Photodegradation of Methylene Blue Dye Using A Novel Nanoscale Photocatalyst Based on Nickel and Titanium Complexes With 2,3-Dihydroxybenzoic Acid

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Methylene blue dye (MB) is a common water pollutant as it is widely used in various industries, primarily textile. This compound is poisonous, carcinogenic, poorly biodegradable and a serious hazard to human health and environment. Currently, degradation using nanoscale photocatalysts is supposed to be a promising approach to water purification. Titanium dioxide (TiO_2) is one of the most attractive photocatalysts, but it is activated only when irradiated with ultraviolet light. The development of (TiO_2)-based photocatalysts functioning under visible light is a relevant research field, as it will allow for efficient use of sunlight. Our study aimed at producing a (TiO_2)-based photocatalyst, which is active under visible light, by including a transition metal (Ni) in its composition. To meet green chemistry requirements, complexes of Ti and Ni with 2,3-dihydroxybenzoic acid (DHBA) were used as precursors. Synthesis of nanoscale nickel titanate ($NiTiO_3$) included the production of Ti and Ni complexes with DHBA followed by their precipitation, collection by filtering, mixing the obtained powders, and calcination in muffle furnace at 560°C to get nickel titanate nanoparticles. The ($NiTiO_3$) formation was confirmed by X-ray diffraction (XRD) analysis. To confirm the photocatalytic activity, the MB decomposition in the presence of the obtained nanoparticles was evaluated. The results show that the use of ($NiTiO_3$) has reduced the MB concentration from 6.83 μM to 4.82 μM in 48 hours, i.e. by 30%.

Keywords: water contamination, methylene blue, 2,3-dihydroxybenzoic acid, nickel titanate, photodegradation

Introduction

Water is the most important resource necessary for a person to maintain life. The fast development of the economy coupled with irresponsible human actions has resulted in a variety of pollutants entering natural waters with a negatively environmental effect. One of the most common types of pollutants are organic dyes[1], which are compounds with high water solubility, making water purification by conventional methods ineffective[2]. Organic dyes have a harmful effect on aquatic organisms by reducing the light transmission of water and thereby reducing the metabolic rate and water oxygen level[3]. Methylene blue dye (MB, Figure 1) is a representative of this class of compounds, and is widely used in various industries, primarily textile[2,4]. It is poisonous, carcinogenic, poorly biodegradable, is a health risk with a negative impact on the ecosystem. Ingestion of MS can lead to serious disorders including vomiting, nausea, anemia and high blood pressure[5].

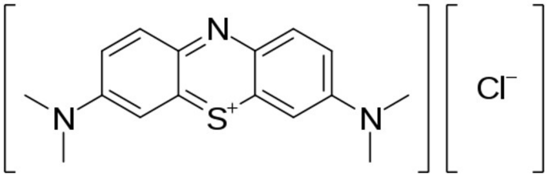

Fig. 1 Methylene blue structure.

Various purification processes are used to remove dyes from the contaminated water, such as oxidation, coagulation, filtration, ozonation, reverse osmosis processes, ion exchange, electrochemical decomposition, adsorption, and photodegradation[2]. Currently, photodegradation is one of the most promising methods, and the possibility of using inexpensive renewable energy is its advantage. Among various methods of photocatalysis, the use of nanoscale photocatalysts is very much in focus as the dye adsorbs on the active site of the catalyst, and in turn converts it to carbon dioxide and water[4]. The degradation efficiency of the photocatalysts reaches the maximum when the target dye is effectively adsorbed on the surface of the photocatalyst, therefore, nanoscale catalysts look particularly promising[4].

