Photocatalytic Degradation of Nonionic Surfactant Using Zinc Oxide Nanoparticles

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In this paper, the photocatalytic degradation of nonylphenol polyethoxylate (10 ethylene oxide units, NP10EO), a nonionic surfactant, was investigated in aqueous solution using ZnO nanoparticles. The degradation was studied under different conditions such as the amount of photocatalyst, illumination time, reaction temperature and initial concentration, presence of electron acceptor. The results showed that photocatalytic degradation of NP10EO was strongly influenced by these parameters. The best conditions for the photocatalytic degradation of NP10EO were obtained. The optimum amount of the photocatalyst used was found to be 0.2 g/L. The photodegradation efficiency of NP10EO increased with the increase of the illumination time. The degradation efficiency is enhanced by increasing reaction temperature and the photodegradation efficiency decreased with an increase in the initial concentration of NP10EO. Analysis of kinetic showed that the amount of surfactant photocatalytic degradation could be fitted into pseudo-second-order model.

Key Words: Zinc oxide nanoparticles, Photocatalytic, Surfactant, Degradation.

INTRODUCTION

Non-ionic surfactants in aqueous solution are excessively used in many formulations applied in various industrial areas such as detergent, agrochemisty, cosmetics, textiles and metallurgy[1]. Surfactants, being the common chemical pollutant of sewage, are hardly removable by classical physicochemical and biological methods. Because the alkylphenol polyethoxylates (APE) surfactants display a low biodegradability and high toxicity for biologically active deposits, their pretreatment should be considered in an efficient oxidation procedure. In recent years, as a promising tool to substitute the traditional wastewater treatment, semiconductor-assisted photocatalysis among the advanced oxidation processes (AOPs), has attracted the public concern for its ability to convert the pollutants into harmless substances directly in the wastewater. Till now, various kinds of semiconductor have been studied as photocatalysts including TiO_2, ZnO, CdS, WO_3, *etc*.[2-4]. TiO_2 is used most widely because of its high effective photocatalyst, photochemical stability, non-toxic nature and low cost. In contrast, ZnO is a semiconductor with similar band gap to TiO_2. However, the most important advantage of ZnO in comparison with TiO_2 is that it absorbs[5] over a wide range of UV spectrum and its corresponding threshold is 425 nm. Some researches have highlighted the performance of ZnO on degradation of some organic compounds. ZnO nano-powder has been reported to be more efficient than TiO_2 with efficiency

noticeable in the advanced oxidation of pulp mill bleaching wastewater[6,7], photo oxidation of 2-phenylphenol and photo catalyzed oxidation of phenol[8].

In this paper, we selected a nonionic surfactant as a model compound for organic pollutants and ZnO nanoparticles as photocatalyst. The effects of various parameters, such as the concentration of the photocatalyst, illumination time, reaction temperature, electron acceptor, initial concentration and pH of the reaction on photocatalytic degradation of nonylphenol polyethoxylate (NP10EO) were studied. In this way, the optimum conditions for photocatalytic degradation of NP10EO and the different effects of these parameters on the photo-catalytic degradation of NP10EO were obtained. The possible role of the additives on the reactions and proposed mechanisms of their effect were also investigated.

EXPERIMENTAL

Nonylphenol polyethoxylate having 10 ethoxy units (NP10-EO) was purchased from Merck™ Chemical Company. The adsorption maximum of the surfactant was 223 nm. Zinc oxide nanopowder (particle size, *ca*. 20 nm, BET area, 50 m^2/g, 99.5 %) was obtained from Nanoamor™ (USA). $K_2S_2O_8$ was purchased from Merck™ Chemical Company. The pH of solution was adjusted to the desired value between 4 and 10 using dilute solutions of HCl or NaOH. The degradation of NP10EO was more enhanced in the range of pH 6-7 than the other pH values.

Photocatalytic reactor: The photodegradation studies were carried out in a batch reactor system. A rectangular tray made of MDF was used through all experiments. The slurry was composed of surfactant solution and catalyst was kept in a reactor (a cylindrical Pyrex vessel of 2 cm diameter with capacity of 50 mL) while stirring on a magnetic stirrer. The radiation source was a high-pressure mercury vapour lamp (400 W) fitted on the top of the reactor.

