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Photocatalytic Degradation of Triton X-100 by Zinc oxide Nanoparticles

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ABSTRACT

In this study the application of ZnO nanoparticles to UV photocatalytic degradation of nonionic surfactant Triton X-100 in aqueous media was investigated. The affecting factors on the photodegradation such as Triton X-100 initial concentration, nanocatalyst weight, pH, temperature and other parameters were studied and described in details. The degradation rate was found to be strongly influenced by all the above parameters .The optimized conditions for maximum amount of degradation were also determined .Results showed that the photocatalytic degradation process using UV light as an irradiation source, and Nanoparticles of ZnO as a photocatalyst, was applicable for the degradation of Triton X-100 in aqueous solution and wastewater samples.

Keywords: Zinc oxide nanoparticles; Photocatalytic; Triton X-100; Surfactant; degradation

INTRODUCTION

Application of semiconductor colloids as photocatalyst in various chemical reactions, due to their peculiar optoelectronic and photocatalytic properties, is well known [1]. Under photo-oxidation, semiconductors undergo charge separation and initiate oxidation of the organic compounds at the interface. Nano structured semiconductors are a potential candidate to photodegradation of organic compounds [2, 3]. Photocatalytic electron and hole Redox potentials of size quantized semiconductor nanocrystals can be tuned of achieve increased catalytic effect for selective photochemical reaction. Moreover, as photocatalytic reaction occurs at nanoparticles surface, nano-sized semiconductor high surface to volume ratio will contribute to increase the decomposition rate. ZnO has been found to be a suitable alternative to TiO_2. ZnO is a kind of semiconductor that has the similar band gap as TiO_2, but is not thoroughly investigated. The greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum and more light quanta comparing to TiO_2 [4]. Some research have highlighted the performance of ZnO on degradation some organic compounds [5, 6]. In addition, ZnO has more functions that TiO_2 [7] and recently it is mentioned that ZnO can also be used in the acidic or alkaline conditions through the proper treatment [8, 9].

Non-ionic surfactants in aqueous solutions are excessively used in many formulations applied in various industrial areas such as detergent industry, agro-chemistry, cosmetics, textiles and metallurgy. The alkyl phenol polyetoxylates (APE) surfactants display a low biodegradability and high toxicity for biologically active deposits their pretreatment should consist in an efficient oxidation. One of the advanced oxidation processes (AOPs) is an effective oxidation combined with the use of photocatalysts. The main advantages of AOP are as follows: high yield, fast reaction rate and total mineralisation

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of organic compounds into CO_2 and water and eco-friendly nature. Radical reactions can be applied to decomposition of many different chemical compounds, e.g. phenols, dyes, pesticides and surfactants [10-12].

The aim of this study was to investigate the photolytic degradation of Triton X-100 in different aqueous media. The effect of concentration of Triton X-100, pH, irradiation time, and amount of nanoparticles of ZnO and other parameters on photodegradation of surfactant was evaluated. It might provide a new method for the treatment of nonionic surfactant in wastewater.

EXPERIMENTAL

Materials

Triton X-100 was purchased from Merck, Germany, and used without further purification. Chemical structure of Triton X-100 is presented as Fig. 1. The Zinc oxide nano powder (particle size, ca.20 nm; BET area, 50 m^2/g, 99.5%) was obtained from Nanoamor (USA). The pH of solution was adjusted of the desired value between 4.0 and 10.0 by using dilute solution of HCl or NaOH.