Due to its chemical inertia, high stability over a wide pH range, compatibility with other materials, rather low cost and environmental friendliness, titanium dioxide (TiO_2) is one of the most attractive photocatalysts[6]. However, it is activated only when irradiated with ultraviolet light, which accounts for only a small proportion (∼5%) of the solar radiation compared to the visible region (∼45%)[6]. Therefore, the development of TiO_2-based photocatalysts functioning under visible light is a relevant research field, as it will allow for an effective use of sunlight. Various approaches are used to impart the photocatalytic activity of TiO_2 in the visible range, in particular, introducing transition metals in its structure[7]. For example, it has been shown that nickel titanate ($NiTiO_3$) is an effective photocatalyst for the MB decomposition under visible light[8]. However, the method of $NiTiO_3$ synthesis proposed by the authors[8] was based on the use of inorganic compounds of titanium chloride ($TiCl_4$) and nickel nitrate ($Ni(NO_3)_2$) as starting reagents, requiring a long synthesis procedure and high energy consumption. In addition, $TiCl_4$ is a poisonous liquid, which is boiling in the air at room temperature. Thus, developing a safe and less energy-consuming method for obtaining a nanoscale $NiTiO_3$ photocatalyst is relevant. A possible solution to this problem is the use of Ti and Ni complexes based on natural organic compounds as precursors.

The purpose of the study was to evaluate the possibility of obtaining nanoscale $NiTiO_3$ particles with photocatalytic activity in the visible range of the spectrum based on Ti and Ni complexes with a natural organic compound – 2,3-dihydroxybenzoic acid (DHBA, Figure 2).

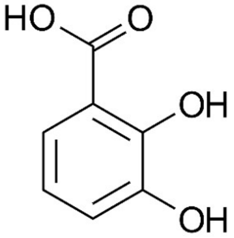

Fig. 2 2,3-dihydroxybenzoic acid (DHBA) structure.

The choice of DHBA was due to its high prevalence in various living organisms, including plants and animals, as well as the fact that DHBA is not classified as either acute toxic or hazardous substance to the aquatic environment[9]. To meet this purpose, the synthesis of Ni and Ti compounds with DHBA followed by production of nanoscale nickel titanate $NiTiO_3$ and verification of its photocatalytic activity with respect to MB have been conducted.

Methods

Synthesis of nanoscale $NiTiO_3$ included the production of Ti and Ni complexes with DHBA followed by their precipitation, collection by filtering, drying, mixing powders, and calcination in muffle furnace at 560°C to get nickel titanate nanoparticles. Synthesis of Ti and Ni complexes with DHBA was performed at room temperature. The $NiTiO_3$formation was confirmed by X-ray diffraction (XRD) analysis. To confirm the photocatalytic activity, the decomposition of MB in the presence of the obtained nanoparticles was evaluated.

Preparation of Ni-DHBA Complex

DHBA is characterized by pronounced chelating properties and can act as a diprotonic ligand of a salicylate (COO–, ortho-O–) or catecholate (ortho-O–, meta-O–) type[9]. Though DHBA is known to effectively chelate Fe^{3+}, Al_{3+}, Mn^{3+}, Cu^{2+} and Cd^{2+}[10], relatively little is known about the complexation of divalent transition metal ions such as Ni^{2+}[9]. Therefore, at the first stage, conditions for obtaining a complex of DHBA with Ni were selected, namely, the optimal ratio of DHBA to Ni. To do this, 60 μL of 0.05M NaOH was added to 5 ml of 0.05M DHBA solution in 50% ethyl alcohol solution to convert DHBA into a deprotonated form. Then the electronic spectrum of the obtained DHBA solution was taken in the ultraviolet (UV) range on a Cary 50 spectrophotometer and a wavelength corresponding to the maximum absorption of the acid acting as a ligand (A_L) was determined. Next, aliquots of 0.05M $NiCl_2$ solution in 50% ethyl alcohol solution were added dropwise to the solution in increments of 20 μL under constant stirring at room temperature. The duration of time between the introductions of an aliquot of the Ni solution was about 1-2 minutes. The formation of a complex of DHBA with Ni was confirmed by the shift of the maximum spectrum absorption to the long–wavelength region. A decrease in the concentration of free DHBA was monitored by a decrease in A_L. Based on the data obtained, the dependence of A_L on the volume of the added $NiCl_2$ solution was plotted. In the plot obtained the inflection point corresponded to the equivalence point, when further addition of the metal did not lead to additional formation of its complexes with DHBA. The inflection point was found by constructing tangents to the two sections of the graph. Based on the established volume of $NiCl_2$ solution and its concentration, the ratio of ligand to metal salt n required to obtain the complex was calculated:

$$n = \frac{C_L \cdot V_L}{C_{Ni} \cdot V_{Ni}}$$

where CNi and CL are the concentration of Ni and DHBA solution, respectively, M; V_{Ni} and V_L are the volume of Ni and DHBA solution, respectively, L.