Procedure: Photodegradation studies were carried out with a 400 W high-pressure mercury vapour lamp as the light source. The experiment was performed by mixing 0.2 g/L ZnO and 1 mM of $S_2O_8^{2-}$, in 25 mL of the synthetic surfactant solution with an initial concentration range of 30-120 g/L. The pH was chemically controlled at 6. The mixtures were mixed by stirring at 80 rpm for 2 h under UV irradiation. The temperature was kept constant at (25 ± 2) ºC. Suspended solids were then separated out and concentration of surfactant measured using spectrophotometer (Model Jenway 6405). Experiments were repeated at least three times to ensure the accuracy of the results. More repetitions were carried out in cases where % relative standard deviation exceeded 15 %. COD tested were used to assay the mineralization of NP10EO.

Degradation kinetics: To estimate the kinetic parameters (k and n) as well as the nth-order rate, an equation of from was used.

$$-r_{surfactant^-} = \frac{dC}{dt} = kC^n$$

In this equation, k is the degradation rate constant, mol/L min, the second-order kinetic model (n = 2) as shown below:

$$\frac{1}{C} - \frac{1}{C_0} = Kt$$

RESULTS AND DISCUSSION

Effect of electron acceptor on NP10EO photodegradation: One practical problem in using ZnO as a photocatalyst is the undesired electron hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and represents the major energy-wasting step, thus, limiting the achievable quantum yield. One strategy to inhibit electron hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects, such as; (i) increasing the number of trapped electrons and, consequently, avoid recombination; (ii) generating more radicals and other oxidizing species, (iii) increasing the oxidation rate of intermediate compounds and (iv) avoiding problems caused by low oxygen concentration. Keeping these points in mind, we have studied the effect of potassium peroxydisulphate as an electron acceptor.

The effect of sulphate radical $(SO_4^{\bullet-})$, as an oxidant, on the degradation of NP10EO was investigated and compared with the ZnO (only), $S_2O_8^{2-}$ (only), UV/$S_2O_8^{2-}$, UV/ZnO and UV/ZnO/$S_2O_8^{2-}$ systems. As can be seen from Fig. 1, ZnO alone in the absence of sulphate radical and UV irradiation was found to have no measurable effect on the degradation of the surfactant during an irradiation time of 2 h. A similar behaviour was also observed in the UV system alone. In the case of sulphate
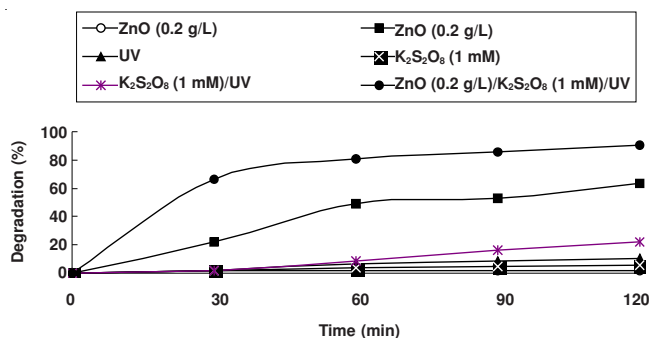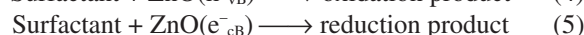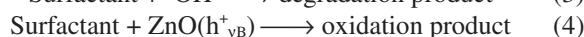

Fig. 1. Degradation of $[NP10EO]_0$ = 30 ppm

radical alone, the degradation yield was determined as *ca.* 6 % after 2 h for 30 mg/L. The degradation yield of surfactant in UV/$S_2O_8^{2-}$ system without ZnO was obtained *ca.* 22 % after 2 h treatment which is, probably, due to the production of radical species. The photocatalytic decomposition of peroxydisulphate potassium under UV radiation involves the formation of a number highly reactive radical $(^{\bullet}OH, SO_4^{\bullet-})$ and the non-radical species (OH^-, SO_4^{2-})[9,10]. As can be seen in Fig. 1, UV/ZnO/$S_2O_8^{2-}$ system had more significant effect on the degradation of surfactant than the UV/$S_2O_8^{2-}$ system.

