Catalytic Photodegradation and Mineralization of Cationic Dye
Methylene Blue from Aqueous Solution
onto Copper Doped Zeolite

ÁGÉNJS JAKAB, LILIANA ANDREEA COLAR, RODICA PODE*, LAURA COCHECI, FLORICA MANEA
Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Victoriei Sq., 300006, Timisoara, Romania

In this study, the photodegradation and the mineralization of a cationic dye Methylene Blue (MB) from aqueous solution was investigated, in the presence of hydrogen peroxide, using a photocatalyst based on copper modified natural zeolite (Z-Cu). Comparative studies of photolysis, photocatalysis on the monocationic form of zeolite (Z-Na) and photocatalysis on Z-Cu, quantified in terms of processes efficiencies, expressed as intensities of absorbance peaks as well as apparent rate constants, revealed that the presence of copper in zeolite network has a significant effect on photocatalytic activity. The addition of hydrogen peroxide (50 mM) in the photocatalytic process on Z-Cu (H₂O₂/UV/Z-Cu) practically doubled the efficiencies achieved by the process of photocatalysis on Z-Cu (UV/Z-Cu) after 120 min of irradiation. The effect of H₂O₂ dose on the MB degradation/discoloration efficiency by photocatalysis on Z-Cu highlighted that in the applied working conditions, 10 mM H₂O₂ was sufficient to degrade 50 mg/L MB solution initial concentration.

Keywords: photolysis, photocatalysis, copper doped Zeolite, methylene blue, hydrogen peroxide, mineralization.

Textile industries are major consumers of water [1] and as consequence large volume of wastewaters is produced [2], mainly from the dyeing and finishing processes. The waste effluents contain a wide range of environmental contaminants, suspended solids, unstable pH, temperature, acidity, chemical oxygen demand, surfactants and strong color [3].

Dyes from textile wastewater are characterized by complex aromatic molecular structures, which offer physicochemical, thermal and optical stability. They may also be carcinogenic, mutagenic and highly toxic to human beings [1, 4] and need to be removed from industrial wastewaters. This has always been a major problem because they can not be easily treated by conventional methods, i.e., coagulation, chemical flocculation or biological procedures [5, 6]. Also, conventional oxidation treatment encounters difficulty to oxidize dyestuffs and complex structure of organic compounds.

Recently, advanced oxidation processes (AOPs) have been proposed as alternative for treatment of wastewater containing organic compounds hard biodegradable produced by textile industry [7-9]. These processes primarily involve the generation of hydroxyl radicals, which attack quickly and destroy hazardous pollutants [7]. Generation of HO· is commonly accelerated by combining O₂, H₂O₂, catalyst, UV radiation, electron-beam irradiation and ultrasound. The eco-friendly oxidant H₂O₂ is known as a liquid substance, thermally stable under room temperature conditions [8], which could offer an attractive alternative for colored wastewater treatment [9].

Other promising advanced treatment method is heterogeneous photocatalysis, which seems to reach the highest efficiencies in degradation and mineralization of organics [10], based on the direct and indirect adsorption of visible or UV radiant energy by a solid semiconductor. When the catalyst is excited by UV irradiation, electrons are promoted from the valence band to the conduction band, under these conditions electron-hole pairs are produced and can migrate to the catalyst surface and react easily with adsorbed species, while others tend to recombine [11]. Main benefits of this process are the low cost, the relatively high chemical stability of the catalyst and the possibility of using sunlight as the source of irradiation [12].

Natural zeolites and their modified forms have been widely used as eco-friendly catalyst in photocatalytic processes [13]. These materials are characterized by high specific surface area, high adsorption capacity, cation exchange capacity, catalytic activity, low cost extraction, availability and an excellent stability in thermal and chemical processes [14].

Copper has been used for treating various organic compounds. The catalytic activity of this metal can be improved by encapsulating in any support matrix, like zeolite or some mesoporous materials [15, 16].

