

## Preparation and comparative photocatalytic study of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO materials for the removal of Malachite Green dye from aqueous solution

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*Dedicated to Acad. Ivan Juchnovski on the occasion of his 80<sup>th</sup> birthday*

The NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO materials were synthesized by precipitation technique (using different precursors – nitrates or chlorides and sodium hydroxide or sodium bicarbonate as precipitant) followed by calcination at 450°C. The existence of NiMnO<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>, ZnO phases were established in the investigated samples by the powder X-ray diffraction analysis and FT-IR spectroscopy. The photocatalytic activity of prepared NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO samples was tested and compared in the degradation of Malachite Green dye (MG) as model contaminant in aqueous solution under UV-irradiation. The photocatalytic tests determined that the degree of degradation of Malachite Green dye after 120 minutes over the NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> samples (99% and 91%) synthesized using nitrates as starting materials is higher compared with that over materials prepared by chlorides (89% and 83%). The results show that synthesized NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials in this study are promising photocatalysts for removal of MG dye as model pollutant from aqueous solution under UV illumination.

**Key words:** preparation, material, photocatalytic efficiency, degradation, Malachite Green, dye.

### INTRODUCTION

Synthetic dyes find application in industries such as the leather tanning, textile, food technology, paper production, hair colorings, etc. The wastewaters released from these industries are usually contaminated with dyes. Malachite Green is used for the dyeing of cotton, silk, leather, paper as well as in manufacturing of printing and paints inks. Malachite Green is broadly used in distilleries for coloring purposes [1]. Malachite Green has strong effects on the reproductive and immune systems and possesses potential genotoxic and carcinogenic effects. The use of photocatalysts to degrade organic compounds in polluted water or air or to convert them into harmless substances has been widely investigated to decrease the damage bred by organic dye contamination to the people and environment [2]. For example Zn<sub>x</sub>Ni<sub>1-x</sub>O thin films were tested in photodegradation of Methylene

Blue [3]. V. Eskizeybek et al. [4] have studied the photocatalytic properties of PANI homopolymer and PANI/ZnO nanocomposites in the degradation of Methylene Blue and Malachite Green dyes in aqueous medium under natural sunlight and UV light irradiation [4]. L. Saikia et al. [5] have established that the photocatalytic degradation of MG dye by ZnO samples in the form of nanoparticles and flowers were very effective in removal of this dye from aqueous solution [5]. Several research groups have investigated the photocatalytic properties of Mn<sub>2</sub>O<sub>3</sub> composites. The photocatalytic activities of Mn<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> material were studied by photooxidation of Rhodamine B, Thymol Blue, Methyl Orange and Bromocresol Green dyes under visible light [6]. R. Talebi [7] tested the photocatalytic ability of Mn<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanocomposites about the degradation of Methyl Orange under ultraviolet light irradiation [7]. The photocatalytic activity of α-Mn<sub>2</sub>O<sub>3</sub> particles were investigated for photodegradation of the Remazol Red B dye, using a multilamp photo reactor [8]. M.

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Pudukudy and et al. [9] are shown that the Mn<sub>2</sub>O<sub>3</sub> microstructures have a moderate photocatalytic efficiency for the degradation of Methylene Blue dye under UV light irradiation [9]. In [10] the photocatalytic activity of graphene–Mn<sub>2</sub>O<sub>3</sub> nanocomposite about photocatalytic degradation of eosin, methylene blue and rhodamine B was tested [10]. G. Panthi et al. [11] determined that the photocatalytic activity of the Mn<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanofibers was higher than that of TiO<sub>2</sub> nanofibers for the photodegradation of Methylene Blue dye [11]. D. Mehandjiev et al. [12] were prepared and compared the catalytic activity of the ilmenite-type and spinel-type nickel-manganese oxide materials in the reactions of complete oxidation of hydrocarbons [12].

The present study deals with the synthesis, physicochemical characterization and comparative photocatalytic investigations of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials. For that the investigated samples were prepared by precipitation procedure using different starting materials – nitrates or chlorides and NaOH or NaHCO<sub>3</sub> as precipitating agent. The physicochemical properties of prepared materials were investigated by powder X-ray diffraction analysis (PXRD) and infrared (FT-IR) spectroscopy. The photocatalytic efficiency of synthesized NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> samples was tested and compared in the reaction of degradation of Malachite Green dye in aqueous solution under UV illumination. The aim of this study was to investigate the effect of the type of precursors and precipitant on the photocatalytic activity of prepared NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials.

