CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 4, No. 4, 2010 Chemistry

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THE EFFECT OF UV/TiO$_2$/H$_2$O$_2$ PROCESS AND INFLUENCE OF OPERATIONAL PARAMETERS ON PHOTOCATALYTIC DEGRADATION OF AZO DYE IN AQUEOUS TiO$_2$ SUSPENSION

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Received : May 05, 2010 / Revised: May 21, 2010 / Accepted : September 30, 2010

Abstract. In this work a detailed investigation of heterogeneous photocatalytic degradation of Navy blue HE2R **1** (NB), azo dye of the reactive class is presented using UV/TiO$_2$/H$_2$O$_2$ process in the aqueous suspension under 8W low-pressure mercury vapor lamp irradiation. Here we also report about optimization of various experimental parameters such as effect of catalyst concentration, effect of substrate concentration, effect of H$_2$O$_2$ addition. The effect of the UV/TiO$_2$/H$_2$O$_2$ process employment and selection of optional operational parameters on complete decolorization and substantial decrease of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of dye solution has been established.

Keywords: photocatalysis, textile dye Navy blue HE2R 1 (NB), titanium dioxide, hydrogen peroxide.

1. Introduction

Azo dyes are an abundant class of synthetic, colored, organic compounds, which are characterized by the presence of one or more azo bonds (–N=N–). About half of the textile dyestuffs manufactured worldwide is used in a variety of applications [1]. Such colored dye effluents pose a major threat to the surrounding eco-system. It is well known that soluble azo dyes when incorporated into the body are split into corresponding aromatic amines by liver enzymes and intestinal flora, which can cause cancer in human [2]. The toxicity and potentially carcinogenic nature of these substances and their manufacturing precursors represent an increasing danger to aquatic life. Therefore, it is necessary to treat these effluents before being discharged to the natural water bodies.

Several studies have been conducted on the issues of biological, physical and chemical treatment of effluents containing dyes, biotreatment of azodyes is, in general ineffective firstly due to its resistance to aerobic degradation [3] and secondly due to the formation of more hazardous intermediates under anaerobic conditions [4]. Furthermore, the azo dyes that undergo reductive cleavage through anaerobic biological treatment, potentially, generate carcinogenic aromatic amines in the process [5]. The conventional physical methods such as adsorption on activated charcoal, flocculation, reverse osmosis, *etc*. simply transfer the pollutants from one phase to another causing a secondary pollution [6]. Chemical methods using chlorine or ozone can be used for destruction of dyes but doses required are so high that they are not economically feasible [7].

Currently, chemical methods such as advanced oxidation processes (AOP's) seem to be more promising for treatment of textile industrial effluents [8]. Among various advanced oxidation processes (AOP's) heterogeneous photocatalysis on metal oxide semiconductor particles has been found to be very effective for removing the organic pollutants from wastewater [9-11]. The basic principles of heterogeneous photocatalysis using semiconductor oxide are well-established [12] and can be briefly summarized in the following simplified processes. The photo-excitation of semiconductor particles promotes an electron from the valence band to the conduction band thus leaving an electron deficiency or the hole in the valence band, in this way electron/hole pairs are generated. Both reductive and oxidative processes can occur at/or near the surface of the photoexcited semiconductor particle. In aerated aqueous suspensions, oxygen is able to scavenge conduction band electrons forming superoxide ions ($O_2^{\cdot -}$) and its protonated form, the hydroperoxyl radical ($HO_2^{\cdot}$)

$$O_2 + e^- \rightarrow O_2^{\cdot -} \quad (1)$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \quad (2)$$

In this way, electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. $HO_2^{\cdot}$ can lead to the formation of H_2O_2.

$$HO_2^{\cdot} + e^- \rightarrow HO_2^- \quad (3)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (4)$$

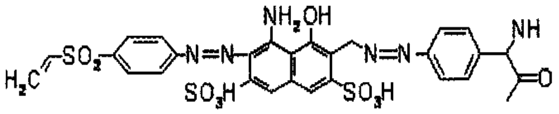
Photogenerated holes can react with adsorbed water molecules (or hydroxide anions) to give hydroxyl radicals:

$$H_2O + h^+ \rightarrow HO\cdot + H^+ \qquad (5)$$

or they can also be filled by an adsorbed organic donor. The whole process can end in complete mineralization of organic compounds. Further, the addition of H_2O_2 to this heterogeneous system increases the concentration of $\cdot$OH radicals and it also inhibits electron hole recombination process at the same time and hence consequently increases the degradation rate dramatically.

