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Investigations of abiotic and biotic materials based on iron oxyhydroxides for photocatalytic decolourization of dyes in aqueous solutions

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Photocatalytic ability of abiotic and biotic materials was investigated in the reaction of decolourization of Methylene Blue and Malachite Green dyes under UV illumination. Tests were carried out with aqueous solution of studied dyes at a concentration of 5 ppm. Biotic material containing lepidocrocite was synthesized by cultivation of *Leptothrix* genus of bacteria in a *Sphaerotilus-Leptothrix* group bacteria isolation medium (ICCL). A reference abiotic sample was prepared in a sterile ICCL not infected by bacteria. Photocatalytic efficiency of examined materials was compared with lepidocrocite synthesized by precipitation. Abiotic, biotic, and synthesized materials were studied by infrared spectroscopy. The biotic material demonstrated a higher photocatalytic activity in Methylene Blue dye decolourization than abiotic sample. In contrast, a higher decolourization degree for Malachite Green dye (83%) was determined using abiotic material in comparison with a biotic sample (70%). Synthesized lepidocrocite demonstrated a higher degree of decolourization of Malachite Green dye (89%) in comparison with that of Methylene Blue dye for the same period of 120 minutes.

Key words: photocatalytic discolouration, Malachite Green, Methylene Blue, lepidocrocite, biogenic material.

INTRODUCTION

In the field of heterogeneous catalysis, materials synthesis by biogenic or biomorphic methods may provide promising resources. Biogenically obtained iron oxyhydroxides and iron oxides have been attractive objects in view of their catalytic application. Interesting subjects of study have been iron oxyhydroxides produced by *Leptothrix sp*. *Leptothrix* is a filamentous bacterium and its sheath can be coated with iron oxyhydroxide or analogous manganese compounds [1].

Water is very important for life and the presence of undesirable chemical components leads to its pollution and makes it unsuitable for use by living organisms. Industrial effluents containing dyes and going into aquatic ecosystems cause environmental pollution. Dyes may induce harmful effects on plants and animals [2–5]. Photocatalytic oxidation is an efficient method for removal of various contaminants [6].

Using photocatalytic oxidation of Fe(II) in the presence of traces of citric acid Chen *et al*. have synthesized Lepidocrocite (γ-FeOOH) under visible light illumination [7]. The obtained low-crystalline γ-FeOOH was easily dissolved in aqueous solution and demonstrated high ability for degradation of Orange II dye by homogeneous photo-Fenton reaction [7]. Jelle *et al.* have prepared and investigated the relationship among goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and feroxyhyte (δ-FeOOH) and their photocatalytic properties for degradation of Methylene Blue dye under visible light irradiation [8]. Chen *et al.* have studied adsorption and degradation of Rhodamine B dye during lepidocrocite formation by air oxidation of $Fe(OH)_2$ under visible light illumination in the presence of trace ethylenediaminetetracetic acid (EDTA) [9]. Sheydaei *et al.* have prepared nanosized lepidocrocite using iron(II) sulphate solution. These authors reported that optimum adsorption conditions of Lanacron Brown S-GL dye (LBS-GL) removal from aqueous solution involved lepidocrocite dosage of 0.015 g, pH 3.5, temperature of 38 °C, and contact time of 100 min [10]. Lin *et al.* have obtained lepidocrocites by aerial oxidation using a ferrous solution under different LED visible light in the presence of trace EDTA. Catalytic studies have shown the ability of lepidocrocite about decolourization of Crystal Violet dye with traces of H_2O_2 under visible light illumination [11].

Many researchers have yet synthesized lepidocrocite using $FeCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, and other salts by different techniques [12-16]. Ristić *et al.* synthesized γ-FeOOH, α-FeOOH, and α-Fe_2O_3 by hydrolysis of Fe^{3+} ions in aqueous solution of perchlorate [17].

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The present work deals with investigations of photocatalytic efficiency of abiotic and biotic iron-containing substances obtained in sterile medium and infected ICCL medium by *Leptothrix* bacteria, respectively. Particularly synthesized lepidocrocite activity is reported for photocatalytic decolourization of model pollutants as Malachite Green and Methylene Blue dyes under UV illumination.

EXPERIMENTAL

Biogenic material was synthesized by cultivation of *Leptothrix* genus of bacteria in a *Sphaerotilus-Leptothrix* group bacteria isolation medium (ICCL). A reference abiotic sample (AR) was prepared in a bacteria-uninfected sterile ICCL. The medium contained glucose, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, K_2HPO_4, $MgSO_4$, KCl, $CaCO_3$, vitamin B12, and vitamin B1. An abiotic (synthetic) material (AS) was prepared using a modified procedure described elsewhere [12, 14–16] by precipitation technique from 0.05M aqueous solution of $FeCl_2 \cdot 4H_2O$ (Sigma Aldrich, p.a.) and 0.8M NaOH (Valerus Co.) as precipitating agent. NaOH was added to reach pH = 6. After that, the mixture underwent continuous stirring in air flow for three hours. The precipitate was filtered and washed with distilled water several times and dried in air at room temperature.