Then the Ni complex with DHBA was obtained at the ratio determined in the experiments described above. The resulting complex was designated as $Ni(C_7H_6O_4)$.

Additionally, the conditions under which it is possible to obtain a stable Ni complex with DHBA were determined. For this purpose, a comparative potentiometric titration of DHBA and its complex with Ni 0.05M NaOH was performed, assuming that the interaction of the metal with the diproton ligand should be accompanied by the solution acidification due to the replacement of protons in the structure of DHBA with Ni.

Preparation of Ti-DHBA Complex

Titanium tetrabutoxide (TBT, Figure 3) was chosen as the initial compound of Ti.

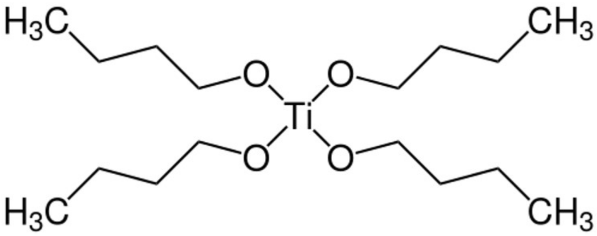

Fig. 3 Titanium tetrabutoxide (TBT) structure.

In an aqueous environment, it is easily hydrolyzed to form titanium oxide and butyl alcohol. Hydrolysis proceeds very quickly with the formation of a dense polydisperse residue, which may further interfere with the production of nanoparticles by thermal degradation; chelating agents are introduced into the reaction mixture to slow down this process[11]. In our work, we used DHBA as a ligand, assuming that 2 moles of DHBA are needed to form a complex per 1 mole of metal. To obtain the complex, TBT was mixed with a solution of DHBA with stirring at room temperature, and the stirring was continued for another hour; the resulting complex was further designated as $Ti(C7H6O_4)_2$.

Production of $NiTiO_3$ Nanoparticles

For the synthesis of $NiTiO_3$ nanoparticles, gels of DHBA complexes with Ni and Ti were obtained by heating solutions of the complexes to a temperature of 100 °C for 1 hour and leaving it in the room temperature for 1 week. The formed precipitate was separated by filtration through a blue-ribbon filter and dried on a filter at a temperature of 120 °C for 2 hours. Next, the air-dry mass of the obtained complexes was determined as the difference between the mass of filters with precipitate and the mass of filters. The precipitate was detached from the filter using a glass spatula and a mixture of $Ni(C_7H_6O_4) : Ti(C_7H_6O_4)_2$ was prepared in a ratio of 1 : 2 (wt.). The resulting mixture was ground in a ceramic mortar using a ceramic pestle. After that, the crushed precipitate was placed in a muffle furnace for 1.5 hours at a temperature of 560 °C. The production of nanoscale particles during thermal decomposition was due to the formation of a large amount of gas during the DHBA decomposition:

$$Ti(C_7H_6O_4)_2 + Ni(C_7H_6O_4) + 21O_2 \rightarrow NiTiO_3 + 21CO_2 + 9H_2O$$

To confirm the composition of the obtained photocatalyst, XRD analysis was performed.

Assessment of photocatalytic activity of $NiTiO_3$ nanoparticles. After obtaining the nanoscale photocatalyst $NiTiO_3$, its effectiveness for the MB decomposition was tested. To do so, 0.85 mg of the resulting photocatalyst was added to 200 mL of MB at a concentration of 6.83 μM giving catalyst concentration 4.25 mg/L The suspension was left at room temperature under natural light conditions without any additional light irradiation source. The change in the concentration of MB was evaluated spectrophotometrically after 30 minutes and after 48 hours at a wavelength of 668 nm corresponding to the MB maximum absorption. The MB concentration was calculated based on the values of the MB molar absorption coefficient which is 266,885 L/(mol×cm). The blank reaction was carried out following the same procedure without adding catalyst. The experiment was performed in triplicate. Data presented as an average ± standard deviation.

