

PHOTOCATALYTIC DEGRADATION OF LINEAR ALKYL BENZENE SULFONATE FROM AQUEOUS SOLUTION BY TiO₂ NANOPARTICLES

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ABSTRACT

The possibility of linear alkyl benzene sulfonate (LAS) photocatalytic degradation through application of TiO₂ nanoparticles was investigated. 10(mg/L) of LAS has been affected by either UV or TiO₂ and simultaneous use of both of them in separated experiments. Moreover, the effect of initial concentrations of LAS and TiO₂, pH, present various anions and different UV power was studied to determine the optimal operating conditions for LAS degradation in water. The amount of mineralization of LAS was reported by measuring the primary and final COD of the solution that was irradiated under optimized conditions. Maximum degradation was obtained at acidic pH, 50 mg/L of TiO₂ and 30 minute irradiation time. It was also shown that 99.5% of LAS was degraded in optimal conditions. Kinetic analysis indicated that photo catalytic degradation rates of LAS can be approximated by pseudo-first order model. Measuring the initial and final COD of illuminated solution under optimized conditions, indicated that almost complete mineralization of LAS was occurred. Based on the results, UV/TiO₂ process may be effectively applied in LAS removal in low concentrations but this process is not economically efficient in high concentrations.

Key words: Photocatalytic degradation; Linear alkyl benzene sulfonate; UV irradiation; TiO₂ nanoparticles

INTRODUCTION

Anionic surfactants are synthetic organic chemicals that are used in various industries and household cleaning products (Hosseinia *et al.*, 2006). Today the consumption of surfactants is increasing world wide because of the population growth and economic development. The average concentration of surfactant in sewage is 1 to 10

(mg/L) (Guo, 2008). One of the major groups of anionic surfactants is linear alkyl benzene sulfonate which have a lot of usage because of its high cleaning power and efficiency (Hassan *et al.*, 2007; Guo, 2008). Therefore, a significant amount of LAS exists in municipal and industrial wastewater such as textile, leather, food, paint, cosmetics, polymer, oil recovery, mining and paper industries (Savaş *et al.*, 2006; Dehghani *et al.*, 2007).

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LAS can be toxic for aquatic organisms in higher than 0.1 mg/L (Hosseinia *et al.*, 2006). Moreover, it can be accumulated in fish and consequently spread in the whole ecosystem. As a result it alters the natural balance of water which changes water into a harmful source for the aquatic organisms and human. It also has some pathological, physiological, biological and other effects on aquatic animals. For specific aquatic plants, LAS damages their chlorophyll-protein and membrane leading to delay in growth and metabolism of cells (Savaş *et al.*, 2006). Due to negative effects that anionic surfactants can have on organisms and environment, many environmental and public health regulatory authorities have considered restrictions, typically < 1.0 mg/L, as MBAS (Methylene-Blue-Active-Substance), for anionic surfactants in wastewaters discharged to the environment (Adak *et al.*, 2005; Guo, 2008).

Various procedures have been considered for the removal of organic compounds and anionic surfactants from wastewater. Biological treatment, being time-consuming with high cost, are considered not to be effective (Savaş *et al.*, 2006). Physical and chemical procedures include processes such as air flotation, coagulation-flocculation and settling, membrane technology, adsorption with alumina and activated carbon, ionizing radiation, oxidation and photo oxidation have also been applied (Gupta *et al.*, 2003; Savaş *et al.*, 2006; Mahvi *et al.*, 2007).

