Photodecolourization of congo red dye in presence of Ni^{3+} layered double hydroxide

Irina Ryltsova*, *Evgenia* Tarasenko, *Olga* Lebedeva

Institute of Pharmacy, Chemistry and Biology, Belgorod State National Research University, Belgorod, Russia

Abstract. Layered double hydroxide containing Ni^{3+} (Mg/AlNi-LDH) was successfully synthesized by co-precipitation in an oxidizing media. The resulted product was characterized using X-ray diffraction, wavelength dispersive X-ray fluorescence spectrometry. The activity of Mg/AlNi-LDH in the process of photodegradation of Congo red dye using UV light irradiation was evaluated. The initial rate of photodegradation of the dye in the presence of LDH is 1.6 times higher than that of UV irradiated solution. The kinetic data obtained for photodegradation process can be adequately described by pseudo-first-order kinetic model. The presence of Mg/AlNi – LDH leads to increased photodegradation yield compared to destruction only by UV irradiation.

1 Introduction

Layered double hydroxides (LDHs) also known as hydrotalcite-like compounds are natural or synthetic layered materials. LDHs consist of positively charged metal hydroxide layers with a brucite-like structure and anions located in the interlayer space and compensating the excessive positive charge of the layers. The interlayer space also contains water molecules, which are involved in stabilizing the structure of LDH. The general formula for compounds of this class is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n}) \cdot mH_2O$, were M^{2+} and M^{3+} are divalent and trivalent cations, An is the interlayer inorganic or organic anion. The nature of metal cations and interlayer anions as well as molar ratio M^{2+}/M^{3+} can be varied in a wide range, and that ability allows to obtain materials with given physical and chemical properties [1].

LDHs find applications for removal of organic and inorganic pollutants from aqueous solutions [2,3], as catalysts and catalyst precursors [4,5], as drug delivery systems [6].

One of the promising directions is the synthesis of LDH exhibiting photoactivity for purification of wastewater from organic pollutants by exposure to radiation in the visible or UV region of light [7]. Several publications describe high photocatalytic activity of Zn-containing LDHs and the products of their thermal decomposition for the degradation of organic dyes under UV-irradiation [8-10]. Wei et al. reported the family of MCr–LDHs (M=Cu, Ni, Zn) to exhibit pronounced photocatalytic activity in the process of dyes and phenols degradation under visible light irradiation [11].

In the present study photodegradation of Congo red dye in the presence of LDH containing Ni^{3+} in hydrotalcite matrix is described. The assumption concerning the activity of the compounds containing Ni^{3+} in the process of dyes degradation is based on the known fact that nickel oxide exhibits photocatalytic activity. E.g. Zhao et al. reported that that doping with Ni_2O_3 improves the photocatalytic activity of titanium oxide in the degradation of trichlorophenol, 2,4-dichlorophenol, and sodium benzoate [12]. Recently Shaban et al. showed Ni_2O_3 supported on MCM-48 to be an effective photocatalyst for degradation of Congo red dye [13]. The degradation in the presence of Ni_2O_3/MCM-48 increased comparing to the degradation using bulk Ni_2O_3.

2 Experimental

Mg/AlNi-LDH was synthesized by precipitation from solution at room temperature at variable pH as described in ref. [14]. The degree of substitution of aluminum cations for nickel in the hydrotalcite structure specified during the synthesis was 25 at. %. Nitrates $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were used as metals sources. The starting reaction mixture consisted of appropriate amounts of metal salts dissolved in distilled water while the total concentration of metal ions being 1 M. The molar ratio of the ions in the solutions of metal salts (M^{2+}:M^{3+}) was 3:1. Precipitant solution containing NaOH and Na_2CO_3 was added dropwise to the metal salts solution until pH reached 9-10. Ni^{2+} was oxidized into Ni^{3+} during the synthesis by sodium hypochlorite. The resulting precipitate was aged at room temperature for 24 h and then at 98°C for 48 h. After that, the sample was washed with distilled water and dried at 120°C.

The chemical composition of synthesized sample was determined by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry on a spectrometer ARL PerformX (Thermo Fisher Scientific) with 2.5 kW Rh tube. The WDXRF experiment was carried out using 0.2 g of sample pressed into a disk with boric acid after heat treatment at 600°C for 1 hour. Analysis of the results was performed using UniQuant program.

