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## Using ZnO supported on clinoptilolite as a catalyst for photocatalytic degradation of metil orange dye in water

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### ABSTRACT

In this investigation photocatalytic degradation of dye Metil Orange (MO) in water was studied. Zinc oxide was supported on Clinoptilolite (Iranin Natural Zeolite) using solid-state dispersion (SSD) method. The results show that the ZnO / Clinoptilolite (SSD) is an active photocatalyst. The maximum effect of photo degradation was observed at 10 wt.% ZnO, 90 wt% Clinoptilolite. A first order reaction with  $K = 0.0119 \text{ min}^{-1}$  was observed. the photocatalytic degradation reaction. The effects of some parameters such as pH, amount of photocatalyst, initial concentration of dye were also examined. © 2013 Trade Science Inc. - INDIA

### KEYWORDS

Photodegradation;  
Photocatalysts;  
ZnO/zeolites;  
MO;  
Clinoptilolite (CP).

### INTRODUCTION

From the viewpoint of green chemistry, the photocatalytic decomposition of organic compounds in wastewater has attracted a great deal of attention<sup>[1-9]</sup>. ZnO is one of the most effective photocatalysts because it is biologically and chemically inert and photostable with near-UV band gap energy. ZnO can be used as a fine powder or crystals dispersed in water wastewater treatment applications. However, the need to filter ZnO after reaction makes such a process troublesome and costs. Thus, in order to solve this problem, many researchers have examined some methods for fixing ZnO on supporting materials including glass beads<sup>[10-12]</sup>, fiber glass<sup>[13-15]</sup>, silica<sup>[16,17]</sup> and zeolite<sup>[18,19]</sup>. When using zeolite as ZnO support, care should be taken that ZnO does not loose its photo activity and adsorption properties of zeolite is not affected. Matthews<sup>[11]</sup> showed the

photoefficiency of ZnO is suppressed when Ti is in interaction with the zeolite. In this work ZnO was supported on a zeolite without losing photoefficiency and affecting the adsorption properties of zeolite. This mixture was used for degradation of Metal Orange.

### EXPERIMENTAL

#### Material

The Metil orange (Kimia Goster Chem. Co., Iran) shown in Figure 1 as a target dye and Zinc Nitrate was (Merk.Co.germany). And the raw zeolite material was an Iranian commercial clinoptilolite (CP) (Afrand Tuska Company, Iran) from deposits in the region of Semnan. According to the supplier specification, it contains about 90 wt % CP (based on XRD internal standard quantitative analysis) and the Si/Al molar ratio is 5.78. The concentration of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MnO,

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P<sub>2</sub>O<sub>5</sub> and Loss on Ignition (LOI) impurities were reported to be 70.16, 20.95, 0.82, 1.30, 0.30, 0.04, 0.04, 0.01 and 6.42 wt %. Another materials were purchased from Merck (Germany). Double distilled water were used for preparation of requisite Solutions.

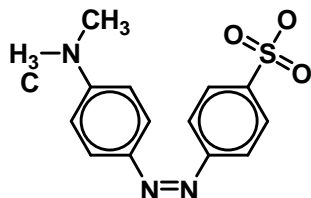


Figure 1 : Molecular structure of direct metal orange

The dye used in this study was MO, Mw=327.8,  $\lambda_{max} = 628.48$  nm, an anionic diazo direct dye, supplied by Kimia Gostar Company (Iran), without further purification. other material prepared from Merck Company.

### Preparation of ZnO-supported CP catalysts

Preparation of ZnO - Supported Clinoptilolite Catalysts The solid state dispersion (SSD) method was used for preparing the Zeolite-based photocatalyst. In this method, ZnO was mixed with zeolite using ethanol as a solvent using agate pestle and mortar; the solvent was then removed by evaporation. Samples prepared by this method were dried at 110 °C and calcined in air at 450 °C for 2 h to obtain ZnO supported zeolite catalysts.

