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## Zn-Al LAYERED DOUBLE HYDROXIDES FOR ADSORPTION AND PHOTOCATALYTIC REMOVAL OF CATIONIC DYE

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The removal of hazardous substances from wastewater is a major problem in the world. The advantages of application of Zn-Al layered double hydroxides (LDHs) and their derivatives for removal of organic contaminants consist in the combination of high adsorption capacity of LDHs and the presence of a photoactive component. Therefore, the present paper focuses on study of the adsorption and photocatalytic capabilities of Zn-Al LDHs to remove cationic dye methylene blue (MB) from aqueous solutions. Zn-Al LDHs with Zn:Al ratio 2 were synthesized by coprecipitation method. Zn-Al LDHs were characterized by XRD, thermogravimetric and spectroscopy analysis. The reconstruction of calcined Zn-Al LDHs in sodium dodecyl sulfate (SDS) solutions in the range of concentrations from  $0.012 \text{ mol}\cdot\text{L}^{-1}$  to  $0.205 \text{ mol}\cdot\text{L}^{-1}$  was performed to obtain organo/Zn-Al LDHs. The partial SDS intercalation was clearly evidenced by the appearance of a peak at low  $2\theta$  values. SDS-modified LDHs demonstrate the high adsorption capacity to MB. About 90 % of dye was adsorbed with organo/Zn-Al LDHs from  $2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  MB solution. The study on optical properties of calcined and reconstructed Zn-Al LDHs has detected the presence of ZnO that makes possible the using of Zn-Al LDHs as photocatalysts. About 50 % of dye was destructed by irradiation of MB solution in the presence of Zn-Al LDHs from  $2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  MB solution in the presence of calcined at  $450 \text{ }^\circ\text{C}$  Zn-Al LDHs. It has been found that the most complete removal of the dye from highly concentrated solutions is achieved by MB adsorption with organo/Zn-Al LDH. The investigation of the irradiation influence on the optical spectra of MB adsorbed on the surface of organo/Zn-Al LDH is needed to clarify the photocatalytic activity of ZnO-contained organo/Zn-Al LDH. The high adsorption capacity of organo/Zn-Al LDHs and the ease of both synthesis and separation processes rendered this adsorbent to be a promising candidate for environmental remediation.

**Keywords:** layered double hydroxides, organo/inorganic nanocomposites, intercalated surfactants, cationic dye adsorption, photocatalytic destruction, wastewater treatment

### INTRODUCTION

The removal of hazardous substances from wastewater and remediation of contaminants in surface water, groundwater is a major problem in the world. Various methods of treatment and processes have been used to remove the pollutants from contaminated water [1]. Adsorption is an inexpensive technique which does not require any special set up. In the recent years, many kinds of adsorbents with the catalytic function were developed and used for removal of nitrate, heavy metals, and organic pollutants from water. The use of layered double hydroxides (LDHs) as an adsorbent in the water treatment was focused by many researchers [1–3]. LDHs or hydrotalcite-like compounds are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and solvation molecules. The metal cations occupy the centers of edge sharing octahedra, their vertices contain hydroxide ions that connect to form infinite 2D

sheets. The chemical composition of LDHs is expressed by the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot z\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  may be common;  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , or  $\text{Ni}^{2+}$ , and  $\text{M}^{3+}$  may be common;  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Mn}^{3+}$ .  $\text{A}^{n-}$  is a nonframework charge compensating inorganic or organic anion, e.g.  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{RCO}_2^-$ , and  $x$  is normally between 0.2–0.4. LDHs layers gain a positive charge by isomorphous substitution of  $\text{M}^{3+}$  for  $\text{M}^{2+}$ , which is compensated by interlayer anions and water [4].

Due to their anionic exchange capacity, LDHs are suitable for intercalation and sorption of negatively charged species but are not applicable for positively charged ones. The modification of LDH's surface with anionic surfactants allows obtaining composites that are capable to adsorb many types of organic molecules [5, 6]. The organic phase in the interlayer formed by the intercalated organic ions acted as an adsorbilization medium increasing the affinity of LDHs for organic compounds. Sodium dodecyl sulfate (SDS) modified LDHs demonstrated the

greatly enhanced sorption of ionizable and nonionic organic contaminants such as pesticides, herbicides, and aromatic hydrocarbons [6, 7].