*Corresponding author: ryltsova@bsu.edu.ru

The phase composition of the synthesized sample was determined by X-ray phase analysis on a Rigaku diffractometer with CuKα radiation (λ =1,5406Å) in the range 2θ = 5 - 75°. The data were collected with a scan step 2θ = 0.02°/step and a scan rate 2θ = 3°/min.

The investigation of the kinetic of Congo red dye adsorption was performed by inserting 20 mg of the synthesized Mg/AlNi-LDH into 10 ml 0.05 mmol/L of dye solution for different time intervals from 2 to 60 min.

The photodegradation experiments were conducted under UV irradiation using photolysis chamber VOLTA FK-12M equipped with a 1000 W mercury lamp, the radiation flux of which lied in the spectrum range of 240-320 nm. The effect of contact time on the degradation of Congo red dye was investigated by mixing 20 mg of Mg/AlNi-LDH with 10 ml 0.05 mmol/L of Congo red solution for different time intervals from 2 to 60 min. For comparison, a similar experiment was performed in the absence of LDH.

In both types of experiments (sorption and photodegradation) the residual dye solutions were centrifuged and collected for analysis. The concentration of the dye in solutions was determined spectrophotometrically using a SPECORD 50 instrument, registering the optical density of the solutions at 500 nm.

3 Results and discussion

The synthetic Mg/AlNi-LDH exhibited the typical XRD peaks of highly crystalline layered double hydroxides [1]. Analysis of diffraction pattern (Fig 1.) confirmed that the sample was a single-phase product with hydrotalcite-like structure.

Based on the data of wavelength dispersive X-ray fluorescence analysis and the general formula of LDH, the following semi-empirical formula of the synthesized sample can be proposed: $Mg_{0.692}Al_{0.297}Ni_{0.011}(OH)_2(CO_3)_{0.154}\cdot nH_2O$. The experimental ratio of metal cations for synthesized sample slightly differs from that in starting solution. This difference may be due to the difference in radii and electronegativity of Al^{3+} and Ni^{3+} and due to the presence of the oxidizing agent (NaClO) during the synthesis.

The photodegradation of Congo red dye was chosen to test the photoactivity of the Mg/AlNi – LDH. The kinetic curves of photodegradation of Congo red in the presence of Mg/AlNi – LDH and without it are shown in Fig. 2. For comparison, the kinetic curve of sorption in the same time interval is shown. The initial rate of sorption and photodegradation was determined by selecting an empirical equation describing the kinetic curves, followed by differentiation (Table I). As follows from the data presented in Fig. 2 and in Table I, the introduction of LDH into dye solution leads to an increase in the rate and conversion of the Congo red dye.

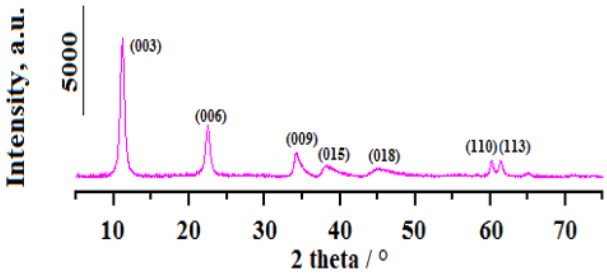

Fig. 1. X-ray diffraction pattern of Mg/AlNi – LDH.

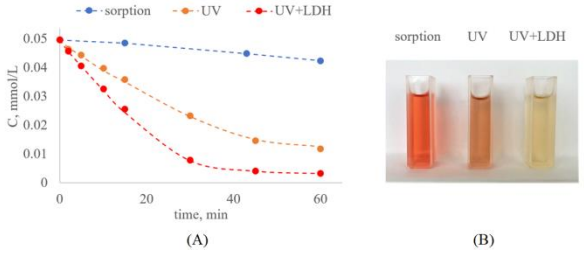

Fig. 2. (A) Kinetic curve of adsorption of Congo red dye on Mg/AlNi - LDH and kinetic curves of photodegradation of Congo red dye in the presence of LDH and without it; (B) Images of residual dye solutions after adsorption and after photodegradation during 60 min.