This result could be explained by the fact that ZnO is exposed to UV radiation; an electron is promoted from the valence band to the conduction band and thus an pairs is produced (eqn. 1). The photocatalyst, zinc oxide, is a wide band gap (3.37 eV) semiconductor, corresponding to radiation in the near -UV:
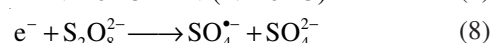
$$ZnO + h\nu \longrightarrow e_{eB}^- + h_{vB}^+ \tag{1}$$
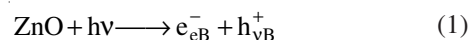
The highly oxidative h_{vB}^+ can react easily with surface bound H_2O to produce hydroxyl radicals or can directly react with the surface adsorbed organic molecules (R) to from R^+[11,12].

$$h_{vB}^+ + H_2O_{(ads)} \longrightarrow {}^{\bullet}OH + H^+ \tag{2}$$

$$\text{Surfactant} + {}^{\bullet}OH \longrightarrow \text{degradation product} \tag{3}$$

$$\text{Surfactant} + ZnO(h_{vB}^+) \longrightarrow \text{oxidation product} \tag{4}$$

$$\text{Surfactant} + ZnO(e_{cB}^-) \longrightarrow \text{reduction product} \tag{5}$$

When potassium peroxydisulphate was added to the UV/ZnO system, surfactant degradation increased from 63 to 90 % after 2 h (Fig. 1).

Effect of amount of $K_2S_2O_8$: Acceleration in degradation rate of photocatalytic oxidation on ZnO occurs by photo-generated holes. It is well known that oxidation rate increases when recombination process is suppressed. Peroxydisulphate has been shown to be a more reliable and low cost electron acceptor[13]. The effect of peroxydisulphate as the electron acceptor was examined and is presented in Fig. 2.

The degradation of NP10EO was remarkably accelerated by addition of peroxydisulphate: 30 mg/L NP10EO and in the presence of 0.2 g/L, ZnO was completely degraded under irradiation of 6 to 2 h in the absence and presence of 1 mM $K_2S_2O_8$, respectively.
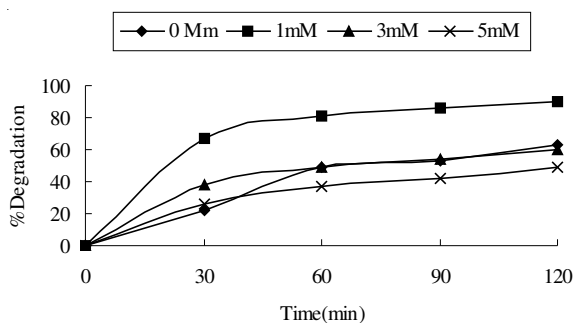
$$h^+ + e^- \longrightarrow ZnO(\text{recombination}) \tag{6}$$

$$h^+ + NP10EO \longrightarrow (NP10EO)^+ \tag{7}$$

$$e^- + S_2O_8^{2-} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \tag{8}$$

Fig. 2.   Effect of $S_2O_8^{2-}$ concentration on the degradation of NP10EO. Conditions: $[NP10EO]_0$: 30 mg/L, ZnO: 0.2 g/L, pH = 6 , V_t: 25 mL

The $SO_4^{\bullet-}$ radical is a strong oxidant, capable of mineralizing phenolic compounds such as butylated hydroxyanisole in water[14] and the resulting SO_4^{2-} ion is not considered as a pollutant. The inhibition of reaction occurs at a high dosage of $S_2O_8^{2-}$ due to an increase in concentration of SO_4^{2-} ion (eqn. 8). The excess SO_4^{2-} ion is absorbed on the ZnO surface and reduces the catalytic activity. At the same time, the excess adsorbed SO_4^{2-} ion also reacts with the photogenerated holes (eqn. 9) and hydroxyl radicals (eqn. 10)[12].