The adsorption greatly reduces the pollution but is not enough to assess its effectiveness at high concentration and does not comply with the standards of the World Health Organization [8]. At this level, the photocatalysis appears to be quite promising because of its simplicity. Recently, LDH have been intensively investigated as promising heterogeneous photocatalysts because of their excellent intrinsic photo-response characteristics, low cost, as well as facile preparation and modification [9]. LDHs as photocatalysts are expected to possess large energy-conversion efficiency as a result of the high dispersion of active species in a layered matrix, which facilitates the charge separation. Many LDH-based photocatalysts have been developed via appropriate incorporation of photoactive components into LDH host layers, sensitizing by interlayer functional molecules and construction of nanocomposites. Mixed oxides with semiconducting properties may be obtained by calcination of appropriate transition metal-containing LDHs. A wide variety of metal cations, such as  $Zn^{2+}$  and  $Ti^{4+}$ , may be introduced into the layers [10, 11]. Their relative proportions may be varied in a fairly wide range. This affords the possibility of preparing semiconducting oxides with tunable properties. Photocatalytic applications of LDHs are an interesting emerging field. Several semiconducting mixed oxides derived from LDH have been studied for the photocatalytic degradation of contaminants, such as Zn-Al [11, 12], Zn-Ce, ZnFe, Zn-Cr [13], and Mg-ZnAl [14] LDHs.

Therefore, the present paper focuses on study of the adsorption and photocatalytic capabilities of Zn-Al LDHs to remove cationic dye methylene blue from aqueous solutions.

## EXPERIMENTAL

**Preparation of Zn-Al LDHs.** All chemicals were analytical grade and used without further purification. Zn-Al LDHs with carbonate as the interlayer anion, with  $[Zn]/[Al]=1/2$  were synthesized by co-precipitation at a constant pH 10, following the method described in [4]. A mixed solution of 0.1 mol of  $Zn(NO_3)_2$  and 0.05 mol of  $Al(NO_3)_3$  in 200 ml of distilled water was added dropwise under vigorous stirring to 200 ml of an aqueous solution containing 0.3 mol of NaOH and 0.1 mol of  $Na_2CO_3$ . The pH 10 was maintained

constant by the addition of NaOH. Once addition was completed, the temperature was raised up to 85 °C and the slurry was being kept for 6 h at this temperature under continuous stirring. After that, the slurry was cooled down to the room temperature within several hours. The product was isolated by filtration and washed several times with the deionized water until pH 7. Afterwards, the solid was dried at 100 °C. The sample was labeled as ZnAl LDH.

The Zn-Al LDHs were modified with sodium dodecyl sulfate ( $CH_3(CH_2)_{11}SO_4Na$ ) by reconstruction method. Zn-Al LDHs have been calcined at 450 °C over 2 h to destroy the layered structure. The suspensions contained 1 g of calcined LDHs and 50 ml of  $CO_2$ -free aqueous solutions of DS were stirred for 24 h at room temperature. The concentration of SDS ranged from 0.012 to 0.205 mol·L<sup>-1</sup>. The ratios of Al (Zn-Al LDH) to SDS in solutions for LDH modification were 1:0.16; 1:0.33; 1:0.55; 1:1; 1:1.5. The SDS modified LDHs were labeled as ZnAl LDH/DS/0.16; ZnAl LDH/DS/0.33; ZnAl LDH/DS/0.55; ZnAl LDH/DS/1.0; ZnAl LDH/DS/1.5.

**Characterization.** XRD patterns of the samples were recorded with a DRON-4-07 diffractometer ( $CuK_\alpha$  radiation). Calculation of apparent crystallite size for LDHs has been performed by Debye-Scherrer formula:  $\beta(2\theta) = 0.94\lambda / (D \cos\theta^\circ)$ , using (003) and (110) reflection, employing the FWHM procedure. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Derivatograph Q-1500 D MOM (Hungary) equipment operated under a flow of an air at the heating rate of 10 °C·min<sup>-1</sup>. Infrared spectra were obtained in the range of 4000–400 cm<sup>-1</sup> on a Thermo Nicolet NEXUS FT-IR spectrophotometer (Nicolet, USA). The morphology and microstructure of Zn-Al LDHs were examined by a scanning electron microscope (SEM, JSM-6490-LV, JEOL, Japan). Diffuse reflectance spectra were obtained with a Lambda 35 UV-Vis (Perkin Elmer) spectrometer equipped integrated with a Labsphere RSA—PR-20 in the range of wavelength 200–1000 nm. The UV-visible spectra of the solutions were recorded on a Lambda 35 UV-Vis (Perkin Elmer) spectrometer using a quartz cell (1 cm path length), with distilled water as a blank.