### Apparatus

For UV/photocatalyst process, irradiation was performed in a batch photoreactor of 4 liter in volume with six mercury lamps, Hitachi 8W (UV-C). A magnetic stirrer was used to ensure complete mixing in the tank (stirring speed=250 rpm) and air was dispersed at a flow rate of 1 lit.min<sup>-1</sup> by using an air diffuser to supply oxygen for the enhancement of photo-oxidation. Figure 2. UV-VIS Spectrophotometer, Perkin-Elmar lambda25 was employed for absorbance measurements using silica cells of path length 1 cm. XRD analysis of the samples was done using a D-500 diffractometer (Simemens). BET surface areas of CP and ZnO/CP were measured in an all-glass high vacuum system by N<sub>2</sub> adsorption at 77 k. The morphology of the resultant was pure, and loaded ZnO was obtained with a transmission electron microscope (SEM; JEOL JSM-5800

Philips, 515 SEM).

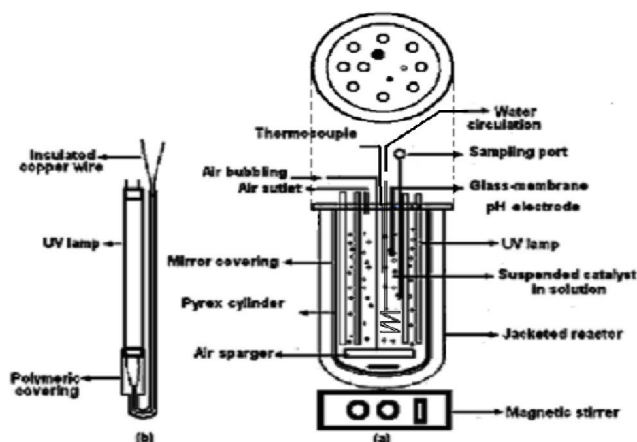


Figure 2 : Schematic diagram of the batch photocatalytic reactor ( cross- section) (a), and UV lamp immersed directly in aqueous solution (b).

### Procedures

For the photodegradation of MO, a solution containing known concentration of dye and photocatalyst was prepared and it was allowed to equilibrate for 30 min in the darkness. The suspension PH values were adjusted at desired level using dilute KOH and H<sub>2</sub>SO<sub>4</sub> (the pH values were measured with pH meter (Sartorius PT-10P and Py-P12 PH meter). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. The concentration of dye in each degraded sample was determined with a spectrophotometer (UV/VIS Spectrophotometer, Perkin - Elmer lambda25) at  $\lambda_{max} = 628.48$  nm and a calibration curve. By this method conversion percent of MO can be obtained in different intervals. The degree of photodegradation (X) as a function of time is given by:

$$x = \frac{C_0 - C}{C_0} \quad (1)$$

Where C<sub>0</sub> and C are the concentration of the dye at t=0 and t, respectively.

## RESULTS AND DISCUSSION

### UV-Vis spectra

The absorbances of MO solutions during the photocatalytic process at initial and after 2 h irradiation time

verses  $\lambda$  are shown in the Figure 3. The spectrum of MO in the visible region exhibits a main band with a maximum at 628.48 nm. The decrease of absorption peaks of MO at  $\lambda_{max} = 628.48$  nm in this figure indicates a rapid degradation of the dye. Complete discoloration of dye was observed after 3h under optimum conditions.

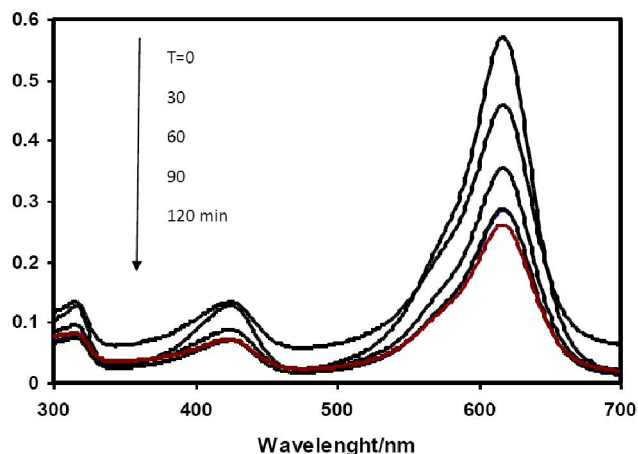


Figure 3 : UV-Vis spectra of MO (40 ppm) in aqueous photocatalyst (10 wt % ZnO/CP) dispersion with concentration of 20 ppm, irradiated with a mercury lamp light at PH=7, T=298K, at: t=0,30, 60, 90, 120