The aim of this study is to investigate the photodegradation and the mineralization of a cationic dye Methylene Blue (MB) from aqueous solution in the presence of hydrogen peroxide, using a copper modified zeolite catalyst.

Experimental part

Materials

Romanian zeolitic mineral from Mirsid, used as support for Cu²⁺ loading, was supplied by CEMACON Company, Romania. The mineral was powdered and sieved with a Multilab sieve shaker. The diameter of grains size selected to carry out the experiments ranged between 315 and 500 μm and the mass composition of the mineral was: 62.20% SiO₂, 11.65% Al₂O₃, 1.30% Fe₂O₃, 3.74% CaO, 0.67% MgO, 3.30% K₂O, 0.72% Na₂O, 0.28% TiO₂.

Methylene Blue (MB – analytical grade), selected as a model for the dye, was supplied by Pekin Chemical Works Peking (China). MB (C₁₆H₁₈N₃SCl·3H₂O) is a basic blue dyestuff with a molecular weight 373.9 g·mol⁻¹ [17, 18], whose structure is presented in figure 1.

*email: rodica.pode@chim.upt.ro

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The dye solution pH was adjusted with analytical grade NaOH (0.1 N). The chemicals used for this study, i.e., hydrochloric acid (HCl), sodium chloride (NaCl), cupric nitrate (Cu(NO₃)₂. 3H₂O), hydrogen peroxide (H₂O₂) and sodium sulphite (Na₂SO₃) were purchased from Merck Company. For all experiments distilled water was used.

**Synthesis of photocatalyst based on copper doped zeolite**

The preparation of the chemically modified zeolite presumes two stages:

1. The first step to reach acid form (H form) by using 1M HCl solution, under magnetic stirring, with a S/L weight ratio of 1/10, for 8 h at 25° C. The resulted H form of zeolite (Z-H) was washed with distilled water, until reach the pH of distilled water.

2. In the second step, the acid form of zeolite was treated with 1M NaCl solution, at a S/L ratio of 1/5, for 8 h at 25° C, to achieve the monocationic form (Z-Na). This process was repeated three times with the replacing of NaCl solution after each step, to improve the cation exchange capacity. Finally, the Z-Na material was separated by vacuum filtration and washed with deionized water until free of chloride ions and dried at 100°C over night.

Therefore, zeolite as Na form was treated with 0.1M Cu(NO₃)₂ solution, at a S/L weight ratio of 1/100, under continuous stirring for 8 h at 25° C. The modified zeolite was washed with distilled water and dried at 100°C for 8 h.

**Photocatalytic experiments**

All experiments regarding adsorption and photocatalysis processes were carried out under magnetic stirring at 20°C into a RS-1 photocatalytic reactor (Heraeus, Germany), which consisted of a submerged lamp surrounded by a quartz shield. Solutions of MB (prepared from an initial stock solution of 1 g . L⁻¹) were placed into the photoreactor and irradiated with an UV light set between 280 and 360 nm. A system of water recirculation maintained a constant temperature of 20°C for the whole period of irradiation.

The results of the previous studies regarding the effect of pH on degradation and discoloration efficiencies of the cationic MB dye indicated as optimum pH 9. For this reason, all experiments in this study were conducted at pH 9.

The pH 9 of MB solutions was adjusted by adding diluted NaOH solutions using an Inolab pH-meter to control the pH value.

The catalyst was placed into 400 mL MB solution. Prior to irradiation, all the reaction mixtures were allowed to reach the adsorption equilibrium by stirring in dark, for 10 min. At different time intervals, samples were collected and filtered through a Millipore filter (pore size 0.45μm). Then, absorption spectra were recorded with a Varian Cary 100 UV-VIS Spectrophotometer.

It can be seen from figure 1 the two major absorbance peaks at 291 nm and 663 nm, which were used to monitor the destruction of benzene rings and heteropolyaromatic linkage. The absorbance at 241 nm is also attributed to aromatic nuclei [19-21].

In the photocatalysis experiments performed with H₂O₂ addition, hydrogen peroxide was added after the adsorption stage, at the same time with UV lamp operation.

