photocatalytic degradation of Triton X-100 in aqueous phase with Zinc oxide as a nanoparticle under UV light irradiation

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ABSTRACT

The photocatalytic degradation of nonionic surfactant Triton X-100 was studied by a batch process using ZnO commercial powders as the catalyst on irradiation with UV light and its behaviour comparatively with respect to ZnO nanoparticles with diameter size 20 nm. The effects of different conditions such as catalyst type, amount of the photocatalyst, pH of the system, initial concentration and electron acceptors were investigated on degradation. The results showed that the photocatalytic degradation of Triton X-100 was strongly influenced by these parameters. Therefore, the best conditions for the photocatalytic degradation of Triton X-100 were obtained.

Keywords: Zinc oxide commercial; Photocatalytic; Triton X-100; Surfactant; Degradation

INTRODUCTION

Alkylphenol ethoxylates (APE) are a group of nonionic surfactants that have been used for many years as detergents, emulsifiers, wetting agents, stabilizers, defoaming agents, intermediates in the synthesis of anionic surfactants and institutional and industrial surface cleaners [1].

During the biodegradation of APE in sewage treatment plants, alkylphenols are produced as metabolites.It has been shown that they have a higher toxicity, estrogenic activity [2–4], persistence, and tendency toward bioaccumulation than the parent substrate. In particular, nonylphenols and octylphenols have been reported to bioaccumulate in the lipids of water organisms [5–7]. Several oxidative methods have been proposed for the remediation of water and wastewater effluents contaminated with APE. It is shown that biological oxidation is not effective, oxidation with H_2O_2 requires long reaction time and oxidation with ozone is costly. Therefore, advanced oxidation processes (AOPs) are alternative for the complete degradation of organic contaminants [8-10]. The effectiveness of the photodegradation processes

has already been tested for different types of matrices and results have been encouraging, literature reports on a large number of successes in the degrading of organic materials in waste water [11-14]. Titanium dioxide (TiO_2) has been extensively investigated as one of the most active semiconductor photocatalysts. It has been known that ZnO is a suitable alternative to TiO_2 so far as band gap energy is concerned and in fact higher photocatalytic efficiency compared with TiO_2 have been reported for ZnO [15-17]. The greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum and more light quanta comparing to TiO_2 [18].

In the present investigation photocatalytic degradation of Triton X-100 in the present of ZnO with UV light as the illuminate has been reported. Comparison between the efficiency of nanocatalyst and its equivalent commercial oxides. The obtained results showed a good efficiency of ZnO commercial powders. It is the most commonly used surfactant in detergent

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industry, agrochemistry, cosmetic, textiles and metallurgy.

EXPERIMENTAL

Materials

The surfactant octhylphenol ethylene oxide known as commercial surfactant Triton X-100 was obtained from Merck. The surfactant showed an adsorption maximum of 223 nm. The Zinc oxide nano-powder (particle size,ca.20 nm;BET area ,50 m^2/g , 99.5%) was obtained from Nanoamor (USA), TiO_2 is from Degussa (P-25) as average primary particle size 21 nm, specific surface area (BET) $50 \pm 15m^2/g$ and ZnO (BET, $<5m^2/g$) and $K_2S_2O_8$ were obtained from Merck. The pH of solution was adjusted to the desired value between 4.0 and 9.0 by using dilute solutions of HCl or NaOH.

Apparatus

A UV-visible spectrophotometers (Jenway 6405) was used for recording and measuring the absorbance at 223 nm. A Metrohm pH meter (model E-632) was used for pH measurements.

Photocatalytic reactor

The photodegradation studies were carried out on a batch reactor system. All of the experiments were done in a rectangular tray of (90 cm ×60 cm× 75cm) made of MDF. The slurry composed of surfactant solution and catalyst was kept in a reactor (a cylindrical Pyrex vessel of 2 cm diameter with capacity of 50 mL) and stirred magnetically.The radiation source were a Xe arc lamp (400 w and tungsten lamp(400 w), lamps were fitted on the top of the reactor.