$$SO_4^{2-} + H^+ \longrightarrow SO_4^{\bullet-} \tag{9}$$

$$SO_4^{2-} + {}^\bullet OH \longrightarrow SO_4^{\bullet-} + OH^- \tag{10}$$
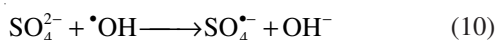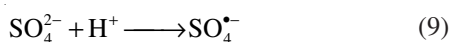
Effect of illumination time: The fixed amount of ZnO was 0.2 g/L. The relationship between the photodegradation efficiency of NP10EO and the illumination time was investigated. The result presented in Fig. 3 indicates that photodegradation efficiency of NP10EO increases with an increase in the illumination time. The photodegradation efficiency of NP10EO increases from 20.5 to 90.5 % when the illumination time increased from 10 to 150 min. It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of ZnO[15], that O_2 and H_2O are necessary for the photocatalytic degradation. Under UV illumination, electron-hole pairs are created on the ZnO surface. Oxygen adsorbed on the ZnO surface prevents the recombination of electron-hole pairs by trapping electrons; superoxide radical ions ($O_2^{\bullet-}$) are thus formed. ${}^\bullet OH$ radicals are formed from holes reacting with either H_2O or OH^- adsorbed on the ZnO surface[4].
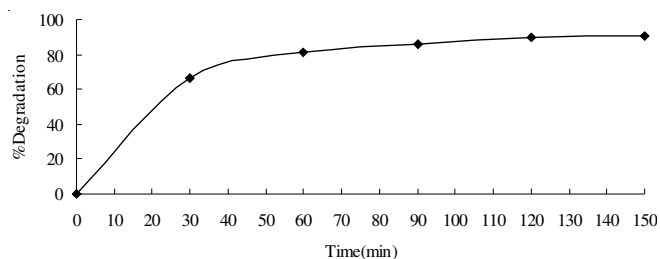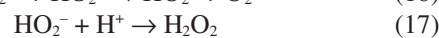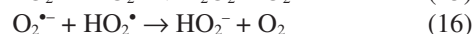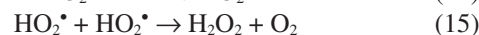

Fig. 3.   Effect of illumination time on the degradation of surfactant solution. Conditions: Surfactant concentration = 30 mg/L, catalyst loading = 0.2 g/L, potassium peroxydisulfate concentration = 1 mM, initial pH value = 6
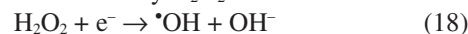
The entire course is as follows:

$$O_2 + e^- \rightarrow {}^\bullet O_2^- \tag{11}$$

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \tag{12}$$

$$OH^- + h^+ \rightarrow {}^\bullet OH \tag{13}$$

Correspondingly, H_2O_2 is formed by $O_2^{\bullet-}$.

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{14}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{15}$$

$$O_2^{\bullet-} + HO_2^\bullet \rightarrow HO_2^- + O_2 \tag{16}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{17}$$

${}^\bullet OH$ and O_2^{2-} are also formed by H_2O_2

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^- \tag{18}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^\bullet OH + OH^- + O_2 \tag{19}$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \tag{20}$$

$$H_2O_2 \rightarrow O_2^{2-} + 2H^+ \tag{21}$$

The ${}^\bullet OH$ and O_2^{2-} are widely accepted as primary oxidants in heterogeneous photocatalysis. The oxidizing power of the ${}^\bullet OH$ radicals is strong enough to completely oxidize NP10EO adsorbed on the surface of ZnO into H_2O and other mineral acids[16].

From Fig. 3, it can also be seen that when the illumination time is longer than 70 min, only small enhancement of photodegradation efficiency is observed. When the illumination time is 120 and 150 min, the photodegradation efficiency of NP10EO is 90 and 90.5 %, respectively. These results do 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 increasing the irradiation time. The small organic molecules adsorb on the surface of ZnO, resulting in the decrease of ${}^\bullet OH$ radicals that attack the nonionic surfactant and, therefore, influence the photodegradation efficiency of NP10EO. At the same time, it had been reported that it can be photocatalytically degraded by increasing the illumination time[9].