After sample collecting, the sodium sulfide was introduced in the samples collected for analysis to stop the oxidation reaction.

The concentration of the dye in the bulk solution at the end point of adsorption was considered as the initial concentration value for the investigation of the photodegradation process. Total organic carbon (TOC) parameter measured with Shimadzu TOC analyzer was used to assess the mineralization process.

The discoloration and degradation efficiencies expressed as \( \eta_{\text{663}} \) and \( \eta_{\text{291}} \) (%) are usually calculated from the decrease of MB concentration at the selected wavelengths (663 and 291 nm),

\[
\eta = \frac{C_0 - C_t}{C_0} \times 100
\]

where \( C_0 \) represents the change in the dye concentration determined spectrophotometrically, during the experiments corresponding to various reaction time.

The mineralization degree was assessed also based on equation (1) using TOC parameter instead of dye concentration determined spectrophotometrically.

**Results and discussion**

**Study on the photocatalytic oxidation of MB**

The doping effect of natural zeolite with Cu²⁺ on the MB photocatalytic oxidation efficiency was revealed by comparative studies of photolysis, photocatalysis on Z-Na and photocatalysis on Z-Cu. The results regarding the
variation of degradation/discholoration efficiencies of MB dye in time are shown in figure 2 a,b.

It can be observed that the photolysis of MB allowed to reach low efficiencies for both discoloration (32.56%) and destruction of benzene nuclei (24.09%). Moreover, for photoactivation of MB solution, about 90 min of irradiation time is required. In the case of photocatalysis on Z-Na, after achieving the adsorption equilibrium, the discoloration/degradation efficiencies reached similar values (about 24%) after only 10 min irradiation, and increase after 240 min irradiation at 58.14% for discoloration and at 50.20% for degradation, respectively. The results obtained by applying the photocatalysis on Z-Cu also indicate similar efficiencies for discoloration/degradation after 10 min of irradiation (about 29%), with a progressive increase after 240 min to 72.15% for discoloration and 66.24% for degradation, respectively.

Since by the photocatalysis on Z-Cu, after 240 min irradiation the efficiencies of discoloration/degradation were higher than the ones recorded on Z-Na, doping of the natural zeolite with Cu²⁺ enhanced the photocatalytic activity.

The aspects presented above are highlighted also by the MB spectra recorded after 240 min irradiation for the studied processes (fig. 3).

\[ r = \frac{dC}{dt} = kKC / (1 + KC) \]  \hspace{1cm} (2)

\[ \ln \left( \frac{C_0}{C} \right) = klt = k_{app}t \]  \hspace{1cm} (3)

where:
- \( r \) – rate of dye degradation and discoloration
- \( C_0 \) – the initial dye concentration (mg·L⁻¹);
- \( C \) – concentration of the dye at time \( t \) (mg·L⁻¹);
- \( t \) – irradiation time (min);
- \( k \) – reaction rate constant (min⁻¹).

The apparent rate constant, \( k_{app} \), was calculated from the intercept of the plot of \( \ln(C_0/C) \) versus time, \( t \).

The kinetics results presented in table 1 showed that the rates of the benzene ring-opening and discoloration processes depend on the type process.

For all studied processes, the rate constants corresponding to discoloration have been higher than the ones corresponding to degradation. Also, the rate constants for the process of photocatalysis on Z-Cu were about 2 times higher than those obtained for the photocatalysis on Z-Na, indicating that the doping of natural zeolite with Cu²⁺ is also justified in terms of kinetic.

**Influence of the hydrogen peroxide addition**

To increase the efficiency of Z-Cu catalyst, the influence of the addition of an oxidizing agent (hydrogen peroxide) on MB photocatalytic oxidation process was studied. For this purpose, a set of experiments was conducted, aiming to evaluate the efficiencies of discoloration/degradation of MB under the following conditions: oxidation (50 mM H₂O₂/UV), photo-oxidation (50 mM H₂O₂/UV) and photocatalytic-oxidation (50 mM H₂O₂/UV/Z-Cu).

