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# Photocatalytic degradation of nonionic surfactant in water with ZnO nanoparticles supported on clinoptilolite as a catalyst

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## ABSTRACT

The use of nanophotocatalysts supported on adsorbents is receiving substantial attention. Supporting ZnO nanoparticles with zeolites is found to be one of the best solutions to increase the efficiency of ZnO-based photocatalysts. This work was focused on simple preparation of a ZnO/Clinoptilolite (CP) (Iranian Natural Zeolite) composite catalyst by the solid state dispersion (SSD) method and Comparison of ZnO nanoparticles and ZnO/CP on the photocatalytic degradation of Triton X-100. The degradation of Triton X-100 was systematically studied by varying the experimental parameters in order to achieve maximum degradation efficiency. The obtained results demonstrated a high photocatalytic activity of nanosize zinc oxide supported on Clinoptilolite.

## KEYWORDS

Photodegradation;
Photocatalysts;
ZnO/zeolites;
Triton X-100;
Peroxydisulfate.

## INTRODUCTION

Nanometer-sized zinc oxide as an important inorganic function material was widely used in rubber, coat, catalyst, electronic engineering fields[1-3]. In the past two decades, zinc oxide has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity[4-7], stability and wide band gap[8]. Zinc oxide is thought as a low cost alternative photocatalyst to $TiO_2$ for degradation of organics in aqueous solutions[9]. As a contrast, ZnO, a kind of semiconductor that has the similar band gap as $TiO_2$, is not thoroughly investigated. However, the biggest advantage of ZnO in comparison with $TiO_2$ is that it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425nm[10]. Some researches have highlighted the performance of ZnO on degradation of some organic compounds. ZnO nanopowder has been reported, sometimes, to be more efficient than $TiO_2$ and its efficiency has been pointed out to be particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater[11,12], the photooxidation of 2-phenylphenol and photocatalysed oxidation of phenol[13]. Despite the positive attributes of ZnO, poor adsorption properties, the rapid recombination of photogenerated electron ($e^-$)/hole ($h_{vB}^{+}$) pairs and the

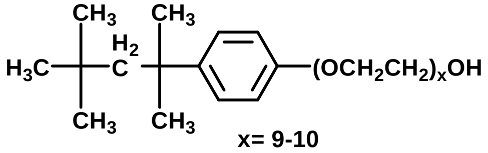

**Figure 1 : Structure of Triton X-100**

ZnO powders are easy to lose and not suitable for recycling lead to great limitation in exploiting this photocatalyst for its maximum efficiency. To circumvent this limitation, several attempts have been made to improve the efficiency of ZnO by using suitable supports such as glass, polymers, stainless steel, quartz, pyrex, paper, fabric, monoliths and zeolites[14-17]. Among the supports, zeolites have more advantageous owing to their special features such as high surface area, hydrophobic and hydrophilic properties, tunable chemical properties, high thermal stability and eco-friendly nature[18]. In this work ZnO nanoparticles was supported on a zeolite without losing photoefficiency and affecting the adsorption properties of zeolite. This mixture was used for degradation of aqueous non-ionic surfactant TX-100 as a model compound of organic pollutants that they are excessively used in many formulations applied in various industrial areas such as detergent industry, textiles and metallurgy.

## EXPERIMENTAL

### Materials

The Zinc oxide nano powder (particle size, ca.20nm; BET area, 50m$^2$/g, 99.5%) was obtained from Nanoamor (USA), 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 50 wt % CP (based on XRD internal standard quantitative analysis) and the Si/Al molar ratio is 5.78. The concentration of $Fe_2O_3$, $TiO_2$, MnO, and $P_2O_5$ impurities were reported to be 1.30, 0.30, 0.04, and 0.01 wt %. The nonionic surfactant Triton X-100(TX-100) was obtained from the company Paxan (Iran) and used without further purification. $K_2S_2O_8$, isopropyl alcohol was from Merck. The pH of solution was adjusted to the desired value between 4.0 and 11.0 by using dilute solution of HCl or NaOH.