Advanced treatment technologies such as Fenton process have been applied to treat the surfactants (Mousavi *et al.*, 2011), and photocatalytic degradation has an important role among them. An advantage of photocatalytic method includes low temperature, low expenses and also radically low level of energy consumption in this method. These factors have caused the photocatalysts to be used in commercial scales (Rezaee *et al.*, 2008; Rajeswari and Kanmani, 2009). The process gradually breaks down the contaminant molecules, no residue of original material remains and therefore no sludge is produced. Photocatalytic degradation of pollutants by using TiO₂ is more appropriate with high efficiency for removal of organic substances such as LAS

because of the excellent pigmentary properties, high ultraviolet absorption, nonpoisonous, insolubility in water and high stability which allow it to be used in different applications. By far TiO₂ is the most important semiconductor with wide application as a photocatalyst for the degradation of water chemical pollutants (Aceituno *et al.*, 2002; Zendeh del *et al.*, 2011). It has been used in the form of a suspension, or a thin film in water treatment (Zhu *et al.*, 2006). The process of photocatalysis is simple; when TiO₂ suspension is illuminated with the light of $\lambda < 390$ nm, valence band holes (h_{vb}^-) and conduction band electron (e_{cb}^+) are generated as (Eq.1):



The potential of valence band (h_{vb}^-) for generation of hydroxyl radical is positive enough and the potential of conduction band is negative enough for the reduction of molecular oxygen (Al-Rasheed, 2005; Rezaee *et al.*, 2008; Mahvi *et al.*, 2009a). Hydroxyl radical is a powerful oxidation element and attacks the organic molecules which cause the degradation of the organic pollutants (Mahvi *et al.*, 2009b; Al-Rasheed, 2005). Produced hydroxyl (OH) along with other oxidants such as superoxide radical anion (O_2^-), can further mineralize organic compounds to end products (water and CO₂) (Yang *et al.*, 2008). In the present study, we investigated the photochemical degradation of LAS through using TiO₂ suspension in aqueous solution and UV radiation was investigated. Moreover, the effects of initial concentration of LAS, TiO₂ concentration, presence of mineral anions and pH have been surveyed.

MATERIALS AND METHODS

Chemicals

The surfactant used in this study contained linear sodium alkyl benzene sulfonate (LAS) 88%, provided by ACROS ORGANIC. Other chemicals such as H₂SO₄, HCl, NaNO₃, NaHCO₃, Na₂CO₃ and NaCl were supplied from Merck

Co. Titanium dioxide (TiO₂, P25, Degussa AG, Germany) with primary particle diameter of 21 nm, specific surface area of 50±15 m²/g, and a crystal distribution of 80% anatase and 20% rutile was used as the photocatalyst.

Samples Preparation and pH Adjustment

A stock solution was made by LAS through standard method and a solution with the required concentration was made by successive dilution of the stock solution by water. The main concentration was 10 mg/L. The solution pH was controlled by addition of NaOH or HCl.

Instruments

A UV-C 18 W lamp (Philips) with constant intensity=1.8 mW/cm² was used as the main irradiation source. Two types of UV light sources were used, one with 27 watt, and the other with 150 watt which could induce the formation of ozone from dissolved oxygen followed by generation of H₂O₂. A UV/Vis (Perkin-Elmer, Lambda 25) spectrophotometer was used for determination of the degradation rate of LAS. The pH of the solution was measured using (Metrohm E520) pH meter.

Photocatalyst reactor

The photo-catalyst reactor utilized consisted of a 2 L volume rectangular tank. A UV lamp was positioned vertically in the solution, protected by a quartz jacket. The batch reactor was placed on a simple magnetic stirrer with a circle flow which could mix consistently the solution to generate a proper environment for all the particles to have contact with the lamp. The whole system was wrapped in an aluminum foil to avoid reflection.

LAS measurement

LAS was measured by using Methylene-Blue-Active-Substance (MBAS) on basis of 5540.C method in the Standard Methods (APHA, 2005). The measurement was based on the formation of a blue salt or ion pair when methylene blue, a cationic dye, reacts with anionic surfactants such as LAS. MBAS bring about the transfer of methylene blue from an aqueous solution into an immiscible organic liquid upon equilibration. The

intensity of the resulting blue color in the organic phase is a measure of the concentration of LAS (Hassan *et al.*, 2007).

