

## Effect of synthesis conditions on the photocatalytic efficiency of $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ , $\text{NiMn}_2\text{O}_4/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ and $\text{Ni}_6\text{MnO}_8/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ for the degradation of Malachite Green dye under UV-light

K. L. Zaharieva<sup>1\*</sup>, K. I. Milenova<sup>1</sup>, S. S. Dimova<sup>2</sup>, S. V. Vassilev<sup>3</sup>,  
I. D. Stambolova<sup>4</sup>, V. N. Blaskov<sup>4</sup>

<sup>1</sup> Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl. 11, 1113 Sofia, Bulgaria

<sup>2</sup> Institute of Polymers, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl.103A, 1113 Sofia, Bulgaria

<sup>3</sup> Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl. 10, 1113, Sofia, Bulgaria

<sup>4</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl. 11, 1113 Sofia, Bulgaria

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The influence of the type of precursors salts (nitrates or chlorides) and calcination temperatures (450 °C and 650 °C) on the photocatalytic activity of  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ ,  $\text{NiMn}_2\text{O}_4/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  and  $\text{Ni}_6\text{MnO}_8/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  prepared by precipitation was investigated in this study. The synthesized samples were characterized using the Powder X-ray diffraction analysis and Fourier-transform infrared spectroscopy. The photocatalytic efficiency of obtained materials was tested in the reaction of oxidative degradation of Malachite Green dye as model contaminant from aqueous solution under UV illumination. The results established that the degree of degradation of Malachite Green dye after 120 minutes increases in the following order:  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ , 450 °C, chlorides (83%) <  $\text{NiMn}_2\text{O}_4/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ , 650 °C, chlorides (86%) <  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ , 450 °C, nitrates (91%) <  $\text{Ni}_6\text{MnO}_8/\text{NiMnO}_3/\text{Mn}_2\text{O}_3$ , 650 °C, nitrates (97%). The photocatalyst prepared at the higher calcination temperature (650 °C) using nitrate precursors demonstrates the highest photocatalytic efficiency.

**Keywords:** photocatalyst, photocatalytic efficiency, Malachite Green.

### INTRODUCTION

The cotton, paper, pulp, leather, wool industries uses many toxic dyes for coloring their final products. The water discharged effluents of these manufactures containing large amount of organic contaminants, leads to pollution of environment. Malachite green dye is cationic dye, which is widely used all over the world in the textile industry as well as in the fish farming industry as fungicide, ectoparasiticide and disinfectant [1–4]. The existence of pigments and dyes in water causes serious damage to the aquatic environment. The color blocks the sunlight access to aquatic flora and fauna, and it decreases the photosynthetic action within the ecosystem [5]. Heterogeneous photocatalysis is a discipline, which includes a large diversity of reactions:

water detoxification, dehydrogenation, mild or total oxidations, hydrogen transfer,  $\text{O}_2^{18}\text{--O}_2^{16}$  and deuterium-alkane isotopic exchange, metal deposition, gaseous pollutant removal, etc. [6, 7]. Photocatalytic degradation of organic contaminants in water by single metal oxides and oxide compounds has attracted the attention of researchers [8]. T. Larbi et al. have investigated photocatalytic degradation of Methylene blue dye by  $\text{Mn}_3\text{O}_4$ ,  $\text{NiMn}_2\text{O}_4$  and alloys of Ni-Manganates thin films [9].  $\text{NiO}_{0.8}\text{ZnO}_{0.2}/\text{ZnO}$  and  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  materials were tested as photocatalysts for degradation of Malachite Green dye under UV-light [10]. Xiaobo He et al. have been synthesized  $\text{NiMnO}_3/\text{NiMn}_2\text{O}_4$  oxides with the aid of pollen using a two-step annealing method [11]. Spinel nickel manganese oxide with large specific surface area and suitable pore size has been synthesized from an epoxide-driven sol-gel process and followed by thermal treatment [12]. K. Vijaya Sankar et al. have been obtained sub-micron sized polyhedral shaped  $\text{NiMn}_2\text{O}_4$  particles by a gly-

\* To whom all correspondence should be sent:  
E-mail: zaharieva@ic.bas.bg

cine assisted solution combustion method [13]. Murdochite-type Ni<sub>6</sub>MnO<sub>8</sub> with variable specific surface areas has been synthesized by H. Taguchi et al. [14].

