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Sorption of phosphates and thiocyanates on isomorphic substituted Mg/Zn–Al-type hydrotalcites

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Abstract: The sorption equilibriums of phosphate and thiocyanate anions on isomorphic substituted Mg/Zn–Al-type hydrotalcites were investigated in this study. Langmuir and Freundlich isotherms were used to interpret the equilibrium data for phosphate. The sorption equilibriums of phosphate on Mg_3Al, Mg_2ZnAl and $Mg_{1.5}Zn_{1.5}Al$ hydrotalcites were well described by the Langmuir isotherm. The highest maximum sorption capacities for these adsorbents were as follows: 111, 101 and 95 mg g^{-1}. The equilibrium constant and standard Gibbs energy changes were also calculated from the sorption data. Standard Gibbs energy changes of about –20 kJ mol^{-1} indicated that the process might be considered as physical adsorption. The sorption equilibriums of phosphate on isomorphic substituted samples of $MgZn_2Al$ and Zn_3Al were well described by the Freundlich isotherm. Thiocyanate showed a relative low affinity for the studied materials, as indicated by both the "S"-shaped isotherms and low sorption capacities. The sorption of phosphate and thiocyanate on the investigated hydrotalcites showed a continuous decrease of the sorption capacity in the following order: $Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$.

Keywords: Mg/Zn–Al-type hydrotalcites; sorption; equilibrium; phosphate; thiocyanate.

INTRODUCTION

Layered double hydroxides (LDHs), hydrotalcite-type solids or anionic clays, are described by the general formula $[\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2]^{x+}(\mathrm{A}^{n-}_{x/n})\cdot m\mathrm{H_2O}$, where M is a divalent or trivalent metals and A^{n-} charge-compensating group.[1] The general formula underlines the possibility of obtaining a large number of compounds with different stoichiometry.

Many studies have considered the synthesis and characterization of LDHs with a variety of divalent (Mg and/or Ni, Zn, Co, Zr) or trivalent (Al and/or Fe,

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Ga, Cr) metal cations within the layers of an LDH. Several kinds of charge-compensating group, mono- or multivalent (HO^-, CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}) were intercalated at the interlayer of the LDH because the volume of the interlayer gallery is variable and the interlayer distance between adjacent layers is enhanced or reduced in proportion to the molecular size of the anion.[2]

There are numerous studies on synthesis, structure and physico–chemical characteristics of these compounds.[3–5]

The layered double hydroxides, particularly anionic hydrotalcite compounds, have gained a large importance for pollution abatement due to their sorption and catalytic properties.[6–11]

The anion exchange properties of LDHs and the anion sorption ability under the LDHs reconstruction process have been investigated for the removal of environmentally undesirable anions. Among oxyanions, the sorption of phosphate species by LDHs has been the subject of many studies because of its consequences for water pollution.[12–15] The presence of phosphate anions in surface water leads to the serious problems of eutrophication, which requires a decrease of the phosphate concentration to stipulated limits. Thiocyanate-containing wastewaters result from a variety of industrial processes, such as, herbicide and insecticide production, acrylic fibre production, manufacturing of thiourea, electroplating, *etc*. The removal of thiocyanates from wastewater is a necessity since this anion is well-known as a priority dangerous pollutant.[16]

The aim of this work was to investigate the influence of the isomorphic substitution ratio Mg/Zn on the sorption equilibriums of phosphate and thiocyanate on Mg/Zn-Al-type hydrotalcites.

EXPERIMENTAL

A series of hydrotalcite-type solids with various compositions were synthesized in order to obtain various substitution ratios ($r_{Mg(II)}$ = 0.065 nm; $r_{Zn(II)}$ = 0.074 nm). The M(II)/Mg mole ratios were 0:3, 1:2, 1.5:1.5, 2:1 and 3:0.

The synthesis was performed by a classic procedure, the co-precipitation method, under conditions of low supersaturation.[7] An aqueous 1.0 mol l^{-1} solution of nitrates, *i.e.*, $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Sigma), was slowly added to a solution of NaOH, under magnetic stirring. The pH was maintained between 7.0 and 7.5 (Hanna HI 991003 pH-meter).

The mixing step was performed under stirring for 1 h at room temperature and then on an oil bath at 60 °C under reflux for 18 h. The hydrotalcite powders were isolated by centrifugation and washed several times with demineralised water until pH 7.0. This step was followed by drying at 80 °C overnight. Then the dried samples were ground and sieved. The fraction between 0.060 and 0.125 mm was used as an adsorbent. The sample activation was performed in an oven at 500 °C in air and a heating rate of 1.0 °C min^{-1} for 4 h.