### Effect of UV irradiation and photocatalyst employed

#### Particles

The effects of UV irradiation, ZnO and clinoptilolite on photodegradation of MO are shown in Figure 4. This Figure indicates that, in the presence of mixed photocatalyst (10% ZnO and 90% clinoptilolite) and UV irradiation 94% of dye was degraded at the irradiation time of 2.5 h while it was 52.7% for ZnO (without clinoptilolite) and UV irradiation. This was contrasted with 9.8% degradation for the same experiment performed in the absence of ZnO, and the negligible 0.30 % when the UV lamp had been switched off and the reaction was allowed to occur in the darkness. These experiments demonstrated that both UV light and a photocatalyst, such as mixed photocatalyst (10% ZnO + 90% clinoptilolite) are needed for the effective degradation of MO. This is due to the fact that when ZnO is illuminated with the light of  $\lambda < 390$  nm, electrons are promoted from the valence band to the conduction band of the semi conducting oxide to give electron-hole pairs. The valence and (h) potential is positive enough to gen-

erate hydroxyl radicals at the surface, and the conduction band ( $e_{cb}$ ) potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of ZnO. It causes photooxidation of dye according to the following reactions<sup>[11-13]</sup>:

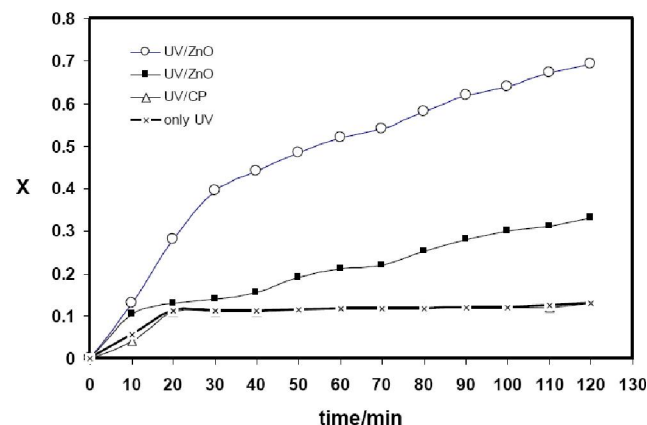
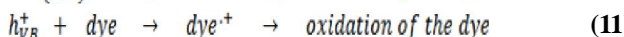
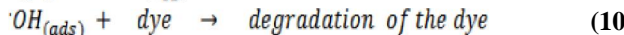
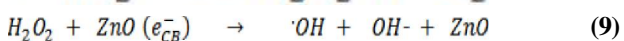
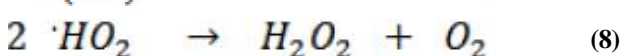
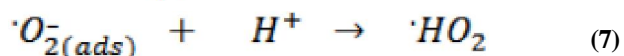
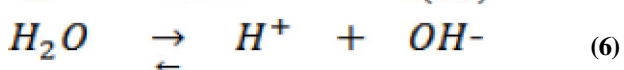
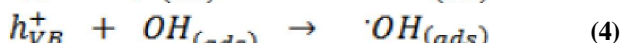
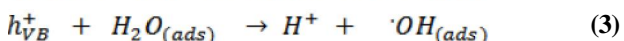
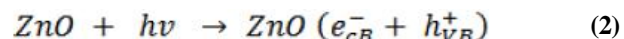