### Preparation of ZnO-supported CP catalysts

The sodium form of zeolite of clinoptilolite was converted into the H-form by repeated ion exchange with 1M ammonium nitrate solution at 80°C, and subsequent calcination at 550°C in air. The resultant H-form of zeolite was abbreviated and 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 with an 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 5 h to obtain ZnO-supported zeolite catalysts.

### Apparatus

The conditions used in the present study was a batch reactor(a cylindrical Pyrex vessel of 2 cm diameter with capacity of 50mL), 20cm distance between UV source (high pressure mercury vapor lamp 400 w) and solution with a stirring speed of 80 rpm and 30 min time for adsorption equilibrium. The quantitative estimation of the surfactant was carried out using a UV-Vis spectrophotometer (model Jenway 6405) at $\lambda_{mAX}$ = 223nm.

## RESULT AND DISCUSSION

### Effect of 50Wt. %ZnO/CP on TX-100 photodegradation

The effects of UV irradiation, ZnO and CP presence on the photodegradation of TX-100 are shown in figure 2. This figure indicates that in the presence of mixed photocatalyst (50 Wt. %ZnO/CP) and UV irradiation 95.4% degraded at the irradiation time of 8 h while it was 83.2% for ZnO (without clinoptilolite) and UV irradiation. This was contrasted with 8.1% degradation for the same experiment performed in the absence of ZnO, and 4.6% when the UV lamp had been switched on and the reaction was allowed to occur in the presence of CP.

### Effect of electron acceptor on TX-100 photodegradation

The effect of sulfate radical ($SO4^{\cdot -}$) as an oxidant on the degradation of Triton X-100 was investigated and compared with the (50 Wt.%ZnO/CP) (only), $S_2O_8^{2-}$ (only), UV / $S_2O_8^{2-}$, UV /(50Wt.%ZnO/CP) and UV/(50Wt.%ZnO/CP) / $S_2O_8^{2-}$ systems. As can be seen from Figure 3 (50Wt. %ZnO/CP) alone in the absence of sulfate radical and UV irradiation was found to have no measurable effect on the degradation of the surfactant during of 120 min irradiation time. A similar behavior was also observed in the UV system alone. In

