Photocatalytic Degradation of an Anionic Surfactant by Tio$_2$ Nanoparticle under UV Radiation in Aqueous Solutions

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ABSTRACT

In this paper the photocatalytic degradation of the anionic surfactant, linear alkylbenzene sulfonic acid (LABSA) was investigated using UV radiation in the presence of TiO$_2$. Our findings demonstrate that various parameters exert their individual influence on the photocatalytic degradation of surfactant in wastewaters. The mentioned parameters have been categorized as follow: the initial pH of the solution to be degraded, the impacts of oxidizing agents on photocatalytic degradation, amount of TiO$_2$, initial concentration of pollutant and irradiation time. The optimal degradation conditions of LABSA are: 200 mg/L TiO$_2$, pH 6.0, 1mM K$_2$S$_2$O$_8$ and concentration of LABSA 20 mg/L. Finally, about 96.14% of LABSA was removed by irradiation in 150 min.

Keywords: Photocatalytic degradation; Surfactant; UV/TiO$_2$

INTRODUCTION

Drinking water, as a vital component in our ecosystem, is of extremely important. Due to the fact that supplies of drinking water are so limited in a large-scale, considerable attention has been given to this challenge particularity with aim of re-using wastewater sources [1-6]. In this regard, various techniques and methodologies should be incorporated in order to refine the wastewater taking into consideration physical, mechanical, chemical and biological processes. In other words, well-known operations are required such as filtration, coagulation, precipitative softening, sedimentation, chlorination and so on [7, 8].

Aforementioned techniques are often ineffective for completely removing contaminations and pollutants and there is therefore a need for effective methodologies to be put in place. Literature review shows that Advanced Oxidation Processes (AOPs) have attracted remarkable attention due mainly to the fact that, generation of Oxidizing Hyrdoxyl Radicals (OHR) is generally capable of degrading recalcitrant molecules into biodegradable compounds [9-12]. On the other hand, published works have demonstrated the applicability of semiconductors, UV light and oxidizing agent either in individual or combined forms. Generally speaking, semiconductors are appropriate candidates to be used for photocatalysis. For example, TiO$_2$ has a number of interesting characteristics; from

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the stability point of view, TiO$_2$ is really reliable. In addition, it has low levels of toxicity and inertness. Other features can be attributed to TiO$_2$ such as being available that makes it suitable candidate for the problems under discussion. Furthermore, there are several examples in which a high level of effectiveness is observed by using TiO$_2$. In [13-21] researchers have employed TiO$_2$ in order to mineralize a vast range of toxic and bi-recalcitrant organic compounds including herbicides, organic acids, dyes, pesticides and organochloride compounds.

Above mentioned techniques have motivated us to use this framework in case of LABSA surfactant, which is an agent of contamination in the water. LABSA is an acronym of linear alkylbenzenesulfonic acid that is referred to a category of anionic surfactants. LABSA has traditionally been used as important agent of detergents, dispersing and emulsifier. In different scales ranging from domestic to industrial applications, the family of LABSA has proved satisfying results from the viewpoint of water pollution. It is generally accepted that, water contaminated by Surfactants is extremely difficult to be used and refined again since conventional methods based on chemical-physical-biological techniques cannot effectively remove the contamination in such a case [22-34]. For this purpose, we have focused on using UV light and TiO$_2$nanophotocatalyst in order to degrade LABSA. Moreover, to show the robustness of output results and concluding remarks, various conditions are examined and different criteria are met. For instance, the authors are interested to evaluate the impacts of variable PH on the performance of proposed degradation. The case when taking into account different amounts of photocatalyst is also of interest. Similarly, initial concentration of LABSA, concentration and type of Oxidizing agents

can fall into group of variables that corresponding effects are assessed too.

