Photocatalytic Degradation of Methylene Blue from Water using UV Irradiation

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ABSTRACT

The aim of this study was to investigate the influence of various parameters on the photocatalytic activity of a copper doped zeolite in the degradation of cationic dye Methylene Blue (MB) from aqueous solution under UV irradiation. The experimental studies revealed that the removal efficiency expressed in terms of discoloration and aromatic ring- opening depended strongly of the initial pH, initial concentrations of the dye solution and catalyst doses. Some mechanistic aspects have been investigated in relation with Zeta potential measurements correlated with adsorption and heterogeneous photocatalysis principles at various pH values.

INTRODUCTION

Dyes from textile wastewaters are characterized by complex aromatic molecular structures, which offer them physicochemical, thermal and optical stability. For this reason, these pollutants need to be removed from industrial effluents. Among the various AOPs, heterogenoues photocatalysis is a promising treatment method with the highest efficiencies [1], based on the direct and indirect absorption of visible or UV radiant energy by a solid semiconductor. Natural zeolites and its modified forms have been widely used as eco-friendly catalyst in various photocatalytic processes [2]. The aim of this study is to investigate the photodegradation of Methylene Blue cationic dye (MB) from aqueous solution using a copper doped zeolite catalyst.

MATERIALS and METHODS

Romanian zeolitic mineral from Mirsid was supplied by CEMACON Company, Romania. Methylene Blue ($C_{16}H_{18}N_3SCl \cdot 3H_2O$) is a basic blue dyestuff with a molecular weight 373.9 $g \cdot mol^{-1}$, selected as a model for the dye. MB (analytical grade) was supplied by Pekin Chemical Works Peking (China). The chemicals used for this study, *i.e.,* hydrochloric acid (HCl), sodium chloride (NaCl), sulfuric acid (H_2SO_4), sodium hydroxid (NaOH) and cupric nitrate ($Cu(NO_3) \cdot 3H_2O$) were purchased from Merck Company. For all experiments distilled water was used. Natural zeolite was previously calcinated and treated with 1M HCl aqueous solution. The activated zeolite as H^+ form was mixed with 1M NaCl aqueous solution and then, the Z-Na form was modified by ion exchange in Z-Cu form with 0.1M $Cu(NO_3)_2 \cdot 3H_2O$ solution. All experiments regarding adsorption and photocatalysis processes were carried out under magnetic stirring at 20 °C into a RS-1 photocatalytic reactor (Heraeus, Germany). Solutions of MB (prepared from an initial stock solution of 1 $g \cdot L^{-1}$) were placed in the photoreactor and irradiated with an UV light set between 280 and 360nm. The first step was to investigate the pH influence on the MB degradation and discoloration efficiency. Similar experiments were carried out at several of dye concentrations (20–100 $mg \cdot L^{-1}$) and catalyst loading (0.5 – 2 $g \cdot L^{-1}$). Prior to irradiation, all the reaction mixtures were stirred in dark for 10 min to reach the adsorption equilibrium.

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. The absorbance values at 291 nm and 663 nm were used to monitor the degradation of aromatic part and discoloration of the dye. The dye solution pH was adjusted with 0.1N H_2SO_4 and 0.1N NaOH solutions. Zeta potential measurements were carried out by a Zeta Meter 3.0+.

RESULTS and DISCUSSION

Zeta potential measurements

The results of the electrokinetic potential (ζ) measurements for 50 $mg \cdot L^{-1}$ MB solutions, Z-Cu suspension in water, Z-Cu suspension in MB solution at the three different pH values are presented in Table 1.

Table 1. Zeta potential measurement results:

System	ζ/mV		
	pH 3	**pH 6**	**pH 9**
MB solution 50$mg \cdot L^{-1}$	+37.57	+52.11	+50.77
Z-Cu suspension in water	-61.00	-69.75	-63.37
Z-Cu suspension in MB	+32.05	+43.5	+33.65

The natural unmodified zeolite has a net negative charge derived from its framework structure, and for the three pH studied, the copper doped zeolite presents a negative surface charge in water, and no izoelectric point was reached. Methylene Blue is a cationic dye, the cationic properties originating from positively charged nitrogen or sulfur centers in its molecular structure. Z-Cu suspension in MB solution has positive charge but slight lower as absolute value.