Procedure

The conditions used in the present study was a batch volume of 50 ml, 20 cm distance between UV source and solution with a stirring speed of 80 rpm and 30 min time for adsorption equilibrium. In all of the experiments, the surfactant solution of known concentration containing a suspension of known weight of catalyst powder and potassium peroxydisulfate of known concentration was irradiated with UV light. 3 ml samples were taken by drowning at regular intervals of time and centrifuged. The supernatant solution was returned to the reactor after measurement of its absorbance. The quantitative estimation of the

surfactant was carried out using a UV-Vis spectrophotometer (model Jenway 6405) at λ_{mAX}=223 nm. 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 Triton X-100.

RESULTS AND DISCUSSION

Catalyst type, catalyst loading, initial pH and initial surfactant concentration were investigated for their effects on the efficiency of the degradation process, defined as:

$$\% \text{ Degradation} = 100 \times (C_o - C)/C_o \qquad (1)$$

where C_o is the initial surfactant concentration.

Catalyst type

Initially, blank experiments were performed under UV radiation without addition of any catalyst and negligible degradation efficiency was observed. To enhance the efficiency, different catalysts were tried under various process conditions. Typical results are shown in Fig. 1 at surfactant concentration = 40 mg/L, initial solution pH = 6, catalyst loading = 0.36 g/L, reaction time = 180 min. The results showed that ZnO exhibits higher photocatalytic activity than the others, especially TiO_2. The same trend was also obtained in other studies with nonionic surfactant [19,20], and this was explained as ZnO having a greater quantum efficiency than TiO_2. The low cost is another important advantage of ZnO. Thus, subsequent experiments were carried out using Merck ZnO.
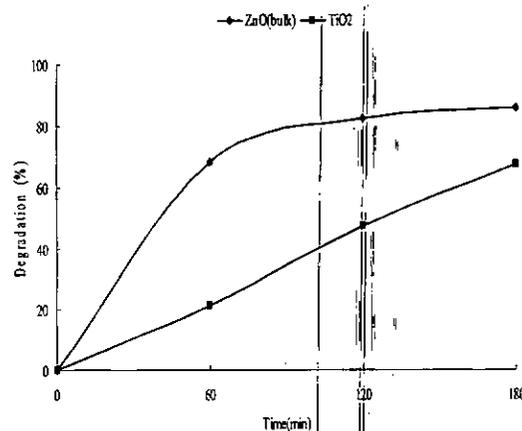
Fig. 1. The effect of the catalyst type on the degradation efficiency.

Effect of electron acceptor on TX-100 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) to increase the number of trapped electrons and consequently, avoid recombination; (ii) to generate more radicals and other oxidizing species, (iii) to increase the oxidation rate of intermediate compounds and (iv) to avoid problems caused by low oxygen concentration. With this view, we have studied the effect of potassium peroxydisulfate as an electron acceptor.

The effect of sulfate radical (SO_4^-) as an oxidant on the degradation of Triton X-100 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. 2, ZnO the absence of sulfate radical and UV irradiation alone had no measurable effect on the degradation of the surfactant during of 180 min irradiation time. A similar behavior was also observed in the UV system alone. In the case of sulfate radical alone, the degradation yield was determined as approximately 3.1% after 120 min for 40 mg/L. The degradation yield of surfactant in UV/ $S_2O_8^{2-}$ system without ZnO was obtained approximately 12.4% 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 ($O H, SO_4^-$) and the non-radical species (OH^-, SO_4^{2-}). As can be seen in Fig. 2, 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 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 an h_{VB}^+ / e_{cB}^- pairs is produced (Eq.(2)). The photocatalyst, zinc oxide, is a wide band gap (3.37ev) semiconductor, corresponding to radiation in the near –UV range:

$$ZnO + hv \longrightarrow e_{cB}^- + h_{VB}^+ \qquad (2)$$
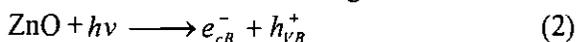
The highly oxidative h_{VB}^+ can react easily with surface bound H_2O to produce hydroxyl radicals or can directly react with the surface sorbed organic molecules (R) to from R^+ [21-24].