Keeping in view the concept of zero discharge and emerging strict environmental legislations for the disposal of wastewater in the rapidly developing countries, the exhaustive research on photocatalytic treatment at the laboratory scale and probing its suitability at an industrial level is a need of current research and development activities.

The aim of the present work is to investigate an effective and economical AOP for the degradation of azo dye of the reactive class. Here we have undertaken detailed study on photodegradation of Navy Blue HE2R 1(NB) azo dye, which is extensively used in textile industry, and to the best of our knowledge; this is the first report on the photocatalytic degradation of this dye. We have employed $UV/TiO_2/H_2O_2$ processes for complete decolorization and substantial decreases of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of dye solutions under optimized conditions of experimental parameters.



Navy blue HE2R (Reactive Blue 172)

2. Experimental

2.1. Reagent and Chemicals

TiO_2 (LR grade Merck with 99 % purity: mixture of anatase and rutile) of band gap = 3.2 eV, H_2O_2 (30 % w/w, Merck),) Reactive textile dye Navy Blue HE2R (Reactive blue 172) was obtained from the local textile industry, Solapur India. All chemicals were used in the form as received without further purification. The solutions were prepared in Millipore water.

2.2. Photoreactor

The experiments were carried out in the batch immersion well photocatalytic reactor procured from "Scientific Aids and Instruments Corporation" Chennai, India. (Fig.1) The reactor consists of the double wall immersion well made of quartz, which was placed inside the glass reactor fitted with the standard joint. The whole assembly of the reactor as procured from the manufacturer also consists of 8W low-pressure mercury vapor lamp (peak emission at 254 nm) which was placed inside the immersion well. Water circulated through the inlet and outlet provided by the reactor in order to maintain the constant temperature between 303 ± 1 K.

2.3. Procedure

The photodegradation of NB was carried out with different AOP's such as (i) UV (ii) UV/TiO_2 (iii) $UV/TiO_2/H_2O_2$ to identify the most suitable and economical process for complete decolorization and substantial mineralization of the dye. The effect of various experimental parameters such as irradiation time, catalyst concentration, substrate concentration and H_2O_2 addition was carried out to arrive under optimized experimental conditions. For that, from the stock solution of NB of concentration 0.01 mol/l, various solutions of desired concentrations were prepared in Millipore water**.** The photodegradation experiments were carried out in the photoreactor in which 250 ml of NB solution were taken. The solution was agitated with the help of aeration pump and magnetic stirrer. To study the effect of irradiation time of photocatalytic degradation experiments were carried within the range of 3–8 h. The effect of the catalyst concentration was studied by varying the amounts of TiO_2 ranging from 50 to 125 mg/250ml. To study the effect of substrate concentration, the photocatalytic degradation experiments were carried out at the optimized catalyst concentration. For this the substrate concentration, *i.e.* concentration of NB was varied from $1.0\cdot10^{-5}$ to $2.5\cdot10^{-4}$mol/l. For each experiment, thealiquot was taken out after every one hour with the help of the syringe, which was then filtered through 0.2 µm, 13 mm diameter Millipore disc and analyzed for its concentration with Schimadzu UV-visible Spectrophotometer to study the decolorization and degradation. The degree of mineralization of the dye was confirmed by COD and TOC analysis.