Figure 4 : Effect of UV light and different photocatalysts on photocatalytic degradation of MO. [MO]<sub>0</sub> = 40 ppm, ZnO and photocatalyst (10 wt. % ZnO/CP) concentration=20 ppm, T= 298 K, PH= 7

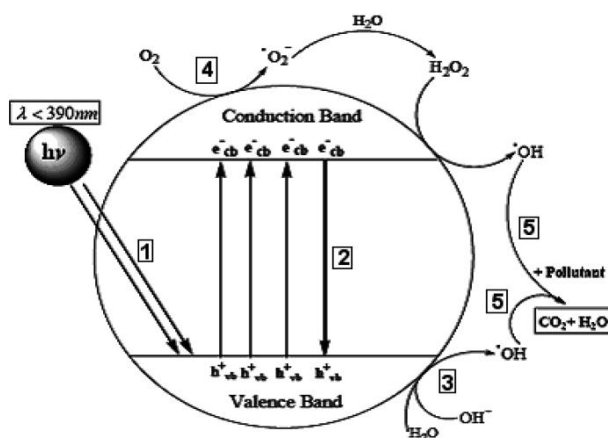


Figure 5 : General mechanism of the photocatalysis

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The mechanism is assumed up in Figure 5.

### Effect of the composition of the supported photocatalyst

The effect of the ratio of ZnO /CP on MO removal is shown in figure 6. The effective decomposition of MO after 120 min irradiation time was observed when the photocatalyst contained 10% ZnO and 90% CP, prepared by using the solid state dispersion (SSD) method.

To comment on this result, we propose that the  $\cdot\text{OH}$  (hydroxyl radical) on the surface of ZnO is easily transferred onto the surface of zeolite. This means the organic pollutants, which have already been adsorbed on the nonphotoactive zeolite, have a chance to be degraded due to the appearance of  $\cdot\text{OH}$ , resulting in the enhancement of the photodegradation performance of ZnO-zeolite. Experimental results show that about 10 wt % of ZnO with respect to zeolite is the best condition to achieve the synergism between ZnO and CP. This synergic effect may be due to the fact that the presence of zeolite maintains the molecules of dye near the photocatalyst (local concentration effect) as depicted in Figure 6. The enhanced photocatalytic activity over the composite ZnO + CP reflects the beneficial adsorption properties of CP. If the amount of ZnO in the composition of the photocatalyst decreases (Less than 10 wt %), the rate of  $\cdot\text{OH}$  production will not be enough. In this condition a few of the dye molecules that have been absorbed on the surface of zeolite can react with  $\cdot\text{OH}$ . If the amount of ZnO increases in the composition of the photocatalyst (more than 10 wt %), the rate of dye absorption will not be enough. In this condition few of the  $\cdot\text{OH}$  can react with dye molecules.

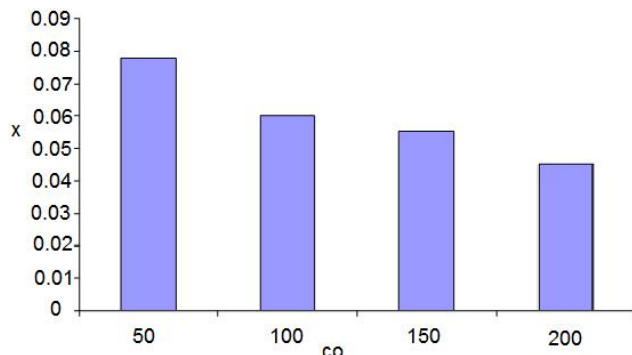


Figure 6 : Effect of composition of photocatalyst (wt % ZnO in mixture of ZnO and clinoptilolite) on photocatalytic degradation of MO.  $[\text{MO}]_0 = 20 \text{ ppm}$ . Concentration of photocatalyst=40 ppm,  $T = 298\text{K}$ ,  $\text{PH} = 7$ , irradiation= 120 min

