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SORPTION OF PERCHLORATE ON Mg–Al–CO_3 LAYERED DOUBLE HYDROXIDES PREPARED VIA FINE INORGANIC SOL–GEL PROCESS: THE TREATMENT OF AQUEOUS SOLUTIONS WITH pH 5, 7 AND 8

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Perchlorate anion is dangerous to human and able to affect the brain functions. Ion exchange is one of the main approaches, which allows separating ClO_4^- anion and controlling its concentration in water solutions. In this work, we evaluated the ability of Mg–Al–CO_3 layered double hydroxides (LDHs) to remove perchlorate ions at various, yet relevant to drinking water treatment conditions, pH values: 5, 7 and 8. LDHs were prepared via an original fine inorganic synthesis which includes sol–gel routes. It was shown that Mg–Al–CO_3 LDHs can effectively sorb perchlorate even at pH 8, whereas most inorganic anion exchangers exhibited much lower adsorptive potential to anions. Experimental adsorption isotherms obeyed the Freundlich model and the Linear equation which confirmed favorable sorption. The process proceeds according to the mechanism of physical sorption based on an electrostatic interaction of an adsorbent and an adsorbate. Although these Mg–Al–CO_3 LDHs demonstrated high adsorptive capacity to perchlorate (as compared with the literature) which is equal to 37 mg of ClO_4^- per 1 gram of dry adsorbent at pH 5, an improvement in their adsorptive affinity can be achieved by the optimization of the material chemical composition and/or its calcination. To improve the removal properties of the anion exchanger toward ClO_4^-, several pathways have been suggested. One of them is a thermal treatment of these unique LDHs, which maintain their layered structure even after calcination at 300–600°C. The paper also presents an overview of the literature data on perchlorate sorption by various materials.

Keywords: perchlorate anion, sorption, inorganic anion exchangers, layered double hydroxides, sorption isotherms, pH effect.

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Introduction

Perchlorate is one of the ions which maximum permissible concentration is strictly controlled by World Health Organization and local authorities. For instance, Environmental Protection Agency of the United States set a limit for perchlorate at 24.6 ppm; however, several states of this country adopted much lower maximum permissible concentration for this anion. California, in particular, accepted even 6 ppb after they detected high levels of this anion in drinking water (up to 100 ppb) [1]. Biochemical studies revealed that perchlorate physiologically mimics iodine and can be absorbed by the thyroid gland which consequently interferes with the endocrine systems of the brain.

Perchlorate anion is stable enough and cannot be easily destroyed in natural waters, which requires advanced technologies for its removal during drinking water treatment. Anion exchange is one of the most promising water purification approaches to remove ClO_4^-. However, ion exchange resins are rarely selective to lowering the concentrations of aqueous ions till ppb levels as often requested by World Health Organization. Inorganic anion exchangers are the best alternative to anion exchange resins within the task of the removal of inorganic anions. Layered structure double hydroxides are the most advanced class of inorganic adsorptive material due to their capability to take an additional amount of aqueous anions by their interlayer space.

Most layered double hydroxides (LDHs), often called hydrotalcites, being an ideal anion exchanger, can be produced by the most popular conventional precipitation synthetic approach. However, it has been recently demonstrated that they are incapable to directly exchange their interlayer carbonate (or other anions) with aqueous anions [2]. In other words, they do not use their advantageous interlayer space acting at the interface with aqueous phase as bulk structure materials. An exception from this list is the Mg–Al–CO_3 LDHs developed by original fine inorganic synthesis with a stage of purely inorganic sol–gel routes [3]. This material exhibited an exceptional or competitive adsorptive capability to many anions among which are arsenate, selenite, selenate, and phosphate (on the one hand) and arsenite, fluoride, bromate, and bromide (on the other hand). It was reasonable to test the adsorptive characteristics of these Mg–Al–CO_3 LDHs towards ClO_4^- anions. Thus, the key task of this work was to assess the Mg–Al–CO_3 LDHs, synthesized by an original fine inorganic sol–gel method, in the process of the removal of perchlorate.