Experimentation method

Photocatalytic decomposition was conducted through using 1.7 L of LAS with supposed concentration and by adding TiO₂ nanoparticles suspension. The reactor on the mixer was placed in the dark for 10 minutes to create a balance between attraction and repulsion. The sample was removed from the reaction environment every 15 minutes and passed through a 0.45 microfilter to separate TiO₂; then the remained LAS was measured. Total time of experiment for each solution was 1 hour. Effect of various concentrations of TiO₂ (10, 50,100,200, 300 mg/L) on photocatalytic degradation of LAS was examined. To investigate pH effect on the degradation of detergent, acidic (pH=3), neutral (pH=7) and alkalic (pH=11) pHs of the solution were provided for 10 mg/L of LAS and measure by a pH meter. To determine impact of mineral anions on the process, 2.5 mM of salts (NaCl, NaNO₃, NaHCO₃, Na₂CO₃, and Na₂SO₄) was separately added to the solution and to determine the impact of initial concentrations of LAS on the process 2, 5, 10, 50, mg/L solutions of LAS have been used. Finally, the experiment was conducted in two separate sessions in the darkness with only TiO₂ and with UV alone.

RESULTS

Fig. 1 shows the degradation of LAS with an initial concentration of 10 mg/L under four reaction conditions (rate constants are shown in table 1). The degradation of LAS in water can be approximately modeled following pseudo-first-order kinetics. Fig.1 shows $-\ln C/C_0$ of LAS versus irradiation time. In the presence of TiO₂ with UV (150 W and 27 W), much faster degradation of LAS occurred compared to reactions without TiO₂ and radiation only. Under UV radiation (150 W), the first-order rate constant in the presence of TiO₂ was more than two times higher than that with UV (18 W) (Table 1). In this stage UV lamp with various powers have been employed (150 W with medium pressure (MP), 18 W and 27 W with

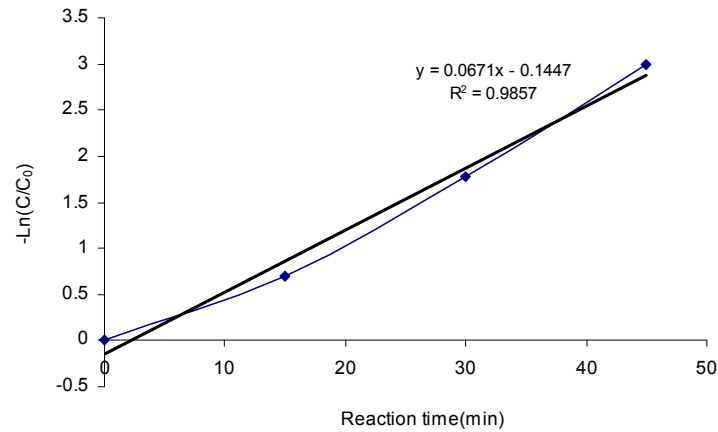


Fig. 1: Pseudofirst-order degradation rate of LAS.

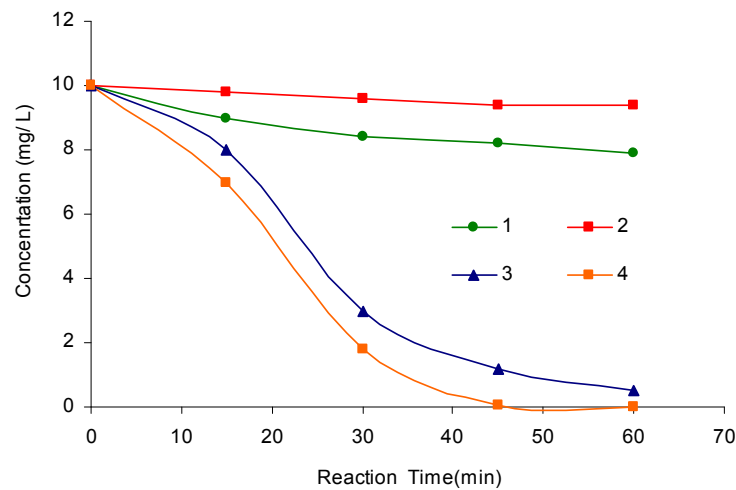


Fig. 2: Photocatalytic degradation of LAS (10mg/L) using four conditions: (1)with TiO₂(50mg/L) without UV(initial pH=7);(2)without TiO₂,with UV 18 W(initial pH=7);(3)with TiO₂(50mg/L), UV 18W(initial pH=7);(4)with TiO₂(50 mg/L),with UV150 W(initial pH=7)