$$h_{VB}^+ + H_2O_{(ads)} \longrightarrow O H + H^+ \qquad (3)$$

$$\text{Surfactant} + O H \longrightarrow \text{degradation product} \qquad (4)$$

$$\text{Surfactant} + ZnO (h_{VB}^+) \longrightarrow \text{oxidation product} \qquad (5)$$

$$\text{Surfactant} + ZnO (e_{cB}^-) \longrightarrow \text{reduction product} \qquad (6)$$
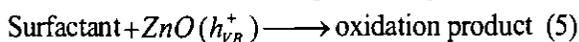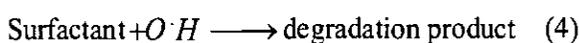
When potassium peroxydisulfate was added to the UV/ ZnO system, surfactant degradation increased from 82.7% to 96.1% after 120 min (Fig. 2).
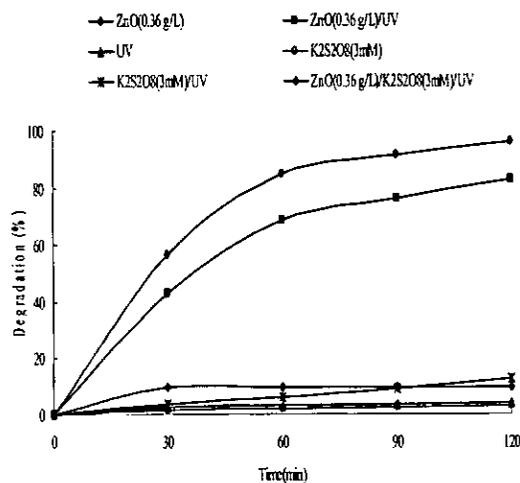
Fig. 2. Degradation of Triton X- 100.

Effect of amount of $K_2S_2O_8$

Acceleration of the degradation rate of 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 [25]. The effect of peroxydisulfate as the electron acceptor was examined as shown in Fig.3.

The degradation of Triton X-100 was remarkably accelerated by adding peroxydisulfate:

40 mg/L Triton X-100 and in the presence of 0.36 g/L ZnO.

$$ZnO + hv \longrightarrow h^+ + e^- \tag{7}$$

$$h^+ + e^- \longrightarrow ZnO \, (recombination) \tag{8}$$

$$h^+ + Tx - 100 \longrightarrow (Tx - 100)^{+} \tag{9}$$

$$e^- + S_2O_8^{2-} \longrightarrow SO_4^- + SO_4^{2-} \tag{10}$$
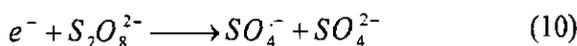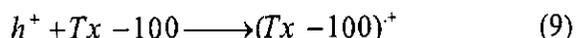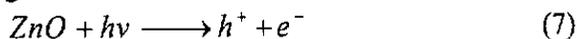
The SO_4^- radical is a strong oxidant capable of mineralizing phenolic compounds such as butylated hydroxyanisole in water [26]. The produced SO_4^{2-} ion is not considered to be a pollutant. The decrease in the mineralization efficiency of surfactant with increasing SO_4^{2-} concentration is mainly due to scavenging the valuable hydroxyl radicals with SO_4^{2-} ion as shown in Eq.(11).

$$\cdot OH + SO_4^{2-} \longrightarrow OH^- + SO_4^- \tag{11}$$
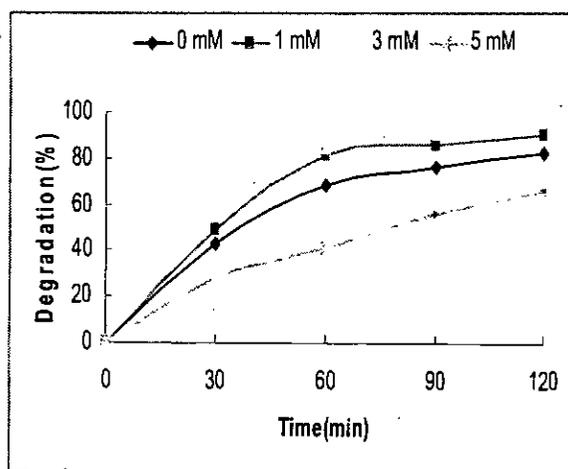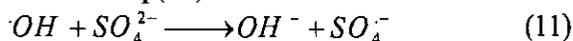
Fig. 3. Effect of $S_2O_8^{2-}$ concentration on the Degradation of Triton X-100