Experimental

Materials

A strategy for the synthesis of the Mg–Al–CO_3 LDHs, which are tested in the present study, was initially developed to remove toxic anions from water, first of all, arsenate. The preparation of this material was described in detail elsewhere [3], and its adsorptive performance toward several anions was presented in work [4]. Briefly, several requirements were set by the researchers when developing the synthetic methodology for this anion exchanger. First of all, they wanted to use advantages of sol–gel routes that give a chance to maximize an access surface energy of the final product (since sol is the most heterogeneous system known till now). Secondly, they tried to provide an abundance of surface OH^- groups by preserving hydration of both interlayer space and physically sorbed water in the structure of these LDHs. And, finally, the above requirements should be satisfied simultaneously with making this material strong and stable enough in water solutions which is usually done by thermal or hydrothermal treatments. The development of the synthetic strategy for advanced anion exchanger was successful and the best ways of treatments of hydrogel or xerogel were chosen. The method yields Mg–Al–CO_3 LDHs with exceptionally high removal capabilities to many anions [3,4].

Comparison of the three samples of layered double hydroxides, Mg–Al–CO_3, produced by the three different advanced synthetic methods revealed the reasons for such exceptional properties of these alkoxide-free sol-gel generated LDHs [5]. It was demonstrated that this material differed from the other ones by its rich speciation of the main chemical elements (Mg, Al), interlayer carbonate, surface chemistry and hydration. Comparison with the literature conducted few years afterwards showed that it is the only hydrotalcite which is capable to directly exchange its interlayer carbonate with the aqueous anions [2]. Other LDHs are mainly used via a stage of calcination (resulted in ruining the layered structure) and their further reconstruction during the contact with water phase combined with anion removal function which is known as «memory effect». Having such a promising material, it was reasonable to study its adsorptive properties also to ClO_4^- which is done in this paper.

Methods

Adsorption isotherms were obtained at three pH values, all of which are close to pH of purifying drinking water which varies from 5.5 to 8.5. Investigations were conducted with an adsorbent dose of 2 g (dry weight) per liter (g_{dw}/L) using 0.01 N NaCl as a supporting electrolyte. The ambient temperature was 20±2^{0}C and the speed of shaker rotation was 200 rpm. The values of pH 5; 7 and 8 (±0.2) were adjusted using 0.1 M HCl and 0.1 M NaOH. The initial concentration of perchlorate was in the range of 25–350 mg[Cl]/L. Adsorption capacity was calculated using the following empirical formula:

$$q = \frac{(C_o - C_{eq.})V}{m}, \qquad (1)$$

where q (mg/g_{dw}) is the amount of anion sorbed per gram of adsorbent (dry weight); C_o (mg/L) is the initial concentration of ClO_4^-; C_{eq} (mg/L) is the final (or equilibrium) concentration of the anion in solution; V (mL) is the volume of the solution; and m (mg) is the dry weight of the adsorbent.

The concentration of ClO_4^- ions was measured by ion chromatography method. Adsorption data were fitted by using three known models (Linear sorption, Freundlich and Langmuir theories).

Results and discussion

Experimental equilibrium adsorption isotherms at pH 5, 7 and 8

Fig. 1 presents experimental data on the adsorptive capabilities of the investigated Mg–Al–CO_3 LDHs to ClO_4^- at pH 5, 7 and 8, the data are given in the form of equilibrium adsorption isotherms.

The curves in Fig. 1 show adsorptive capacities using classical units of measurements of complex anion sorption (mg[Cl]/g_{dw}). However, in order to be consistent with the most literature articles, we also present these results in mg[ClO_4^-]/g_{dw} which are written in the graph as maximum adsorption (capacity). Quick glance at the curves (Fig. 1) allows concluding that adsorptive capacities of this anion exchanger are among the highest, however, its affinity to perchlorate can be improved.