Effect of initial pH

As a consequence of the Zeta potential evolution, it should be expected a favorable electrostatic interactions between the cationic dye molecules and catalyst surface

The best results were obtained at pH 9 with a degradation efficiency of 66.24 % and a discoloration efficiency of 72.15 % versus 38.73 % degradation efficiencies obtained at pH 3 and 43.74 % for discoloration. A possible reason for this behavior is that alkaline pH range favors the formation of higher ·OH concentrations due to the presence of a large quantity of hydroxide ions in the alkaline medium, which enhanced the photocatalytic degradation of the dye. The presence of transition metal cations doped zeolite may prevent the recombination between the photo-generated holes and electrons or elongate the time of charge separation, because it acts as an electron acceptor center.

In agreement with literature [3] it can assumed that the hydroxyl groups on the surface of prepared catalyst act as an electron donor for photo-generated Cu^{2+}, forming a reactive hydroxyl radicals (·OH) which attack MB via reactions (1) and (2):

$$OH^- + Cu^{2+} \rightarrow \cdot OH + Cu^{2+} \quad (1)$$

$$\cdot OH + MB^+ \rightarrow MB_{ox} \quad (2)$$

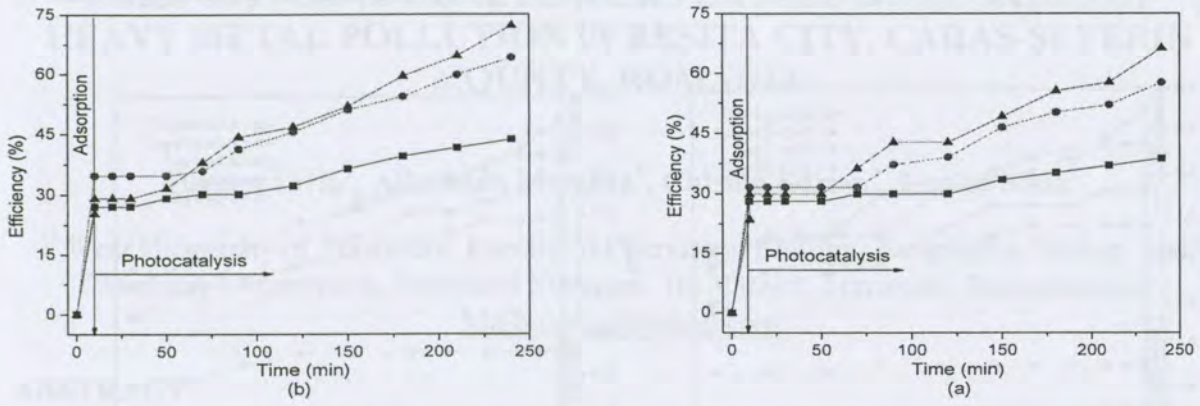

Fig.1. Time evolution of the (a) degradation, (b) discoloration efficiencies of MB after 240 min irradiation: ■ – pH 3 ; ● – pH 6; ▲ – pH 9.
Conditions: 50 mg·L^{-1} MB dye solution; 1 g·L^{-1} catalyst loading.

Effect of initial concentration of Methylene Blue

Fig.2. shows the effect of initial concentration of MB (20-100 mg·L^{-1}) on the degradation and discoloration efficiency (calculated for an irradiation time of 240 min). The increase of the initial dye concentration determined decreasing discoloration/degradation efficiencies. Thus, for 20 mg·L^{-1} initial dye concentration the degradation efficiency was 94.62 % and 25.55 % for 100 mg·L^{-1} initial dye concentration .

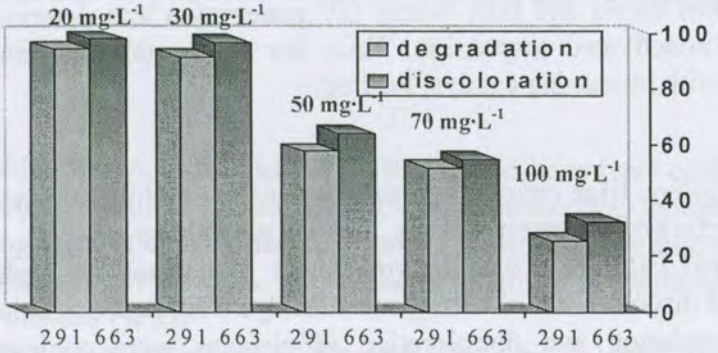

Fig.2. Removal efficiencies of cationic dye Methylene Blue for different initial dye concentrations, at pH 6, 1 g·L^{-1} catalyst loading.