CHEMICALS
Linear alkylbenzene sulfonic acid was obtained from paxan detergent producer. HCl, NaOH, H$_2$O$_2$, K$_2$S$_2$O$_8$, KIO$_3$ and KBrO$_3$supplied by Merck Chemical Company. All reagents were used without further treatment. TiO$_2$nanopowders were synthesized in the laboratory of physical chemistry of Lahijan Branch and the crystallite size of the samples was estimated from XRD and TEM analyses. The average crystallite size is about 9.65nm.

EVALUATION OF PHOTOCATALYTIC ACTIVITY
Photocatalytic testing was conducted in a thermostatic cylindrical Pyrex reactor with a 50 mL capacity. 36-W mercury lamp was used as the UV light source. In a 50 mL flask, 25 mL of the LABSAsolution with an initial concentration range of 20 mg/L was placed. A known amount of TiO$_2$nanopowder was added to the surfactant and oxidant. The solution pH was adjusted by diluted HCl and NaOH solutions. The mixture was irradiated with the UV lamp for 90 min. The aqueous suspension was magnetically stirred (speed of 64 rpm) throughout the experiment. 5 mL samples were withdrawn on regular intervals of time and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor. The quantitative estimation of the surfactant was carried out using a UV-Vis spectrophotometer (Model Jenway 6405) at λ_{max}= 222 nm. The Photocatalytic degradation was calculated as follows:

$$\text{Photocatalytic degradation \%} = \frac{C_0 - C}{C_0} \times 100$$

where C$_0$ is the initial concentration of

surfactant and C the concentration of surfactant at time t.

RESULTS AND DISCUSSION
Effect of UV Irradiation and TiO₂Nanopowder
Fig. 1 shows a typical time-dependent UV-Vis spectrum of linear alkylbenzene sulfonic acid (LABSA) solution during photo-irradiation. These experiments demonstrated that both UV light and a photocatalyst, were needed for the effective destruction of LABSA.It is established that the photocatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst (Eq. (1)).The high oxidative potential of the holes (h^+_{VB}) in catalyst permits the direct oxidation of organic matter (surfactant) to reactive intermediates (Eq. 2).

Highly reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. 3) or by the reaction of the hole with OH^-(Eq. 4). The hydroxyl radical is an extremely strong, non-

selective oxidant which leads to the partial or complete mineralization of several organic chemicals.

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB}) \qquad (1)$$

$$h^+_{VB} + surfactant \rightarrow surfactant^{\bullet+} \rightarrow\ oxidation$$
$$of\ the\ surfactant \qquad (2)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + OH \qquad (3)$$

$$h^+_{VB} + OH^- \rightarrow OH^\bullet \qquad (4)$$
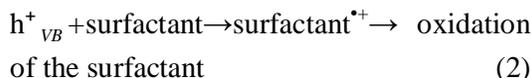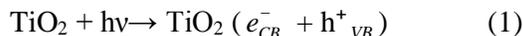
Electron in the conduction bond (e^-_{CB}) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. 5). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. 6) or hydrogen peroxide (Eq. 7).

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet-} \qquad (5)$$

$$O_2^{\bullet-} + surfactant \rightarrow surfactant\text{-}OO^\bullet \qquad (6)$$

$$O_2^{\bullet-} + H_2O^\bullet + H^+ \rightarrow H_2O_2 + O_2 \qquad (7)$$
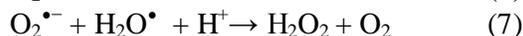
Electrons in the conduction bond are also responsible for production of hydroxyl radicals, species which have been indicated as the primary cause of organic matter mineralization (Eq. 8).