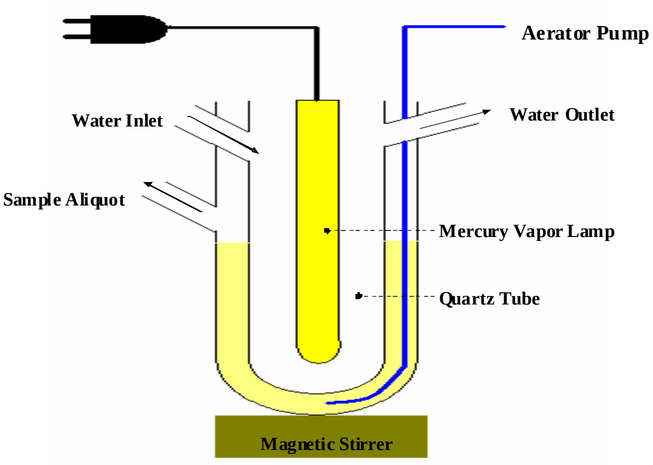


Fig. 1. Photoreactor

2.4. Analysis

The optical absorption spectrum for NB was determined by the double beam Schimadzu UV-visible Spectrophotometer. The characterized wavelength of NB was found to be 610 nm, which was used to monitor the decolorization and degradation of the dye. The chemical oxygen demand (COD) was measured by the dichromate reflux method [13] and total organic carbon (TOC) was measured using commercially available test kits (NANOCOLOR TOC 60) from Macherey-Nagel, Germany [14] to determine the mineralization of the dye solution under optimized conditions.

3. Results and Discussion

The photodegradation of NB was carried out with different AOPs such as (i) UV, (ii) UV/TiO_2, (iii) UV/TiO_2/H_2O_2 to identify the most suitable and economical process for complete decolorization and substantial mineralization of the dye.

3.1. Optimization of Various Experimental Parameters

(i) The effect of irradiation time; (ii) the effect of catalyst concentration; (iii) the effect of substrate concentration; (iv) the effect of H_2O_2 addition.

3.1.1. Effect of irradiation time

The effect of irradiation time on photocatalytic degradation of NB was studied in the range of 3–8 h. The obtained results show that maximum degradation of NB can be achieved in the first 3 h. The minimum time of irradiation for maximum degradation was found to be 5 h. Beyond this, the rate of degradation of NB is almost constant.

3.1.2. Effect of catalyst concentration

The effect of catalyst concentration was studied by varying the amounts of TiO_2 ranging from 50 to

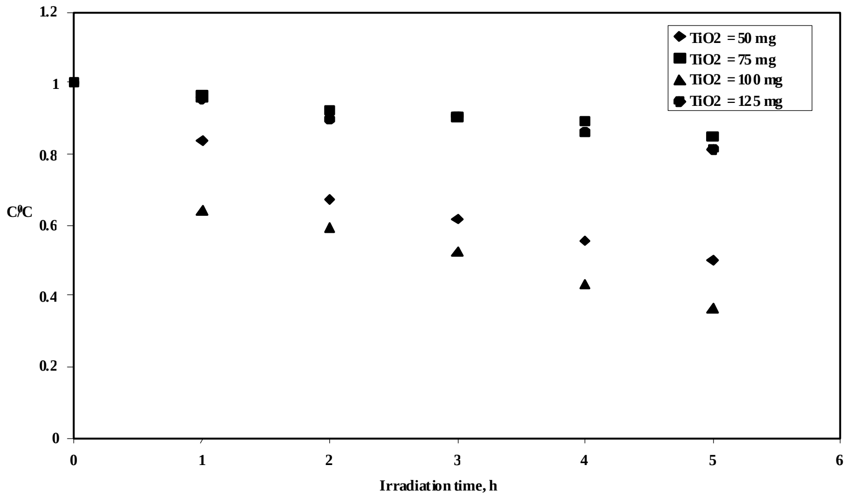


Fig. 2. Influence of catalyst concentration on the degradation rate for decomposition of Navy Blue HE2R 1 (NB) in the presence of TiO_2. Experimental conditions : dye concentration is $2.5 \cdot 10^{-5}$ mol/l ; catalyst concetration (50, 75, 100 and 125 mg /250 ml) ; T = 303 K ; V = 250 ml ; irradiation time is 5 h. Photocatalyst : Merck TiO_2.