**Batch adsorption.** The batch adsorption technique was used to obtain the MB adsorption data. Typically, 0.02 g of ZnAl LDH was

introduced into 100-mL glass tubes containing 40 mL of freshly prepared aqueous MB solutions. The adsorption process was allowed to last 4 h under continuous stirring. Particles were removed by centrifugation at 6000 rpm, and the residual concentration of MB in the solution was determined using UV-Vis spectrometry at the detecting wavelength of 663 nm. The equilibrium adsorption amount of MB in the sample has been calculated according to equation:  $q_e = (C_0 - C_e)V/m$ , where  $q_e$  is the amount of MB adsorbed at equilibrium,  $C_0$  is the initial MB concentration,  $C_e$  is the equilibrium concentration in solution,  $V$  is the total volume of solution, and  $m$  is the sorbent mass.

MB adsorption isotherm was obtained for ZnAl LDH/DS/1.5 in MB concentrations range from  $10^{-5}$  to  $2 \times 10^{-3}$  mol·L<sup>-1</sup>.

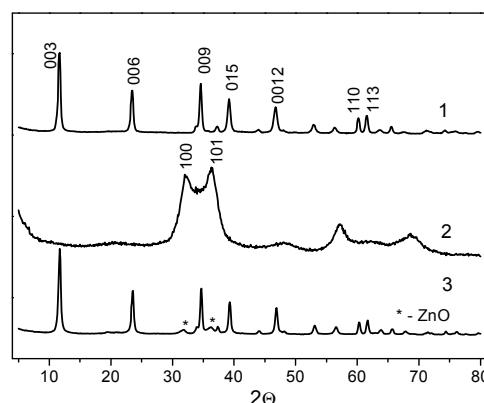
**Photocatalytical experiment.** For the degradation of MB, 0.020 g of Zn-Al LDHs was dispersed in 40 mL of  $9 \times 10^{-5}$  MB aqueous solution in 100-mL quartz reactor. Before illumination, the suspensions were stirred for 4 h in dark in order to reach an adsorption-desorption equilibrium between the photocatalyst and MB. Then, the solution was irradiated 3 h with UV light under magnetic stirring. At given time intervals, the solution was analyzed by measuring the absorption band maximum using a UV-Vis spectrometry at a detecting wavelength of 663 nm.

## RESULTS AND DISCUSSION

**Characterization.** The XRD pattern of the as-synthesized ZnAl LDH contains the characteristic reflections of layered double hydroxides with the basal planes of (003), (006), and (009) peaks at low  $2\theta$  angles and the other peaks for (101), (015), (0012), (110), and (113) planes at high  $2\theta$  angles (Fig. 1). All the reflections are sharp indicative of a highly crystalline material.

ZnAl LDH was calcined in air at 450 °C for 2 h to obtain a mixture of zinc and aluminium oxides. The reflections in XRD pattern of calcined Zn-Al LDHs are characteristic of ZnO (Fig. 1). It is known that at certain temperature the original hydrotalcite is converted into a mixture of oxides which have «memory» of the original structure [15]. In fact, in the presence of aqueous solutions the oxides regenerate the double hydroxides in the form of brucite-like sheets and the positive charges are balanced by anions presented in solutions. The hydration of calcined Zn-Al LDHs in aqueous suspension caused to the reconstruction of the hydrotalcite phase (Fig. 1). The source of anions in

this case is atmospheric CO<sub>2</sub> from which CO<sub>3</sub><sup>2-</sup> ions are formed.