The goal of the current work is to study the influence of different precursors (nitrates and chlorides) and calcination temperatures (450 °C and 650 °C) on the photocatalytic properties of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials about degradation of aqueous solution of Malachite Green dye as a model contaminant under UV-light. The tested samples prepared by precipitation and thermally treatment were investigated by Powder X-ray diffraction analysis and Fourier-transform infrared spectroscopy.

## EXPERIMENTAL

### Preparation and investigation

The tested photocatalysts NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> were synthesized by precipitation using 0.25M Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (VWR Prolabo BDH chemicals); 0.25M Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Alfa Aesar); 0.75M NaHCO<sub>3</sub> (Valerus Co.) or 0.25M NiCl<sub>2</sub>·6H<sub>2</sub>O (Valerus Co.); 0.25M MnCl<sub>2</sub>·4H<sub>2</sub>O (Valerus Co.); 0.75M NaOH (Valerus Co.) aqueous solutions. The precipitant NaHCO<sub>3</sub> and NaOH were added dropwise to the mixtures of nitrates or chlorides and at continuous stirring until reaching pH 7 and 12, respectively. The suspension was stirred for one hour after precipitation. The precipitates were filtered and washed with distilled water several times. The obtained precipitates were dried at 35 °C and thermally treated at 450 °C or 650 °C for 3 hours and 30 minutes in air media. The samples obtained by nitrates and calcined at 450 °C and 650 °C were assigned as **MN1** and **MN2** and materials prepared using chlorides and thermally treated at 450 °C and 650 °C – **MC3** and **MC4**.

The Powder X-ray diffraction patterns of the obtained materials were carried out on Philips PW 1050 with Cu K<sub>α</sub>-radiation. The presence of the phases in the prepared materials was determined by the ICDD database. The FT-IR investigations were performed on a Fourier infrared spectrometer Bruker-Vector 22 in the region 400–4000 cm<sup>-1</sup> and using KBr tablets.

### Photocatalytic tests

The photocatalytic activity of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> for the oxidative degradation of 5 ppm aqueous solution of Malachite Green dye was investigated.

The photocatalytic test was performed as 0.15 g catalyst sample and 150 ml of dye solution were put in a semi-batch reactor under constant stirring, air flowing at room temperature. The first experiment was performed in the dark in a period of 30 minutes to achieve adsorption-desorption equilibrium. Second UV lamp with power 18 W and λ<sub>max</sub> 365 nm was turned on and irradiation was carried out for 120 min. To separate the powder from the liquid phase, centrifugation of the samples was performed for a period of 10 minutes. Spectrophotometrically were measured absorption peaks of MG dye – with maximum wavelength at 615 nm using UV-1600PC Spectrophotometer. The degree of degradation of Malachite Green dye was established using dependence:

$$Degradation = \frac{(C_0 - C)}{C_0} 100\%$$

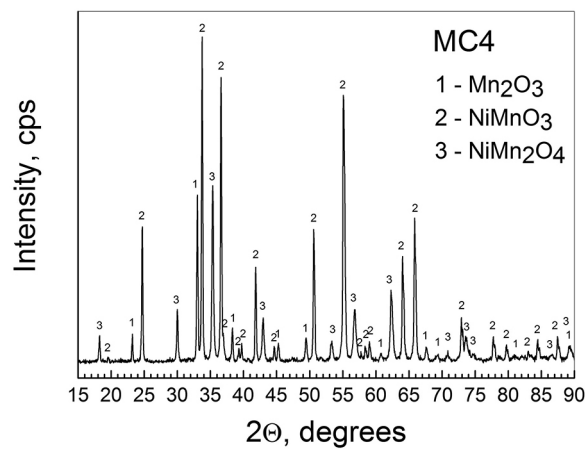
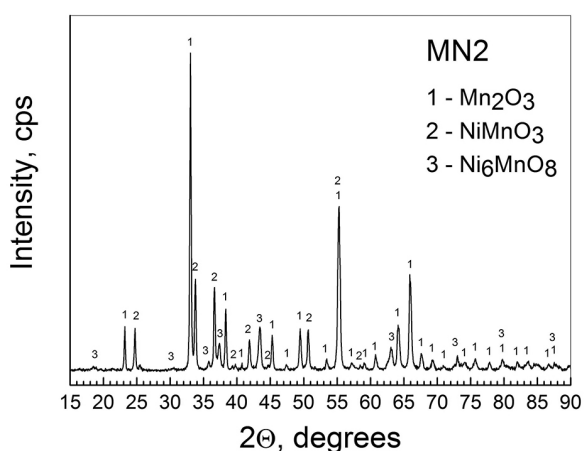
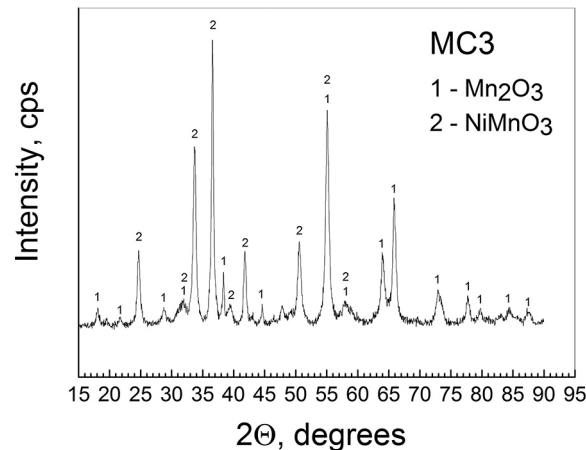
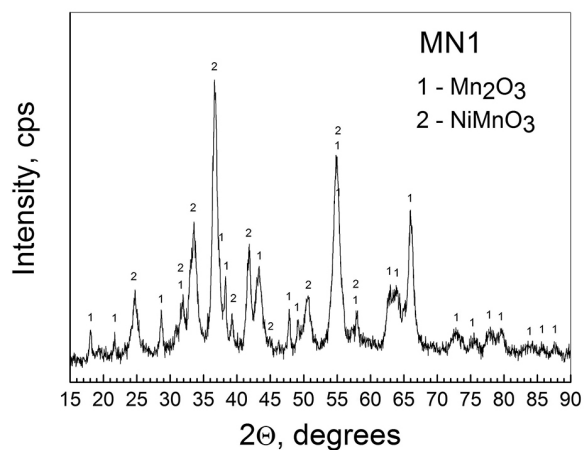
where C<sub>0</sub> and C were initial concentration before turning on the illumination and residual concentration of the dye solution after illumination for selected time interval.

## RESULTS AND DISCUSSION

The Powder X-ray diffraction results (see Figures 1 and 2) show that material prepared using nitrate precursors and thermally treatment at 450 °C contains NiMnO<sub>3</sub> (PDF-653695); Mn<sub>2</sub>O<sub>3</sub> (PDF-721427) and three phases – NiMnO<sub>3</sub> (PDF-895878); Mn<sub>2</sub>O<sub>3</sub> (PDF-651798); Ni<sub>6</sub>MnO<sub>8</sub> (PDF-894619) are established in the sample calcined at 650 °C. The existence of NiMnO<sub>3</sub> (PDF-653695) and Mn<sub>2</sub>O<sub>3</sub> (PDF-721427) are registered in the PXRD pattern of material synthesized using chlorides as starting materials after thermally treatment at 450 °C. The NiMnO<sub>3</sub> (PDF-895878); Mn<sub>2</sub>O<sub>3</sub> (PDF-651798) and NiMn<sub>2</sub>O<sub>4</sub> (PDF-894619) phases are determined in the Powder X-ray diffractogram of sample thermally treated at 650 °C.

FT-IR spectra of prepared materials are shown in the Figure 3. The absorption peaks at around 3440–3442 cm<sup>-1</sup> and 1631–1636 cm<sup>-1</sup> are attributed to the stretching and bending mode of the OH group of absorbed water molecules [15, 16]. It is known that in the region of 400–1000 cm<sup>-1</sup>, the characteristic bands of inorganic solids are usually assigned to the vibration of metallic ions in the crystal lattice [17]. The peaks at about 1195–1198 cm<sup>-1</sup> and 1051–1058 cm<sup>-1</sup> could be assigned of some impurities in the investigated materials.

Photocatalytic degradation of Malachite Green (MG) dye on NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> samples was



**Fig. 1.** PXRD patterns of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials prepared using nitrate precursors.

**Fig. 2.** PXRD patterns of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> samples prepared using chloride precursors.

investigated under UV-light irradiation. Attention is paid to the influence of different calcination temperatures (450 °C and 650 °C) and precursors (chlorides and nitrates) on the photocatalytic properties of **MN1**, **MN2**, **MC3** and **MC4**. Table 1 shows the data for adsorption capacities and apparent rate constants of the studied materials.

The following formula is used for calculation of the adsorption capacities:

$$Q = \frac{(C_0 - C)V}{m}$$

where C<sub>0</sub> and C are the initial and after 30 minutes in the dark concentrations of the dye, V is the volume of the solution and m is the weight of the samples.

