

NICKEL FERRITE-ACTIVATED CARBON MATERIALS – PREPARATION AND PHOTOCATALYTIC EFFICIENCY FOR CLEANING OF MALACHITE GREEN AND REACTIVE BLACK 5 DYES UNDER UV-ILLUMINATION

НИКЕЛОВ ФЕРИТ-АКТИВЕН ВЪГЛЕН МАТЕРИАЛИ – ПОЛУЧАВАНЕ И ФОТОКАТАЛИТИЧНА ЕФЕКТИВНОСТ ЗА ОЧИСТВАНЕ НА МАЛАХИТОВО ЗЕЛЕНО И РЕАКТИВНО ЧЕРНО 5 БАГРИЛА ПОД УВ ОБЛЪЧВАНЕ

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Abstract: Nickel ferrites having different stoichiometry supported on activated carbon ($Ni_{0.25}Fe_{2.75}O_4$ -AC, $Ni_{0.5}Fe_{2.5}O_4$ -AC, $NiFe_2O_4$ -AC) were prepared by co-precipitation using nitrate precursors and activated carbon from peach stones and calcination procedure in nitrogen atmosphere. The physicochemical properties of these materials were studied by powder X-ray diffraction analysis (PXRD) and Mössbauer spectroscopy. The presence of spinel ferrite and additional hematite phases was established by PXRD. The photocatalytic properties of the so synthesized nickel ferrite-AC materials were tested and compared in oxidative degradation of Malachite Green (MG) and Reactive Black 5 (RB5) dyes under UV-light irradiation. The photocatalytic tests show that investigated samples lead to much higher degree of degradation of MG (86%-92%) compared with that of RB5 (17%-35%) due to their structure. The results proved that nickel ferrite-AC materials are more efficient photocatalysts for removal of MG as model contaminant from aqueous solution under UV light than RB5.

Keywords: NICKEL FERRITES-AC, MALACHITE GREEN, REACTIVE BLACK 5, PHOTOCATALYTIC DEGRADATION

1. Introduction

The development of efficient methods to reduce environmental contamination is of great practical importance. The heterogeneous photocatalysis is an outstanding method for purification of polluted waters [1]. Hazardous organic compounds are among the major factors of environmental pollution, especially in water media [2]. Synthetic dyes find wide application for coloring purposes in leather, textile, printing, food, cosmetic and plastic industries [3]. The water contamination caused by dyes is posing a problem throughout the world. Colour is the first aspect to be recognised in wastewater [4]. Spinel ferrites MFe_2O_4 , $M = Ni, Mg, Ca, Co$ have narrow band gaps (~2.0 eV), magnetic separability, and chemical stabilities so their nanoparticles could be potentially applied as photocatalysts for decontamination of environment because of their superiority in complete utilization of natural sunlight [5,6]. The application of magnetic semiconductor nanoparticles for treatment of polluted waters is attractive research field. Nickel ferrites with general formula (AB_2O_4) are among the most versatile magnetic materials due to the high Curie temperature, high saturation magnetization, chemical stability and relatively high permeability [7]. The use of activated carbons as materials for the photocatalysts' support shows many advantages because of the high specific surface areas, easy control of the surface chemistry and excellent adsorption capacity for organic compounds, high porosity and ability for recovering of active metal phase by burning the carbon support. The oxidative degradation rate under UV-light illumination is enhanced due to the porosity of the carbon feeding desorbed pollutant molecules to the photocatalytically active sites, suggesting also possible own photoactivity of the carbon support [8].

The nanosized composite $NiFe_2O_4$ /active carbon has already been used to remove Alizarine Yellow R and Methyl Orange azo dyes, from water [9]. The adsorption property of AC/ $NiFe_2O_4$ magnetic composite was investigated with respect to Methyl Orange dye in ref. [10]. Another research group used the AC- $NiFe_2O_4$ as photo-Fenton catalyst for photo-Fenton degradations of Methylene Blue, Rhodamine B and Malachite Green as model pollutants, carried out in the presence of oxalic acid under $\lambda > 400$ nm visible light [11]. Zhao et al. [12] determined that $NiFe_2O_4$ -graphene

