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Homogeneous and heterogeneous AOPs for rapid degradation of Triton X-100 in aqueous media via UV light, nano titania hydrogen peroxide and potassium persulfate

J. Saien a,∗, Z. Ojaghloo a, A.R. Soleymani a, M.H. Rasoulifard b

a Department of Applied Chemistry, Bu–Ali Sina University, Hamedan 65174, Iran
b Department of Applied Chemistry, University of Zanjan, Zanjan, Iran

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ABSTRACT

Feasibility of degradation of Triton X-100 as a widely used and resistive surfactant in aqueous media was studied via some homogeneous and heterogeneous AOPs of UV/TiO2, UV/H2O2 and UV/S2O82−. For treatment of solutions containing 20 mg/L of Triton, the optimum obtained conditions are: 5.0 mg/L of nano TiO2, 270.3 mg/L of KPS, and 34.0 mg/L of H2O2 (1 mM of the oxidants), initial natural pH of 5.4 and temperature of 45 °C. Under these conditions, the degradation efficiency for the UV/TiO2, UV/H2O2 and UV/S2O82− processes exceeds 71.9% (in 60 min), 80.9% (in 60 min) and 98.5% (in only 30 min) respectively. It was found that simultaneous application of these heterogeneous and homogeneous AOPs (UV/TiO2/H2O2 or S2O82−) is not desirable due to some physico-chemical retarding effects. The influence of temperature on the reactions was examined in the range of 15–45 °C. Under these conditions, the degradation efficiency for the UV/TiO2, UV/H2O2 and UV/S2O82− processes under optimum conditions, while this order for UV/H2O2 process is 2.27. Meanwhile, the initial rates of degradation in UV/TiO2 process can be described well by the Langmuir–Hinshelwood–Hougen–Watson kinetic model. Analysis of energy consumptions (thermal and electrical) revealed that increasing in temperature is an effective factor for lowering the energy cost of the preferred process of UV/S2O82−.

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1. Introduction

Synthetic surfactants have become a significant fraction of dissolved organic pollutants in water ecosystems. The contribution of non-ionic surfactants is still growing, and at present the non-ionic surfactants of alkylphenyl polyethoxylate type (Triton X-n) where “n” can be within the range of 3–40 are most widely industrial scale used surfactants, including production of detergents, emulsifiers, wetting agents, solubilizers and dispersants [1–3].

Alkylphenyl polyethoxylate surfactants can mimic natural hormones and thus have the potential to act as endocrine disrupters in aquatic organisms, wildlife and even humans [1]. The low affinity of alkylphenyl polyethoxylate surfactants for biological degradation and their high toxicity for biological active deposit require efficient oxidation treatments [4].

As the most famous surfactant in the category of non-ionic surfactants, Triton X-100 with n ≈ 9.5 (TX-100) is compatible with anionic, cationic and other non-ionic surfactants, and it possesses wide practical applications in almost every type of liquid, paste, and powdered cleaning compounds, ranging from heavy-duty industrial and agrochemical products to gentle detergents [5]. The increasing consumption of this surfactant generates lots of wastes during production, use and disposal.

Advanced oxidation processes (AOPs) can be used as promising techniques for in situ destruction and mineralization of many organics in water and wastewater [6,7]. AOPs are based on the generation of very reactive species such as •OH and SO4•− radicals that quickly oxidize a broad range of organic pollutants [8,9]. But unlike the non specific oxidation ability of hydroxyl radicals, sulfate radicals act as a relatively selective oxidant that react with certain organic compounds, especially benzene derivatives with ring activating groups [10]. AOPs can be separated into heterogeneous (e.g. UV/TiO2) and homogeneous (e.g. UV/H2O2 and UV/KPS) systems.