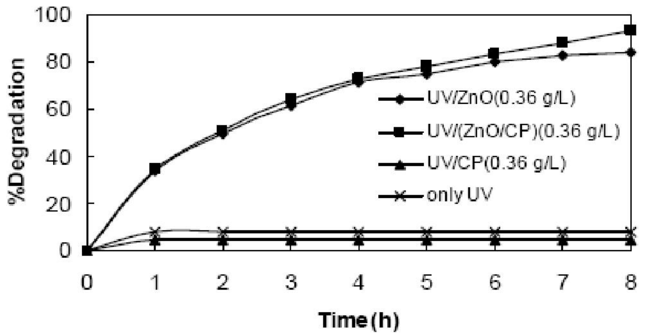

Figure 2 : Degradation of $[TX\text{-}100]_0 = 30ppm$

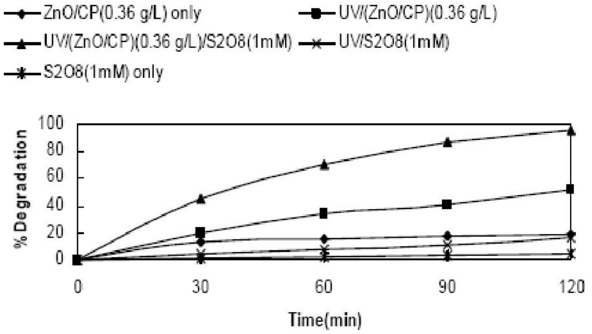

Figure 3 : Degradation of $[TX\text{-}100]_0 = 30ppm$

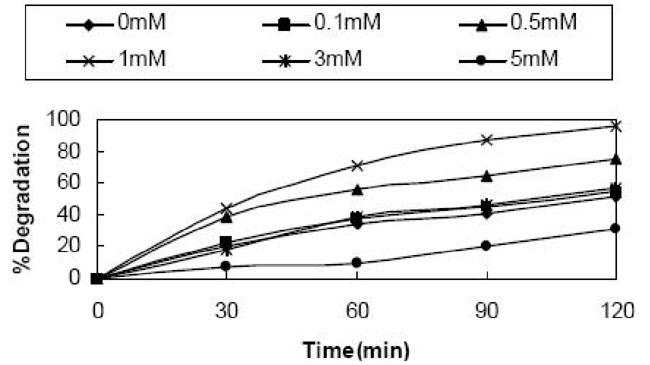

Figure 4 : Effect of $S_2O_8^{2-}$ concentration on the Degradation of Triton X-100 Conditions:$[Triton\ X\text{-}100]_0$: 30mg/L, ZnO/CP: 0.36 g/L, pH = 7, V: 25ml

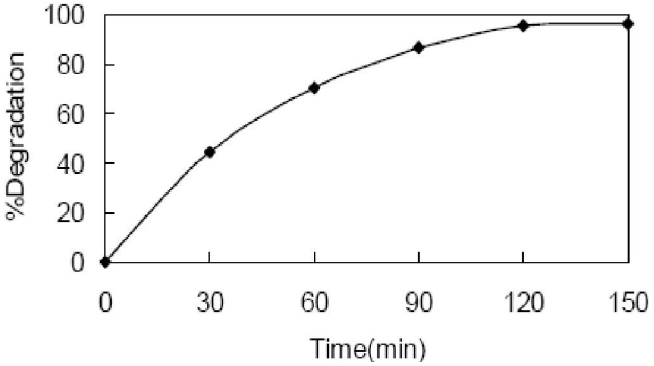

Figure 5 : Effect of Time on the Degradation of Triton X-100 Conditions: 30mg/L of Triton X-100; ZnO: 0.2 g/L; pH = 6; V: 25mL

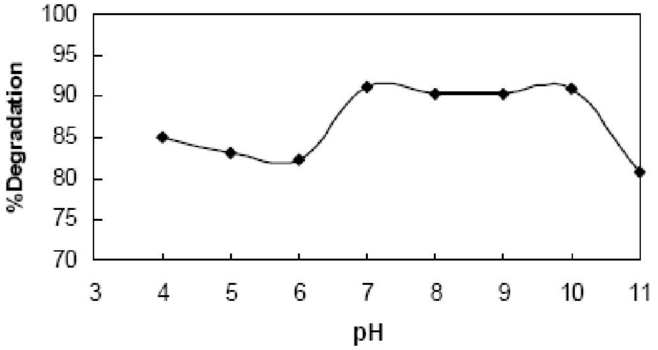

Figure 6 : Effect of pH. Conditions: ZnO/CP: 0.36 g/L,[S2O82-]:1mM, V: 25ml

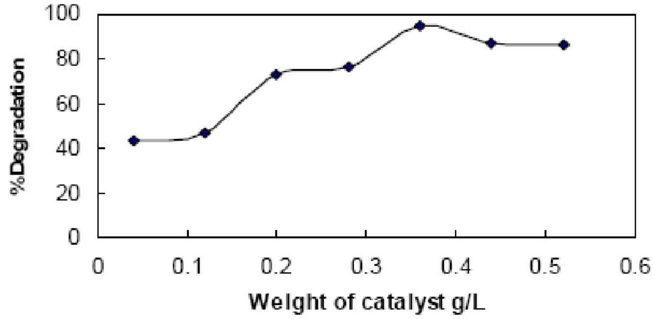

Figure 7 : Effect of catalyst weight. Conditions: Triton X-100 = 30mg/L;$[S_2O_8^{2-}]$ = 1mM; pH = 7; Irradiation Time: 120; V: 25ml