All sorption experiments were performed on activated Mg/Zn–Al hydrotalcite samples. To study the retention capacity at equilibrium, identical quantities of synthesized solids were contacted with identical volumes of aqueous solutions containing phosphate and thiocyanate, the initial concentrations of which ranged from 10 to 500 mg l^{-1} for phosphate and from 5.0 to

100 mg l^{-1} for thiocyanate. The solution pH was 7.0±0.2 and the solid/liquid ratio was 1.0 g l^{-1}. The samples were maintained at a constant temperature (25±1 °C) in a thermostated shaker bath for 12 h to reach sorption equilibrium. The kinetic studies preceded the determination of the equilibrium isotherm in order to determine the time demand for attaining thermodynamic equilibrium.

At equilibrium, the solid was separated by centrifugation and the phosphate and thiocyanate concentration in the supernatant was analysed by using a Varian Carry 50 UV–Vis spectrophotometer. The phosphate concentration in the aqueous solution was determined at 450 nm in line with the vanado-molybdate method.[17] The concentration of thiocyanate was also determined spectrophotometrically at 475 nm.[18]

X-Ray diffractions patterns were recorded on a Philips PW 1830 power diffractometer (45 kV, 25 mA) using Ni filtered Cu_{α} (0.154 nm) radiation.

The thermal analysis was performed under an inert atmosphere (nitrogen), from 20 to 990 °C, at a heating rate of 10 °C min^{-1} using a TG 209 analyzer (Netzsch, Germany). A Proteus Analysis (Netzsch) program was used for data processing.

RESULTS AND DISCUSSION

Samples characterization

The X-ray diffraction analysis enabled the computation of the unit cell parameters *a* and *c*, which highlighted the rhombohedric symmetry of the synthesized hydrotalcite-like compounds (Table I).

TABLE I. Parameters of the cell unit, *a* and *c*, for the synthesized samples

M(II)/Mg mole ratio	Sample	*a* / Å	*c* / Å	Symmetry
3	Zn_3Al	3.03	22.94	3R
2	Zn_2MgAl	3.03	23.06	3R
1	$Zn_{1.5}Mg1_{1.5}Al$	3.03	23.20	3R
0.5	$ZnMg_2Al$	3.04	23.25	3R
0	Mg_3Al	3.04	23.37	3R

The *a* parameter corresponds to the cation–cation gap within the brucite layer and the *c* = 3*c*' parameter is the thickness of the layer made of a brucite-like film and an interlayer. The numbers are characteristic of a rhombohedric symmetry and they were calculated using the following relationships:

$$1/d^2 = 4/3(h^2+hk+k^2)/a^2 + l^2/c^2 \quad (1)$$

where:

$$d = \lambda/2 \sin \theta \text{ and } \lambda = 1.54051 \text{ Å} \quad (2)$$

The influence of the degree of isomorphic substitution on the thickness of the layer can be seen.

In addition, the thermal behaviour of the samples was influenced by the degree of isomorphic substitution, indicating changes in the hydroxyl surface structure (Table II). Firstly, dehydration occurred due to the loss of adsorbed water molecules in one minor step at 100 °C. The second step was caused by the loss of interlayer water molecules in the Mg_3Al sample at about 212 °C. For the Zn-substituted samples, the temperature of this step was lower. In addition, the dehydroxylation of the Mg/Zn/Al hydroxide sheets and decarbonisation decreased with increasing Zn content.

TABLE II. Thermal analysis results

Stage	Mg/Zn mole ratio									
	3:0		2:1		1.5:1.5		1:2		0:3	
	t / °C	Mass loss %	t / °C	Mass loss %	t / °C	Mass loss %	t / °C	Mass loss %	t / °C	Mass loss %
1	100.0	2.35	100.0	2.29	89.4	2.04	100.0	2.17	100.0	1.40
2	212.2	12.67	175.8	8.16	100.0	2.61	183.1	9.85	176.5	9.01
3	379.0	31.85	302.3	15.56	182.6	9.01	270.5	17.80	216.6	14.62
4	–	–	363.2	23.89	261.0	17.01	372.1	28.42	–	–

Sorption equilibrium of phosphate on Mg/Zn–Al-type hydrotalcites

The results showed that for the Mg_3Al sample, at the upper limit of the equilibrium concentration range, the sorption capacity for phosphate remained practically constant (Fig. 1). Thus, the equilibrium was well described by the Langmuir isotherm (Eq. (3)):

$$q_e = q_{max}K_Lc_e/(1 + K_Lc_e) \tag{3}$$

where q_e is the quantity of anion sorbed at equilibrium (mg g^{-1}), q_{max} is the maximum sorbed quantity (mg g^{-1}), c_e is the equilibrium concentration (mg l^{-1}) and K_L is the equilibrium constant (l mg^{-1}).