The activated H₂O₂ by UV irradiation was decomposed into two moles of hydroxyl-free radicals by the following reaction [23]:

\[ H_2O_2 + hν \rightarrow 2OH \]  \hspace{1cm} (4)

The OH· radical formed during the reaction (4) is responsible significantly for the oxidation of the cationic dye MB.

Figure 4 a,b present the evolution of the degradation and discoloration processes efficiency versus time for above mentioned processes.

After only 120 min oxidation time, it was found that the obtained efficiencies for discoloration (59.48%) and degradation (70.33%) by oxidation with hydrogen peroxide were comparable to those achieved by photocatalysis on Z-Cu after 240 min of UV irradiation.

It can also be said that the combined processes efficiency, i.e., H₂O₂/UV and H₂O₂/UV/Z-Cu, was much higher compared to oxidation by hydrogen peroxide. After the same time of oxidation processes, i.e., 120 min, the discoloration efficiency was practically the same (about 99%) for both H₂O₂/UV and H₂O₂/UV/Z-Cu processes.

The achieved efficiency for the degradation of benzene nuclei was also appreciable, i.e., 85.66% for photo-oxidation and 87.27% for photocatalytic-oxidation.

Another aspect to be emphasized regards the efficiencies of discoloration/degradation achieved by the photocatalytic-oxidation process after 120 min of

<table>
<thead>
<tr>
<th>Process type</th>
<th>Apparent rate constants</th>
<th>Correlation coefficient, ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis</td>
<td>( k_{app291nm, \text{min}^{-1}} ), ( k_{app663nm, \text{min}^{-1}} )</td>
<td>291 nm, 663 nm</td>
</tr>
<tr>
<td>Photocatalysis Z-Na</td>
<td>0.0014, 0.0018</td>
<td>0.9510, 0.9680</td>
</tr>
<tr>
<td>Photocatalysis Z-Cu</td>
<td>0.0018, 0.0025</td>
<td>0.9301, 0.9559</td>
</tr>
<tr>
<td></td>
<td>0.0034, 0.0040</td>
<td>0.9395, 0.9724</td>
</tr>
</tbody>
</table>

**Table 1**

**APPARENT RATE CONSTANTS FOR DISCOLORATION, AROMATIC RING-OPENING AND CORRELATION COEFFICIENTS. CONDITIONS: 50 mg·L⁻¹ MB DYE SOLUTION; 1 g·L⁻¹ CATALYST LOADING; pH 9
irradiation, which were doubled compared to the efficiencies achieved by the process of photocatalysis on Z-Cu, after the same irradiation time (fig. 5).

The MB spectra profile recorded for the initial solution and also for MB solutions obtained after 15 min of oxidation time by applying 50 mM H₂O₂, photo-oxidation and photocatalytic-oxidation, respectively, (fig. 6) indicate some issues which will be discussed below.

\[ \text{HO.} + \text{MB} \rightarrow I \rightarrow \text{CO}_2 + \text{H}_2\text{O} \] (5)

The increasing of photo-oxidation process efficiency compared with oxidation process with hydrogen peroxide is reflected in the shape of the spectrum (c), where the absorbance maximum at 663 nm is slightly lower compared with the one recorded by oxidation process (b), indicating a more intense discoloration process in the employed working conditions. The peak corresponding to the wavelength of 291 nm overlaps the one corresponding to the process (b), indicating the destruction of benzene nuclei and the formation of intermediate compounds.

High efficiency of the H₂O₂/UV/Z-Cu process is revealed by the spectrum shape (d), indicating the disappearance of the dye. But, increasing absorbance after 500 nm to UV spectrum shows that complete mineralization did not take place.

In the spectrum corresponding to the oxidation with H₂O₂ (b), the absorbances of the initial solution spectrum (a) are found, noting that the maximum of the absorbance at 663 nm is appreciably smaller, and the one corresponding to the wavelength of 291 nm is almost invisible.