$$OH^\bullet + surfactant \rightarrow\ degradation\ of\ the$$
$$surfactant \qquad (8)$$
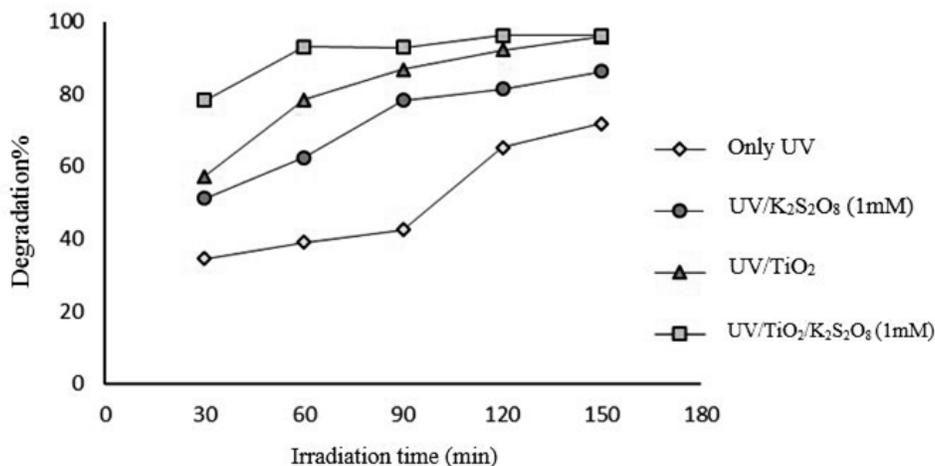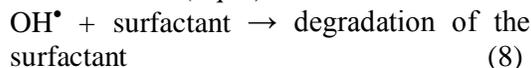
Fig. 1. Effect of UV irradiation and TiO₂nanopowder, Conditions: LABSA=20 mg/L, pH=6.0, TiO₂: 0.2 g/L, Irradiation time: 150 min, V_t: 25 mL.

Effect of the Amount of TiO2 Nanopowder

In order to obtain the optimum TiO_2 suspension concentration, the effect of photocatalyst dosages on the degradation of LABSA in aqueous solution was studied. The experiments were carried out employing different concentrations of TiO_2 varying from 0.04 to 0.44 g/L. The result is illustrated in Fig. 2.

It is obvious from this Fig. that when illumination time is fixed at 150 min, the photodegradation efficiency is directly proportional to the mass of catalyst. As the concentration of the photocatalyst increases from 0.04 to 0.2 g/L, the photodegradation efficiency of LABSA increases rapidly from 68% to 96.14%. Then the efficiency decreases slightly when the amount of TiO_2 reaches above 0.2 g/L. It is believed that the increase in the number of TiO_2 particles will increase the number of photons and the number of the LABSA molecules absorbed. Therefore, the degradation efficiency can be enhanced by increasing TiO_2 concentration. Due to the increase in total surface area available for contaminant adsorption and a further increase of the catalyst concentration, beyond 0.2 g/L may cause light scattering and screening effects. The excessive C, N-doped TiO_2photocatalyst leads to opacity of the suspension, which prevents the catalyst farthest in solution from being illuminated. The scattering and screening effects reduce the specific activity of the catalyst. At high catalyst concentration, particle aggregation may also reduce the catalytic activity. This may be the reason for decrease in photodegradation efficiency of LABSA. In this study, the optimum amount of catalyst is found to be 0.2 g/L for the degradation of LABSA.
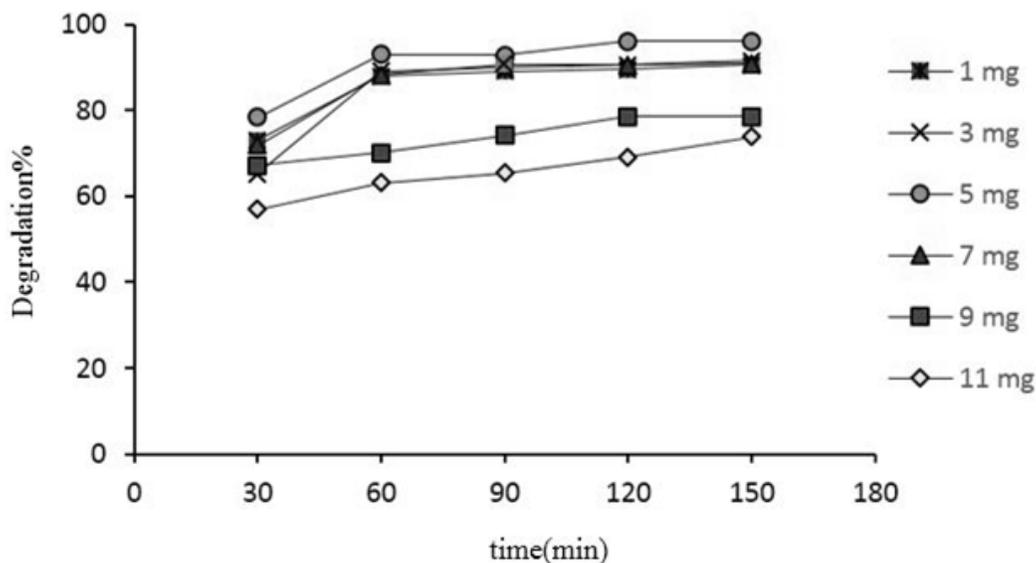