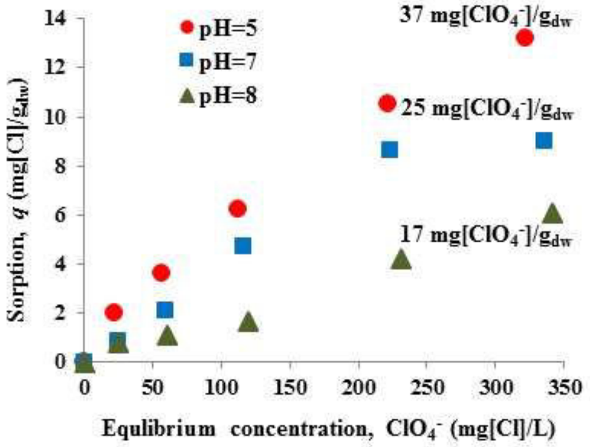

Fig. 1. Isotherms of ClO_4^- sorption on Mg–Al–CO_3 LDHs at pH 5, 7 and 8. Experimental conditions: adsorbent dose is 2g/L; supporting electrolyte is 0.01 N NaCl; temperature is 20±2°C

The shape of the obtained adsorption isotherms is not steep-like to expect an outstanding removal performance in dynamic adsorption conditions (in columns). A high affinity of adsorbent to adsorbate is usually recognized (and reflected) from steep isotherms of adsorption.

Fitting the experimental data according to three models: Linear, Freundlich and Langmuir

The experimental curves cannot be described by Langmuir model which commonly better fits the data involved chemisorption mechanism of cation/anion removal. We tried to describe the experimental data by Linear and Freundlich theories. Fig. 2 shows the results of fitting the experimental data to the Linear adsorption model based on the following simple equation:

$$q_{eq}=K_{lin}\cdot C_{eq}, \qquad (2),$$

where q_{eq} is the equilibrium value of adsorption (mg/g); K_{lin} is the coefficient of linear adsorption (L/g); and C_{eq} is the equilibrium concentration of adsorbate (mg/L).

Freundlich equation is based on two parameters, Freundlich constant (K_f), which shows the affinity of an adsorbent for an adsorbate, and parameter n, which is characteristic of the system and indicates the strength of adsorption:

$$q_{eq}=K_f C_{eq}^{1/n}. \qquad (3).$$

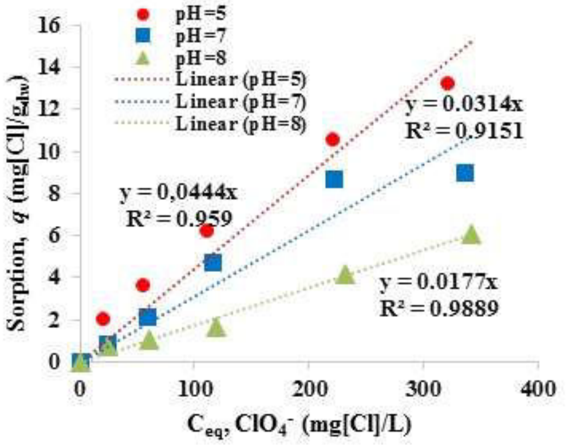

Fig. 2. Fitting the experimental data given in Fig. 1 according to Linear adsorption model

Logarithmic form of Eq. (3) was used to determine the coefficients K_f (Freundlich constant) and n (adsorption strength) by plotting dependency of log q_{eq} vs. C_{eq}:

$$\log q_{eq} = \log K_f + \frac{1}{n}\log C_{eq}. \qquad (4)$$

Fig. 3 demonstrates the results of Freundlich equation fitting using Eq. (4).