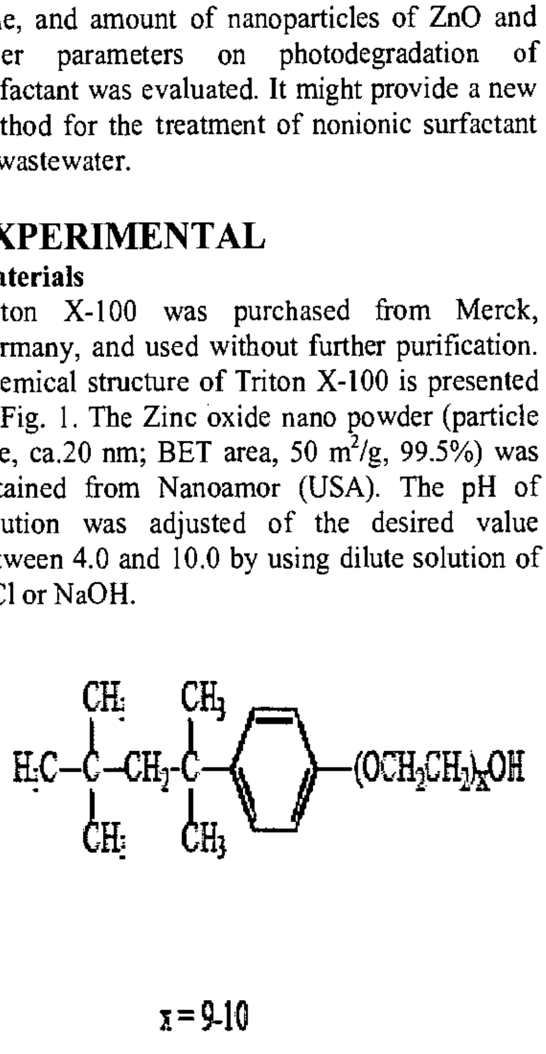

Fig. 1. Structure of Triton X-100.

Photocatalytic reactor

The photodegradation studied were carried out a batch reactor system. All the experiments done in a rectangular tray of (90 cm × 60 cm× 75 cm) 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) was placed on a magnetic stirrer and stirred magnetically. The radiation source was a Xe arc lamp (400 w) and it was fitted on the top of the reactor.

Procedure

Photodegradation studies were carried out with a 400 W Xe arc lamp house as the light source. The experiment was performed by mixing 0.2 g/L ZnO, 1 mM of $S_2O_8^{2-}$, in 25 mL of the synthetic surfactant solution with an initial concentration in the range of 30-120 g/L. The pH was chemically controlled at 6. The mixtures were mixed in a stirrer at a rate of 80 rpm for 2 h under UV irradiation light. After that Suspended solids were separated out and concentration of surfactant was then measured with spectrophotometer(Jenway 6405) at 223 nm. Experiments were repeated at least three times to ensure the accuracy of the results.

RESULTS AND DISCUSSION

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. 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 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 behaviour was also observed in the UV system alone. In the case of sulfate radical alone, the degradation yield was determined as approximately 4% after 120 min for 30 mg/L. The degradation yield of surfactant in UV/ $S_2O_8^{2-}$ system without ZnO 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 ($^{\cdot}OH$, $SO_4^{\cdot-}$) 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 a 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:

$$ZnO + h\nu \longrightarrow e_{cB}^- + h_{VB}^+ \qquad (1)$$

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

$$h_{VB}^+ + H_2O_{(ads)} \longrightarrow {}^{\cdot}OH + H^+ \qquad (2)$$

$$\text{Surfactant} + {}^{\cdot}OH \longrightarrow \text{degradation product} \qquad (3)$$

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

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

When potassium peroxydisulfate was added to the UV/ ZnO system, surfactant degradation increased from 62.2% to 98.1% after 120 min (Fig. 2).

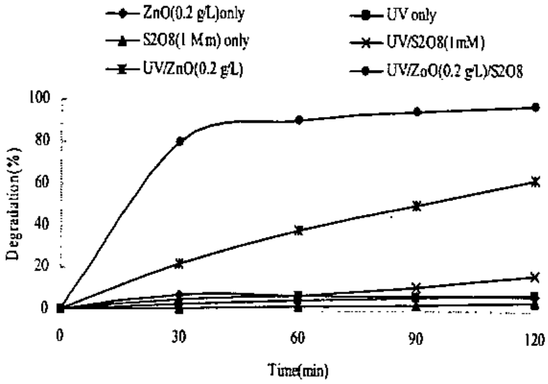

Fig. 2. Degradation of Triton X- 100.

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 Fig. 3.

$$h^+ + e^- \longrightarrow ZnO\,(recombination) \qquad (6)$$

$$h^+ + Tx-100 \longrightarrow (Tx-100)^{\cdot+} \qquad (7)$$

$$e^- + S_2O_8^{2-} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} \qquad (8)$$

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. (9).

$$^{\cdot}OH + SO_4^{2-} \longrightarrow OH^- + SO_4^{\cdot-} \qquad (9)$$

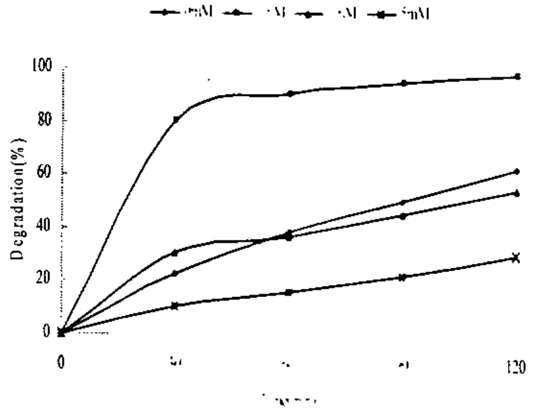

Fig. 3. Effect of $S_2O_8^{2-}$ concentration on the Degradation of Triton X-100
Conditions: 30 mg L of Triton X-100; ZnO: 0.2 g/L; pH-6; V: 25 mL.