The explanation of this behavior arises from the fact that when the number of the dye molecules adsorbed on the surface of the catalyst is increased, the number of active sites that generate hydroxyl radicals is reduced. Other responsible factor could be the intense color of the dye solution for high concentration, as a result the UV radiation penetration in the solution is cluttered and the number of photons adsorbed on the catalyst surface is lowered.

Effect of the dose of copper doped zeolite catalyst

Subsequent experiments were carried out with different concentrations of catalyst (0.5; 0.75; 1; 1.5; 2 g·L^{-1}) at the same cationic dye concentration (70 mg·L^{-1}), at pH 6 for 240 min irradiation. From Fig.3. it can be noticed that sorption process of MB onto the catalyst is enhanced at the highest catalyst dose (2 g·L^{-1}) while the photocatalysis performance in relation with the MB

discoloration and degradation was slightly affected negatively by the catalyst dose higher than 1 $g \cdot L^{-1}$.

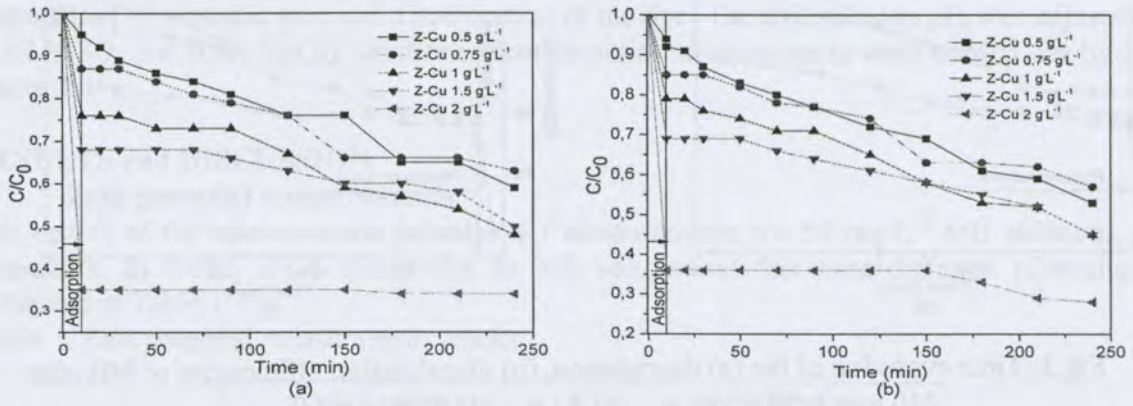

Fig.3. Influence of catalyst loading on (a)-aromatic ring-opening and (b)-discoloration efficiency under UV irradiation; 70 $mg \cdot L^{-1}$ initial MB dye concentration; pH 6.

When the catalyst dose is increased, the quantity of the photons adsorbed and the quantity of the MB molecules adsorbed are higher because of the larger number of active surface centers. Beyond a certain level of the catalyst dose, dye molecules amount is not sufficient for adsorption onto the increased catalyst surface, and as a result of this the Z-Cu powder surplus is involved in the photocatalytic activity [3]. Also, after a certain limit of catalyst amount (1 $g \cdot L^{-1}$ in this study), the solution becomes turbid and thus blocks UV penetration and determines a decrease in the volume of the photoactivated suspension. Thus, the photocatalytic contribution in the global process decreased with increasing catalyst loading.

CONCLUSIONS

- Based on Methylene Blue cationic properties, it is expected that the adsorption take place on the negative surface of the catalyst at the different pH values.
- The optimum pH value of 9 was determined for photocatalysis application using Z-Cu in degradation and discoloration of Methylene Blue dye from aqueous solutions.
- The good degradation and discoloration efficiencies were achieved especially at low concentrations of the dye.
- The increase of the catalyst dose above 1 $g \cdot L^{-1}$ produced a decrease in the photocatalytic activity due to the solution turbidity increasing, which blocked the UV radiation penetration.

LIST OF REFERENCE

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