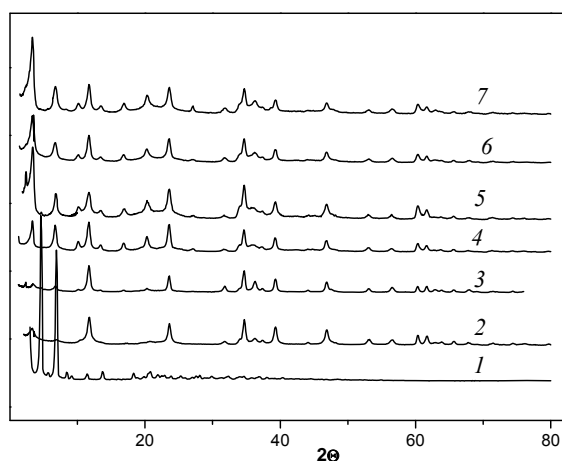


**Fig. 1.** X-ray diffraction patterns of as-synthesized – 1, calcined – 2, and reconstructed – 3 Zn-Al LDH

The layered structure reconstruction of calcined Zn-Al LDHs was performed in aqueous solutions of different SDS concentrations that corresponded to Al (ZnAl LDH): SDS molar ratio in the range of 0–1.5. The appearance of new diffraction peak signed the formation of a new phase was observed at small angles indicating SDS anion incorporation into the interlayer space (Fig. 2). The intercalated amount of SDS ions was gradually accumulated with increasing of its concentration in solutions used for modification of Zn-Al LDHs. The ratio of integral intensities of reflections that correspond to the intercalated ( $2\theta=3.4^\circ$ ) and hydrotalcite ( $2\theta=11.7^\circ$ ) phases was calculated (Table 1). The main type of intercalated derivatives was obtained having the mean interlayer spacing 26 Å,  $2\theta=3.4^\circ$  (Table 1). These interlayer distances depend upon the orientation of the chains within the interlamellar space. As the length of sodium dodecylsulfate molecule is 20.8 Å [16], the basal spacing of 26.8 Å corresponds to a perpendicular monolayer arrangement of SDS ions between the host layers [17]. The characteristic reflections of SDS are absent in the XRD pattern of the organo/Zn-Al LDHs. The diffraction peaks at  $2\theta$  equal to 10.2°, 13.5°, 16.9°, and 20.3° (Fig. 2) are suggested to correspond to the formation of a superlattice consisted probably of ordered SDS ions in the interlayer spaces.

The thermal decomposition of Zn-Al LDHs modified with various concentration of SDS was studied. Figure 3 displays the TG-DTG-DTA curves of the as-synthesized, reconstructed and SDS modified Zn-Al LDHs. The three events have been assigned to the thermal decomposition of

LDH-carbonate: in the first one (60–190 °C), the mass loss is attributed to the removal of water from internal gallery surfaces and the external non-gallery surface; in the second interval (190–300 °C), the loss is ascribed to the dehydroxylation of the brucite-like sheets and removal of interlayer anions; in the last one (300–500 °C), the mass loss is recognized as the total dehydroxylation and collapse of the structure due to the removal of the remaining interlayer anions [18]. In order to study the contribution of water and CO<sub>2</sub>, mass losses were divided into three intervals: 60–190, 190–300 and 300–500 °C (Table 2). The small mass loss observed in the interval 500–1000 °C can be ascribed to the loss of some carbonate anions strongly adsorbed on the mixed oxides crystallites [19].



**Fig. 2.** X-ray diffraction patterns of: sodium dodecylsulfate – 1; reconstructed ZnAl LDH – 2; ZnAl LDH/DS/0.16 – 3; ZnAl LDH/DS/0.33 – 4; ZnAl LDH/DS/0.55 – 5; ZnAl LDH/DS/1.0 – 6; ZnAl LDH/DS/1.5 – 7

**Table 1.** Al (ZnAl LDH): SDS molar ratio and *d*-spacing of Zn-Al LDH modified with SDS

Al(ZnAl LDH):SDS molar ratio	Basal spacing $d_{003}$ , Å	Integral intensities $I(3.4^\circ)/I(11.7^\circ)$ ratio
1:0	7.60	0
1:0.08	7.6; 26.4; 38.4	0.3
1:0.16	7.6; 26.4	0.4
1:0.33	7.6; 26.4	0.8
1:0.55	7.6; 26.4	2.4
1:1.00	7.6; 26.4	2.3
1:1.50	7.6; 26.4	3.8

The smaller total mass loss of the reconstructed Zn-Al LDHs is explained by the fact that some part of calcined LDH was not restored by hydration. So, the reconstructed LDHs contained fewer hydroxides and carbonate ions in comparison with the as-synthesized Zn-Al LDHs. As shown by XRD analysis, the traces of ZnO are remained in the pattern of the reconstructed Zn-Al LDH (Fig. 1).