The Henry domain was also well defined for this situation.

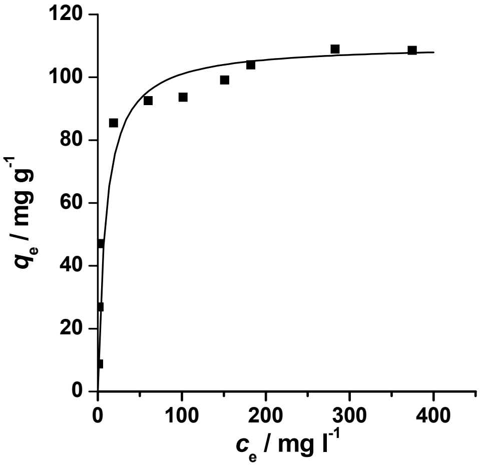

Fig. 1. Sorption isotherm of phosphate on Mg_3Al hydrotalcite.

The experimental data obtained from the sorption of phosphate on Mg/Zn–Al-type hydrotalcites (Figs. 2–5) were interpreted by means of the Langmuir (full line) and Freundlich (dotted line) isotherms (Eqs. (3) and (4)):

$$q_\mathrm{e} = \alpha c_\mathrm{e}^{\beta} \tag{4}$$

where q_e and c_e have the same meaning as previously mentioned; and α and β are constants.

The isotherms for the sorption of phosphate on Mg_2ZnAl and $Mg_{1.5}Zn_{1.5}Al$ hydrotalcites (Figs. 2 and 3) displayed a typical Langmuir plateau, while those for Mg_2ZnAl and Zn_3Al hydrotalcites (Figs. 4 and 5) did not reach the plateau at up to 450 mg l^{-1}, the maximum equilibrium concentration employed in this study.

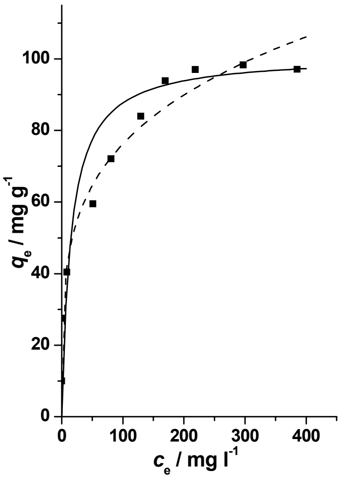

Fig 2. Sorption isotherm of phosphate on Mg_2ZnAl hydrotalcite: full line – Langmuir isotherm; dotted line – Freundlich isotherm.

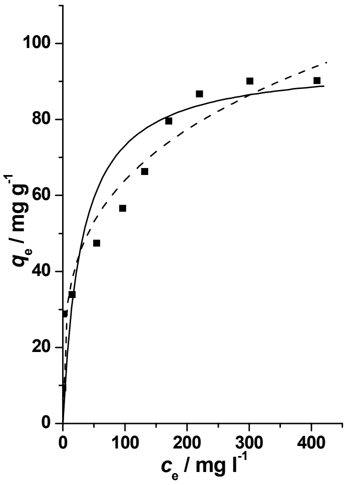

Fig. 3. Sorption isotherm of phosphate on $Mg_{1.5}Zn_{1.5}Al$ hydrotalcite.

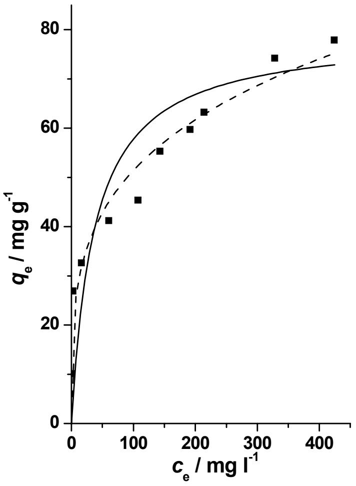

Fig. 4. Sorption isotherm of phosphate on $MgZn_2Al$ hydrotalcite.