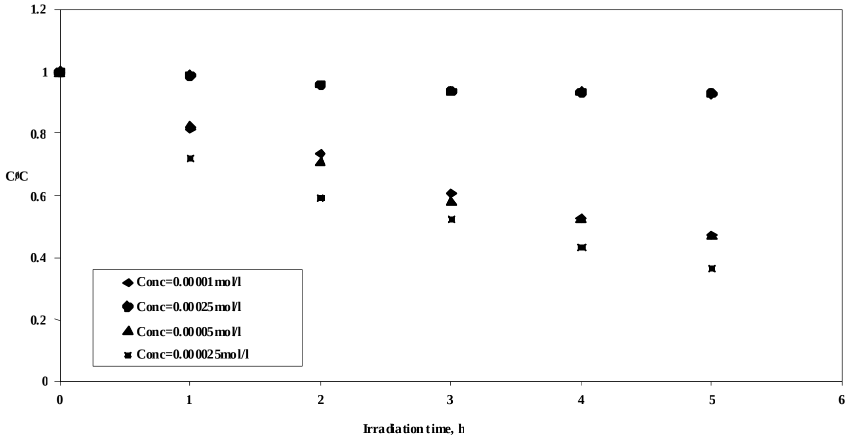


Fig. 3. Influence of substrate concentration on the degradation rate for decomposition of Navy Blue HE2R 1 (NB) in the presence of TiO_2. Experimental conditions: substrate concentrations ($1 \cdot 10^{-5}$, $2.5 \cdot 10^{-5}$, $5 \cdot 10^{-5}$ and $2.5 \cdot 10^{-4}$ mol/l); T = 303 K; V = 250 ml; irradiation time is 5 h. Photocatalyst: Merck TiO_2 = 100 mg.

125 mg/250ml, in order to obtain an optimum catalyst concentration for the maximum photodegradation, which could save unnecessary use of photocatalyst excess. For these studies, the substrate concentration was kept constant ($2.5\cdot10^{-5}$ mol/l). Fig. 2 shows that the degradation efficiency increases up to 100 mg/250 ml of the dye solution, above which it shows reduction in degradation efficiency. Beyond this dose, the substrate molecules available are not sufficient for adsorption by the increased number of TiO_2 particles. Hence, the additional amount of the catalyst is not involved in catalyst activities and the rate does not increase with an increase in the amount of the catalyst [15]. Also at high TiO_2 concentrations particles aggregate reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface decreases. The surplus addition of the catalyst makes the solution more turbid and the reduction in degradation efficiency may be due to the reduction in penetration of light with the surplus amount of TiO_2. In the present investigation, 100 mg of TiO_2 in 250 ml of the dye solution was found to be the optimized dose for maximum degradation of NB.

3.1.3. Effect of substrate concentration

The effect of the substrate initial concentration on the degradation of NB dye was studied at different concentrations varying from $1\cdot10^{-5}$ to $2.5\cdot10^{-4}$ mol/l since the pollutant concentration is a very important parameter in water treatment. Experimental results are presented in Fig. 3, which shows that the degradation rate depends on the initial concentration of the dye NB. The rate of degradation was found to increase with the increasing concentration of NB up to $2.5\cdot10^{-5}$ mol/l. The further increase of the concentration decreases the rate of degradation. This may be explained on the basis that upon increasing the concentration of NB, the reaction rate increases as more molecules of the dye are available for degradation. Also with an increase in dye concentration, the solution becomes more intensely colored and the path length of photons entering the solution is decreased thereby fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals are reduced [15]**.** Therefore the photodegradation efficiency is reduced. Moreover, at the higher concentration, the number of collisions between dye molecules increases whereas the number of collisions between dye molecules and $^{\cdot}OH$ radical decreases. Consequently, the rate of reaction is retarded [16]. Hence in the present investigation the optimized substrate concentration of NB was found to be $2.5\cdot10^{-5}$ mol/l.

3.1.4. Effect of H_2O_2 addition

The effect of H_2O_2 addition to the system with optimized catalyst concentration and optimized initial substrate concentration was studied by varing the amount of H_2O_2 ranging from 0.175 g/250 ml to 0.475 g/250 ml. Fig. 4 shows the variation in the photodegradation rate of NB for different amounts of H_2O_2. The highest rate of degradation was found for H_2O_2 = 0.375 g and beyond this the rate of degradation of NB was not significant. The addition of H_2O_2 to the heterogeneous system increases the concentration of $^{\cdot}OH$ radicals.