UV/TiO2 process is based on the use of ultraviolet light (λ ≪ 400 nm) and TiO2 semiconductor photocatalyst. TiO2 has received increasing attention because of its low cost, relatively high chemical stability, and the possibility of using sunlight as a source of irradiation [11–13]. The process is initiated by UV irradiation of the semiconductor to excite an electron from the valence band (VB) to the conduction band (CB) resulting in formation of...
a high energy electron-hole pairs (Eq. (1)). The highly oxidative valence band hole (redox potential of 2.8 V) may directly react with the surface-sorbed organic molecule or indirectly via the formation of \(^{•}\)OH radicals [14]. The reaction of the photo-generated holes with hydroxyl ions and water molecules adsorbed on the surface of TiO₂ yields hydroxyl radicals (Eq. (4)) [15,16] as well. Also, the conduction band electron (\(e_{\text{CB}}\)) is negative enough to reduce the oxygen molecules, present in the solution (Eq. (3)). The generated hydroxyl radicals are powerful oxidizing agents and attack organic pollutants, present at the surface of TiO₂ or near it (within 500 \(\mu\)m) and of course the reaction rate of hydroxyl radicals with pollutants decreases as the distance from surface increases [17]. Dissolved oxygen plays an important role in TiO₂ photocatalysis reaction to assure sufficient electron scavengers present to trap the excited conduction-band electron from recombination [18]. These functions cause the degradation of dye according to the following reactions (\(R\) is an organic compound) [7,17,19]:

\[
\begin{align*}
\text{TiO}_2 + h\nu (E_c \geq 3.2 \text{ eV}) & \rightarrow \text{TiO}_2(\text{e}_{\text{CB}}^- + h\nu^+) \quad (1) \\
\text{h}^+ + \text{e}_{\text{CB}}^- & \rightarrow \text{heat}(\text{recombination}) \quad (2) \\
\text{O}_2(\text{ads}) + \text{C}_\text{B}^- & \rightarrow \text{O}_2^{•-} \quad (3) \\
(\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-)^\text{ads} + \text{h}^+ + \text{OH}^- & \rightarrow \text{H}^+ + \text{•OH} \quad (4) \\
\text{O}_2^{•-} + \text{H}^+ & \rightarrow \text{HO}_2^- \quad (5) \\
2\text{HO}_2^• & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (6) \\
\text{H}_2\text{O}_2 + \text{e}_{\text{CB}}^- & \rightarrow \text{•OH} + \text{OH}^- \quad (7) \\
\text{R} + \text{•OH} & \rightarrow \text{degradation} \quad (8) \\
\text{R} + \text{h}^+ & \rightarrow \text{oxidation} \quad (9) \\
\text{R} + \text{e}_{\text{CB}}^- & \rightarrow \text{reduction} \quad (10)
\end{align*}
\]

Dissolved oxygen also provides sufficient buoyant force for complete suspension of TiO₂ particles [20]. However, the viability of this kind of process is debatable, mainly due to the extreme difficulty encountered in the separation of the solid photocatalysts at the end of the process. From this point of view, the use of homogeneous systems appears to be a good alternative [21].

In UV/H₂O₂ process, main interactions between hydrogen peroxide with UV irradiation and free radicals are represented by reactions as below [22,23]:

\[
\begin{align*}
\text{H}_2\text{O}_2^{\text{UV}} & \rightarrow 2 \cdot \text{OH} \quad (11) \\
\text{H}_2\text{O}_2 + \text{•OH} & \rightarrow \text{HO}_2^• + \text{H}_2\text{O} \quad (12) \\
2\text{•OH} & \rightarrow \text{H}_2\text{O}_2(\text{onlyinacidicdioxide}) \quad (13) \\
\text{•OH} + \text{HO}_2^• & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (14) \\
2\text{HO}_2^• & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (15)
\end{align*}
\]

Persulfate ion (\(\text{S}_2\text{O}_8^{2-}\)), on the other hand, is a strong oxidant (with redox potential of 2.05 V) [8]. This oxidant is normally available as a salt associated with ammonium, sodium, or potassium. Potassium persulfate (KPS) recently was shown to be an effective disinfectant and/or oxidant for the Norwalk virus, foot and mouth disease and Coro-naviridae (causing severe acute respiratory syndromes SARS) [24]. It has also been reported to be effective for degrading organics in hazardous wastewaters in acidic or basic media through direct chemical oxidation [25]. Since \(\text{S}_2\text{O}_8^{2-}\) slowly reacts with many organics, it is activated via thermal, photochemical, radiolytic or reduct decomposition to generate the stronger oxidant of sulfate radicals (\(\text{SO}_4^{•-}\)) [9]. These radicals with redox potential of 2.6 V [26] accompanied with generated \(\text{•OH}\) radicals are responsible for degradation of pollutants in the solution [27–29]:

\[
\begin{align*}
\text{S}_2\text{O}_8^{2-} + h\nu & \rightarrow 2\text{SO}_4^{•-} \quad (16)
\end{align*}
\]

In the oxidation process, sulfate ions will be generated as the end-product, which leads to an increase in salt content in the effluent. But this does not seem to be a serious drawback, because there are no legal restrictions on sodium/potassium sulfate in waste water [30,31]. Alternatively, potassium persulfate (KPS) is much cheaper than other oxidants like hydrogen peroxide and ozone as well as its safe handling and its solubility in water makes it an excellent additive for waste treatment [8,27].