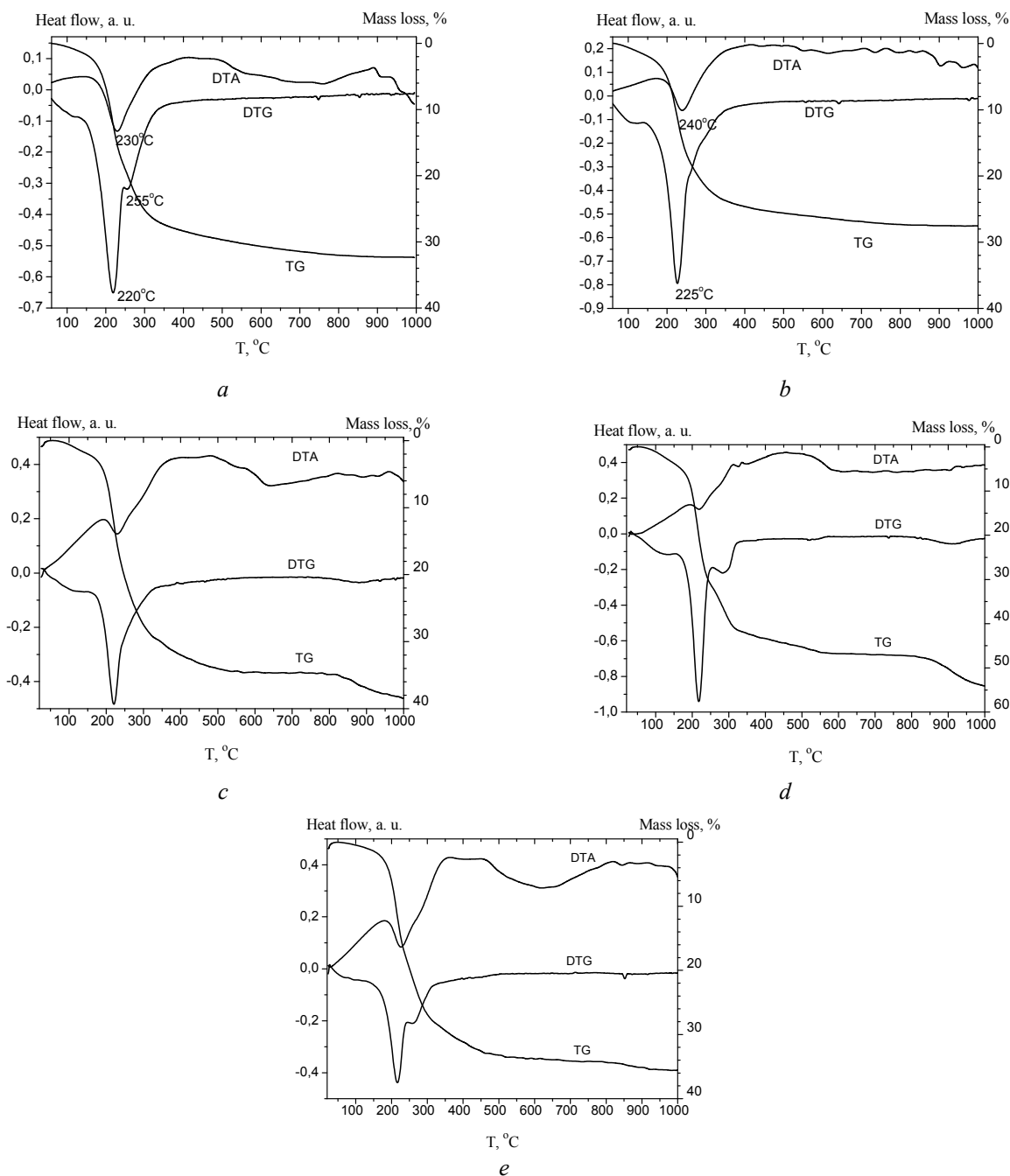
The thermal decomposition of SDS modified LDH is almost identical to ZnAl LDH (Fig. 3 c, d). The temperature of interlayer water loss seems to be lower than that of the as-synthesized and the reconstructed Zn-Al LDHs indicating the changes of LDHs structure. It can be caused by the fact that SDS ions intercalated into interlayer of LDH reduce the interactions of water with the environment in ZnAl LDH. In other words, SDS intercalation into Zn-Al LDHs increase the hydrophobic nature of its interlayer surface [6]. The second step of dehydroxylation of the brucite-like sheets is accompanied by SDS destruction. The decomposition of SDS takes place in the range 210–250 °C [20] and therefore, a greater loss is observed above 200 °C. The mass loss of SDS modified LDHs at 300–500 °C occurs due to the total dehydroxylation and the collapse of the layered structure. The thermogravimetric analysis coupled with mass spectroscopy revealed that the pyrolysis of the organic anion takes place under thermal treatment of LDHs [21]. The mass loss between 800–900 °C can be ascribed to SO<sub>3</sub> evolution as a result of the decomposition of (Zn, Al) sulfate formed by decomposition of SDS anions during the second mass loss stage [22]. The total mass loss of SDS-contained Zn-Al LDHs is higher than that for Zn-Al LDHs reconstructed in aqueous suspensions. This increase in mass loss is resulted from the loading of SDS, their decomposition being reflected by the mass loss in 400–900 °C and the exothermal peak at 642 °C. The total mass loss of ZnAl LDH/SDS/1:0.33, ZnAl LDH/SDS/1:0.55, ZnAl LDH/SDS/1:1 and ZnAl LDH/SDS/1:1.5 does not change drastically (Table 2). It is likely that these samples contain the same amount of SDS.