Effect of illumination time

The relationship between the photodegradation efficiency of Triton X-100 and the illumination time was investigated. As can be seen from figure 4, it can be seen that the photodegradation efficiency of Triton X-100 increases with the increase of the illumination time. But when the illumination time is longer than 60 min, only small enhancement of photodegradation efficiency is observed. 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, 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, when the illumination time is 120 and 150 min, the photodegradation efficiency of Triton X-100 is 98.1% and 98.7%, respectively.

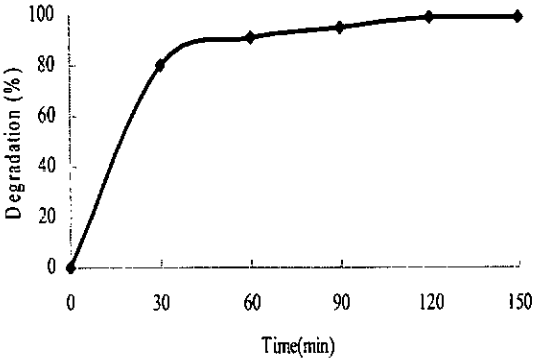

Fig. 4. Effect of Time on the Degradation of Triton X-100.
Conditions: 30 mg/L of Triton X-100; ZnO: 0.2 g/L; pH=6; V: 25 mL.

Effect of pH

Fig. 5. indicates the effect of pH on the degradation efficiency of Triton X-100 by UV/ZnO/$S_2O_8^{2-}$ system is range of 4-10. The lower rate of degradation at acidic and alkaline pH maybe 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.

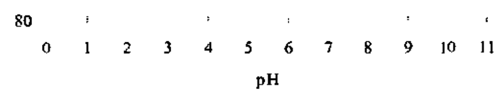

Fig. 5. Effect of pH Conditions: 30 mg/L of Triton X-100; ZnO: 0.2 g/L;.
$[S_2O_8^{2-}]$=1mM; Irradiation Time: 120 min; V: 25mL.

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. Further increase in catalyst weight resulted in the decrease of the reaction rate as show in Fig.6. 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.

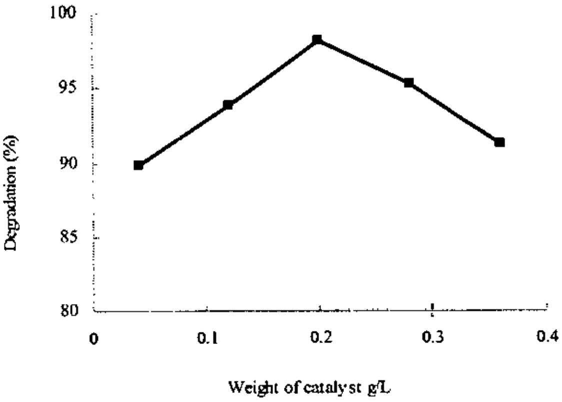

Fig. 6. Effect of catalyst weight Conditions: 30 mg/L of Triton X-100; $[S_2O_8^{2-}]$ =1mM; pH=6; Irradiation Time: 120 min; V: 25mL.

Effect of surfactant concentration on the photocatalytic degradation

Photocatalytic process was investigated at the Triton X-100 concentration ranging from 30 mg/L to 120 mg/L (Fig. 7). It can be seen from figure 7 that degradation efficiency is inversely affected by the surfactant concentration. As the surfactant concentration is increased, the equilibrium adsorption of surfactant on the catalyst surface active sites increases resulting in lower photon adsorption on catalyst particle and, consequently, lower photodegradation rate.

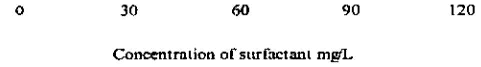

Fig. 7. Influence of initial surfactant concentration on the photodegradation.
Conditions: $[S_2O_8^{2}]$:1mM, ZnO: 0.2 g/L, PH: 6, Irradiation Time: 120 min, V=25mL.

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CONCLUSION

The optimal degradation conditions of Triton X-100 were: the dosage of catalyst 0.2 g/L, pH 6-7, the amount of $k_2S_2O_8$ 1 Mm and the photodegradation precent of Triton X-100 was 98.1 % when the solution was irradiation by the 400w high pressure mercary –vapour lamp for 2h.

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