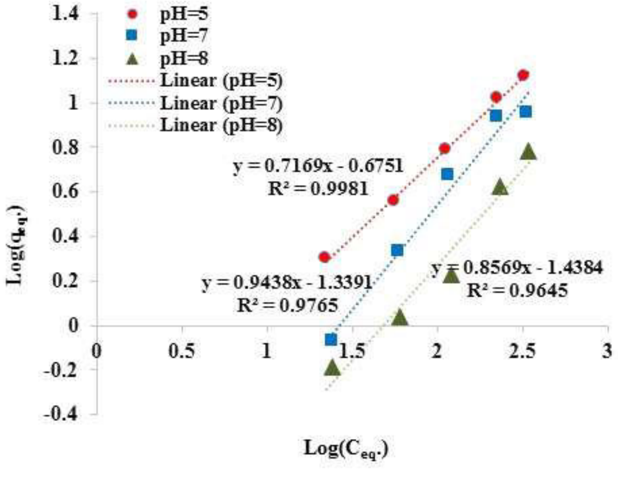

Fig. 3. Fitting the experimental data given in Fig. 1 according to Freundlich adsorption model

The data resulted from the fitting the

experimental data by Linear and Freundlich adsorption models are summarized in Table 1.

Table 1

Parameters obtained from fitting the data by Linear and Freundlich adsorption models

Sample	Linear model	Freundlich theory	
pH	K_{lin} (L/g)	K_f	n
5	0.044	0.211	1.395
7	0.031	0.046	1.060
8	0.018	0.036	1.167

It can be concluded from Table 1 that while the coefficient of Linear model gradually increases (from 0.018 to 0.044) as pH decreases (from 8 to 5), Freundlich fitting results demonstrate that the sorption of perchlorate is stronger at pH 5 than at pH 7 and 8. However, the values of the intensity of adoption calculated from Freundlich model (n) is higher than 1 at all investigated pH values which indicates a favorable adsorption. At the same time, Freundlich coefficient is low enough which suggests that further improvements (modifications or treatments) of this material might be useful to increase its affinity to ClO_4^-. Fitting the experimental data according to these three models (Freundlich, Linear and Langmuir theories) demonstrated that perchlorate is sorbed by these Mg–Al–CO_3 LDHs via physical sorption mechanism (electrostatic interaction). However, high affinity of adsorbent to adsorbate is mostly resulted from chemi-sorption mechanism which obviously did not involve the removal of ClO_4^- by this anion exchanger.

Adsorptive performance of Mg–Al–CO_3 LDHs in comparison with the literature data

Table 2 shows the data on adsorptive removal capabilities of various materials toward perchlorate given in literature.

Perchlorate belongs to those inorganic anions which are difficult to remove by adsorption method. Consequently, literature data on its adsorptive performance on various adsorbents and anion

Table 2

Adsorptive performance of various adsorbents towards ClO_4^-

Adsorbent	q, (mg/g) mg[ClO_4]/g	pH	Ads. dose	Ref.	Comments
Mg–Al–CO_3 LDHs	37 25 17	5 7 8	2	this work	Provides realistic data at pH of purifying drinking water and an adsorbent dose of >1 g/L
Granular activated carbon	~30	3	0.5	[6]	pH is very low which suggests low adsorption at higher pH values. Dose is higher than 1 g/L which indicates much lower adsorption at dose of >1 g/L
Modified inorganic-bentonites	~10	–	–	[7]	–
Granular ferric hydroxide, Fe_2O_3	~20	6.0–6.5	–	[8]	Data are comparable to this work
Aluminum-based drinking-water treatment residual	–	–	–	[9]	No data on adsorptive capacity in mg/g presented, only in % with hidden experimental conditions
Graphene	0.024	–	–	[10]	At initial perchlorate concentration of 2 mg/L. Very different experimental conditions. Impossible to compare
Granular activated carbon modified with cetyltrimethyl ammonium chloride	~20	–	0.1	[11]	Adsorbent dose was 0.1 g/L which results in artificially high adsorptive capacity. These data cannot be used for comparison. Realistic adsorption is expected to be approximately 10 times lower
Cetyltrimethyl ammonium chloridectivated carbon fibers	26.74	Acidic	~0.7	[12]	Authors assumed that adsorptive capacity in alkaline solutions (typical for water treatment conditions) is very low. Adsorbent dose is lower than 1
Calcined Mg/(Al–Fe) hydrotalcite	~5	–	–	[13]	–
Single-walled carbon nanotubes (SWCNTs)	~10	–	–	[14]	–