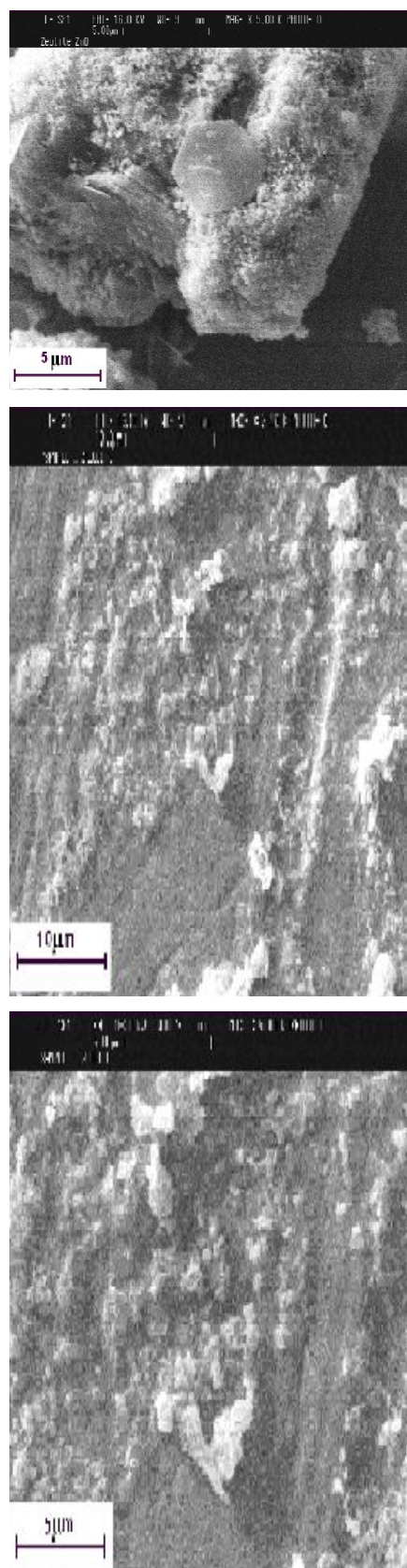


Figure 7 : SEM images of (a) purer ZnO particles and (b) ZnO particles loaded on the surface of CP

### Characterization of photocatalysts

As is known, the pore size of CP is 0.4-0.7 nm<sup>[19]</sup>. Figure 7. shows the SEM images of pure ZnO nanoparticles and ZnO particles loaded on the surface of CP. As can be seen. The particle size of pure ZnO is The photodegradation efficiency increases with an increase in the amount of photocatalyst, reaches the higher value of catalyst amount (40 ppm) and then decreases. The most effective decomposition of MO was observed with 40 ppm of mixed photocatalyst. The reason of this observation is thought to be the fact that when all dye molecules are adsorbed on photocatalyst, the addition of higher quantities of photocatalyst would have no effect on the degradation efficiency. Another cause for this is supposedly an increased opacity of the suspension, brought about as a result of excess of ZnO particles<sup>[14]</sup>.

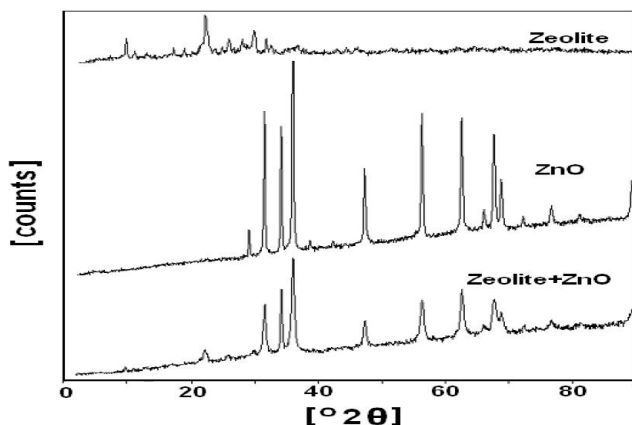


Figure 8 : XRD pattern of 10 wt. % ZnO/CP prepared by the (SSD) method after calcinations in air at 450°C for 5 h (CP), raw ZnO after calcinations in air at 450°C for 5 h and ZnO/CP after calcinations in air at 450°C for 5 h