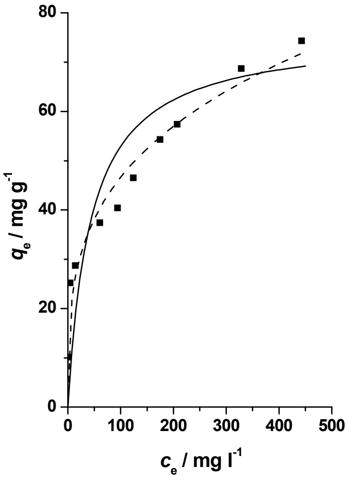

Fig.5. Sorption isotherm of phosphate on Zn_3Al hydrotalcite.

On analysing the results, it followed that the Mg_3Al sample had the best sorption behaviour. The maximum sorption capacity of phosphate on this adsorbent was 111 mg g^{-1}. In addition, as the isomorphic substitution degree increased, the sorption capacity decreased continuously. This finding is in agreement with the low values of cell unit parameters, which impeded the access of phosphate ions to the space between the brucite layers (Table III).

TABLE III. The sorption equilibrium characteristics of phosphate on Mg/Zn–Al-type hydrotalcites

Sample	Langmuir isotherm				Freundlich isotherm	
	$q_{\max}$	Equilibrium constant, K_L		$\Delta_{ads}G^{\ominus}$ (298 K)	α	β
	mg g^{-1}	l mg^{-1}	10^3 l mol^{-1}	kJ mol^{-1}		
Mg_3Al	111	0.107	10.1	–22.9	–	–
Mg_2ZnAl	101	0.066	6.25	–21.7	25.4	0.239
$Mg_{1.5}Zn_{1.5}Al$	95	0.033	3.14	–20.0	18.2	0.273
$MgZn_2Al$	79	0.027	2.56	–19.4	15.3	0.263
Zn_3Al	76	0.023	2.19	–19.1	12.3	0.290

For all samples, in the low concentration range, a decrease in the slope of the Langmuir isotherm with increasing degree of substitution of Mg^{2+} by Zn^{2+} could be seen. This decrease might be attributable to the decrease of the phosphate affinity of the hydrotalcites within the Mg/Zn–Al series. Both the decrease of the isotherm slope and the maximum sorption capacities led to the following order for phosphate affinity for the studied hydrotalcites:$Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al >$ $> MgZn_2Al > Zn_3Al$.

The Langmuir model allowed the computation of the sorption equilibrium constant, K_L, and standard Gibbs energy change, $\Delta_{ads}G^{\ominus}$ (298 K). The equilibrium constant decreased by a factor of 1.4 from Mg_3Al to Zn_3Al, showing that the sorption process was not favoured as the degree of substitution of Mg^{2+} by Zn^{2+} increased. In accordance with the calculated standard Gibbs energy changes, about –20 kJ mol^{-1}, the process could be considered as physical adsorption.[15]

An examination of the Langmuir isotherms showed that there was deviation from the experimental data at higher isomorphic substitution ratios ($MgZn_2Al$ and Zn_3Al). The sorption equilibrium of phosphate on these samples followed the Freundlich isotherm closely. In addition, the interpretation of experimental results using the Freundlich isotherm can be justified by the fact that advanced wastewater treatment does not assume operation at the quite high concentrations used in this study.

In all cases, both the subunit β (Table III) and the $\Delta_{ads}G^{\ominus}$ (298 K) values underlined that the interaction forces between phosphate and the studied adsorbents were weak and thus the process was physical adsorption.[15]

Sorption equilibrium of thiocyanate on Mg/Zn–Al -type hydrotalcites

The experimental sorption isotherms for thiocyanate are shown in Fig. 6

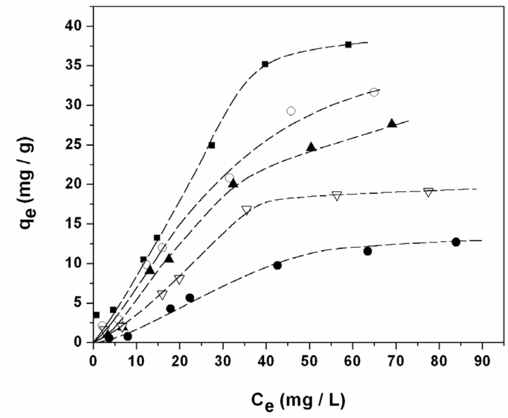

Fig. 6. Sorption isotherms for thiocyanate on: Mg_3Al (■); Mg_2ZnAl (○); $Mg_{1.5}Zn_{1.5}Al$ (▲); $MgZn_2Al$ (∇); Zn_3Al (●). Lines are drawn to guide the eye.