The presence of photoactive ZnO extends range of applications of LDHs and LDH-based composites, particularly as photocatalysts, UV filters, dye sensitized solar cells. The effect of phase transformations on Zn-Al LDHs capability to absorb UV light was examined. The optical absorption spectra of as-synthesized ZnAl LDH,

calcined ZnAl LDH and Zn-Al LDHs with different content of SDS are shown in Fig. 4.

Since  $\text{Al}_2\text{O}_3$  has a wide band gap (5.55 eV), the absorption of light in the UV range caused by the presence in the samples of ZnO, the band gap of which is 3.37 eV at room temperature [23]. The calculated values of ZnO band gap are presented in Table 3. The reconstruction of calcined oxides promotes the formation of additional quantity of

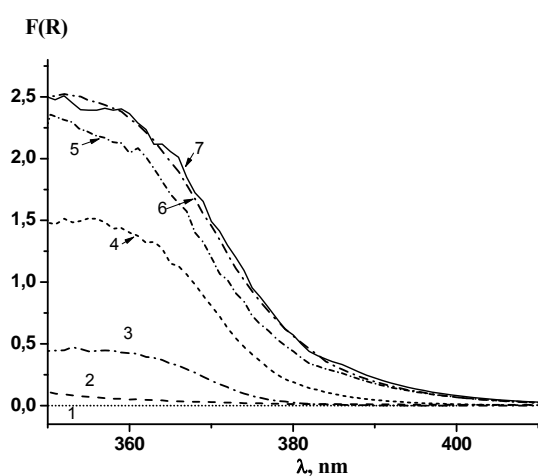
crystalline ZnO that causes the red shift of absorbance band of reconstructed Zn-Al LDHs Fig. 4, spectrum 3. The light absorbance bands of Zn-Al LDHs modified with SDS are more shifted to visible region. It is suggested that the reconstruction of calcined LDHs in SDS solutions causes the formation of ZnO-containing Zn-Al LDHs with smaller sizes of ZnO crystallites.



**Fig. 3.** TG, DTA and DTG curves as-synthesized ZnAl LDH (a), reconstructed ZnAl LDH (b), ZnAl LDH/SDS/1:0.16 (c), ZnAl LDH/SDS/1:1.5 (d), ZnAl LDH SDS adsorbed (e)

**Table 2.** The thermal decomposition stages of Zn-Al LDH

Samples	Temperature intervals, °C				Total mass loss, %
	60–190	190–300	300–500	500–950	
ZnAl LDH	4.2	20.9	4.4	2.6	32.1
ZnAl LDH reconstructed	3.9	17.6	4.0	2.0	27.5
ZnAl LDH/SDS/1:0.16	4.7	22.8	6.3	3.0	36.8
ZnAl LDH/SDS/1:0.33	6.7	28.3	7.6	8.8	51.4
ZnAl LDH/SDS/0.55	7.0	28.1	8.1	5.2	48.4
ZnAl LDH/SDS/1:1.0	8.3	29.7	5.8	5.0	48.8
ZnAl LDH/SDS/1:1.5	6.9	32.5	5.7	4.9	50.0
ZnAl LDH SDS adsorbed	4.1	22.7	6.3	2.0	35.1



**Fig. 4.** UV-Vis diffuse reflectance spectra of ZnAl LDH – 1; calcined ZnAl LDH – 2; ZnAl LDH/SDS/0.16 – 3; ZnAl LDH/SDS/0.33 – 4; ZnAl LDH/SDS/0.55 – 5; ZnAl LDH/SDS/1.0 – 6; ZnAl LDH/SDS/1.5 – 7

**Table 3.** The band gap of ZnO in Zn-Al LDH

Samples	$E_g$ , eV
ZnAl LDH rehydrated	3.81
ZnAl LDH/SDS/0.16	3.31
ZnAl LDH/SDS/0.33	3.32
ZnAl LDH/SDS/0.55	3.31
ZnAl LDH/SDS/1.0	3.29
ZnAl LDH/SDS/1.5	3.29