## EXPERIMENTAL

### *Synthesis and physicochemical characterization of the materials*

The NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO samples named as Sample 1 and Sample 2 were prepared by precipitation technique. The Sample 1 and Sample 2 was synthesized using aqueous solutions of 0.25M Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (VWR Prolabo BDH chemicals); 0.25M Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Valerus Co.) (sample 1) and 0.25M NiCl<sub>2</sub>•6H<sub>2</sub>O (Valerus Co.); 0.25M ZnCl<sub>2</sub> (Valerus Co.), (sample 2) mixed in ratio 1:2. The aqueous solutions of used starting materials (nitrates or chlorides) were prepared separately and then mixed. The mixture was stirred for 15 minutes. After that the precipitant - aqueous solution of 0.75M NaOH (Valerus Co.) was added drop by drop in the mixture until pH reached 12 at

continuous stirring. The NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials labeled as Sample 3 and Sample 4 were synthesized by the similar precipitation procedure. Sample 3 was prepared from 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.), while the sample 4 was prepared using 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.). The precipitants NaHCO<sub>3</sub> and NaOH were added in the mixtures of aqueous solutions of nitrate and chloride precursors until pH became 7 and 12 respectively. After precipitation the suspension was stirred for one hour. The precipitates was filtered and washed with distilled water several times to remove the traces of NaOH or NaHCO<sub>3</sub> respectively. The obtained materials were dried at 35 °C. The precipitates were calcined at 450 °C for 3 hours and 30 minutes in air atmosphere. The Powder X-ray diffraction analysis (PXRD) and FT-IR spectroscopy were used to study the phase composition and structure of the synthesized materials. The PXRD analysis of the samples was performed using Philips PW 1050 with Cu K<sub>α</sub>-radiation. The phases were established using the ICDD database. FT-IR spectra of the samples were collected on a Fourier infrared spectrometer Bruker-Vector 22. The prepared materials using KBr tablets were investigated in the 400-4000 cm<sup>-1</sup> range.

### *Photocatalytic tests*

The photocatalytic experiment of degradation of Malachite Green (MG) with initial concentration of aqueous solution of the dye - 5 ppm was carried out under UV-A illumination (18 W). The photocatalytic test was performed in semi-batch slurry reactor using 0.15 g photocatalyst and 150 ml of dye solution under constant stirring and air flowing. To reach adsorption-desorption equilibrium state the studied systems were left in the dark for about 30 min before switching on the UV irradiation for 2 hours. The powder was separated from the aliquot solution by centrifugation (4ml of the suspension). After that the change of absorbance during the photocatalytic tests was monitored by UV-Vis absorbance spectrophotometer UV-1600PC in the wavelength range from 200 to 800 nm ( $\lambda_{\max} = 615$  nm).

The degree of dye degradation was calculated using the dependence:  $(Co-C/Co) \times 100$ , where Co and C were initial concentration of the dye solution before turning on the illumination and residual concentration of the dye solution after illumination for the selected time interval.

## RESULTS AND DISCUSSION

On the Figures 1 and 2 are illustrated the results of the studied samples recorded by powder X-ray diffraction (PXRD) analysis. The presence of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}$  (PDF-750271) and  $\text{ZnO}$  (PDF 897130) phases are registered in the powder X-ray diffraction spectra of the Sample 1 and Sample 2. The PXRD patterns of the Sample 3 and Sample 4

show the existence of the  $\text{NiMnO}_3$  (PDF-653695) and  $\text{Mn}_2\text{O}_3$  (PDF-721427) phases. Figures 3 and 4 presented FT-IR spectra of synthesized  $\text{NiO}_{0.8}\text{ZnO}_{0.2}/\text{ZnO}$  and  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  materials. The absorption bands at around 3440 and 3444  $\text{cm}^{-1}$  can be ascribed to the hydroxyl groups bonded through hydrogen bonds. The peak at wave numbers about 1630  $\text{cm}^{-1}$  corresponds to the adsorbed molecular  $\text{H}_2\text{O}$  [8].