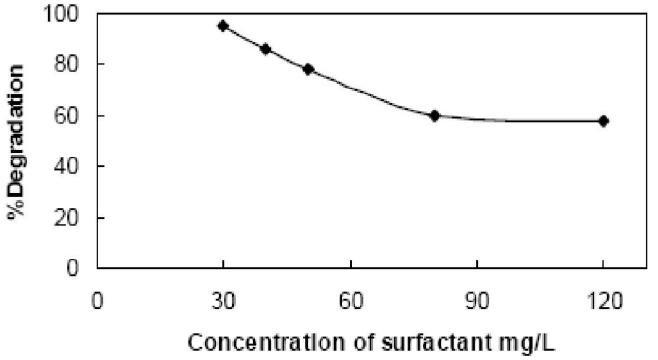

Figure 8 : Influence of initial surfactant concentration on the photodegradation. Conditions: $S_2O_8^{2-}$:1mM, ZnO/CP: 0.36 g/L, PH: 7, Irradiation Time: 120min, V = 25ml

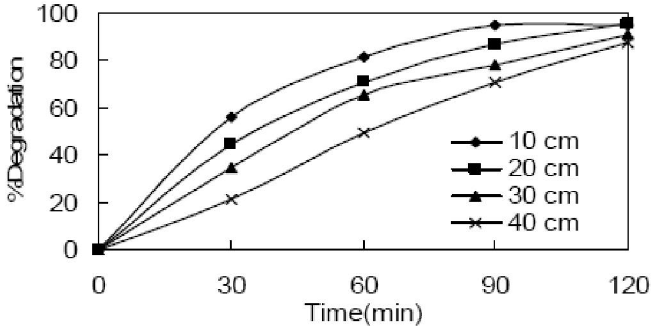

Figure 9 : Effect of distance between UV source and solution on photodegradation rate. Conditions: ZnO/CP: 0.36 g/L; Triton X-100 = 30mg/L;$[S_2O_8^{2-}]$ = 1mM; pH = 7; Irradiation Time: 120 min; V: 25ml

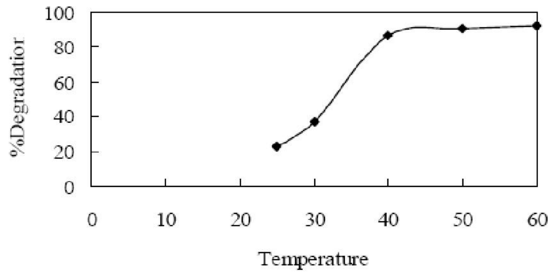

**Figure 10 : Temperature effect, Conditions: ZnO/CP: 0.36 g/L; Triton X-100 = 30mg/L;[$S_2O_8^{2-}$] = 1mM; pH = 7; Reaction Time: 120 min; V: 25ml**

the case of sulfate radical alone, the degradation yield was determined as approximately 4% after 120 min for 30mg/L. The degradation yield of surfactant in UV/ $S_2O_8^{2-}$ system without (50Wt. %ZnO/CP) was obtained approximately 17 % after 120 min treatment which is probably due to the production of radical species. The photocatalytic decomposition of peroxydisulfate potassium under UV radiation involves the formation of a number highly reactive radical ($O^{\cdot}H$, $SO_4^{\cdot -}$) and the non-radical species ($O_3$, $SO_4^{2-}$). As shown in figure 3 UV/(50 Wt. %ZnO/CP) system had more significant effect on the degradation of surfactant than the UV/ $S_2O_8^{2-}$ system. This result is explained by the fact that ZnO is exposed to UV radiation; an electron is promoted from the valence band to the conduction band. Thus a $\frac{h^+_{VB}}{e^-_{cB}}$ pairs is produced (Eq. 1). The photocatalyst, zinc oxide, is a wide band gap (3.37ev) semiconductor, corresponding to radiation in the near –UV range:

$$ZnO + hv \rightarrow e^-_{cB} + h^+_{VB} \qquad (1)$$

The highly oxidative $h^+_{vB}$ can react easily with surface bound $H_2O$ to produce hydroxyl radicals or can directly react with the surface sorbed organic molecules (R) to from R $^{+}$.