possesses significantly enhanced photocatalytic activity for the degradation of Methylene Blue under illumination of artificially simulated sunlight compared to bare $NiFe_2O_4$ nanoparticles. Photocatalytic activity of $NiFe_2O_4$ /MWCNTs hybrids has been studied in the photocatalytic decolorization of Congo Red in aqueous solution under simulated solar light irradiation in ref. [13]. The multi-walled carbon nanotubes CNTs and $NiFe_2O_4$ -MWCNTs were efficient adsorbents for the removal of Methylene Blue from polluted water [14]. The high photoactivity of $NiFe_2O_4$ /MWNT was established in the degradation of phenol and nitrophenols (o-nitrophenol, p-nitrophenol and picric acid) under UV light [15]. Ikenaga and coworkers determined that investigated activated carbon-supported ferrite had ten times higher hydrogen sulfide absorption rate than that of the ferrite prepared by the dry process [16]. The adsorptive ability of fly ash/ $NiFe_2O_4$ composites has been tested for removal of Congo Red dye from an aqueous solution by the authors [17]. Singh et al. [18] showed that cobalt-doped nickel ferrite/MWCNTs nanocomposites demonstrated a significant catalytic activity in the photo-Fenton process in the degradation of Rhodamine B dye, which completely degraded the dye molecule in 15–25 min. The photocatalytic activity of nickel ferrite samples $Ni_xFe_{3-x}O_4$ ($0 \leq x \leq 1$) in the degradation of Malachite Green dye under UV irradiation was discussed in previous investigations [19].

The present paper is focused on the synthesis, physicochemical and photocatalytic properties of nickel ferrite-activated carbon materials having different compositions in the degradation of aqueous Malachite Green and Reactive Black 5 dyes under UV light.

2. Experimental

2.1. Synthesis of the nickel ferrite-activated carbon samples

The nickel ferrite-activated carbon (AC) materials having different compositions $Ni_{0.25}Fe_{2.75}O_4$ -AC, $Ni_{0.5}Fe_{2.5}O_4$ -AC and $NiFe_2O_4$ -AC (denoted as S1, S2 and S3) were synthesized by the co-precipitation technique. The starting aqueous solutions of 0.03M $Ni(NO_3)_2 \cdot 6H_2O$ (VWR Prolabo BDH chemicals) and

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar) were mixed at a preset ratio. After that 2g of activated carbon were added to the mixture. The carbon was produced from peach stones (supplied by Laboratory for "Chemistry of Solid Fuels" at the Institute of Organic Chemistry with Centre of Phytochemistry). The 0.3M NaOH solution (Valerus Co.) was used as precipitant by adding it dropwise slowly into the mixture upon continuous stirring. The addition of precipitating agent was discontinued at $\text{pH} = 12.5$ and then the mixture was continuously stirred for one more hour. The so synthesized materials were then centrifuged and washed with distilled water until neutral reaction medium ($\text{pH}=7$) was reached. Further the obtained precipitates were dried at 110°C for 3 hour in air media. The co-precipitated samples were thermally treated at 400°C for 3 hours and 30 minutes in inert nitrogen atmosphere.

2.2. Powder X-ray diffraction analysis (PXRD)

The powder X-ray diffraction analysis was carried out on a Bruker D2 Phaser diffractometer within the range of 2θ values between 5° and 65° using Cu K_α radiation ($\lambda = 0.154056 \text{ nm}$) at 40 kV. The present phases were identified by using of JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997).

2.3. Mössbauer spectroscopy

The Mössbauer measurements were performed on apparatus Wissenschaftliche Elektronik GmbH, working at a constant acceleration mode, $^{57}\text{Co}/\text{Rh}$ source (activity $\approx 50 \text{ mCi}$) and $\alpha\text{-Fe}$ standard. The parameters of hyperfine interactions of Mössbauer spectral components: isomeric shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the sites of iron nuclei (H_{eff}), line widths (FWHM) and component relative weights (G) were calculated by computer fitting.