To reveal the interaction between the ZnO and the zeolite, the crystal structures of the raw zeolite and the ZnO-zeolite calcined at 450 °C after 5 h were measured, as shown in Figure 8. It is clear that the XRD patterns of ZnO-zeolite consist with the raw zeolite very well as calcined at 450°C for 5 h, and no diffraction peaks corresponded to typical ZnO, including anatase and rutil, can be observed. And similar results have also been reported by other researchers<sup>[21,22]</sup> It implies that the frame structure of zeolite after ZnO loading has not been destroyed.

### Effect of pH

The pH is one of the main factors influencing the rate of degradation of some organic compounds in

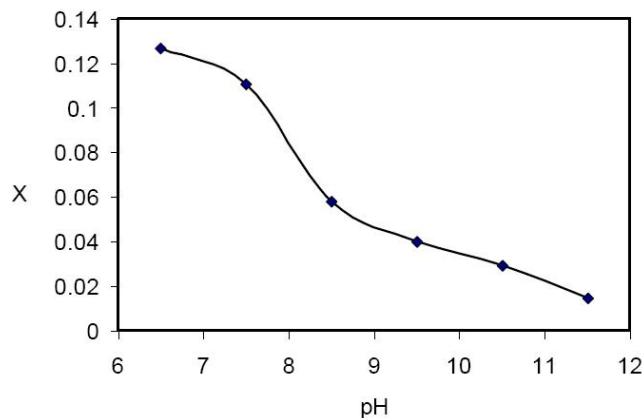
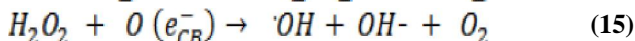
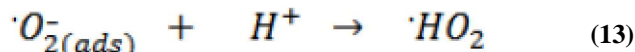
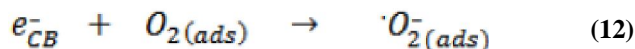


Figure 9 : Effect of pH on photodegradation efficiency of MO at the = 40 ppm, photocatalyst (10% irradiation time of 150 min).  $[MO]_0 = 20$  ppm, concentration of photocatalyst (10 wt. % ZnO/CP) = 40 ppm, T = 298 K

the photocatalytic process<sup>[15,16]</sup>. It is also an important operational variable in actual wastewater treatment. Figure 9. shows the photodegradation of MO at different pH from 6.5 to 11.5, which clearly shows that the best results were obtained in acidic solution, (pH = 6.5 or 7, X = 100%). The ZnO surface is presumably positively charged in acidic solution and negatively charged in alkaline solution<sup>[17,18]</sup>. For the above reasons, for dyes that have a sulfuric group in their structure, which is negatively charged, the acidic solution favors, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of MO in acidic solution, which is probably due to the formation of  $\cdot OH$  as it can be inferred from the reactions (12)-(15)<sup>[20]</sup>.



### Kinetics of photocatalytic degradation of MO

Several experimental results indicated that the degradation rates of photocatalytic oxidation of various dyes over illuminated ZnO fit by the first-order kinetic model<sup>[23-29]</sup>.

Figure 7 shows the plot of  $\ln([dye]_t/[dye]_0)$  versus irradiation time for MO. The linearity of plot suggests that the photodegradation reaction approximately follows the pseudo-first order kinetics with a rate coefficient  $K=0.0009 \text{ min}^{-1}$ .

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### CONCLUSIONS

- 1 The SSD method is an effective method for supporting of ZnO on Clinoptilolite.
- 2 Photocatalyst containing 10% ZnO and 90% clinoptilolite has the maximum on photodegradation efficiency of MO.
- 3 The photodegradation conversion of MO decreases with an increase in the initial concentration of MO.
- 4 pH is one of the main affecting factors and the optimum pH was obtained about 6.5 or 7.
- 5 Kinetics of photocatalytic degradation of MO is pseudo-first order with  $K=0.0009 \text{ min}^{-1}$ .

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