ADSORPTION KINETICS FOR THE REMOVAL OF METHYL ORANGE USING ADSORBENTS BASED ON Zn Al-LAYERED DOUBLE HYDROXIDES

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Abstract
The adsorption phenomena of adsorbents based on ZnAl layered double hydroxides was studied. Methyl orange was used as test pollutant. The emphasis of the study was the analysis of Methyl Orange removal kinetics. The synthesized and thermally treated adsorbents were characterized by X-ray diffraction. The analysis of adsorption kinetics was conducted using the pseudo-second order kinetic model. The results showed that the samples have adsorptive removal properties, particularly the adsorbent derived from thermally treated layered double hydroxides. The findings give an insight into the adsorption phenomena of ZnAl-layered double hydroxides based materials which could be considered as promising adsorbents for the removal of Methyl Orange in wastewaters.

Introduction
From various industries, organic dyes have been detected as one of the toxic pollutants in wastewaters and have recently become a serious concern due to the increased quantity discharged into the environment. Considering their stable nature, these dyes can cause severe problems not only to the environment, but also to humans [1]. Therefore, an urgent need for a rapid and efficient removal method for coloured dyes from water is of essential importance and has been set as a priority in the scientific world. Lately, layered double hydroxides (LDHs) have received considerable attention in the environmental friendly processes. These materials consist of stacked hydroxide layers with charge-balancing anions in the interlayer [2]. Additionally, the properties of the LDHs can be tailored through variation of numerous synthesis methods and parameters enabling abundant possibilities for preparation of materials with targeted characteristics. After thermal treatment, their layered structure collapses triggering the formation of non-stoichiometric metastable mixed oxides with developed surface area and specific acid-base and redox properties. One of the most interesting property of the obtained mixed oxides is the so-called “memory effect” that gives the thermally treated oxides the ability to easily reconstruct the original layered structure in an aquatic environment [3].
Therefore, the motivation for this study was to investigate the behaviour of synthesized ZnAl-LDHs and their mixed oxides (thermally treated at 500°C/5h) in the Methyl Orange (MO) removal processes and to determine the adsorption kinetics of the process.

Experimental
For the synthesis of layered double hydroxides with carbonate anions in the interlayer low supersaturation coprecipitation method at constant pH (9–9.5) was used. Metal salts solution $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, were continuously (4 $cm^3 min^{-1}$) added at constant temperature (40°C) maintaining the required constant pH with the base solution of 0.67 M Na_2CO_3 and 2.25 M NaOH. The precipitates were aged for 15 h, thoroughly washed with distilled water until neutral pH = 7. The obtained samples were dried 24 h at 100°C (ZnAl-100) and then calcined for 5 h, at 500°C in air (ZnAl-500).
The phase composition of samples was analysed by X-ray powder diffraction (XRD), using Rigaku MiniFlex 600.

Adsorption experiments were conducted in an open cylindrical thermostated Pyrex reaction vessel containing 100 ml of MO solution (C_0 = 20 mg dm^{-3}) and 50 mg of powdered adsorbents (ZnAl-100 and ZnAl-500). At defined intervals, aliquots were centrifuged and MO concentrations were determined using UV-VIS spectrophotometer at 464 nm.
The pseudo-second-order kinetic model was used for the analysis of the MO adsorption kinetics.

Results and discussion

XRD spectra of the synthesized (ZnAl-100) and thermally treated (ZnAl-500) samples are presented in Figure 1. XRD pattern of ZnAl-100 sample corresponds to the characteristic reflections for the layered structure of the hydrotalcite-like materials (Zinc Aluminium Carbonate Hydroxide Hydrate JCPDS 38-0486) and the observed sharp and highly intensive peaks suggest a well-defined crystal structure [4]. Additional peaks were also detected that could be attributed to the presence of the crystalline ZnO phase in the ZnAl-100 sample [5]. After thermal treatment at 500°C, layered LDH structure collapsed and the formation of the spinel phase $ZnAl_2O_4$ with additional ZnO peaks was detected. Besides that, the intensities of the diffraction peaks are much lower suggesting that the newly formed mixed-oxide phase has lower crystallinity than starting LDH phase. The results of the XRD analysis show that thermal treatment of layered double hydroxides leads to the collapse of the layered structure verified by the formation of new phases detected in sample ZnAl-500.

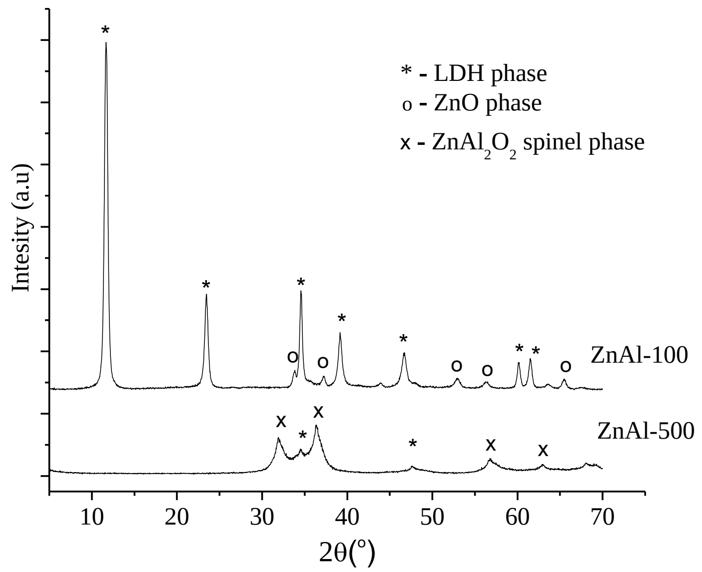

Figure 1. XRD diffraction patterns for samples ZnAl-100 and ZnAl-500

The absorption process of the MO is presented as a function of MO concentration decrease with contact time (adsorbent-pollutant) in Figure 1. It can be observed that the decrease in MO concentration was detected with both adsorbents. The concentration decrease for the sample ZnAl-100 was only around 30% after 120 minutes of adsorbent-pollutant contact, whereas outstanding concentration decrease was observed for sample ZnAl-500. After only 1 min of adsorbent-pollutant contact the MO concentration decreased to complete decolourisation of the pollutant (~0 mg/l). This higher adsorptive capacity of ZnAl-500 sample could be explained by the memory effect. The thermally treated sample probably reconstructed its starting layered structure after contact with the MO aquatic solution, partially intercalating the MO and CO_3^{2-} ions into the interlayer of LDH, leading to complete removal after only 1 minute of contact.