low pressure (LP) while other conditions (pH and LAS concentration) were constant. As table 1 demonstrates there is no significant difference in rate constant and the radiation length between 18w and 27w lamps. However, in 150W lamps the decomposition rate was extremely high.

The effect of various concentrations of TiO₂ is shown in Fig. 2. As illustration in Table.1, the degradation rate constant of LAS increased with TiO₂ concentration, reached a plateau at a TiO₂ concentration of 50 mg/L, and decreased slightly and became independent of catalyst concentration.

The effect of variation in pH is showed in Fig.3. According to obtained results, there was a significant difference between removal efficiency with various

pH. The faster degradation occurred in lower pH; in fact less time needed for completion of degradation in acidic conditions.

Fig.5 illustrates separately the results of impact of mineral anions on the process. The highest effect on reduction of removal efficiency was related to the carbonate anion. The results related to impact of initial concentrations of LAS are shown in Table.1. The constant rate decreased when LAS concentration changes from 2 to 10 mg/L, while other conditions were constant. There was 95% removal of LAS with 2 mg/L in 15 minutes, while for 10 and 50 mg/L, 84% and 41% removal was obtained respectively.

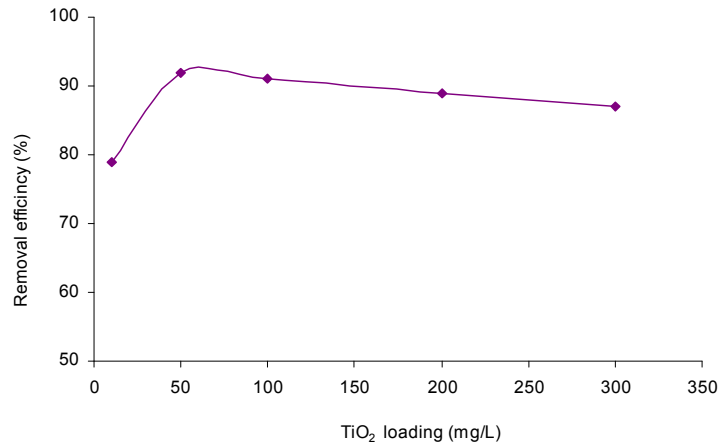


Fig. 3: Photocatalyst degradation of LAS with various TiO₂ concentrations

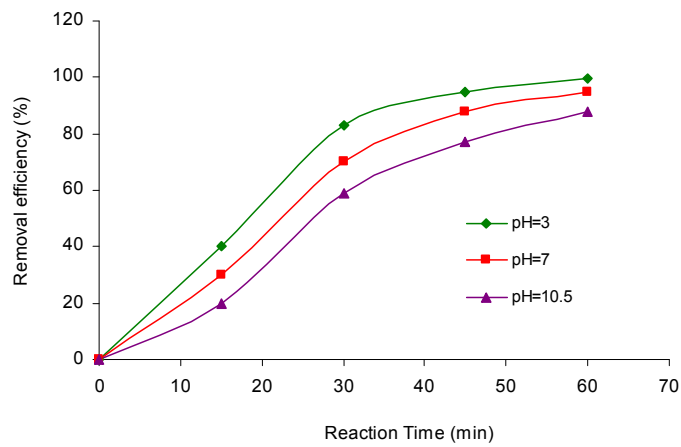


Fig. 4: Effect of pH on the efficiency removal of LAS (LAS:10 mg/L, TiO₂: 50 mg/L)