**Study of MB removal.** The adsorption properties of Zn-Al LDHs modified with solutions of different SDS concentration were investigated in removal of MB from  $2 \times 10^{-4}$  M solution (Table 4). The amount of adsorbed MB is increased with increasing of SDS quantity used for modification of Zn-Al LDHs. The organo/Zn-Al LDHs showed

the high capacity to MB adsorption while the as-synthesized and the calcined Zn-Al LDHs demonstrated very pure MB adsorption (Table 4). The low MB adsorption on inorganic LDH was also observed for Mg-Al LDHs [24]. Zn-Al LDHs in carbonate form was modified in 0.05 M DS solution (the ratio Al(LDH):SDS = 1:0.33) and used for MB adsorption. The adsorption capacity of hydrotalcite with SDS modified external surface has been increased in comparison with the unmodified as-synthesized and the calcined ZnAl LDH but it was still less than that of the organo/Zn-Al LDHs with intercalated SDS ions (Table 4). While SDS modified Zn-Al LDHs with intercalated SDS ions removed 75 % of MB from solution, the SDS modified hydrotalcite eliminated only 33 % of MB under the same conditions. So, the most of MB molecules is adsorbed on internal surface of LDHs.

The results indicate that the organic phase (SDS) greatly increases the affinity of organo/Zn-Al LDHs for MB due to hydrophobic interactions between the surfactants and dye molecules [7].

The MB adsorption isotherm for ZnAl LDH/SDS/1.5 is presented in Fig. 5. The amount of MB sorbed sharply increased at low MB concentration and then reached a plateau at the concentration higher than  $5 \times 10^{-4}$  mol·L<sup>-1</sup>.

As was shown above, the as-synthesized and calcined Zn-Al LDHs possess low adsorption capacity to MB. The photocatalytic activity of unmodified Zn-Al LDHs was studied. The calcined ZnAl LDH demonstrated higher capability to destroy MB under irradiation in comparison with as-synthesized ZnAl LDH (Table 5). It was not possible to compare the photocatalytic activity of SDS modified Zn-Al LDHs as MB was completely adsorbed from  $2 \times 10^{-5}$  M solution of MB.

**Table 4.** Comparison of the MB adsorption over Zn-Al LDHs modified with SDS solutions of different concentration\*

Samples	Adsorption, mmol·g <sup>-1</sup>	% of MB removal
ZnAl LDH/SDS/0.16	0.28	70
ZnAl LDH/SDS/0.33	0.30	75
ZnAl LDH/SDS/0.55	0.30	73
ZnAl LDH/SDS/1.0	0.31	78
ZnAl LDH/SDS/1.50	0.35	89
ZnAl LDH	0.02	5
calcined ZnAl LDH	0.01	2
ZnAl LDH with adsorbed SDS**	0.13	33

\* [MB] =  $2 \times 10^{-4}$  mol·L<sup>-1</sup>, [LDH] = 0.5 g·L<sup>-1</sup>

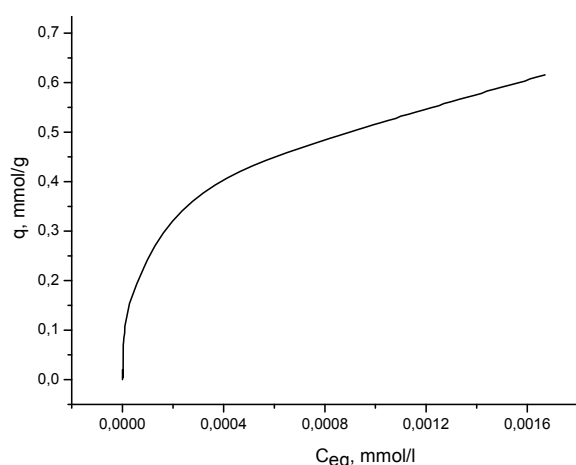
\*\* Al (ZnAl LDH):SDS = 1:0.33

**Table 5.** MB removal with Zn-Al LDHs

Samples	Adsorption, %	Photodestruction, %	Total removal, %
blank	–	18	18
ZnAl LDH	5	26	31
calcined ZnAl LDH	2	46	48
ZnAl LDH/SDS/0.33	100	–	100

\* [MB] =  $2 \times 10^{-5}$  mol·L<sup>-1</sup>, [Zn-Al LDH] = 0.02 g·L<sup>-1</sup>**Table 6.** The adsorption and photocatalytic MB removal with SDS modified Zn-Al LDH

Samples	Adsorption,		Photodestruction		Total removal, mmol/g
	mmol/g	%	mmol/g	%	
ZnAl LDH/SDS/0.16	0.133	74	0.008	4	0.141
ZnAl LDH/SDS/0.33	0.154	86	0.016	8	0.170
ZnAl LDH/SDS/0.55	0.141	78	0.004	3	0.145
ZnAl LDH/SDS/1.0	0.158	88	0.002	3	0.160
ZnAl LDH/SDS/1.50	0.165	92	0.005	2	0.170