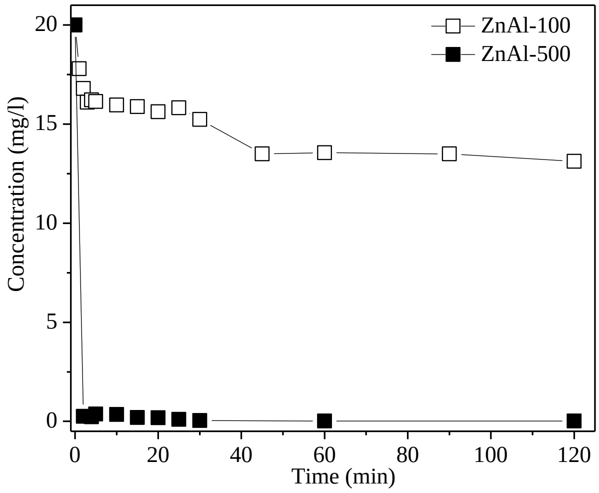

Figure 2. The MO concentration decrease as a function contact time (adsorbent-pollutant)

In order to define the adsorbent efficiency for dye removal processes and to clarify the adsorption mechanism, it is necessary to determine adsorption kinetics. Adsorption kinetics was evaluated using the pseudo-second-order kinetic model given by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium conditions and q_t (mg g^{-1}) is the adsorption capacity at equilibrium at defined time t (min); k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant for the pseudo-second-order model.

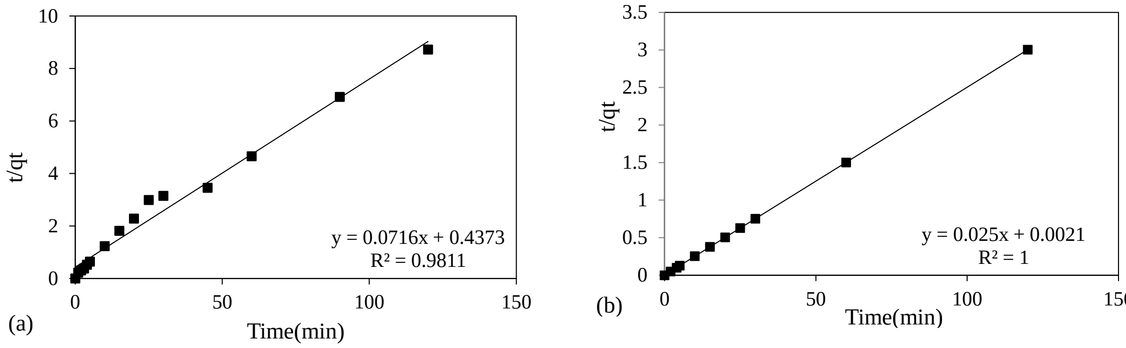

Figure 3. Pseudo-second-order kinetic plot: (a) ZnAl-100 and (b) ZnAl-500

Considering the correlation coefficient (R^2) and the data obtained for MO adsorption, it can be observed that the best fit for both adsorbents was obtained by the pseudo-second-order kinetic model. The results of fitting experimental data for pseudo-second-order kinetic model are given in Table 1. The analysis of data indicates that the pseudo-second-order model is suitable for the explanation of the MO adsorption kinetics on adsorbents based on layered double hydroxides. Considering that the pseudo-second-order model is based on the adsorption loading of the solid phase, the rate-determining step has been described to be the chemisorption [6]. Additionally, it has been suggested that the pseudo-second-order model can predict the behaviour over the whole range of the adsorption process [1].

Table 1. Kinetic parameters and correction coefficient (R^2) for the pseudo-second-order kinetic model

Samples	Pseudo-second order		
	q_e(mg/g)	k_2(g/mgmin)	R^2
ZnAl-100	13.76	0.012078	0.9811
ZnAl-500	39.96	0.2982	1

Conclusion

In this study, ZnAl-LDH and ZnAl-mixed oxides were successfully synthesized and thermally treated at 100 and 500°C. The XRD analysis for ZnAl-100 sample confirmed the presence of the characteristic reflections for the layered structure of the hydrotalcite-like materials with the additional ZnO phase. After thermal treatment at 500°C, sample ZnAl-500 layered LDH structure collapsed and the formation of the spinel phase $ZnAl_2O_4$ with additional ZnO peaks was detected.

The adsorbent treated at higher temperature, ZnAl-500, showed high adsorption properties that could be explained by the memory effect and the ability to intercalate the MO and CO_3^{2-} ions into the interlayer of LDH during the reconstruction of the layered structure. Adsorption kinetics analysis showed that the best fit for both adsorbents was obtained by the pseudo-second-order kinetic model indicating that the rate-determining step is the chemisorption and suggesting possible prediction of the behaviour over the whole range of the adsorption process. These results suggested that the LDHs could be considered as promising adsorbents for the removal of Methyl Orange in wastewaters.

Acknowledgements

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