By analysing the sorption isotherms, their "S" shape is immediately obvious, which suggests low affinity of thiocyanate for the studied hydrotalcites. This finding was also highlighted by the values of the sorption capacities, *e.g.* 38 mg g^{-1} for Mg_3Al and 13 mg g^{-1} for Zn_3Al, at the maximum equilibrium concentration employed in this study (60 mg l^{-1}). These results are in accordance with the literature,[15,19] concerning the affinity of monovalent ions for hydrotalcites as opposed to polyvalent ions, which showed a lower affinity. In addition, the values obtained for the sorption capacity of thiocyanate anion are comparable with those reported by other authors.[14]

For a given equilibrium concentration, there was a 3-times continuous decrease of the sorption capacity in the following order: $Mg_3Al > Mg_2ZnAl > > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$, which emphasizes the negative influence of the isomorphic substitution by Zn^{2+} within the brucite layer on the retention of thiocyanate.

By comparing the sorption of the two anions on Mg/Zn–Al-type hydrotalcites, it follows that phosphate sorption occurred with good results, highlighted by the values of the maximum sorption capacities, while thiocyanate sorption was ineffective; the affinity of the studied adsorbents for this anion was poor. The results are in accordance with literature data,[19] which reported that the affinity of hydrotalcites for monovalent anions was modest. Another finding referred to the negative influence of zinc substitution into the brucite-like layer.

CONCLUSIONS

The equilibrium of phosphate and thiocyanate sorption on Mg/Zn–Al-type hydrotalcites was studied under various Zn/Mg substitution ratios.

Langmuir and Freundlich models were applied to characterize the equilibrium of phosphate sorption on Mg/Zn–Al hydrotalcites.

The Langmuir isotherm can be used to describe all adsorption equilibriums but with increasing substitution of Mg^{2+} by Zn^{2+}, the deviation of the experimental points from the theoretical curve increased. For $MgZn_2Al$ and Zn_3Al hydrotalcites, the experimental data were better described by Freundlich isotherms.

The highest sorption capacity for phosphate was attained with the Mg_3Al sample (111 mg g^{-1}). Phosphate adsorption on hydrotalcites within the Mg/Zn–Al series indicated a decrease of the maximum sorption capacity as the Zn/Mg substitution ratio increased.

Expressing the equilibrium data using the Langmuir model allowed the computation of the sorption equilibrium constant, K_L, and the standard Gibbs energy change, $\Delta_{\mathrm{ads}}G^{\ominus}$ (298 K). Based on results, the process can be considered as physical adsorption.

This finding was confirmed with the assessment of the constant β, which was determined based on the Freundlich isotherm for $MgZn_2Al$ and Zn_3Al.

The experimental sorption isotherms of thiocyanate showed a lower affinity for Mg/Zn–Al series as compared to phosphate. For a given equilibrium concentration, there was a continuous decrease of the sorption capacity in the following order: $Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$.

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ИЗВОД

СОРПЦИЈА ФОСФАТА И ТИОЦИЈАНАТА НА ИЗОМОРФНИМ СУПСТИТУИСАНИМ ХИДРОТАЛЦИТИМА ТИПА Mg/Zn–Al

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У овом раду су испитиване сорпционе равнотеже фосфата и тиоцијаната на изоморфним супституисаним хидроталцитима типа Mg/Zn–Al. За тумачење равнотежних података за фосфате коришћене су Ленгмирова и Фројндлихова изотерма. Сорпционе равнотеже за фосфате на Mg_3Al-, Mg_2ZnAl- and $Mg_{1.5}Zn_{1.5}Al$-хидроталцитима добро су описане Ленгмировом изотермом. Највећи максимални сорпциони капацитети износили су 111, 101 и 95 mg g^{-1}. Такође су израчунати и константа равнотеже и промена стандардне Гибсове енергије сорпције. Промена стандардне Гибсове енергије сорпције од око –20 kJ mol^{-1} указује на то да процес треба сматрати као физичку адсорпцију. Сорпционе равнотеже фосфата на изоморфним супституисаним хидроталцитима $MgZn_2Al$ and Zn_3Al добро су описане Фројндлиховом изотермом. Тиоцијанати су показали релативно мали афинитет према испитиваним материјалима, на шта указују изотерме облика "S" криве и мали сорпциони капацитети. Сорпција фосфата и тиоцијаната на испитиваним хидроталцитима показала је континуално опадање сорпционог капацитета према следећем низу: $Mg_3Al > Mg_2ZnAl > Mg_{1.5}Zn_{1.5}Al > MgZn_2Al > Zn_3Al$.

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