exchangers are scare. Some studies do not reveal clearly the applied experimental conditions [8], while other studies present unrealistic adsorptive data. The latter mainly falls into two categories: those using too lower adsorbent dose (<1), and those not showing the data at full pH range. If an adsorbent dose is less than <1 g/L, then the measured adsorptive capacity will be always wrong (overevaluated) due to the fact that this value is in the denominator in the formula of adsorption calculation (see Eq. (1)). Adsorption characterizes the capacity of one gram of an adsorbent to remove ions/molecules from one liter of adsorbate. 10–20 years ago, a «common» adsorbent dose was ca. 10–20 g/L: it was a period when highly selective synthetic ion exchangers have not been developed yet and researchers used mainly natural materials. Over the last decades, an adsorbent dose of 2 g/L is most acceptable as often it is a minimum amount of the material in batch which produces a plateau on dependences of adsorption capacity upon adsorbent dose. However, some works repoerted an adsorbent dose of 0.5, 0.1 or even 0.02 g/L.

As concerns pH effect, it is known that a typical pH influence on anion sorption is characterized by an adsorption decrease at increasing the pH which is partially due to the competition of inorganic anions with OH$^-$ in solution. Very often, adsorption of inorganic anions at pH≥7 is much lower than at pH<7 or even approaching zero in alkaline solutions. Therefore, many studies reported the results collected only at acid pH values. Another widely spread issue is related to the fact that precise experimental conditions are not shown at all; for instance, an amount of adsorbent may be shown, but a volume of adsorbate to which it was added is not disclosed.

The sample of Mg–Al–CO$_3$ LDHs generated via an original alkoxide-free sol-gel method exhibited a competitive adsorptive removal to perchlorate at pH values close to those of purifying drinking water (pH 5.5–8.5), at which many inorganic adsorbents show unacceptably low sorption. Thus this material seem to be a promising adsorbent for the removal of ClO$_4^-$, however, its adsorptive affinity should be still improved.

How to increase an adsorptive affinity of the Mg–Al–CO$_3$ LDHs to perchlorate – a brief overview

We suppose that adsorptive characteristics of the Mg–Al–CO$_3$ LDHs to perchlorate can be improved. This material has all basic properties expected from high-quality anion exchangers: rich speciation of chemical elements, phases and surface chemistry. However, its affinity to ClO$_4^-$ is relatively low which can be fixed. To this end, two major possibilities can be used: fitting the structural factors and/or changing the chemical composition.

The first factor can be applied by using modification (activation) of the initial Mg–Al–CO$_3$ LDHs by thermal treatment. Analysis of adsorptive performance of this material to different anions (H$_2$AsO$_4^-$, H$_2$PO$_4^-$, SeO$_4^-$, As(III), HSeO$_3^-$, BrO$_3^-$, F$^-$, Br$^-$) demonstrated that its adsorption capacity and affinity to some anions (in particular, As(III) and BrO$_3^-$) was considerably increased by the treatment of this sample at 200–600^{0}C [2]. Major reason for such an improvement is the factor of structural correspondence between an adsorbent and aqueous anion modified by thermal treatment which changes the interlayer space of this layered inorganic anion exchanger [2]. The interlayer distance of the sample is a function of the applied temperature. Moreover, these Mg–Al–CO$_3$ LDHs are the only layered double hydroxides which preserve their layered structure at thermal treatment up to 600^{0}C, while all other hydrotalcites known from the literature are destroyed and transformed into double oxides of bulk structure. The future task within this strategy is to find the right temperature of thermal treatment (within the range of 200–600^{0}C) of these Mg–Al–CO$_3$ LDHs samples which increases their affinity to ClO$_4^-$.