\* [MB] =  $9 \times 10^{-5}$  mol·L<sup>-1</sup>, [Zn-Al LDH] = 0.02 g·L<sup>-1</sup>**Fig. 5.** Isotherm of MB adsorption by ZnAl LDH/SDS/1.50

The comparison of MB removal by adsorption and by photodestruction was performed for SDS

modified Zn-Al LDHs in  $9 \times 10^{-5}$  M MB solutions. As it can be seen from Table 6, the main part of MB was removed by adsorption. The photodestruction of MB was insignificant in the presence of organo/Zn-Al LDHs. Probably the photodestruction of dye occurred on the surface of SDS modified Zn-Al LDHs that was not fixed under the experimental conditions. After the equilibrium achievement, the Zn-Al LDHs with adsorbed MB had an intense blue color. The changes in the intensity of adsorbed MB were not studied.

## CONCLUSION

The study of adsorption and photocatalytic capabilities of Zn-Al LDHs to remove the cationic dye methylene blue from aqueous solutions was carried out. The organo/Zn-Al LDHs show high adsorption capacity to MB. Unmodified Zn-Al

LDHs demonstrated activity in the photodestruction of MB. The photocatalytic activity of organo/Zn-Al LDHs was not observed. The most complete removal of the dye from highly concentrated solutions was achieved by its adsorption with organo/Zn-Al LDH. Further investigation of the behavior of MB adsorbed on the surface of organo/Zn-Al LDH under irradiation

will be carried out to clarify the photocatalytic activity of ZnO-contained organo/Zn-Al LDH.

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### **Zn-Al шаруваті подвійні гідроксиди для адсорбційного та фотокаталітичного вилучення катіонного барвника**

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*Досліджено адсорбцію та фоторозкладання модельного барвника метиленового блакитного (МБ) Zn-Al шаруватими подвійними гідроксидами (ШПГ), модифікованими аніонною поверхнево-активною речовиною. Модифікування Zn-Al ШПГ здійснювалось методом реконструкції із застосуванням розчинів додецилсульфату натрію різної концентрації. Zn-Al ШПГ були охарактеризовані із застосуванням рентгено-структурного, термогравіметричного та спектрофотометричного методів. При дослідженні оптичних властивостей органо/Zn-Al ШПГ виявлено присутність кристалічного ZnO, що робить можливим застосування Zn-Al ШПГ як фотокаталізатора. Немодифіковані Zn-Al ШПГ демонструють активність в реакції фоторозкладання МБ, в той час як фотокаталітичної активності органо/Zn-Al ШПГ не було виявлено. Встановлено, що найбільш повне вилучення барвника з концентрованих розчинів досягається адсорбцією органо/Zn-Al ШПГ. Для подальшого вивчення фотокаталітичної активності ZnO-вмісних органо/Zn-Al ШПГ необхідно дослідити вплив опромінення на оптичні властивості МБ, адсорбованого на поверхні ШПГ.*

**Ключові слова:** Шаруваті подвійні гідроксиди, органо/неорганічні наноконізати, інтеркальовані поверхнево-активні речовини, адсорбція катіонного барвника, фотокаталітичне розкладання, очистка стічних вод

### **Zn-Al слоистые двойные гидроксиды для адсорбционного и фотокаталитического извлечения катионного красителя**

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*Исследованы адсорбция и фоторазложение модельного красителя метиленового голубого (МГ) Zn-Al слоистыми двойными гидроксиды (СДГ), модифицированными анионным поверхностно-активным веществом. Модифицирование Zn-Al СДГ осуществлялось методом реконструкции с применением растворов додецилсульфата натрия различной концентрации. Zn-Al СДГ охарактеризованы с применением рентгено-структурного, термогравиметрического и спектрофотометрического методов. При исследовании оптических свойств органо/Zn-Al СДГ обнаружено присутствие кристаллического ZnO, что*



делает возможным применение Zn-Al СДГ в качестве фотокатализатора. Немодифицированные Zn-Al СДГ демонстрируют активность в фоторазложении МГ, в то время как фотокаталитической активности органо/Zn-Al СДГ не было обнаружено. Установлено, что наиболее полное извлечение красителя из концентрированных растворов достигается его адсорбцией органо/Zn-Al СДГ. Для дальнейшего изучения фотокаталитической активности ZnO-содержащих органо/Zn-Al СДГ необходимо исследование влияния облучения на оптические свойства МГ, адсорбированного на поверхности СДГ.

**Ключевые слова:** слоистые двойные гидроксиды, органо/неорганические нанокмозиты, интеркалированные поверхностно-активные вещества, адсорбция катионного красителя, фотокаталитическое разложение, очистка сточных вод

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