Results

Analysis of the electronic spectrum of DHBA showed that in the UV region the maximum absorption is observed at 305 nm (Figure 4), which corresponds to the previously published data[12]. When $NiCl_2$ solution was added, a gradual shift of the maximum in the electronic absorption spectra to the long-wavelength region occurred, suggesting the formation of a complex compound of DHBA with Ni.

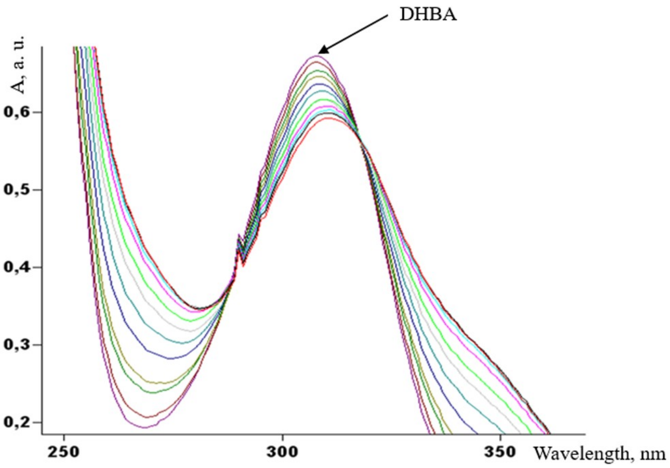

Fig. 4 Electronic absorption spectra of DHBA and its complexes with Ni with different amounts of metal added. The gradual shift of the maximum in the spectra to the long-wavelength region corresponds to an increase in the amount of added Ni solution.

The construction of the absorption dependence at 305 nm (AL) on the amount of Ni introduced (Figure 5) showed that a gradual decrease in$A_L$is replaced by a plateau. Determination of the equivalence point using formula (1) made it possible to establish that the required volume of $NiCl_2$ equals to 151 μL, while the optimal ratio of DHBA to Ni is 1 : 1. Therefore, the calculated ratio of the components was used for further experiments.

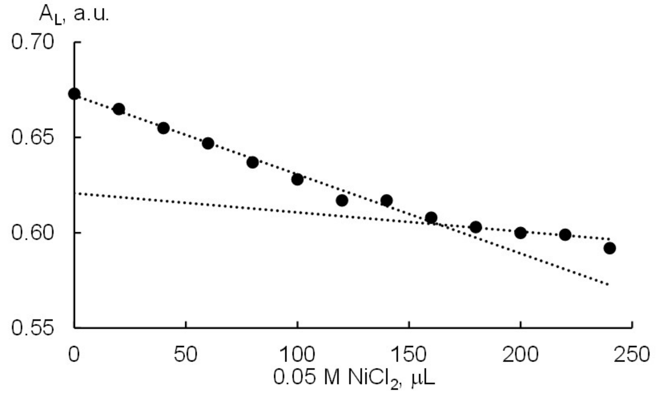

Fig. 5 Dependence of the absorption of$A_L$solution of DHBA with Ni on the amount of metal introduced: determination of the equivalence point.

Assessment of the $Ni(C_7H_6O_4)$ complex stability by potentiometric titration showed that in the entire range studied, pH of its solutions was lower than pH of DHBA (Figure 6) due to the replacement of protons in DHBA with metal ions. The results obtained allow us to conclude that the resulting $Ni(C_7H_6O_4)$ complex is stable in a wide pH range, at least in the 4-11 range.