Fig.2. Effect of the amount of TiO_2nanopowder, Conditions: LABSA=20 mg/L, $K_2S_2O_8$=1 mM, pH=6.0, Irradiation time: 150min, V_t: 25 mL.

Effect of Initial Concentration
The effect of initial concentration of LABSA on the photocatalytic degradation was studied by varying the initial concentration over a wide range. The result, presented in Fig.3.indicates that photodegradation efficiency decreases with the increase in the initial concentration of LABSA. The photodegradation efficiency of LABSA decreased from 96% to 68% when the initial concentration increased from 10 to 40mg/L. The decrease in percent of degradation with increase in concentration of surfactant can be due to two reasons. With increasing the amounts of surfactant, more surfactant molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced.

Therefore, any increase in occupied space of catalyst surface, leads to decrease of hydroxyl radical generation. On the other hand, increasing concentration of surfactant can lead to decreasing the number of photons arrived to the surface of catalysts. The more light adsorbed by the molecules of surfactant, the less is excition of photocatalyst particles by photons.

Effect of pH
Photodegradation of surfactant was studied in pH of 2.0–12.0 in the presence of TiO_2 catalyst (0.2g/L) and $K_2S_2O_8$ (1mM). The results for irradiation time of 150 min are presented in Fig. 4.

In all cases, the maximum degradation efficiency was obtained in acidic pH 6.0 for LABSA. In presence of TiO_2 and in pH 6.0, degradation efficiency 96.14% is obtained. The interpretation of pH effects on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process.The pH influences surface charge of photocatalyst, meaning that pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor particles. In acidic solutions photodegradation efficiency was more than in alkaline solutions. It is because photodecomposition of TiO_2takes place in acidic and neutral solutions.
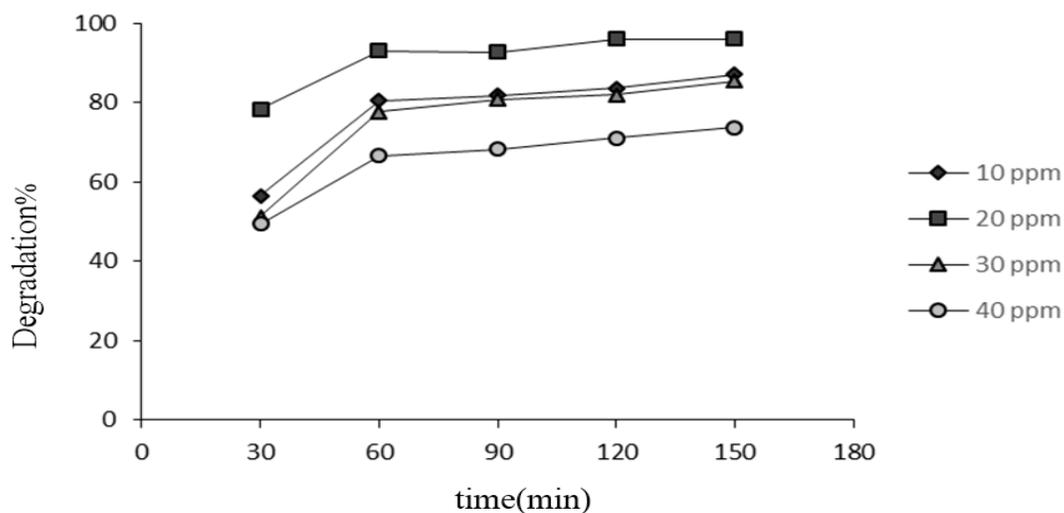