$$h^+_{VB} + H_2O_{(ads)} \rightarrow O^{\cdot}H + H^+ \qquad (2)$$

$$\text{Surfactant} + O^{\cdot}H \rightarrow \text{degradation product} \qquad (3)$$

$$\text{Surfactant} + ZnO\ (h^+_{vB}) \rightarrow \text{oxidation product} \qquad (4)$$

$$\text{Surfactant} + ZnO\ (h^-_{cB}) \rightarrow \text{reduction product} \qquad (5)$$

When potassium peroxydisulfate was added to the UV/ (50 Wt. %ZnO/CP) system, surfactant degradation increased from 51.2% to 95.4% after 120 min (Figure 3).

Acceleration of the degradation rate Photocatalytic oxidation on ZnO occurs by photogenerated holes it is well known that oxidation rate increases when recombination process is suppressed. Peroxydisulfate has been shown to be a more reliable and cheaper electron acceptor effect of peroxydisulfate as the electron acceptor was examined as shown in figure 4. The degradation of Triton X-100 was remarkable accelerated by adding peroxydisulfate:30mg/L Triton X-100 and in the presence of 0.36g/L (50Wt.%ZnO/CP) was completely disappeared under the irradiation of 8 to 2h respectively, in the absence and in the presence of 1mM $K_2S_2O_8$.

$$ZnO + hv \rightarrow h^+ + e^- \qquad (6)$$

$$h^+ + e^- \rightarrow ZnO \text{ (recombination)} \qquad (7)$$

$$h^+ + Tx\text{-}100 \rightarrow (Tx\text{-}100)^{\cdot +} \qquad (8)$$

$$e^- + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} \qquad (9)$$

The $SO_4^{\cdot -}$ radical is a strong oxidant capable of mineralizing phenolic compounds such as butylated hydroxyanisole in water. The produced $SO_4^{2-}$ ion is not considered to be a pollutant. The decrease in the mineralization efficiency of surfactant with increasing $SO_4^{2-}$ concentration is mainly due to scavenging the valuable hydroxyl radicals with $SO_4^{2-}$ ion as shown in eq. (10).

$$^{\cdot}OH + SO_4^{2-} \rightarrow OH^- + SO_4^{\cdot -} \qquad (10)$$

## Effect of illumination time

The relationship between the photodegradation efficiency of Triton X-100 and the illumination time was investigated. The result is shown in figure 5. As can be seen from figure 5, it can be seen that the photodegradation efficiency of Triton X-100 increases with the increase of the illumination time. The photodegradation efficiency of Triton X-100 increases from 10.6% to 95.4% when the illumination time increases from 10 to 150 min. From figure 4, it also can be seen that when the illumination time is longer than 60 min, only small enhancement of photodegradation efficiency is observed. When the illumination time is 120 and 150 min, the photodegradation efficiency of Triton X-100 is 95.4% and 96%, respectively. The result does not seem to lead to full degradation. The possible reason is that there are a large number of small organic molecules produced by photodegradation with the increase of the irradiation time. The small organic molecules adsorb on the surface of ZnO supported on the zeolite, resulting in the decrease in the amount of $^{\cdot}OH$

radicals that attack the nonionic surfactant, and therefore influence the photodegradation efficiency of Triton X-100. At the same time, it had been reported that the can be completely photocatalytically degraded with the increase of the illumination time.