The adsorption capacities in ascending order were: **MC3** (0.004 mg/g) < **MN1** (0.041 mg/g) < **MC4** (0.051 mg/g) < **MN2** (0.060 mg/g).

**Table 1.** Calculated adsorption capacities and apparent rate constants (k) of tested photocatalysts

| Sample | Adsorption capacity, mg/g | k (x10 <sup>-3</sup> min <sup>-1</sup> ) |
|--------|---------------------------|--|
| MC3    | 0.004                     | 14.0                                     |
| MC4    | 0.051                     | 5.5                                      |
| MN1    | 0.041                     | 14.9                                     |
| MN2    | 0.060                     | 12.9                                     |

In Table 1 the apparent rate constants of investigated materials were defined as pseudo first-order kinetics by logarithmic linear dependence:

$$-\ln\left(\frac{C}{C_0}\right) = k.t.$$

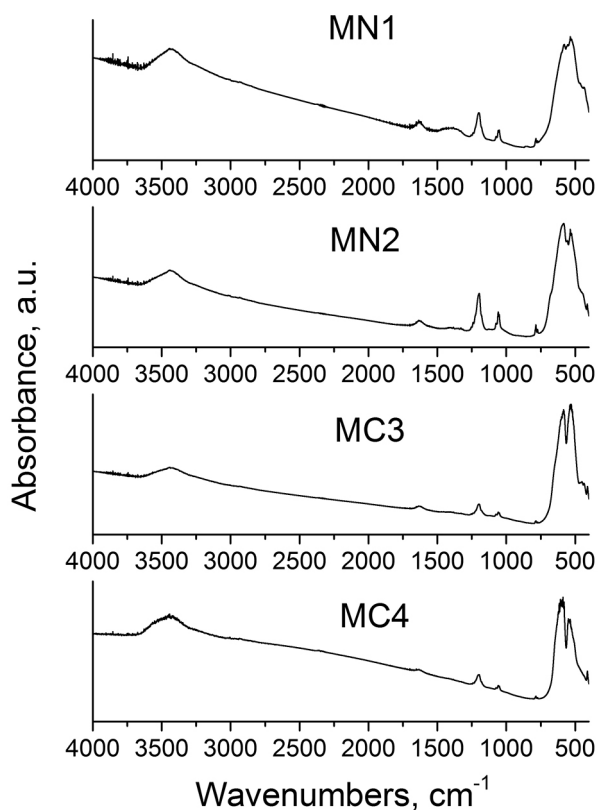


Fig. 3. FT-IR spectra of synthesized materials – MN1; MN2; MC3 and MC4.

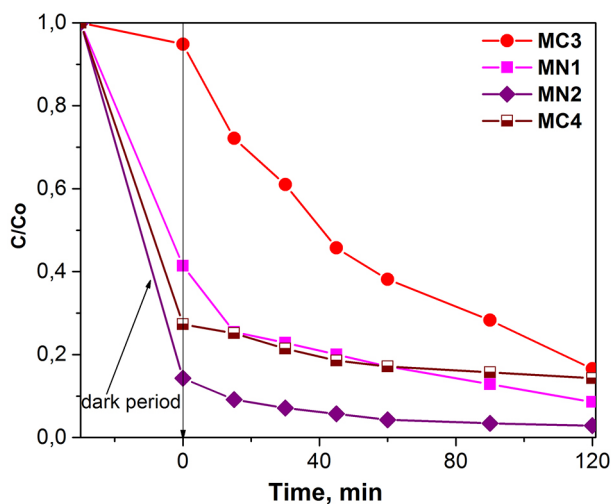


Fig. 4. The concentration ratio  $C/C_0$  of Malachite Green dye as a function of the time of UV illumination.

The lowest value of apparent rate constants was for sample MC4 ( $5.5 \times 10^{-3} \text{ min}^{-1}$ ) until the highest one was MN1, which reached  $14.9 \times 10^{-3} \text{ min}^{-1}$ .