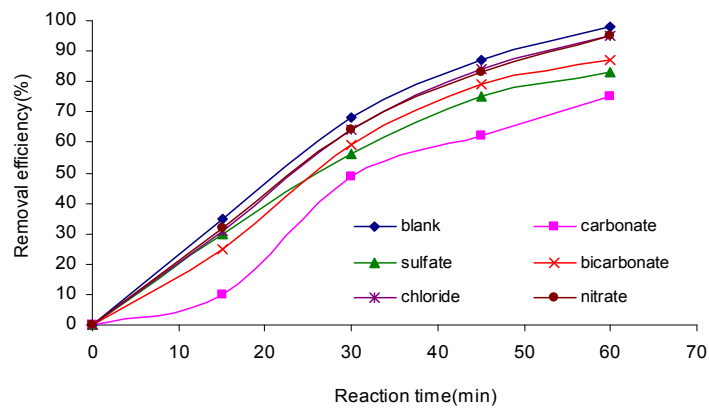


Fig. 5: Effect of anions on the efficiency removal of LAS (TiO₂: 50 mg/L)

DISCUSSION

According to the results as it is clear from Fig. 1 decreasing LAS concentration can be approximately modeled following pseudo-first-

order kinetics. It should be noted that UV-C 18 W radiation alone degraded a negligible amount of LAS; also with TiO₂ alone (without UV

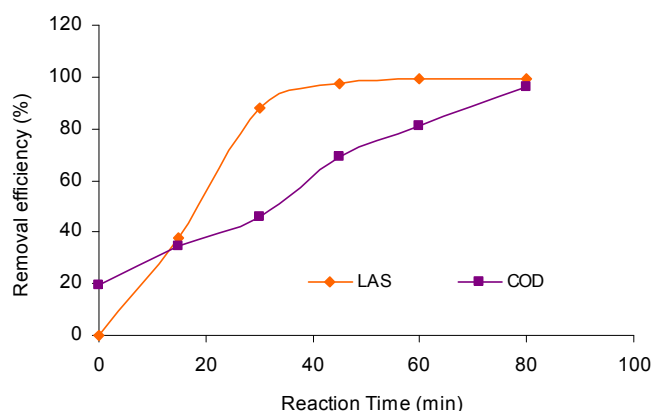


Fig. 6: Efficiency removal of COD and LAS (LAS: 10 mg/L, TiO₂: 50 mg/L,pH:4)

Table. 1: Degradation of LAS under different condition

LAS Concentration (mg/L)	TiO ₂ Concentration (mg/L)	pH	UV power (W)	Rate constant (10 ⁻³ / min)
1. Degradation of LAS				
10	0	acidic	18	3
10	0	neutral	18	3
10	0	alkaline	18	4
10	50	acidic	NA*	0.5
10	50	neutral	NA	NR**
10	50	alkaline	NA	NR
2. Effect of UV				
10	50	neutral	18	20
10	50	neutral	27	20
10	50	neutral	150	50
3. Effect of TiO ₂ concentration				
10	10	neutral	18	17
10	50	neutral	18	21
10	100	neutral	18	20
10	200	neutral	18	20
10	300	neutral	18	19.8
4. Effect of initial concentrations				
2	50	neutral	18	62
5	50	neutral	18	56
10	50	neutral	18	20
50	50	neutral	18	11
5. Effect of pH				
10	50	acidic	18	30
10	50	neutral	18	21
10	50	alkaline	18	16

radiation), removal of LAS was not evident. Fig. 1 also indicated insignificant adsorption of LAS onto TiO₂. This also suggested that stereochemical configuration of LAS is unsuitable to chelate with TiO₂, leading to negligible chemical adsorption \ high temperature.