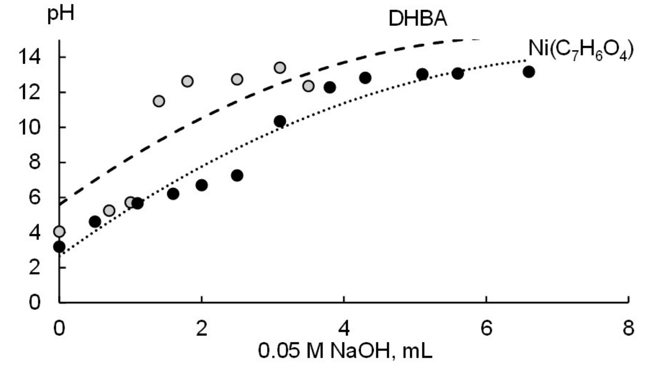

Fig. 6 Potentiometric titration of $Ni(C_7H_6O_4)$ and DHBA solutions.

The mass of $Ni(C_7H_6O_4)$ and $Ti(C7H6O_4)_2$ complexes equaled to 0.075 g and 0.155 g, respectively; the mass of $NiTiO_3$ after calcination was 0.230 g. The XRD analysis of the obtained nanoparticles (Figure 7) showed peaks corresponding to $NiTiO_3$ and TiO_2.

Assessment of the photocatalytic activity of the obtained nanoparticles showed that a decrease in the intensity of the MB color was observed as early as 30 minutes after their application; after 48 hours, the discoloration became even more pronounced.

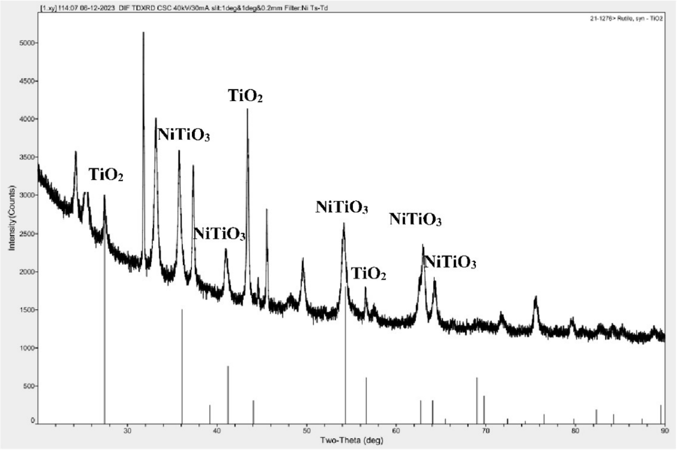

Fig. 7 Diffractogram of the synthetized nanoparticles.

Absorption of MB solutions at 668 nm was confirmed by visual observations. As the calculations show, the use of $NiTiO_3$ reduce the MB concentration from 6.83 μM to (6.62 $\pm$ 0.08) μM and (4.82 $\pm$0.05) μM in 30 minutes and 48 hours, respectively, i.e. by 3% and 30%. No decrease in the intensity of the MB color was detected in the control solution without photocatalyst addition, indicating that there is no self-photolysis of MB dye.

Discussion

The conducted study shows that the complexes of DHBA with nickel and titanium are promising precursors for the production of nickel titanate with photocatalytic activity. It is established that the formation of complexes of DHBA with Ni proceeds effectively at the DHBA to Ni ratio of 1 : 1 and in a wide pH range, at least from 4 to 7. Calcination of a mixture of $Ni(C_7H_6O_4)$ and $Ti(C_7H_6O_4)_2$ complexes at a ratio of 1 : 2 for 1.5 hours at a temperature of 560 °C has made it possible to obtain $NiTiO_3$ nanoparticles with an admixture of TiO_2. The presence of TiO_2 in the mixture after calcination in the obtained nanoparticles may be due to incomplete binding of Ti to complexes with DHBA, resulting in a rapid hydrolysis of TBT to form TiO_2. In addition, presence of TiO_2 in the obtained nanoparticles could also be explained by the calcination conditions not being sufficient to eliminate all the TiO_2. However, verification of these assumption requires additional research on optimizing production of $Ti(C_7H_6O_4)_2$.