Infrared (IR) spectra of the samples were collected on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) using dilution of studied material (0.5%) in a KBr pellet. The spectra were recorded in the middle IR range using 50 scans at a resolution of 4 (data spacing 1.928 cm^{-1}).

The photocatalytic study concerned oxidative decolourization of model pollutants Malachite Green (MG) and Methylene Blue (MB) dyes under UV light for 2 hours. Initial dye concentration in aqueous solution was 5 ppm. A semi-batch slurry reactor containing 150 ml of dye solution was used for tests under constant air flow and stirring. The amount of used catalyst was 0.15 g for biogenic and synthetic (AS) materials and 0.12 g for abiotic reference material. Examined systems were left in the dark for about 30 min in order to reach adsorption-desorption equilibrium. Periodically, after different time intervals of UV illumination, 4 ml of the investigated suspension were taken out of the reactor and centrifuged to separate the powder from the aliquot solution. Absorbance of aliquot solutions during the photocatalytic tests was monitored by UV-1600PC UV-Vis absorbance spectrophotometer in the wavelength range from 200 to 800 nm. Dye concentrations C_0 and C were evaluated from the calibration lines of the absorbance maxima (615 and 664 nm of MG and MB). Dye decolourization degree was determined following a decrease of absorbance maximum at 615 and 664 nm of MG and MB dye, respectively.

RESULTS AND DISCUSSION

Infrared spectra of abiotic and biotic Fe-containing materials are displayed in figure 1. The bands of lepidocrocite (γ-FeOOH) observed in the region 459–3228 cm^{-1} [9,10,15,17] are marked as 'γ'. The bands at about 3400 and 1631 cm^{-1} are due to stretching vibrations of H-bonded OH groups and bending vibrations of physisorbed water molecules, respectively [15]. The band registered at about 1401 cm^{-1} could be attributed to some components of ICCL medium in which the abiotic reference (AR) and biotic materials were obtained. The vibrations at about 1384 and 1976 cm^{-1} could be assigned to impurities obtained during synthesis of lepidocrocite (AS).

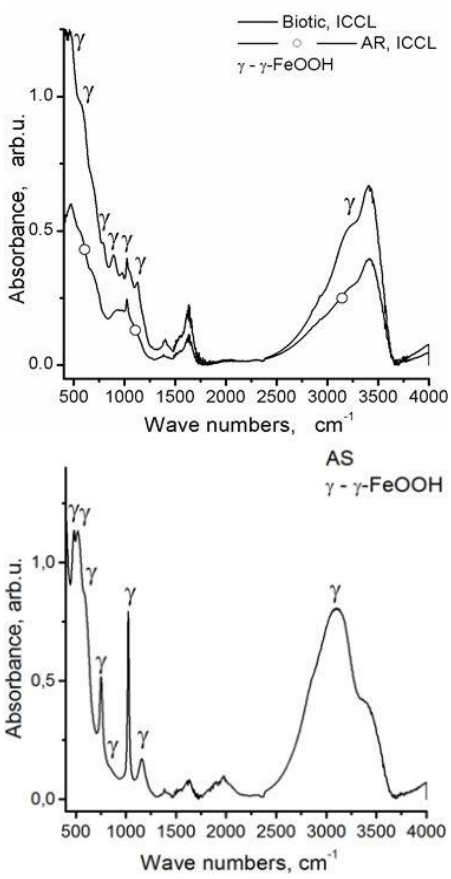

Fig. 1. IR spectra of biotic and abiotic Fe-containing materials.

Photocatalytic ability of biotic, synthetic lepidocrocite (AS), and abiotic control material (AR) was tested in UV-light decolourization of aqueous solution of two model pollutants, Malachite Green (MG) and Methylene Blue (MB), which are used as

textile dyes. Adsorption capacities, apparent rate constants of investigated reaction, and decolourization degree of MG and MB dyes are presented in table 1.

Adsorption capacity of the materials was calculated using the formula (1):

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

where C_0 is initial dye concentration, C is dye concentration after 30 min in the dark, V is solution volume, and m is sample mass. The abiotic reference material (AR) possessed the highest adsorption capacity for both MB and MG dyes – 0.335 and 0.269 mg/g, respectively.

Table 1. Calculated adsorption capacities, apparent rate constants of abiotic and biotic materials, and decolourization degree of MG and MB dyes.

Material	Used dye	Adsorption capacity, (mg/g)	Rate constant k ($x10^{-3}$ min^{-1})*	Degree of decolourization, (%)
abiotic (AR), ICCL	MB	0.335	-	-
abiotic (AR), ICCL	MG	0.269	12.8	83
biotic, ICCL	MB	0.266	-	-
abiotic (AS)	MB	0.215	-	-
biotic, ICCL	MG	0.018	10.1	70
abiotic (AS)	MG	0.027	10.7	89

*Apparent rate constant (k) calculated from slope of logarithmic linear dependence until UV irradiation time 60 minutes.