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\cdot} \qquad (6)$$

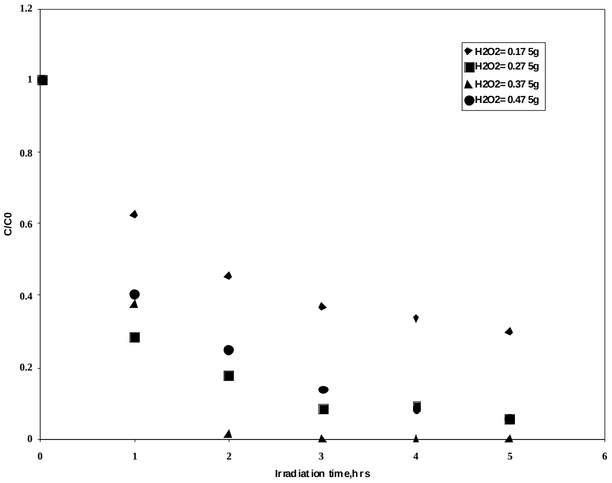


Fig. 4. Influence of H_2O_2 concentration on photodegradation of Navy Blue HE2R 1 (NB) in the presence of TiO_2. Experimental conditions: H_2O_2 concentrations (0.175, 0.275, 0.375 and 0.475 g); T = 303 K; V = 250 ml; irradiation time is 5 h. Photocatalyst : Merck TiO_2 = 100 mg.

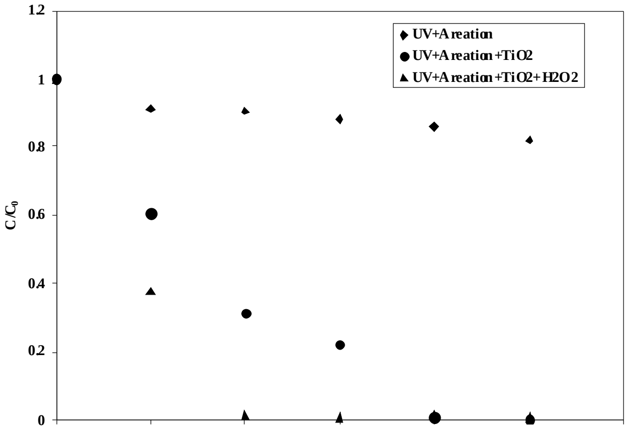


Fig. 5. Comparison of degradation rate for decomposition of Navy Blue HE2R 1 (NB) under different Advance Oxidation Processes. Experimental conditions: dye concentration is $2.5\cdot10^{-5}$ mol/l ; H_2O_2 concentration is 0.375 g; T = 303 K; V = 250 ml; irradiation time is 5 h. Photocatalyst : Merck TiO_2 = 100 mg. Immersion well photoreactor, continuous air purging and stirring

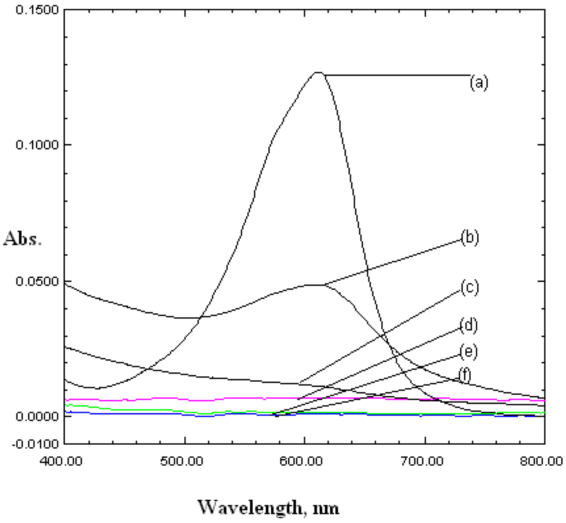


Fig. 6. Change in absorption intensity as a function of time for Navy Blue HE2R 1 (NB) under UV/TiO$_2$/ H$_2$O$_2$ process, light source is 8W low pressure mercury vapour lamp; irradiation time : 0 min (a), 1 h (b), 2 h (c), 3 h (d), 4 h (e) and 5 h (f)

Being an electron acceptor, H$_2$O$_2$ does not only generate ·OH radicals but it also inhibits the electron hole recombination process at the same time, which is one of the most important practical problems in using TiO$_2$ as a photocatalyst. When the H$_2$O$_2$ concentration becomes high, the excess of H$_2$O$_2$ consumes hydroxyl radicals and it performs like hydroxyl radical scavengers [17].