Photodegradation efficiency increased with the increasing time of reaction. Although an MB dye degradation efficiency of only 3% was after 30 minutes, it achieved 30% after 48 hours. The obtained results agreed with the previously published data on gradually increased MB photodegradation from the lowest value after 15 minutes of catalyst immersion into MB solution to the greatest one after about 150 minutes[2]. It should be noted, however, that the MB degradation rate, calculated as a ratio of the amount of decomposed dye to the time of reation, decreased from 0.42 to 0.04 μMol of MB per hour. Considering a relatively high residual concentration of MB at the end of the degradation experiment, this might be indicative for instability of catalyst under prolonged irradiation. So, an established fact needs to be addressed in further investigations aiming assessment the long-term performance and practical applicability of the photocatalyst synthetized.

The ability of the obtained nanoparticles to decompose MB by 30% in 48 hours has been demonstrated. Similar photocatalytic activity was previously shown for $NiTiO_3$ with respect to methylene orange[7]. Taking into account the absence of additional lighting sources during photodegradation, the results obtained suggest a good photocatalytic activity of the synthesized $NiTiO_3$ nanoparticles in the visible range of the spectrum.

Shu and co-authors, however, reported significantly greater degradation efficiency of $NiTiO_3$ nanoparticles in relation to MB[8]. The degradation percentages of MB after 6 hours reached 73%. Overall, the reported values for MB photodegradation varied from 63 to 100% depending used TiO_2-based catalyst and conditions of experiments[13]. The higher photodegradation rate was probably due to a significantly higher concentration of the catalyst used. For example, in work[8] with a similar initial concentration of MB (10 μM), the concentration of the $NiTiO_3$ was 300 mg/L, i.e. 70 times higher than in our experiment (4.25 mg/L). In other studies, the concentration of TiO_2-based catalyst varied from 300 to 5000 mg/L[13]. The amount of the dose used in the photocatalytic reaction may enhance the efficacy of breaking down the pollutants as a result of the good dispersion of the catalyst in the aqueous medium or aggregation, which leads to an increase or decrease in the absorption of photons through the surface area exposed to light. Abd El Khalk and co-authors demonstrated the removal of the MB dye was improved from 35 to 77% using the doses of 0.02 and 0.12 g (corresponded to 20 and 120 mg/L, respectively) of the zeolitic imidazolate framework (ZIF)-8-dot catalyst[2]. In addition, the photocatalytic reaction in[8] was performed under the visible light irradiation source (a 125-W fluorescent mercury lamp), whereas in our work, degradation occurred only under the effect of daylight.

Along with dose of catalyst and irradiation intensity, other important factors affecting degradation efficiency should be also considered such as MB concentration and solution pH[2]. Increasing the dye concentration led to a reduction in the photocatalytic activity due to the increase in the area covered of the catalyst's surface (surface saturation)[14]. The pH, in its turn, affects the charge distribution on the photocatalyst's surface and affects the electrostatic interactions between the MB dye and the surface of the photocatalyst. Therefore, it is important to determine the pH range at which the high dye decomposition efficiency occurs[15].

Finally, the performance of the photocatalytical activity of nanoparticles is very dependent on the synthesis method as it determines appropriate size and nanophase structure[4]. In this study the obtained nanocatalyst was $NiTiO_3$ nanoparticles with an admixture of TiO_2, and the latter could reduce photocatalytical activity under visible light because it is activated only when irradiated with ultraviolet light[6]. In addition, a number of studies have shown that catalytic activity of nanoparticles depends on their size and their shape[16], which were not controlled in our work. On the whole, the analysis of our results indicates necessity of further studies of the obtained catalyst, which should be aimed both at optimizing the process of catalyst synthesis and at determining the conditions for its most effective use. Our study has clearly demonstrated the possibility of producing a nanoscale photocatalyst based on nickel and titanium complexes with 2,3-dihydroxybenzoic acid. Future research directions should be focused on finding optimal ways to synthesize and use $NiTiO_3$ as catalyst. On the other hand, the issue of determining the decomposition products of MB and their impact on the environment is also of a great importance.

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