2.4. Photocatalytic investigations

The photocatalytic degradation of Malachite Green (MG) and Reactive Black 5 (RB5) dyes under UV-light irradiation was studied using obtained nickel ferrite/AC materials as photocatalysts. The photocatalytic experiments were carried out using polychromatic UV-A lamp illumination (18W) with maximum emission at 365 nm and illumination intensity $2.6 \text{ mW}/\text{cm}^2$. The reaction course was followed by UV-Vis spectrophotometer CamSpec M501. The aqueous solutions of Malachite Green ($\lambda_{\text{max}}=615 \text{ nm}$) and Reactive Black 5 ($\lambda_{\text{max}}=599 \text{ nm}$) dyes were with initial concentration 5 ppm and 20 ppm respectively. In order to establish adsorption equilibrium in system, the dye solution and photocatalyst were stirred in the dark for 30 min without any UV illumination. A semi-batch suspension photocatalytic reactor was equipped with two frits blowing tiny bubbles of air in order to saturate the solution in dissolved oxygen. The photocatalytic tests were carried at a constant stirring rate (400 rpm) under ambient conditions. The measurement of the photocatalytic efficiency of nickel ferrite – AC samples was performed by taking aliquot samples of the suspension out of the reaction vessel after regular time intervals. The powder was then separated from the aliquot solution by centrifugation before the UV-Vis spectrophotometric evaluation of the dye concentration, based on previous calibration. After that, the aliquot solution, together with the photocatalyst powder, were returned back into the reaction vessel, which ensured operation under constant volume and catalyst amount. The degree of degradation is estimated using dependence $(C_0 - C)/C_0 \times 100$, where C_0 and C are respectively initial concentration before turning on the illumination and residual concentration of the dye solution after illumination in the course of given time interval.

3. Results and discussions

Figure 1 represents the Powder X-ray diffraction patterns of the obtained calcined nickel ferrite – activated carbon materials showing the characteristic reflexes of non-stoichiometric and stoichiometric spinel nickel ferrite phase (PDF-86-2267; PDF-75-0449) and activated carbon also. The presence of additional hematite phase (PDF-89-0599) is registered in all thermally treated nickel ferrite-AC samples.

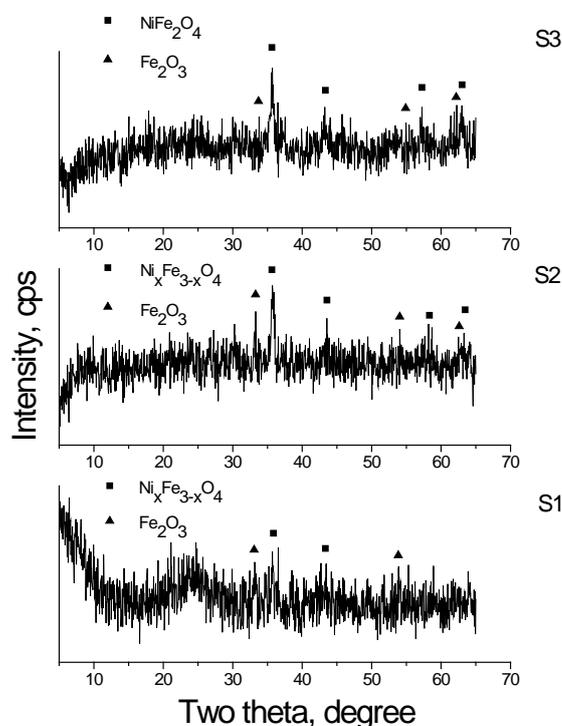


Fig. 1 PXRD patterns of nickel ferrite-AC photocatalysts after calcination.

The recorded room temperature Mössbauer spectra of thermally treated nickel ferrite-AC samples are displayed in Figure 2. The Mössbauer spectra of prepared materials represent a superposition of the sextet and superparamagnetic doublet components. The sextet-type components could be assigned to the presence of spinel ferrite and hematite phases [20].

The photocatalytic activities of the investigated samples were measured using two hazardous textile dyes - Reactive Black 5 (RB5) and Malachite Green (MG) as model pollutants. Figure 3 is illustrating the reaction course of both dyes degradation in solution under UV-A illumination over the investigated photocatalysts. The adsorption capacities of samples S1, S2 and S3 towards model pollutant MG dye are higher than those for RB5 dye, which is probably due to the amino groups in MG reacting readily with acidic sites on the surface of the photocatalysts. After half an hour in the dark the UV lamp was switch on and the photocatalytic degradation is started. The rate of oxidative discoloration reaction of studied powders regarding the RB5 dye is lower than MG dye, which can be attributed to the higher stability of RB5 molecule having a much larger conjugated system of single and double bonds.