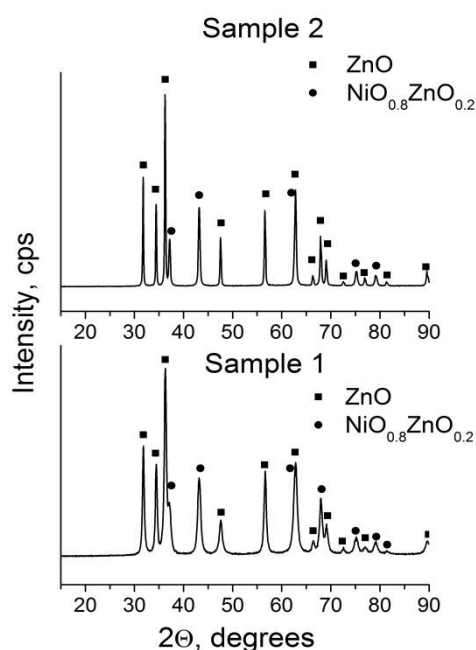


Fig. 1. PXRD patterns of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}/\text{ZnO}$  materials.

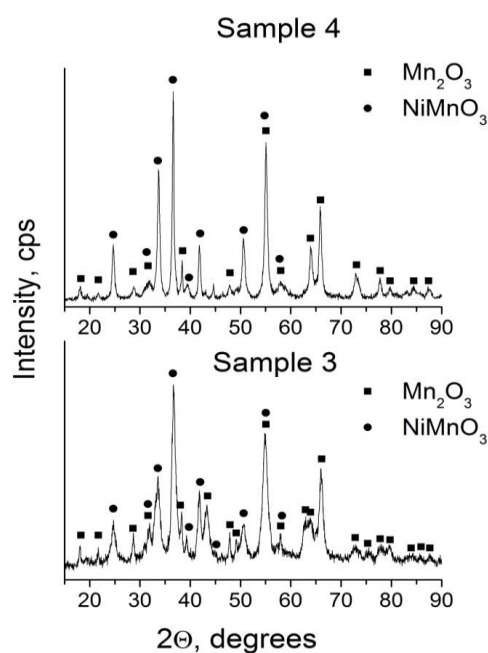


Fig. 2. PXRD patterns of  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  materials.

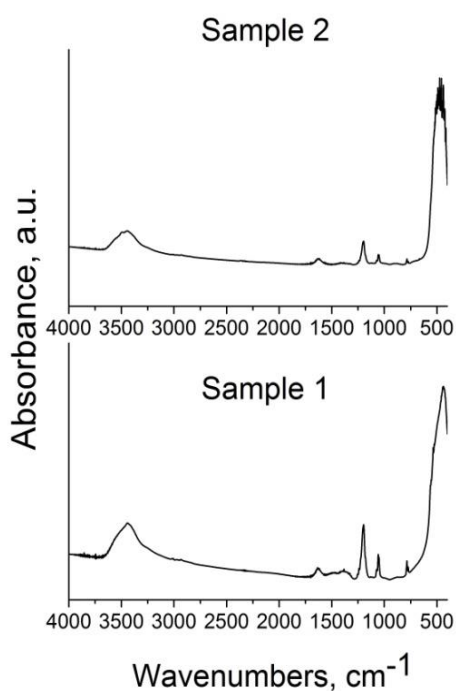


Fig. 3. FT-IR spectra of  $\text{NiO}_{0.8}\text{ZnO}_{0.2}/\text{ZnO}$  materials.

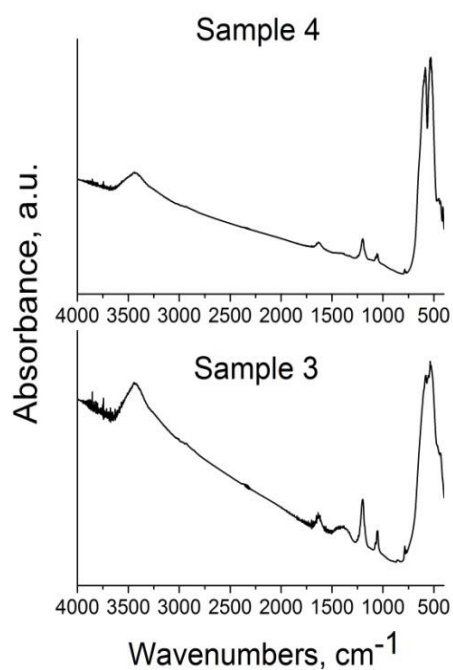


Fig. 4. FT-IR spectra of  $\text{NiMnO}_3/\text{Mn}_2\text{O}_3$  materials.