Effect of nanocatalyst weight: The effect of photocatalyst weight on the photodegradation of the surfactant was studied in the range of 0.04-0.36 g/L. A small, but significant, rate of the degradation observed with an increase in the catalyst weight up to an optimum loading. Further increase in catalyst weight resulted in the decrease of the reaction rate as shown in Fig. 4.
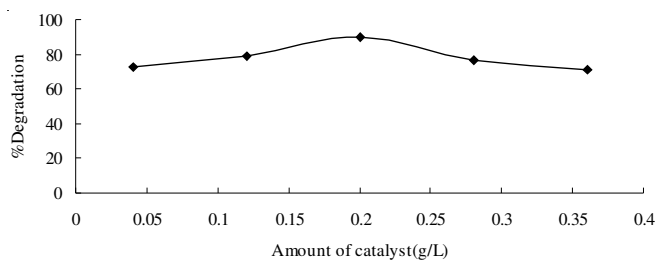

Fig. 4.   Effect of catalyst weight. Conditions: $[NP10EO]_0$ = 30 mg/L; $[S_2O_8^{2-}]$ = 1mM; pH = 6; irradiation time: 2 h; V_t: 25 mL

This type of behaviour 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. However, at the catalyst weights 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: In the typical detergent effluent, surfactant concentration ranges from 80 to 120 mg/L. By changing the initial concentration from 30 to 120 mg/L at constant catalyst loading (0.2 g/L and pH 6), its effect on the degradation rate was determined and the results are presented in Fig. 5. As shown in this figure, degradation efficiency is inversely affected by the surfactant concentration. This negative effect can be explained as follows; as the surfactant concentration is increased, so equilibrium adsorption of surfactant on the catalyst surface active sites increases. Hence, competitive adsorption of OH⁻ on the same site decreases, meaning a lower formation rate of •OH radical, which is the principal oxidant necessary for higher degradation efficiency. On the other hand, considering the Beer-Lambert law, as the initial surfactant concentration increases, resulting in lower photon adsorption on catalyst particle and, consequently, lower photodegradation rate[17].
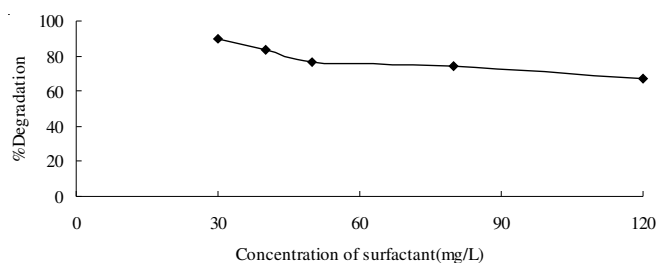

Fig. 5. Influence of initial surfactant concentration on the photodegradation. Conditions: $[S_2O_8^{2-}]$: 1 mM, ZnO: 0.2 g/L, pH: 6.0, irradiation time: 2 h, V_t = 25 mL

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 one outlet connected to the thermostated bath (Haake Model F122). Water was pumped inside cell and after tap off it was returned to the bath. So, the temperature was fixed and controlled. The experiment was carried out in 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 (3.37 eV) to be overcome by the thermal activation energy. 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[18].

Photocatalytic mineralization of NP10EO: In order to access the degree of mineralization reached during the photocatalytic treatment, the COD test was used. It is known that COD normally decreases with increase in irradiation time, whereas the amount of inorganic ions irradiation time. It has shown a decrease in COD from 85 to 28 mg/L with irradiation time.

Performing experiments on the actual wastewater of detergent industry: In this study, after obtaining the optimized conditions of efficiency from nanophotocatalytic process (natural pH, ZnO = 0.2 g/L), experiments were carried out on the actual wastewater of a detergent industry (PaXan). The amount of mineralization of organic substances present in wastewater was identified by the amount of COD. The amount of reduction of actual wastewater COD was in the range of 3782 to 3281 mg/L.

Conclusion

In this study the surfactant NP10EO was appropriately mineralized by a photocatalytic reaction in using nanoparticles of zinc oxide in the form of slurry. The results are summarized as follows: The optimal degradation conditions of NP10EO were: the dosage of catalyst 0.2 g/L, the amount of $K_2S_2O_8$ 1 mM. Under optimal degradation conditions of NP10EO, the photodegradation of NP10EO was 90 % when the solution was irradiated by the 400 W high pressure mercury-vapour lamp for 2 h. Degradation of NP10EO was remarkably accelerated by addition of proxydisulphate. Therefore, when peroxydisulphate was added to the UV/ZnO system, surfactant degradation increased from 63.3 to 90 % after 2 h. The kinetics of photocatalytic degradation for surfactant NP10EO follows a pseudo-second order equation.

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