Analysis of physical properties of various anions revealed that the hydration energy of perchlorate anion in water is among the lowest of «common» inorganic anions which causes serious problems in separation and analysis of perchlorate [15]. It is the reason why its adsorptive affinity to these Mg–Al–CO$_3$ LDHs differs so dramatically from the other tetrahedral anions (H$_2$AsO$_4^-$, H$_2$PO$_4^-$) which are sorbed by this material with outstanding adsorptive characteristics [2–5]. Table 3 shows hydration energies of common inorganic anions and demonstrates that ClO$_4^-$ has the lowest from the list.

Literature data (see Table 2) allows drawing some conclusions on the best adsorbents for the removal of perchlorate ions. The first observation is

Table 3

Hydration energies (ΔG_h) of common inorganic anions [15]

Anion	F$^-$	Cl$^-$	CO$_3^{2-}$	OH$^-$	NO$_3^-$	H$_2$PO$_4^-$	PO$_4^{3-}$	SO$_4^{2-}$	ClO$_4^-$
Thermochemical radius, nm	0.125	0.172	0.178	0.133	0.196	0.200	0.238	0.230	0.240
ΔG_h observed, kJ/mol	–465	–340	–1315	–430	–300	–465	–2765	–1295	–205

that even activated carbon is capable to remove this inorganic anion, ClO_4^-. Granular activated carbons are usually produced at very high temperatures and cannot be a highly hydrated materials required for the removal of most inorganic anions. At the same time, perchlorate is the least hydrated anion. These samples of Mg–Al–CO_3 LDHs are the most hydrated LDHs known till now. It is possible that a decrease in hydration due to thermal treatment of the Mg–Al–CO_3 LDHs will considerably increase their adsorptive properties towards ClO_4^-. The literature data and Table 2 also indicate that carbon or inorganic adsorbents modified with organic molecules can serve as competitive removers of ClO_4^-.

The second option is a change of the chemical composition of inorganic anion exchanger synthesized by fine inorganic sol-gel method which is currently based on hydroxides of Mg and Al [2–5]. Table 2 exhibits that Fe oxide-based (or modified) materials show better adsorptive affinity than others. This factor can be used via two possibilities: one of which is adding Fe salts at the last stage of the synthesis which can also increase adsorptive affinity to ClO_4^-. The other way is to synthesize different layered double hydroxides of similar quality (requested/expected from adsorptive materials), such as rich speciation of chemical elements, phases and surface chemistry, but with different chemical composition (Mg–Fe, Mg–Zr, Ca–Fe, etc.). However, this is a future research goal.

Conclusions

Mg–Al–CO_3 LDHs prepared via an original fine inorganic synthesis, which includes a stage of sol–gel routes, can serve as competitive adsorbents for the removal of perchlorate ion from water solutions. They are capable to sorb ClO_4^- even at pH 8 when most other adsorbents exhibit very low adsorptive properties up to zero levels compared with acidic solutions. Their adsorptive capacity to perchlorate at pH 5, 7 and 8 constitutes 37, 25 and 17 mg[ClO_4^-]/g_{dw}, respectively.

Mechanism of perchlorate uptake by these Mg–Al–CO_3 LDHs involves physical sorption which is based on electrostatic interaction and well-described by Freundlich and Linear adsorption models.