On the Figure 4 are presented the concentration changes  $C/C_0$  of degradation of Malachite Green dye as a function of the time of UV irradiation. The

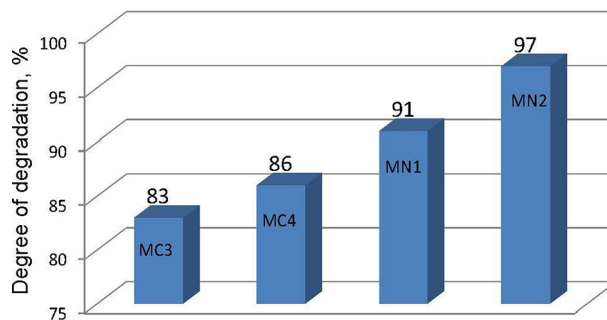


Fig. 5. Degree of degradation of Malachite Green dye after 120 minutes under UV irradiation using prepared photocatalysts – MN1; MN2; MC3 and MC4.

degree of degradation of Malachite Green dye after 120 minutes UV illumination was showed on Figure 5. Samples MN1 (91%) and MN2 (97%) have the best catalytic performance, whereas the degradation degree of MC3 (83%) and MC4 (86%) were lower. The obtained data showed that the used precursor affects the catalytic activity, like the samples from nitrate precursors gave maximum results. The different calcination temperatures have influence on the photocatalytic behavior of the systems under investigation. With increasing of the temperature to 650 °C, the degree of degradation of the dye increases for the samples obtained by both types of precursors.

The authors in [18] reported that the excellent catalytic activity of NiMnO<sub>3</sub> can be attributed to the composite effect of nickel and manganese oxides for the process of visible light-driven water oxidation. NiMn<sub>2</sub>O<sub>4</sub> nanoparticles demonstrated high photocatalytic activity for degradation of Methyl Orange under UV light, due to the proper size distribution of the pores, high hydroxyl amount and high separation rate of charge carriers [19]. The enhancement of oxygen adsorption leading to more available sites for photocatalytic reaction is the reason for the high photocatalytic reactivity of NiMn<sub>2</sub>O<sub>4</sub> films [9]. Other research groups have explained the photocatalytic activity of Mn<sub>2</sub>O<sub>3</sub> towards degradation of Methylene Blue with the d-d transitions involving Mn<sup>2+/4+</sup> ions on the photocatalyst surface [20, 21]. It could be supposed that all these factors play role in the enhanced photocatalytic activity of investigated nickelum-manganite composite powders in the present study.

## CONCLUSIONS

Effect of synthesis conditions on the photocatalytic ability of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/

Mn<sub>2</sub>O<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> about degradation of aqueous solution of Malachite Green dye under UV-light was established in the present study. The photocatalysts prepared using nitrate precursors demonstrate a higher photocatalytic efficiency in comparison with that of the samples synthesized using chlorides. The Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> material obtained from nitrate precursors at higher temperature of thermal treatment (650 °C) exhibits the highest degree of degradation of Malachite Green dye (97%).

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ВЛИЯНИЕ НА УСЛОВИЯТА ЗА СИНТЕЗ ВЪРХУ ФОТОКАТАЛИТИЧНАТА СПОСОБНОСТ НА NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> И Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> ЗА РАЗГРАЖДАНЕТО НА МАЛАХИТОВО ЗЕЛЕНО БАГРИЛО ПОД УВ-СВЕТЛИНА

К. Л. Захариева<sup>1\*</sup>, К. И. Миленова<sup>1</sup>, С. С. Димова<sup>2</sup>, С. В. Василев<sup>3</sup>,  
И. Д. Стамболова<sup>4</sup>, В. Н. Блъсков<sup>4</sup>

<sup>1</sup> *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

<sup>2</sup> *Институт по полимери, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 103А, 1113 София, България*

<sup>3</sup> *Институт по електрохимия и енергийни системи, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 10, 1113 София, България*

<sup>4</sup> *Институт по обща и неорганична химия, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

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(Резюме)

Изследвано е влиянието на типа прекурсори (нитрати или хлориди) и температури на наляване (450 °C и 650 °C) върху фотокаталитичната активност на NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> и Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, получени чрез утаяване. Синтезираните проби бяха охарактеризирани чрез рентгенодифракционен анализ и инфрачервена спектроскопия с Фурие трансформация. Фотокаталитичната способност на получените материали беше тествана в реакцията на окислително разграждане на Малахитово Зелено багрило като моделен замърсител от воден разтвор под UV облъчване. Резултатите установиха, че степента на разграждане на Малахитово Зелено багрило след 120 минути нараства в следния ред: NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, 450 °C, хлориди (83%) < NiMn<sub>2</sub>O<sub>4</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, 650 °C, хлориди (86%) < NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, 450 °C, нитрати (91%) < Ni<sub>6</sub>MnO<sub>8</sub>/NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>, 650 °C, нитрати (97%). Фотокатализаторът, получен при по-висока температура на наляване (650 °C), използвайки прекурсори нитрати, демонстрира най-висока фотокаталитична способност.