After irradiation for 60 min, about 76% of the Congo red was decolorized without LDH, while this value increased to 93% by adding Mg/AlNi – LDH. Dye removal by adsorption was only about 14% for the same time period.

The kinetic behavior was estimated utilizing common kinetic model of pseudo-first order (Lagergren model). Kinetic data in the coordinates of the pseudo-first-order model are shown in Fig. 3. The kinetics appears to fit this model with high R^2 values (table I).

According to the conventional opinion, the heterogeneous photocatalytic degradation involves the following main steps: adsorption of the dye on the catalyst surface, absorption of the light by the catalyst and charge transfer reactions. Shaban et al. [13] proposed the mechanism including the generation of positive holes (photogenerated holes, h_{VB}^{+}) and the hydroxyl radicals in the photocatalytic process upon irradiation of MCM-48/Ni_2O_3. The radicals can be active oxidizing agents for degradation of Congo red (Eqs. 1-4):

$$MCM-48/Ni_2O_3 + h\nu \longrightarrow MCM-48/Ni_2O_3\ (h_{VB}^{+}) \quad (1)$$

$$MCM-48/Ni_2O_3\ (h_{VB}^{+}) + H_2O \longrightarrow$$

$$\longrightarrow MCM-48/Ni_2O_3 + H^{+} + OH^{\cdot} \quad (2)$$

$$MCM-48/Ni_2O_3\ (h_{VB}^{+}) + CR^{+\cdot} \longrightarrow$$

$$\longrightarrow Product\ of\ degradation \quad (3)$$

$$OH^{\cdot} + CR^{+\cdot} \longrightarrow Product\ of\ degradation \quad (4)$$

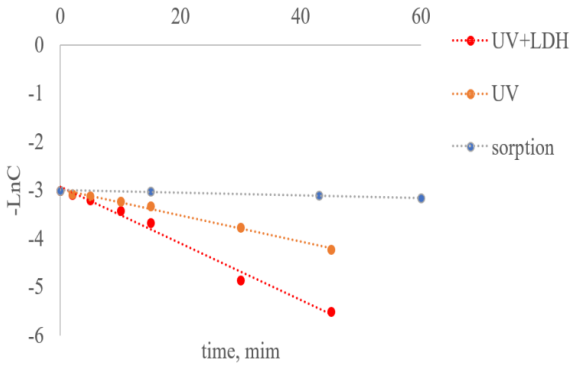

Fig. 3. Pseudo-first-order kinetic plotting of adsorption data and photodegradation.

Table 1. Analysis of Kinetic Data on sorption and photodegradation of Congo Red

Sample	**W_0, mmol/(L·min)**	**R^2 of empirical equation describing the kinetic curves**	**k, (min^{-1}) pseudo-first-order kinetics**	**R^2 of pseudo-first-order kinetics**
sorption	$5.0 \cdot 10^{-5}$	1.0000	0.0027	0.9876
UV	$1.0 \cdot 10^{-3}$	0.9992	0.0268	0.9939
UV+LDH	$1.6 \cdot 10^{-3}$	0.9996	0.0584	0.9879

However, the reference [13] does not contain any information on the oxidation state of nickel in the catalyst after the oxidation process.

It should be noted that during the oxidation of Congo red in the presence of Mg/AlNi - LDH under the UV irradiation, the LDH sample changed its color from black to green. This may indicate the reduction of nickel ($Ni^{3+} \rightarrow Ni^{2+}$) during the photodegradation of the dye. Thus, we can assume that Mg/AlNi - LDH in this case acts as an oxidizing agent, which is activated by light irradiation.

4 Conclusion

Mg/AlNi - LDH was synthesized by co-precipitation in an oxidizing media. Mg/AlNi - LDH is active in the process of Congo red dye destruction under the UV irradiation. The initial rate of the process of the dye destruction under UV light illumination in the presence of Mg/AlNi - LDH is 1.6 times higher than without it. The kinetic data obtained for photodegradation process well pseudo-first-order kinetic model. Using Mg/AlNi – LDH increased photoconversion from 76% (without LDH) to 93 % (with LDH).

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