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O \qquad (7)$$

When H$_2$O$_2$ was added, the maximum degradation was achieved in the first hour only. The complete degradation was achieved in 2 h. Thus in the present investigation the optimized amount of H$_2$O$_2$ was found to be 0.375 g/250 ml**.** The photocatalytic degradation of NB using different AOPs such as (i) UV, (ii) UV/TiO$_2$, (iii) UV/TiO$_2$/H$_2$O$_2$ is shown in Fig. 5 and the corresponding spectral changes observed for UV/TiO$_2$/H$_2$O$_2$ process are depicted in Fig. 6**.**

3.2. Estimation of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)

The COD is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of wastes in terms of the total quantity of oxygen required for oxidation of organic matter to CO$_2$ and water. The COD of the dye solution was estimated before and after the treatment under optimized conditions. The reduction in the COD and TOC values of the treated dye solution indicates the mineralization of dye molecules along with color removal. The percent reduction in the COD values and TOC values of the treated dye solution under above optimized condition was found to be 85 and 65 % respectively in the present study.

4. Conclusions

The results obtained in the present study show the great efficiencies of advanced oxidation processes in removing diazo dyes, which are resistant to other conventional treatment processes. This is the first report on the photocatalytic degradation of NB. The application of heterogeneous photocatalytic treatment using TiO$_2$ for NB degradation has been found to be a promising process. Further addition of H$_2$O$_2$ to the above system made the degradation much faster and could degrade the dye only in couple of hours**.** Degradation of NB was found to increase in the order UV<UV/TiO$_2$<UV/TiO$_2$/H$_2$O$_2$. The employment of UV/TiO$_2$/H$_2$O$_2$ process led to complete decolorization and to 85 % decrease in COD and 65 % decrease in TOC values. The observations of these investigations clearly demonstrated the importance of choosing the optimum degradation parameters, which are essential for any practical application of photocatalytic oxidation process. Thus, UV/TiO$_2$/H$_2$O$_2$ seems to be the most appealing choice for complete degradation and substantial mineralization of NB and may be extended to treat real industrial wastewaters.

Acknowledgements

The author^1 is thankful to University Grants Commission, New Delhi, India, for financial support, and to the Secretary of Gokhale Education Society Nashik, and the Principal of RNC Arts, JDB Commerce and NSC Science College, Nashik-Road for allowing to carry out research work.

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ВПЛИВ UV/TiO_2/H_2O_2 ПРОЦЕСУ ТА ЕКСПЛУАТАЦІЙНИХ ПАРАМЕТРІВ НА ФОТОКАТАЛІТИЧНУ ДЕГРАДАЦІЮ АЗОБАРВНИКА У ВОДНІЙ СУСПЕНЗІЇ TiO_2

Анотація. *У роботі представлені результати досліджень гетерогенної фотокаталітичної деградації темно-синього азобарвника HE2R 1 (NB) за допомогою UV/TiO_2/H_2O_2 процесу у водній суспензії під опроміненням 8W ртутною лампою низького тиску. Показано можливість оптимізації таких експериментальних параметрів, як концентрація каталізатора, концентрація субстрату, добавлення H_2O_2. Встановлено вплив застосування UV/TiO_2/H_2O_2 процесу та вибору додаткових експлуатаційних параметрів на повне знебарвлення та істотне зниження хімічного споживання кисню (ХСК) та загального органічного вуглецю (ЗОВ) в розчині барвника.*

Ключові слова: *фотокаталіз, текстильний барвник темно-синій HE2R 1 (NB), діоксид титану, пероксид водню.*