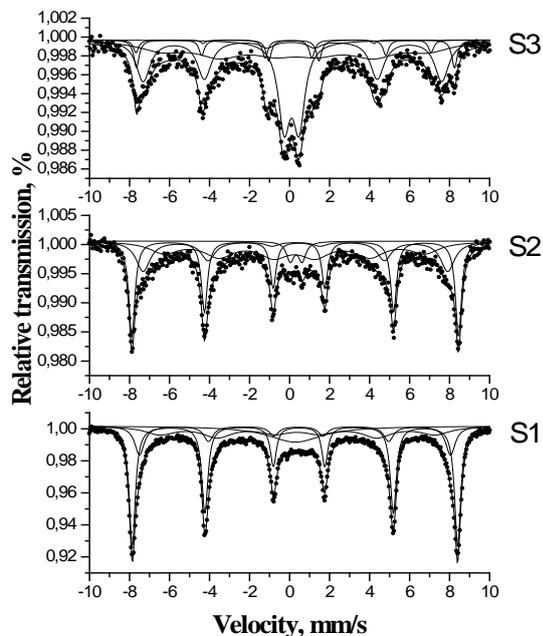


Fig. 2 Mössbauer spectra of calcined nickel ferrite-AC photocatalysts.

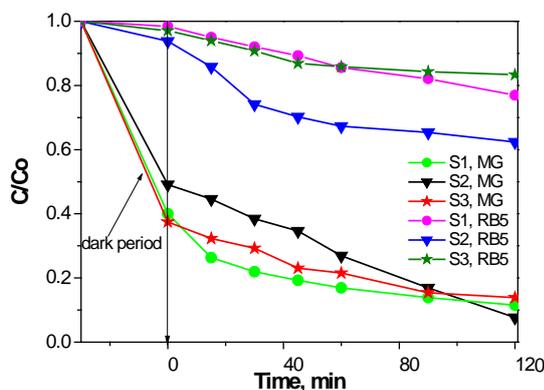


Fig. 3 Concentration changes of tested dyes based on changes in the intensity of the maximal absorbance peak at 599 nm for RB5 dye and at 615 nm for MG dye respectively, with the course of time.

Figure 4 shows degree of degradation of the dyes after 120 min under UV-A illumination over investigated photocatalysts. MG degradation conversion degrees of photocatalytic systems: S1, S2 and S3 are in the range 86÷92%, while they degrade weaker RB5 dye (17÷35 %).

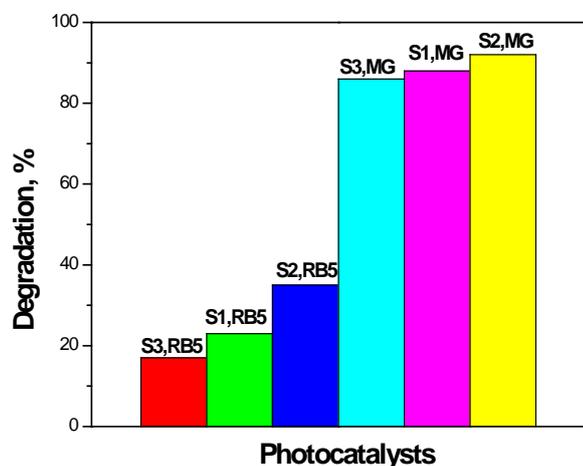


Fig. 4 Degradation degrees of investigated dyes: RB5 and MG using prepared nickel ferrite-AC photocatalysts.

Table 1 lists the rate constants and degradation conversion degrees of studied catalysts in the degradation of MG and RB5 dyes after 120 min work. Rate constants were calculated using the equation $-\ln(C/C_0) = kt$ on the basis of the slope of the linear logarithmic function. The degradation apparent rate constants (pseudo first order kinetics) decreased in the order: S2, MG ($15.1 \times 10^{-3} \text{ min}^{-1}$) > S1, MG ($9.1 \times 10^{-3} \text{ min}^{-1}$) > S3, MG ($8.7 \times 10^{-3} \text{ min}^{-1}$) > S2, RB5 ($3.2 \times 10^{-3} \text{ min}^{-1}$) > S1, RB5 ($2 \times 10^{-3} \text{ min}^{-1}$) > S3, RB5 ($1.3 \times 10^{-3} \text{ min}^{-1}$).