Fig. 3. Effect of initial surfactant concentration, Conditions: TiO_2: 0.2 g/L, $K_2S_2O_8$=1mM, pH=6.0, Irradiation time: 150 min, V_t: 25 mL.
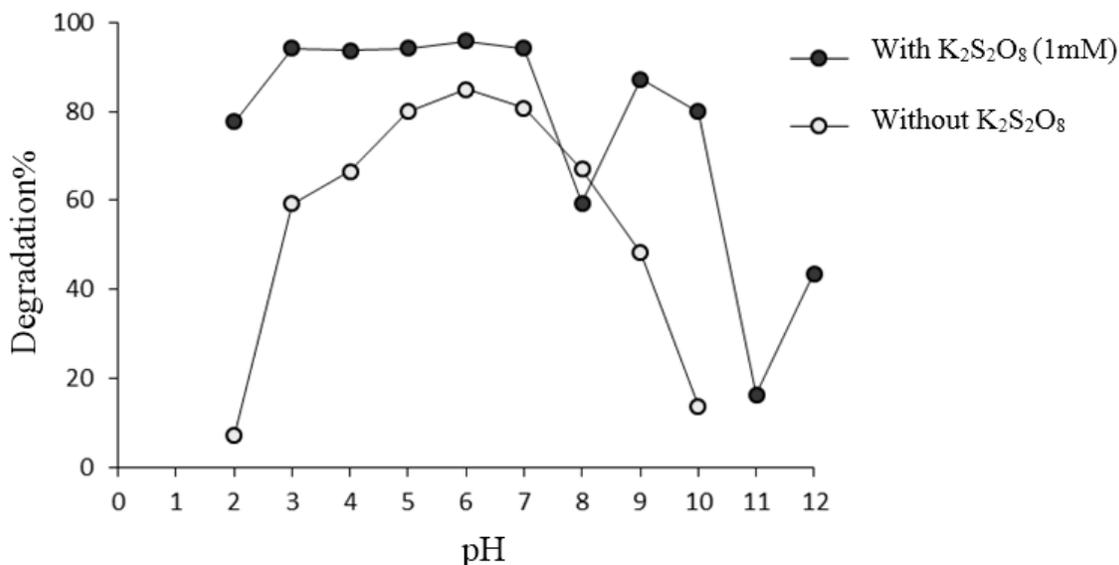
Fig.4. Effect of initial pH value, Conditions: LABSA: 20 mg/L, TiO$_2$: 0.2 g/L, K$_2$S$_2$O$_8$=1mM, Irradiation time: 150 min, V$_t$: 25 mL.

Effect of K2S2O8

Acceleration of the degradation rate photocatalytic oxidation on TiO$_2$ occurs by photogenerated holes. It is well known that oxidation rate increase when recombination process is suppressed. Potassium peroxydisulfate is a more reliable and cheaper electron acceptor. The effect of S$_2$O$_8^{2-}$concentration on the photodegradation efficiency of LABSA is shown in Fig. 5.