In this research rapid degradation of TX-100 in aqueous media using heterogeneous and homogenous AOPs (UV/TiO₂, UV/H₂O₂ and UV/\(\text{S}_2\text{O}_8^{2-}\)) is investigated in a special reactor and the influence of H₂O₂ and \(\text{S}_2\text{O}_8^{2-}\) on UV/TiO₂ process is studied. Effect of operational parameters of catalyst and reagents dosage, pH and temperature are to be studied. The kinetic relationships and the level of required energy for the outstanding process are investigated.

2. Experimental

2.1. Reagents

All reagents were used as received without further purification.

TX-100, was Merck product with purity of more than 99.5%. Fig. 1 displays the chemical structure of this surfactant. Nano catalyst was Degussa P25 titania (Germany), with approximately 70% anatase and 30% rutile structure; BET surface area of 55 ± 15 m²/g and the average particle diameter of 30 nm [32]. Sulfuric acid and sodium hydroxide (used to adjust the pH), hydrogen peroxide (30%, w/w) and potassium persulfate (KPS), were all Merck products. Distilled water was used to prepare the solutions.

2.2. The photo reactor

Fig. 2 demonstrates a schematic view of the reactor and its belongings. A cylindrical photo reactor made of glossy stainless steel with capacity of about 1.25 L and dimensions of 90 mm diameter and 250 mm height was employed. The UV lamp (165 mm body length and 80 mm arc length) was mercury 250 W with the wavelength range of 280–400 nm and the maximum emission (348 mW/cm²) at 365 nm (measured by a TOPCON UV-R-1 spectroradiometer). It was positioned symmetrically in the reactor and immersed directly in the solution. The reactor was equipped with a stainless steel water-flow jacket for regulating the temperature by means of an external circulating flow of a thermostat bath (Julabo F12-ED, Germany) with an accuracy of ±0.1 °C. Since the photocatalyst is sustained by a ready supply of dissolved oxygen, air was supplied to the reaction system at a constant flow-rate using a micro-air compressor.
2.3. Procedure

In the case of UV/TiO₂ process, first TiO₂ stock suspension was prepared and sonicated for 20 min in order to well homogenization. Then solutions containing 20 mg/L of the TX-100 and the appropriate amount of TiO₂ were prepared. The pH of solutions was adjusted to the desired values by means of a pH meter (Denver, UB-10) using dilute H₂SO₄ or NaOH solutions. A prepared solution (1 L for each experiment) was then transferred to the reactor and after adjusting the temperature, the UV lamp was switched on to initiate the process. During the experiments a mild aeration was kept for mixing the content and saturation with O₂. Samples (4 mL) were taken at regular time intervals and centrifuged in two stages for separating the TiO₂ particles perfectly [33]. A maximum total sampling volume of 32 mL was withdrawn during each experimental run which is not significant, compared with the solution volume.

Same procedures were applied in the case of UV/H₂O₂ and UV/S₂O₈²⁻, considering that no sonication or centrifuge steps were needed to be used.

2.4. Analysis method

In a precedent study the UV–Vis absorption spectra of TX-100 were studied using a UV–Vis spectrophotometer (PG Instrument, T80) at different times of UV/TiO₂ process, under conditions of catalyst concentration of 5 mg/L, 25 °C and natural pH of 5.4. As it is presented in Fig. 3, the absorption band relating to different molecular parts of this substrate, at λ_max = 195 nm and 223 nm, is decreased with respect to time. These absorbance peaks are attributed to benzene ring [34]. In this study the absorbance decrease at 223 nm was measured to follow the elimination of TX-100. Absorbance at 195 nm may be accompanied with a number of interfering absorptions.