Zhu et al. [13] proposed the possible mechanism of the dye degradation on NiFe₂O₄/carbon tubes composites. Firstly the dye molecules were adsorbed on the surface of NiFe₂O₄/carbon nanotubes composite. Secondly, electrons in the valence band of NiFe₂O₄ can become excited to its conduction band under light irradiation, causing the photoproduced holes in the valence of NiFe₂O₄ simultaneously. The photoproduced electrons are able to quickly migrate towards the surface of carbon tubes because of the matching between the energy level of NiFe₂O₄ and carbon tubes and the chance of recombination of electrons and holes is greatly reduced. This could be explanation of promising photocatalytic activity of the NiFe₂O₄/AC composites.

The photocatalytic performances and mechanism of dye degradation of the samples in the oxidative degradation of specific classes of dyes were influenced by some factors such as chemical composition, the morphology, degree of crystallinity, crystallites size etc. The functional groups of the dyes have also to be taken into account as well as the acidity/basicity of the photocatalyst surface.

Table 1: Rate constants and degradation conversion degrees for MG and RB5 of investigated nickel ferrite-AC photocatalysts.

Samples	$k \times 10^{-3}, \text{ min}^{-1}$	Degradation, %
S2, MG	15.1	92
S1, MG	9.1	88
S3, MG	8.7	86
S2, RB5	3.2	35
S1, RB5	2	23
S3, RB5	1.3	17

4. Conclusions

The nickel ferrite-AC photocatalysts were prepared by co-precipitation and calcination in inert atmosphere. The physicochemical characterization of the so synthesized samples by PXRD analysis and Mössbauer spectroscopy proved the existence of nickel ferrite and hematite as additional phase. Comparatively study of photocatalytic efficiency of the investigated materials confirmed the easier degradation of MG over RB5 dye in aqueous media. The tested photocatalyst Ni_{0.5}Fe_{2.5}O₄-AC demonstrates the highest degree of degradation of MG (92%) and RB5 (35%) dyes compared to these over the other samples. The studies can be continued and extended further in the direction of involving TOC analysis of the total organic carbon in the decolorized solution thus evaluating not only the degree of discoloration but also the degree of total oxidation, which could shed some light on the different behavior of the two dyes. The present results determined that synthesized nickel ferrite-AC materials could be appropriate photocatalysts for removing of MG as contaminant from aqueous media.