The results indicate that catalysts are hydrated. In the region 400-800 cm<sup>-1</sup> are usually the vibration of metallic ion in the crystal lattice. Two main broad M-O bands are seen in the spectra of normal spinels. The highest peak at around 550 cm<sup>-1</sup> attributed to the stretching vibration of the metal ion at the tetrahedral site (ν(M-O)) [13]. In the infrared spectra of Sample 3 and 4 are seen the lowest band observed in the range 450-490 cm<sup>-1</sup> (NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub>) is octahedral metal ion stretching [13]. The appearance of the two bands in the range of 400-1000 cm<sup>-1</sup> shows the presence of mixed oxides. The peaks at about 1191, 1200 and 1051 cm<sup>-1</sup> could be assigned to the others admixtures in the studied samples [14-16]. The data obtained by FT-IR spectroscopy are in agreement with the results established by PXRD.

In presented study is discussed the degradation of Malachite Green dye as model pollutant under UV irradiation using synthesized NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> as photocatalysts.

The equation (1) was used to calculate the adsorption capacities of investigated samples:

$$Q = \frac{(C_0 - C) \cdot V}{m} \quad (1)$$

where  $C_0$  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 photocatalyst.

The adsorption capacities give the following order: Sample 4 (0.004 mg/g) < Sample 3 (0.041mg/g) < Sample 2 (0.044mg/g) < Sample 1 (0.051mg/g). As can be seen the NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO material prepared by nitrate precursors shows the highest adsorption capacity in comparison with these of the others samples.

The degradation of Malachite Green dye with time of UV-A illumination is presented on Figure 5.

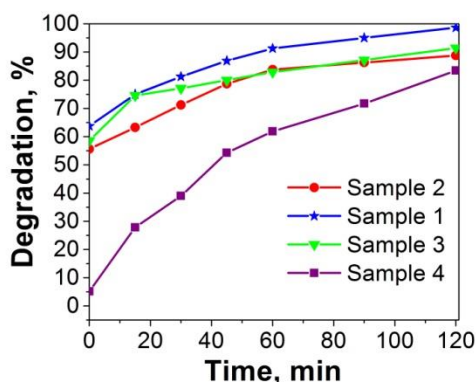


Fig. 5. Degree of degradation of MG dye as a function of the time of UV illumination.

The degree of degradation on Sample 1 (99%) and Sample 2 (89%) was higher in comparison with Sample 3 (91%) and Sample 4 (83%). The catalysts prepared from nitrates possessed better photocatalytic activity than those from chloride precursors. The highest photocatalytic efficiency about degradation of Malachite Green dye is determined for NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO obtained by nitrate precursors.

The apparent rate constants of investigated photocatalysts (Figure 6) were calculated using logarithmic linear dependence  $-\ln(C/C_0) = k \cdot t$ . They followed the pseudo first-order kinetics. NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> samples have demonstrated almost equally rate constants values, no matter of used precursors.

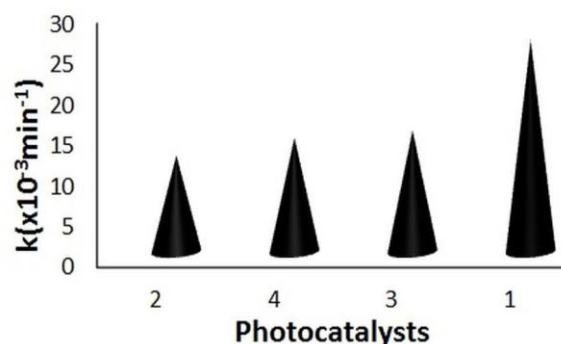


Fig. 6. Comparison data of apparent rate constants of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> photocatalysts in degradation of MG dye.

Unlike apparent rate constant of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO prepared by nitrates increased twice in comparison of this of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO obtained by chlorides.

## CONCLUSION

The precipitation technique followed by calcination in air media at 450°C for 3 hours and 30 minutes was successfully used for the synthesis of NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO samples. The NiMnO<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>, ZnO phases were determined in the prepared materials using PXRD analysis and FT-IR spectroscopy. The impact of the different precursors on the photocatalytic properties of the prepared samples was found. The photocatalytic activity of NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO and NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> materials prepared using nitrates as starting materials is higher than that of the samples synthesized by chlorides. The synthesized NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> and NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO powdery materials exhibit high degree of degradation of the MG dye (83%-99%)

and can be potential photocatalysts for removal of MG from contaminated waters under UV irradiation.