Conditions: 40 mg/L of Triton X-100; ZnO:0.36 g/L; pH=6; V:25 mL.

Effect of pH

The photodeagration process is pH depended and the process exhibits different behavior with the chemical character of surfactant. Figure 4 indicates the effect of pH on the degradation efficiency of Triton X-100 by UV/ZnO/S$_2$O$_8^{2-}$ system is in the range of 4-9. The degradation of TX-100 was more enhanced in the range of pH 6-7 than the other pH values. The lower rate of degradation at acidic and alkaline pH may be attributed to dissolution of ZnO. So, the optimum pH for the removal of Triton X-100 was found to be in natural pH of surfactant solution.
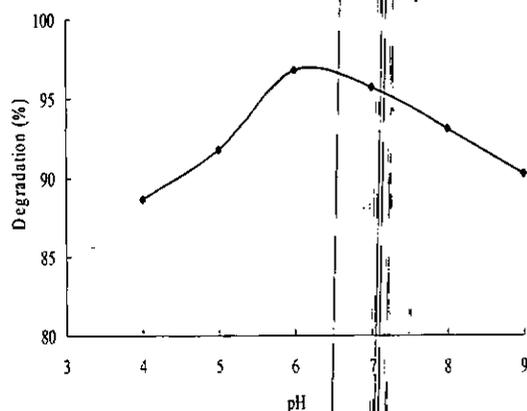
Fig. 4. Effect of pH.
Conditions: 40 mg/L of Triton X-100; ZnO: 0.36 g/L; [S$_2$O$_8^{2-}$]=3mM; Irradiation Time:120 min; V:25ml.

Effect of catalyst weight

The effect of photocatalyst weight on the photodegradation of the surfactant was studied in the range of 0.08-0.52 g/L. A small but significant rate of the degradation was 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 show in Fig.5 .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.
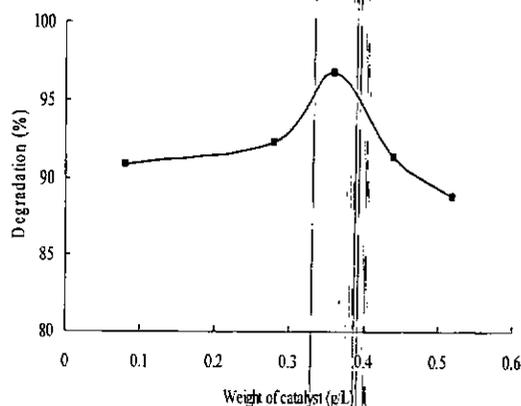
Fig. 5. Effect of catalyst weight.
Conditions: 40 mg/L of Triton X-100; [S$_2$O$_8^{2-}$] = 3mM; pH=6; Irradiation Time:120 min; V:25ml.

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Effect of surfactant concentration on the photocatalytic degradation

Photocatalytic process was investigated at the Triton X-100 concentration ranging from 10 mg/L to 120 mg/L (Fig. 6). It can be seen from Figure 6 that degradation efficiency is inversely affected by the surfactant concentration. This negative effect can be explained as follows; as the surfactant concentration is increased, the 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 $\cdot OH$ radical, which is the principal oxidant necessary for a high 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 [27].

Fig. 6. Influence of initial surfactant concentration on the photodegradation.
Conditions: $[S_2O_8^{2-}]$:3mM, ZnO:0.36 g/L, pH :6, Irradiation Time:120 min ,V=25ml.

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