti-symmetric vibrations of P–O groups were  $\nu_s(\text{P-O})$  at  $1088\text{ cm}^{-1}$  and  $\nu_{as}(\text{P-O})$  at  $1158\text{ cm}^{-1}$ , respectively, and were transformed for adsorbed Gly/ $\text{MgAl}_2\text{-NO}_3$  sample at  $C_e = 0.5$  mmol/L (below the plateau) into a broad vibration band centered at around  $1100\text{ cm}^{-1}$ . At  $C_e = 1.0$  mmol/L these vibration bands shifted down to  $1060\text{ cm}^{-1}$  and to  $1137\text{ cm}^{-1}$ , respectively. The broad and strong absorption band around  $1640\text{--}1580\text{ cm}^{-1}$  centered at  $1630\text{ cm}^{-1}$  should actually be associated with a superposition of the C=O bands, suggesting the formation of carboxylate anion in adsorbed (c) and (d) samples with Gly [26]. These changes clearly indicate the geometric changes of the functional groups. A downshift in adsorption frequency for the P–O groups suggests hydrogen bonds with the surface of LDHs, P–O ... H–O–M (M = Mg or Al). The intensity of absorption band of  $\text{NO}_3^-$  anions ( $\nu_3 \sim 1384\text{ cm}^{-1}$ ) decreases with increasing equilibrium concentration of Gly, also indicating that interlayer nitrate anions have been displayed gradually by Gly anions by anion exchange.

Thus, the adsorption of Gly on LDHs may generally occur through two processes: external surface adsorption and interlayer anion exchange (Fig. 9). The orientation of Gly at the external surface of LDH is probably flat because the equivalent area of the external surface is twice the area in the interlayer space.

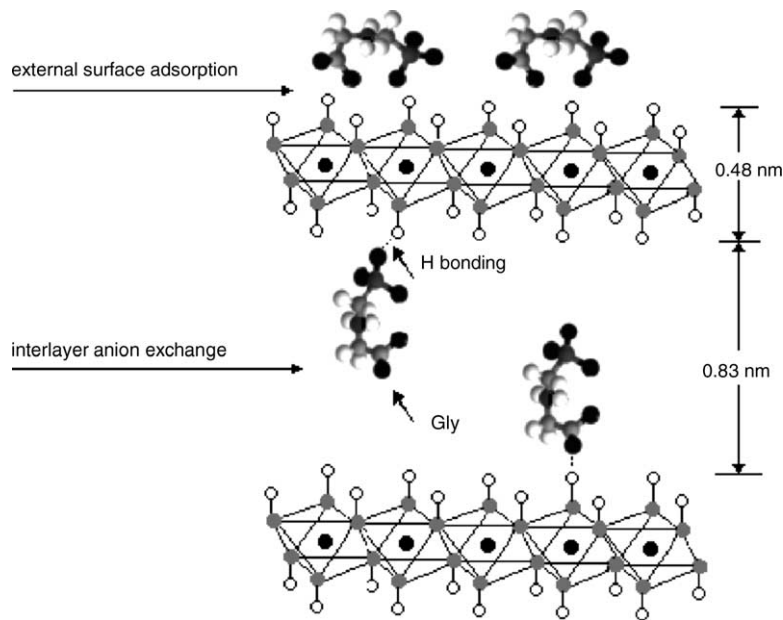


Fig. 9. Schematic diagram of Gly adsorption on MgAl-LDHs nitrate through external surface adsorption and interlayer anion exchange.

### 3.2.2. Influence of the starting interlayer anion on adsorption

Fig. 10 shows the adsorption isotherms of Gly on LDHs with  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  as interlayer anions. Unlike adsorption on  $\text{MgAl}_2\text{-NO}_3$ , adsorption isotherms on  $\text{MgAl}_2\text{-CO}_3$  and  $\text{MgAl}_2\text{-Cl}$  are of the C-type. This is because like for  $\text{MgAl}_3\text{-NO}_3$  the interlayer anion exchange with Gly for  $\text{MgAl}_2\text{-Cl}$  is easy due to the absence of interlayer carbonate ions while carbonate anions in  $\text{MgAl}_2\text{-CO}_3$  are strongly held to the hydroxyl layers and hinder the anion exchange with Gly. The adsorption amount for  $\text{MgAl}_2\text{-NO}_3$ ,  $\text{MgAl}_2\text{-CO}_3$  and  $\text{MgAl}_2\text{-Cl}$  at  $C_e = 1.0$  mmol/L decreases in the order of interlayer anions:  $\text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$ . The  $M^{2+}/M^{3+}$  is for all three samples identical and differences may be explained

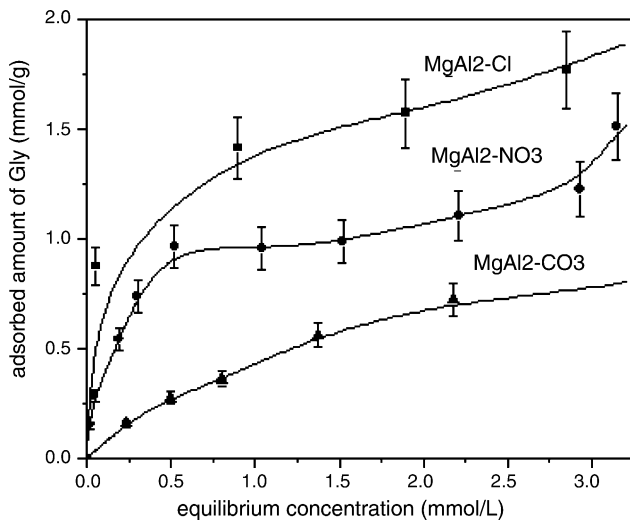


Fig. 10. Influence of starting interlayer anions of MgAl-LDHs on Gly adsorption.

by the competition between the adsorbate and the original anions for adsorption sites on the surface.

## 4. Conclusion

Adsorption experiments examining the removal of the anionic pesticide glyphosate from aqueous solutions by MgAl-LDHs materials indicated two distinguishable adsorption paths, external surface adsorption and interlayer anion exchange. At low concentration of glyphosate, glyphosate only adsorbed at the external surface while interlayer anion exchange occurred at high concentration. The glyphosate adsorption capacity increased with the layer charge density ( $\text{Al}^{3+}/\text{Mg}^{2+}$  molar ratio) of LDHs. The adsorption amount at  $C_e = 1.0$  mmol/L decreased in the order of interlayer anions:  $\text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$ . The result indicates an important role of MgAl-LDHs materials as potential adsorbents for removal of glyphosate pollutants from water.

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