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## REFERENCES

1. B. H. Hameed, M. I. El-Khaiary, *J. Hazard. Mater.*, **154**, 237 (2008).
2. E. S. Baeissa, *J. Alloy. Compd.*, **672**, 564 (2016).
3. R. Dridi, M. BenAmor, N. Mahdhi, A. Amlouk, K. Boubaker, M. Amlouk, *J. Non. Cryst. Solids*, **449**, 1 (2016).
4. V. Eskizeybek, F. Sari, H. Gulce, A. Gulce, A. Avci, *Appl. Catal. B*, **119–120**, 197 (2012).
5. L. Saikia, D. Bhuyan, M. Saikia, B. Malakar, D.K. Dutta, P. Sengupta, *Appl. Catal. A*, **490**, 42 (2015).
6. T. K. Ghorai, S. Pramanik, P. Pramanik, *Appl. Surf. Sci.*, **255**, 9026 (2009).
7. R. Talebi, *J. Mater. Sci.: Mater Electron*, **28**, 8316 (2017).
8. S. Gnanam, V. Rajendran, *J. Alloy. Compd.*, **550**, 463 (2013).
9. M. Pudukudy, Z. Yaakob, *J. Nanopart.*, **2016**, 7 pages (2016).
10. S. Chandra, P. Das, S. Bag, R. Bhar, P. Pramanik, *Mat. Sci. Engin. B*, **177**, 855 (2012).
11. G. Panthi, A. Yousef, N.A.M.Barakat, K. A. Khalil, S. Akhter, Y.R.Choi, H.Y.Kim, *Ceram. Internat.*, **39**, 2239 (2013).
12. D. Mehandjiev, E. Zhecheva, G. Ivanov, R. Ioncheva, *Appl. Catal. A*, **167**, 277 (1998).
13. H. Kumar, Manisha and P. Sangwan, *Internat. J. Chem. Chem. Engin.*, **3**, 155 (2013).
14. D. Mehandjiev, A. Naydenov, G. Ivanov, *Appl. Catal. A*, **206**, 13 (2001).
15. F. Kovanda, T. Grygar, V. Dorničák, *Solid State Sci.*, **5**, 1019 (2003).
16. R. Y. Hong, J. H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, J. Ding, *Powd. Technol.*, **189**, 426 (2009).

## ПОЛУЧАВАНЕ И СРАВНИТЕЛНО ФОТОКАТАЛИТИЧНО ИЗСЛЕДВАНЕ НА NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> И NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO МАТЕРИАЛИ ЗА ПРЕМАХВАНЕ НА МАЛАХИТОВО ЗЕЛЕНО БАГРИЛО ОТ ВОДЕН РАЗТВОР

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(Резюме)

NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> и NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO материали бяха синтезирани чрез утаяване (използвайки различни прекурсори – нитрати или хлориди и натриев хидроксид или натриев хидрогенкарбонат като утаител) последвано от наляване при 450°C. Съществуването на NiMnO<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> и NiO<sub>0.8</sub>ZnO<sub>0.2</sub>, ZnO фази беше установено в изследваните проби посредством рентгенофазов анализ и инфрачервена спектроскопия с фурие трансформация. Фотокаталитичната активност на получените NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> и NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO проби беше тествана и сравнена в разграждането на Малахитово Зелено багрило (МЗ) като моделен замърсител във воден разтвор под действието на УВ облъчване. Фотокаталитичните тестове установиха, че степента на разграждане на Малахитово Зелено багрило след 120 минути с NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO и NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> проби (99% и 91%) синтезирани използвайки нитрати като изходни материали е по-висока сравнена с тази при материалите получени от хлориди (89% и 83%). Резултатите показват, че синтезираните NiO<sub>0.8</sub>ZnO<sub>0.2</sub>/ZnO и NiMnO<sub>3</sub>/Mn<sub>2</sub>O<sub>3</sub> материали в това изследване са обещаващи фотокатализатори за премахване на Малахитово Зелено багрило като моделен замърсител във воден разтвор под действието на УВ светлина.