Concentration changes of MG and MB dyes and decolourization degree with the time under UV irradiation using abiotic and biotic Fe-containing samples are displayed in figures 2 and 3, respectively. The results definitely show that all studied materials were not active in decolourization of Methylene Blue dye. Kinetic curves show that the activity of the materials for decolourization of Malachite Green is not high. Bearing in mind these results, the apparent rate constants (Table 1) of the photocatalytic process with studied materials were estimated using logarithmic linear dependence only for the decolourization of MG dye:

$$-ln(C/C_0) = k.t \quad (2)$$

A clearly lower rate constant of the MG decolourization reaction on the biogenic material could be due to adsorption of the dye, reaction products on biogenic impurities, or some influence of adsorbed components of the ICCL medium.

Iron (hydr)oxides were used as catalysts for purification of waste waters in Fenton-like processes, where reactive species (hydroxyl radicals) are generated at room temperature under atmospheric pressure. Iron oxides (magnetite, maghemite and hematite) were more successful at initiating dye photodegradation than the iron (hydr)oxides [18]. Lepidocrocite was studied for environmental remediation procedures in water treatment for the removal of toxic ions [19].

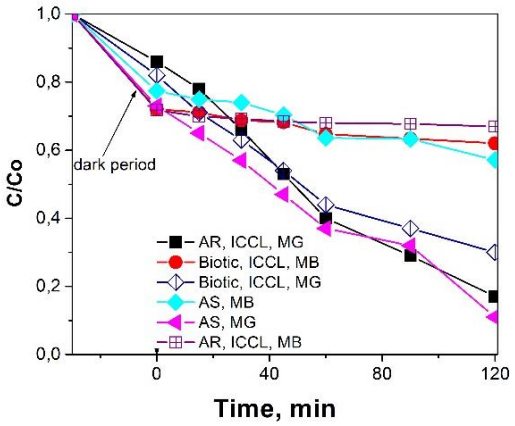

Fig. 2. Concentration C/C_0 ratio of MG and MB dyes in aqueous solution with time under UV illumination using abiotic and biotic Fe-containing samples.

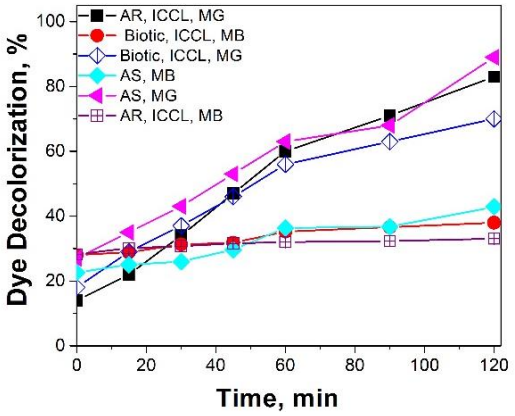

Fig. 3. Decolourization of MG and MB dyes in aqueous solution with time under UV illumination using abiotic and biotic Fe-containing samples.

CONCLUSIONS

Photocatalytic tests of biogenic material from cultivation of *Leptothrix* bacteria in ICCL medium, abiotic (formed in sterile medium), and synthesized iron oxyhydroxide(s) samples, revealed that they were not active in photocatalytic decolourization of Methylene Blue dye. A low decolourization activity of the same substances in aqueous solutions of Malachite Green dye was registered. The presence of bacterial rests so as some ICCL medium components could have a decreasing effect on catalytic activity.

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ИЗСЛЕДВАНИЯ НА АБИОТИЧНИ И БИОТИЧНИ МАТЕРИАЛИ НА ОСНОВАТА НА ЖЕЛЕЗНИ ОКСИХИДРОКСИДИ ЗА ФОТОКАТАЛИТИЧНО ОБЕЗЦВЕТЯВАНЕ НА БАГРИЛА ВЪВ ВОДНИ РАЗТВОРИ

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(Резюме)

Фотокаталитичната способност на абиотичен и биогенен материал е изследвана в реакцията на обезцветяване на багрилата метиленово синьо и малахитово зелено под действието на УВ облъчване. Опитите са проведени във водни разтвори на изследваните багрила с концентрация 5 ppm. Биогенният материал съдържащ лепидокрокит е получен при култивиране на бактерии *Leptothrix* в изолационна среда за бактерии от групата *Sphaerotilus-Leptothrix* (ИССЛ). Абиотичен сравнителен материал (AR) е получен в стерилна ИССЛ (незаразена с бактерии). Фотокаталитичната способност на тестваните материали беше сравнена с тази на синтезиран чрез утаяване лепидокрокит (AS). Абиотичният, биогенният и синтезираният материал бяха изследвани посредством инфрачервена спектроскопия. Биогенният материал демонстрира по-висока фотокаталитична активност в обезцветяването на метиленово синьо от абиотичния сравнителен материал. Обратното бе наблюдавано при обезцветяване на малахитово зелено, като регистрираният ефект е много по-голям (83% с абиотичния сравнителен материал, 70% с биогенния материал). Синтезираният лепидокрокит показа по-висока степен на обезцветяване на разтвора с малахитово зелено (89%) в сравнение с тази на разтвора с метиленово синьо за еднакъв период от 120 минути.