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References

- [1] Matos, J., J. Laine, J.-M. Herrmann. Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania. *Journal of Catalysis*, 200, 2001, 10-20.
- [2] Velasco, L. F., J. B. Parra, C. O. Ania. Role of activated carbon features on the photocatalytic degradation of phenol. *Applied Surface Science*, 256, 2010, 5254–5258.
- [3] Sonar, S. K., P. S. Niphadkar, S. Mayadevi, P. N. Joshi. Preparation and characterization of porous fly ash/NiFe₂O₄ composite: Promising adsorbent for the removal of Congo red dye from aqueous solution. *Materials Chemistry and Physics*, 148, 2014, 371-379.
- [4] Patil, M. R., V. S. Shrivastava. Adsorption of malachite green by polyaniline–nickel ferrite magnetic nanocomposite: an isotherm and kinetic study. *Appl Nanosci.*, 5, 2015, 809–816.
- [5] He, H.-Y., Photocatalytic degradations of Malachite Green on magnetically separable Ni_{1-x}Co_xFe₂O₄ nanoparticles synthesized by using a hydrothermal process. *American Chemical Science Journal*, 6 (1), 2015, 58-68.
- [6] Zhang, D., X. Pu, K. Du, Young Moon Yu, Jae Jeong Shim, P. Cai, Sun Il Kim, Hyo Jin Seo. Combustion synthesis of magnetic Ag/NiFe₂O₄ composites with enhanced visible-light photocatalytic properties. *Separation and Purification Technology*, 137, 2014, 82–85.
- [7] Moeinpour, F., A. Alimoradi, M. Kazemi. Efficient removal of Eriochrome black-T from aqueous solution using NiFe₂O₄ magnetic nanoparticles. *Journal of Environmental Health Science & Engineering*, 12 (1), 2014, 112.
- [8] Kadirova, Z. C., Ken-ichi Katsumata, T. Isobe, N. Matsushita, A. Nakajima, K. Okada. Adsorption and photodegradation of methylene blue by iron oxide impregnated on granular activated carbons in an oxalate solution. *Applied Surface Science*, 284, 2013, 72–79.
- [9] Ranjeh, G., M. Radmanesh, A. Kiafar. Nanosized NiFe₂O₄/Active Carbon composite as adsorbent for azo dyes and colours. *Science Journal of Chemistry*, 3(2), 2015, 28-34.
- [10] Jiang, T., Yao-dong Liang, Yong-jun He, Qing Wang. Activated carbon/NiFe₂O₄ magnetic composite: A magnetic adsorbent for the adsorption of methyl orange. *Journal of Environmental Chemical Engineering*, 3, 2015, 1740–1751.
- [11] Lianrong, F., Hu Fengtian, Liu Chengbao, Chen Feng, Xu Nan, Liu Shouqing, Chen Zhigang. Photocatalytic properties of Activated Carbon-NiFe₂O₄ magnetic catalyst. *Chin. J. Catal.*, 33 (8), 2012, 1417–1422.
- [12] Zhao, D. F., H. Yang, R. S. Li, J. Y. Ma, W. J. Feng. Fabrication of nickel ferrite–graphene nanocomposites and their photocatalytic properties. *Materials Research Innovations*, 18 (7), 2014, 519-523.
- [13] Zhu, H.-Y., R. Jiang, S.-H. Huang, J. Yao, F.-Q. Fu, J.-B. Li. Novel magnetic NiFe₂O₄/multi-walled carbon nanotubes hybrids: Facile synthesis, characterization, and application to the treatment of dyeing wastewater. *Ceramics International*, 41, 2015, 11625–11631.
- [14] Bahgat, M., Ahmed Ali Farghali, Waleed El Roubi, Mohamed Khedr, Mohassab Y. Mohassab-Ahmed. Adsorption of methyl green dye onto multi-walled carbon nanotubes decorated with Ni nanoferrite. *Appl Nanosci.*, 3, 2013, 251–261.
- [15] Xiong, P., Y. Fu, L. Wang, X. Wang. Multi-walled carbon nanotubes supported nickel ferrite: A magnetically recyclable photocatalyst with high photocatalytic activity on degradation of phenols. *Chemical Engineering Journal*, 195–196, 2012, 149–157.
- [16] Ikenaga, Na-oki, N. Chiyoda, H. Matsushima, T. Suzuki. Preparation of activated carbon-supported ferrite for absorbent of hydrogen sulfide at a low temperature. *Fuel* 81,2002, 1569–1576.
- [17] Sonar, S. K., P. S. Niphadkar, S. Mayadevi, P. N. Joshi. Preparation and characterization of porous fly ash/NiFe₂O₄ composite: Promising adsorbent for the removal of Congo red dye from aqueous solution. *Materials Chemistry and Physics*, 148, 2014, 371-379.
- [18] Singh, C., S. Bansal, V. Kumar, S. Singhal. Beading of cobalt substituted nickel ferrite nanoparticles on the surface of carbon nanotubes: a study of their synthesis mechanism, structure, magnetic, optical and their application as photocatalyst. *Ceramics International*, 41, 2015, 3595–3604.
- [19] Cherkezova-Zheleva, Z., K. Zaharieva, M. Tsvetkov, V. Petkova, M. Milanova, I. Mitov. Impact of preparation method and chemical composition on physicochemical and photocatalytic properties of nano-dimensional magnetite-type materials. *American Mineralogist*, 100, 2015, 1257–1264.
- [20] Schwertmann, U., R. Cornell, *Iron Oxides in the Laboratory*, Weinheim, New York-Basel-Cambridge, 1991.