According to the results, addition of a small amount from S$_2$O$_8^{2-}$(1 mM), causes a rapid increase in the photodegradation efficiency of surfactant. It was found that the surfactant degradation increased from 70% to 96.14% after 150 min.

$$e^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad (9)$$
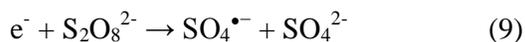
The sulphate radical anion SO$_4^{-\bullet}$may react with photogenerated electron and with watermolecule producing hydroxyl radical. The sulphate radical anion (SO$_4^{-\bullet}$)

is also a very strong oxidant (E$_0$ = 2.6 eV). This radical anion also participates in the degradation process.

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)[35, 36].

$$SO_4^{2-} + h^+ \rightarrow SO_4^{\bullet-} \qquad (10)$$
$$SO_4^{2-} + OH^\bullet \rightarrow SO_4^{\bullet-} + OH^- \qquad (11)$$
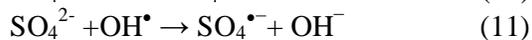
CONCLUSIONS

Linear alkylbenzenesulfunic acid (LABSA), an anionic surfactant of acid class, can be easily degraded by UV radiation in the presence of TiO$_2$ as a photocatalyst.Degradation of LABSA was remarkably accelerated by addition of proxydisulfate. The optimal degradation conditions were contained 20 mg of surfactant, 5 mg of photocatalyst, 1mM of Potassium peroxydisulfate, pH=6 andirradiation time: 150 min. Under this
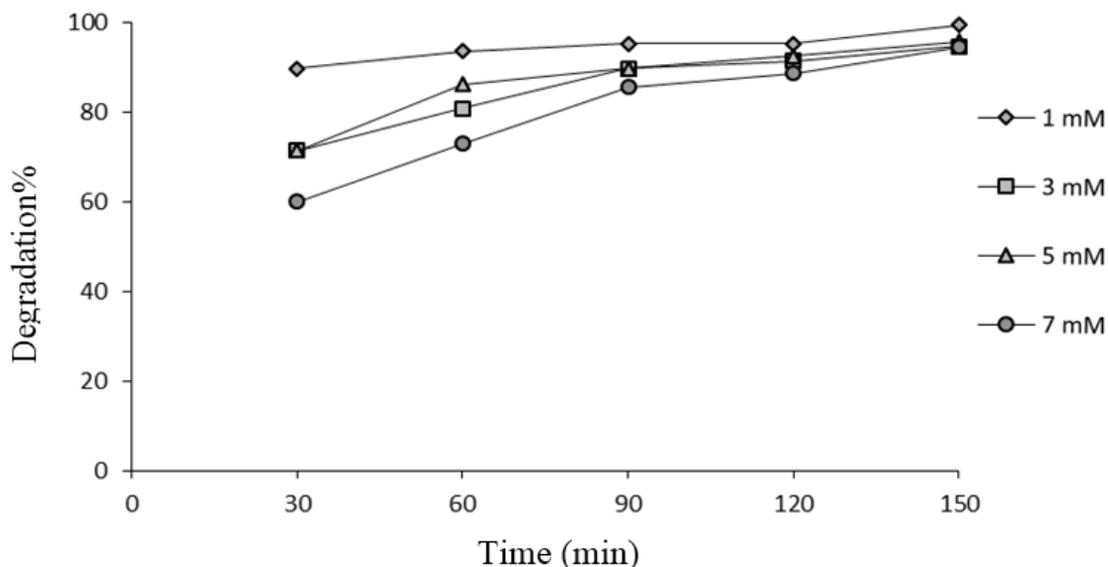
Fig.5. Effect of $K_2S_2O_8$, Conditions: LABSA: 20 mg/L, TiO_2: 0.2 g/L, pH=6.0, Irradiation time: 150 min, V_t: 25 mL.

conditionsthe photodegradation percent of LABSA was 96.14% when the solution irradiated by the 36 W mercury vapor lamp.

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