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СОРБЦІЯ ПЕРХЛОРАТУ НА ШАРУВАТИХ ПОДВІЙНИХ ГІДРОКСИДАХ Mg–Al–CO_3, ВИГОТОВЛЕНИХ ШЛЯХОМ ТОНКОГО НЕОРГАНІЧНОГО ЗОЛЬ–ГЕЛЬ ПРОЦЕСУ: ОБРОБЛЕННЯ ВОДНИХ РОЗЧИНІВ З pH 5, 7 І 8

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Перхлорат є небезпечним для людини аніоном, який може впливати на функції її головного мозку. Іонний обмін є одним із основних методів виділення цього аніона з води і таким чином дозволяє контролювати вміст ClO_4^- в водних розчинах. В цій роботі ми оцінили здатність зразків шаруватих подвійних гідроксидів складу Mg–Al–CO_3 (layered double hydroxides, LDHs) видаляти перхлорат при значеннях pH, які є типовими для умов водоочищення: pH 5, 7 та 8. Зразки LDHs був виготовлений методом тонкого неорганічного синтезу, що містив стадію золь-гель перетворень, Показано, що ці Mg–Al–CO_3 LDHs ефективно сорбують ClO_4^- навіть при pH 8, при якому більшість неорганічних аніонообмінників мають значно нижчий сорбційний потенціал щодо аніонів. Експериментальні ізотерми сорбції описуються моделями Фрейндліха та лінійним рівнянням, що підтвердило сприятливу сорбцію. Процес вилучення перхлорату реалізується за механізмом фізичної сорбції, який базується на електростатичній взаємодії сорбенту і адсорбату. Не дивлячись на те, що сорбційна місткість цього матеріалу до перхлорату є досить високою (порівняно з літературними даними) і становить 37 мг ClO_4^- на 1 г маси сухого адсорбенту при pH 5, його сорбційна спорідненість може бути підвищена шляхом оптимізації хімічного складу матерілу та/або його кальцинування. Запропоновано декілька шляхів покращення сорбційних властивостей аніонообмінника, одним з яких є термічне оброблення цих унікальних зразків LDHs, які зберігають свою шарувату будову навіть при прожарюванні при 300–600^{0}C. В статті також наведено короткий огляд літератури стосовно сорбції перхлорату різними сорбційними матеріалами.

Ключові слова: перхлорат, аніон, сорбція, неорганічні аніонообмінники, шаруваті подвійні гідроксиди, ізотерми адсорбції, залежність від pH.

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Perchlorate anion is dangerous to human and able to affect the brain functions. Ion exchange is one of the main approaches, which allows separating ClO_4^- anion and controlling its concentration in water solutions. In this work, we evaluated the ability of Mg–Al–CO_3 layered double hydroxides (LDHs) to remove perchlorate ions at various, yet relevant to drinking water treatment conditions, pH values: 5, 7 and 8. LDHs were prepared via an original fine inorganic synthesis which includes sol–gel routes. It was shown that Mg–Al–CO_3 LDHs can effectively sorb perchlorate even at pH 8, whereas most inorganic anion exchangers exhibited much lower adsorptive potential to anions. Experimental adsorption isotherms obeyed the Freundlich model and the Linear equation which confirmed favorable sorption. The process proceeds according to the mechanism of physical sorption based on an electrostatic interaction of an adsorbent and an adsorbate. Although these Mg–Al–CO_3 LDHs demonstrated high adsorptive capacity to perchlorate (as compared with the literature) which is equal to 37 mg of ClO_4^- per 1 gram of dry adsorbent at pH 5, an improvement in their adsorptive affinity can be achieved by the optimization of the material chemical composition and/or its calcination. To improve the removal properties of the anion exchanger toward ClO_4^-, several pathways have been suggested. One of them is a thermal treatment of these unique LDHs, which maintain their layered structure even after calcination at 300–600^{0}C. The paper also presents an overview of the literature data on perchlorate sorption by various materials.

Keywords: perchlorate anion; sorption; inorganic anion exchangers; layered double hydroxides; sorption isotherms; pH effect.

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