### Effect of pH

The photodeagration process is pH depended and the process exhibits different behavior with the chemical character of surfactant. Figure 6 indicates the effect of pH on the degradation efficiency of Triton X-100 by UV/(50Wt. %ZnO/CP)/$S_2O_8^{2-}$ system is range of 4-12. The degradation of TX-100 was more enhanced in the range of pH 7-10 than the other pH values. As is inferred in reaction (2), in the alkaline solutions the formation of $\cdot$OH on to photocatalyst surface is favored; thus, the photodegradation efficiency increases in the alkaline solutions for photodegradation of TX-100.The lower rate of degradation at acidic and alkaline pH maybe attributed to dissolution of ZnO.

### Effect of catalyst weight

The effect of photocatalyst weight on the photodegradation of the dye was studied in the range of 0.04-0.52g/L. A small but significant rate as show in Figure 7 this can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalyst weight. But at the catalyst weight above optimum loading there is a decrease in UV light penetration due to screening effect of excess catalyst particle in the solution. Hence, the rate of photodegradation decreases at the higher catalyst loading.

### Effect of surfactant concentration on the photocatalytic degradation

The photocatalytic degradation of the surfactant was carried out at different initial surfactant concentrations ranging from 30 to 120mg/L. Figure 8 shows the rate of photodegradation of the surfactant decreased at higher concentrations. At higher concentration a greater number of surfactant molecules of adsorbed virtually masking the surface of the catalyst particles and preventing the photons interacting with the catalyst.

### Effect of distance between UV source and solution

As shown in figure 9, change in distance between UV source and solution, rate of degradation of surfactant will change. In this work 10, 20, 30 and 40 cm distances were studied. Results showed that when the distance between solution and UV source was decreased, large amount of light absorb by photocatalyst and photodegradation process time was decreased from 120 min to 90 min.

### Effect of temperature of reaction

Temperature effect was studied in a thermal reactor. The reactor was surrounded by a water jacket, consisting of one inlet and another outlet for the passage of water inlet and outlet is connected to thermostat bath) Haake Model F122). Water is pumped inside cell and after tap off it is return to the bath. So the temperature fixed and controlled. Experiment was done alone at dark. Although the temperature in a chemical reaction plays an important role, very little information concerning the temperature effect on the heterogeneous photocatalytic degradation of pollutants in aqueous solutions is available. This is due to the fact that the heterogeneous photocatalytic reactions are usually not very temperature-sensitive because the band-gap energy of ZnO is too high (3.2eV) to be overcome by the thermal activation energy. Figure 10 shows increasing the reaction temperature may increase the oxidation rate of organic compounds at the interface, but it also reduces the adsorptive capacities associated with the organics and dissolved oxygen[19,20].

### Effect of isopropyl alcohol

The photocatalytic degradation of the surfactant, Triton X-100 was carried out in the presence of ZnO by the additional of isopropyl alcohol, a known hole scavenger[33]. Even very low concentration of IPA (10mM) hindered the degradation rate of the surfactant to a large extent and the degradation percent decreased from 55.5% to 46% with an increase of IPA concentration to 20mM. The decrease in the rate was due to the holes that were formed and were trapped by IPA which prevents the formation of hydroxyl radicals. However higher concentration of IPA (50mM) did not stop the oxidation completely, indicating that oxidants other than holes are also involved. Direct oxidation by electron vacancies may be suggested as reported by Richard and Boule[21].

## CONCLUSION

The SSD method is an effective method for supporting ZnO on CP.A photocatalyst containing 50 %ZnO and 50% CP has the maximum photodegradation efficiency of TX-100. The optimal degradation conditions of TX-100 obtained from the present research were:the dosage of catalyst 0.36 g/L, pH 7-10, the amount of $k_2S_2O_8$ 1Mm.Under optimal degradation conditions of TX-100, the photodegradation percent of TX-100 was 95.4% when the solution was irradiated by the 400w high pressure mercury–vapour lamp for 2h. Degradation of NP10EO was accelerated remarkably by adding proxydisulfate. Therefore, when peroxydisulfate was added to the UV/ (50 Wt. %ZnO/ CP) system, surfactant degradation increased from 51.2% to 95.4% after 120 min.

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