The disappearance of the peak at 246 nm can also be remarked. These aspects can be explained by the almost full opening of benzene nuclei and formation of some oxidation intermediates and end products [11]:

\[ r = -dC_{\text{MB}} / dt = k' C_{\text{MB}}^m \] (6)

where:
- \( C_{\text{MB}} \) - concentration of cationic dye Methylene Blue (mg . L⁻¹);
- \( C_{\text{H}_2\text{O}_2} \) - concentration of hydrogen peroxide (mM).

By the pseudo-stationary hypothesis (concentration of hydrogen peroxide can be considered unchanged), the rate expression (6) can be simplified as [25]:

\[ r = -dC_{\text{MB}} / dt = k' C_{\text{MB}}^m \] (7)

Using (7), the representation of \( \ln(r) \) versus \( \ln C_{\text{MB}} \) (initial dye concentration) gave a straight line (fig. 7) with slope (m) indicating the order of reaction.

Fig. 4. Time evolution of the (a) - discoloration, (b) - degradation efficiency of MB cationic dye after 120 min:
- \( \bullet \) - oxidation with H₂O₂;
- \( \bullet \) - H₂O₂/UV;
- \( \Delta \) - H₂O₂/UV/Z-Cu. Conditions: 50 mg . L⁻¹ MB dye solution; 1 g . L⁻¹ catalyst loading; \( \text{pH} \) 9.

Fig. 5. Time evolution of the removal efficiency of MB cationic dye:
- \( \square \) - discoloration, H₂O₂/UV/Z-Cu;  
- \( \bullet \) - degradation, H₂O₂/UV/Z-Cu;  
- \( \Delta \) - discoloration, UV/Z-Cu;  
- \( \bullet \) - degradation, UV/Z-Cu. Conditions: 50 mg . L⁻¹ MB dye solution; 1 g . L⁻¹ catalyst loading; \( \text{pH} \) 9; 50 mM H₂O₂ solution (30%).

Fig. 6. UV-VIS spectra profile of MB dye solution after 15 min oxidation:
- \( a \) - initial dye solution;  
- \( b \) - oxidation with H₂O₂;  
- \( c \) - H₂O₂/UV;  
- \( d \) - H₂O₂/UV/Z-Cu. Conditions: 50 mg . L⁻¹ MB dye solution; 1 g . L⁻¹ catalyst loading; \( \text{pH} \) 9; 50 mM H₂O₂ solution (30%).

Fig. 7. Logarithm of reaction rates vs. logarithm of the concentration of the dye solutions.
The apparent rate constants and the reaction orders for the processes of degradation/discoloration of MB are shown in table 2.

In the case of oxidation process with hydrogen peroxide, the reaction order for the degradation/discoloration of MB was 2, indicated a second-order kinetics. But, the rate constants obtained in this case were much lower (about $2.3 \times 10^{-3}$ L/mg·min$^{-1}$) compared with those obtained for the H$_2$O$_2$/UV and H$_2$O$_2$/UV/Z-Cu processes. Although in terms of degradation and discoloration efficiencies, the H$_2$O$_2$/UV and H$_2$O$_2$/UV/Z-Cu processes are comparable, kinetic data also justify the application of H$_2$O$_2$/UV/Z-Cu process. Indeed, in the case of photocatalysis with hydrogen peroxide added, the apparent rate constant was about 8.5 times higher for discoloration process and about 2.5 times higher for the degradation process than the rate constants of the photo-oxidation process.

**Influence of H$_2$O$_2$ doses**

The effect of H$_2$O$_2$ dose on the degradation/discoloration efficiency of MB by photocatalysis on Z-Cu is highlighted in figures 8 a, b.

The shape of the curves recorded for the variation of MB discoloration/degradation efficiencies in time, revealed for discoloration (fig. 8 a) an overlay of the three curves corresponding to all studied concentrations of H$_2$O$_2$.

Moreover, the efficiencies of discoloration recorded a sharp increase up to 15 min of irradiation (98.50% for 50 mM H$_2$O$_2$; 99.38% for 25 mM H$_2$O$_2$; 98.55% for 10 mM H$_2$O$_2$), and then remained almost constant.