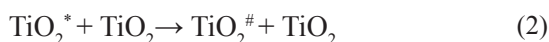
Effect of TiO₂ concentration

As illustrated in Table 1 the degradation rate constant of LAS increased with TiO₂ concentration,

reached a plateau at a TiO₂ concentration of 50 mg/L, and decreased slightly and became independent of catalyst concentration. It can be explained by the availability of access of active areas on the surface of TiO₂ and penetrating of light into the suspension. The accessibility of active areas increases by charging the catalyst, but light penetrating to solution decrease leads to lower degradation of LAS (Yang *et al.*, 2008).

A small amount of TiO₂ suspension would

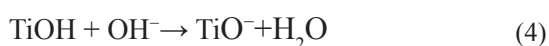
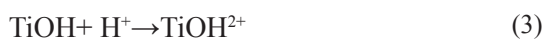
become active when the light penetration decreases; in addition, when TiO₂ concentration is high, a large amount of originally activated TiO₂ would deactivate through collision with ground-state catalysts. According to the following equation (Eq. 2):



Where TiO₂^{*} has active species adsorbed on its surface and TiO₂[#] is the deactivated form of TiO₂ (Nepolian *et al.*, 2002). Moreover agglomeration and sedimentation of TiO₂ occurs in high amounts of catalyst concentration (So *et al.*, 2002; San *et al.*, 2007). To avoid extra and not required catalyst and to adsorb total light photons for light mineralization, enough amount of optimal TiO₂ should be added.

Effect of pH

In photocatalytic processes, pH can also influence the degradation rate (Saien *et al.*, 2003). The zero charge point for TiO₂ particles depending on their anatase form varies from 5 to 7. If the mentioned pH is higher or lower, the TiO₂ surface charge becomes negative and positive, respectively as Eqs 3 and 4 (Brunner *et al.*, 1998).



As a result, TiO₂ surface in acidic conditions has positive charge and anionic surfactant absorption via anion group of SO₃⁻ on the positive surface of TiO₂ is easier in acidic pH (Hidaka *et al.*, 2004). Obviously adsorbing surfactant on the TiO₂ surface increases the reaction between hydroxyl radical of TiO₂ surface and the carbon atom in phenyl circle. Increasing pH gradually increases the electrostatic repulsion between TiO₂ surface and LAS, which is negatively charged at pH above 9.5 (Hidaka *et al.*, 2004).

Effect of mineral anions

According to the results of this study there was a significant difference between the blank sample and the mineral anions samples and the reactions

rate was less for mineral anions. These substances may deactivate the catalyst or compete with the decomposing LAS. Hydroxyl radical is very active and can react with non-aimed compositions non-selectively. As the result, the need for hydroxyl radical would become more and consequently the efficiency of the process would decrease. Moreover, anions may have reaction with positive gaps and hydroxyl radical which causes LAS decomposition period (Konstantinou *et al.*, 2004).

Effect of initial concentration of LAS

The effect of various initial concentrations of LAS in efficiency of removal showed that with increasing concentration of LAS, the efficiency of removal decreased. As the radical densities were equal in all the solutions, a solution with low LAS concentration with the same hydroxyl radical rate, would have higher transformation rate in comparison to solutions with higher density rates (Lopez *et al.*, 2000). Another reason is the intervention of mediating products which were produced as the result of LAS molecules decomposition. In high concentration of LAS, active areas would be covered by LAS ions. As the result, OH radical production on the catalyst decreases. Furthermore, the higher densities of LAS absorb most of photons, thus available photons for TiO₂ activation decrease (Konstantinou *et al.*, 2004). Accordingly the transformation rate is higher for samples with less density in the same period of time.

Photocatalytic mineralization of LAS

The Chemical Oxygen Demand (COD) of samples has been used as the criterion in an optimal condition to assure LAS decomposition and mineralization during the process. As Fig.6 shows, COD reduced significantly in a solution with 10 mg/L LAS after 80 minute radiation. The reason that the organic substances change to transient products and COD does not decrease totally in one hour. Similar studies (Sanchez *et al.*, 1997; Borio *et al.*, 1998) have also proposed that mineralization of LAS may occur with changing benzene group to carbon dioxide and water and also sulfite to sulfate simultaneously.

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