This remark is valid for the degradation efficiencies (figure 8 b) which after 15 min of irradiation were: 80.86% for 50 mM H$_2$O$_2$; 84.19% for 25 mM H$_2$O$_2$; 83.92% for 10 mM H$_2$O$_2$ with a very slow increase up to 120 min irradiation time. These observations lead to the conclusion that in the used working conditions, a dose of 10 mM H$_2$O$_2$ is sufficient to degrade a 50 mg·L$^{-1}$ MB.

The conclusion is supported by MB spectra recorded after 15 min of irradiation time at three concentrations of H$_2$O$_2$ (fig. 9). The disappearance of absorbances corresponding to wavelengths of 663 nm and 291 nm (spectra b, c and d) indicates that a concentration of 10 mM H$_2$O$_2$ is optimum for an initial dye concentration of 50 mg·L$^{-1}$.

The values of rate constants k' and the reaction orders were calculated from the above-presented model fitting and the resulting data are displayed in table 3. R$^2$ value always greater than 0.95 demonstrated that the used model is suitable to describe the experimental results. The reaction rate constant did not increase significantly with the H$_2$O$_2$ dose increasing, emphasized that the concentration of 10 mM hydrogen peroxide is optimum.

### Table 2

<table>
<thead>
<tr>
<th>Process type</th>
<th>Apparent rate constants [L/mg·min$^{-1}$]: $k'_p$(291 nm), $k'_p$(663 nm)</th>
<th>Order m</th>
<th>Correlation coefficient, R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>0.0029$^<em>$, 0.0027$^</em>$</td>
<td>291 nm</td>
<td>0.995</td>
</tr>
<tr>
<td>H$_2$O$_2$/UV</td>
<td>0.0546$^{<strong>}$, 0.1448$^{</strong>}$</td>
<td>663 nm</td>
<td>0.992</td>
</tr>
<tr>
<td>H$_2$O$_2$/UV/Z-Cu</td>
<td>0.145$^{<strong>}$, 1.225$^{</strong>}$</td>
<td></td>
<td>0.952</td>
</tr>
</tbody>
</table>

Fig. 8. Time evolution of photocatalytic (a)-discoloration, (b)-degradation process efficiency of MB cationic dye using different doses of H$_2$O$_2$: • – 50 mM H$_2$O$_2$; • – 25 mM H$_2$O$_2$; ▲ – 10 mM H$_2$O$_2$. Conditions: 50 mg·L$^{-1}$ MB dye solution; 1 g·L$^{-1}$ catalyst loading; pH 9.

Fig. 9. UV-VIS spectra profile of MB dye solution after 15 min photocatalytic-oxidation: a – initial dye solution; b – 50 mM H$_2$O$_2$; c – 25 mM H$_2$O$_2$; d – 10 mM H$_2$O$_2$. Conditions: 50 mg·L$^{-1}$ MB dye solution; 1 g·L$^{-1}$ catalyst loading; pH 9; 50, 25, 10 mM H$_2$O$_2$ solution.

### Table 3

<table>
<thead>
<tr>
<th>H$_2$O$_2$/UV/Z-Cu</th>
<th>k' [L/mg·min$^{-1}$]</th>
<th>m</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM</td>
<td>0.055</td>
<td>2.01</td>
<td>0.951</td>
</tr>
<tr>
<td>25 mM</td>
<td>0.067</td>
<td>1.70</td>
<td>0.971</td>
</tr>
<tr>
<td>50 mM</td>
<td>0.145</td>
<td>1.33</td>
<td>0.952</td>
</tr>
</tbody>
</table>
The degradation kinetics of MB in the photocatalytic-oxidation process obey a pseudo-second-order kinetic for the two concentration of 10 and 25 mM H₂O₂ and for the oxidation process obey a pseudo-second-order kinetic for values of the ratio ηOC/ηH₂O₂ doubled efficiencies of the mineralization process and the rate constants of photo-oxidation process. The addition of H₂O₂ in the photocatalytic process can doubled efficiencies of the mineralization process and values of the ratio ηOC/ηH₂O₂ indicated an effective mineralization of the process (Table 4). In agreement with the literature [3] the process mechanism involves the following reactions, which represented the basis for the kinetics studies:

\[
\begin{align*}
\text{hv} + \text{Catalyst} & \rightarrow \text{Catalyst (hνB^+ + eCB^−)} & (8) \\
\text{OH}^− + hνB^+ & \rightarrow \text{OH} & (9) \\
\text{MB}^+ + \text{OH} & \rightarrow \text{MB}_\text{ox} \rightarrow \text{CO}_2 + \text{H}_2\text{O} & (10) \\
\text{eCB}^− + \text{O}_2 & \rightarrow \text{O}_2^− & (11) \\
\text{O}_2^− + \text{dye} & \rightarrow \text{dye−OO} & (12) \\
\text{O}_2^− + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & (13)
\end{align*}
\]

In UV/Z-Cu/H₂O₂ process in particular, H₂O₂ is added in order to improve dye degradation. Actually, H₂O₂ is an e- acceptor with higher efficiency than that of oxygen and is thought to promote the generation of OH mainly through the following reactions:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{eCB}^− & \rightarrow \text{OH} + \text{OH} & (14) \\
\text{H}_2\text{O}_2 + hνB^+ & \rightarrow 2\text{OH} & (15) \\
\text{H}_2\text{O}_2 + \text{O}_2 & \rightarrow \text{OH} + \text{OH} + \text{O}_2 & (16)
\end{align*}
\]

Conclusions
The effect of natural zeolite doping with Cu²⁺ on the photocatalytic oxidation efficiency of MB dye solution was revealed by comparative studies of photolysis, photocatalysis using Z-Na and respective, Z-Cu. Efficiencies of discoloration/degradation after 240 min of UV irradiation achieved by photocatalysis on Z-Cu were higher than those obtained by photocatalysis on Z-Na under the same working conditions, which proved the enhanced photocatalytic activity of copper modified natural zeolite. This aspect was supported by the shape of MB spectra recorded after application of the processes of photolysis, photocatalysis on Z-Na and photocatalysis on Z-Cu, which showed the similar to the spectrum of the initial dye solution, noting that absorbance peaks corresponding to 291 nm and 663 nm wavelengths exhibited a smaller intensity, and decreased in the following order: photolysis > photocatalysis on Z-Na > photocatalysis on Z-Cu.

The apparent rate constants of the photocatalysis process on Z-Cu were about two times higher than those obtained for the photocatalysis on Z-Na, indicating that the doping of natural zeolite with Cu²⁺ justify the application of photocatalysis on Z-Cu from the kinetic point of view.

The influence of the hydrogen peroxide addition in the process of photocatalysis on Z-Cu revealed the fact that after 120 min of irradiation, the efficiencies of discoloration/degradation achieved by the photocatalytic-oxidation process were doubled with respect to the efficiencies achieved by the photocatalysis on Z-Cu process after the same irradiation time.

By applying the photocatalysis on Z-Cu with hydrogen peroxide addition, the apparent rate constant was about 8.5 times higher for the discoloration process and about 2.5 times higher for degradation process, compared with the rate constants of photo-oxidation process.

The discoloration/degradation kinetics of MB in the oxidation process with hydrogen peroxide obey a pseudo-second-order kinetic.

Study of the H₂O₂ dose effect on the MB degradation/discoloration efficiency by photocatalysis on Z-Cu highlighted that in the applied working conditions, 10 mM H₂O₂ dose represented the optimum for the initial concentration of MB solution of 50 mg - L⁻¹.

The reaction orders in the case of 10 and 25 mM hydrogen peroxide adding in the photocatalytic oxidation process were 2.01 and 1.70 respectively, but for the concentration of 50 mM hydrogen peroxide was 1.33.

The increasing absorbances after 500 nm to UV spectrum shows that complete mineralization did not take place.

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