It is notable that the maximum wavelength and the molar absorption coefficient of TX-100 were not much dependent on pH of solution within the range of 4–9. Using this method, the degradation efficiency (X) was obtained at any time, according to [7]:

\[
X = \frac{C_0 - C}{C_0}
\]

where \(C_0\) and \(C\) are initial and appropriate concentrations of TX-100 at any time.

Chemical oxygen demand (COD) was measured in order to investigate the mineralization of the substrate, using a closed reflux digester reactor (HACH, DRB 200) and the corresponding spectrophotometer (HACH, DR 2800).

3. Results and discussion

3.1. Influence of nano titania dosage

Concentration of TiO₂ in the photo-catalytic water treatment system affects the overall photo-catalysis reaction rate. Adding TiO₂ particles in the solution causes two different effects: (i) rising active catalyst surface which leads to generating more active species in the media and more degradation efficiency, (ii) increas-
ing the media turbidity which leads to a decrease in the amount of lights, reached to the catalyst surface and hence, diminishing the degradation efficiency. These two opposite effects will result an optimum amount for the catalyst dosage. This optimum value is attributed to the geometry and working conditions of the photo-reactor where the surface reaction is initiated upon light photon absorption [35]. When the amount of TiO₂ increases, the solution turbidity will increase and the excess TiO₂ particles can create a light scattering effect that reduces the surface area of TiO₂ being exposed to light illumination and the photo-catalytic efficiency. In general, this phenomenon is called as “inner filtration effect” in photo-catalysis [36]. Therefore, any chosen photo-reactor should operate below this limit of TiO₂ dosage, to avoid excess catalyst and ensure efficient photons absorption [20].

Fig. 4 shows an improvement in degradation efficiency from 13.6% to 41.1% when catalyst concentration is increased and then decreases. The positive effect of adding TiO₂ particle is intense up to 5 mg/L and then will be mild, because of reaching to inner filtration effect. The catalyst concentration, therefore, can be limited to 5 mg/L, while the degradation efficiency is remained around the maximum level. The subsequent relevant experiments were performed using this concentration of TiO₂ particle.

3.2. Effect of pH

pH is one of the factors influencing the rate of degradation of organic compounds in the UV/TiO₂ process. It has influence on substrate and catalyst surface charge and also on the mechanism of hydroxyl radical generation [37]. Fig. 5 demonstrates the variation in the degradation efficiency of TX-100 for pH values within the range of 4–9 for the cases of UV/TiO₂ and only photolysis processes after 60 min. As it is observed, TX-100 can be photo-degraded with UV irradiation. The corresponding degradation after 60 min is around 13.6% under natural pH. When pH is decreased to 4, a mild decrease in degradation efficiency occurs. Also as pH increases to 9, the efficiency decreases considerably and even to levels less than the photolysis process. Diminishes in degradation efficiency at acidic and alkaline media can be attributed to the repulsion between the substrate and catalyst surface charges. Since the pH of zero point of charge (pH_{zpc}) of titania is 6.25 [19]; below and above this pH, titania surface is positively and negatively charged respectively according to the following equations [20]:

$$\text{atpH} < \text{pH}_{zpc}: \quad \text{TiOH}^+ + \text{H}^+ \leftrightarrow \text{TiOH}_2^+$$ (24)
$$\text{atpH} > \text{pH}_{zpc}: \quad \text{TiOH}^+ + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O}$$ (25)

At pH 4, substrate is presumably partial positively charged; therefore, there is a partial repulsion between positive catalyst surface and the substrate, which is not desirable. As the figure shows, this undesirable repulsion has not been able to reduce the degradation, which can be related to the possibility of additional •OH radical formation in the acidic media from the following reaction equations [40]. However, since the life time of superoxide anions is very short [41] at neutral and acidic pH conditions, the portion of this mechanism is minor:

$$\text{e}^- + \text{O}_2(\text{ads}) \rightarrow \cdot\text{O}_2(\text{ads})$$ (26)
$$\cdot\text{O}_2(\text{ads}) + \text{H}^+ \rightarrow \text{HO}_2^-$$ (27)
$$2\cdot\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$$ (28)
$$\text{H}_2\text{O}_2 + \cdot\text{O}_2(\text{ads}) \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$$ (29)

Under pH values of 7–9, on the other hand, the catalyst surface and the substrate are both partial negatively charged and the repulsion between them inhibits the degradation too. pH results interpretation, based on existed repulsions at acidic or alkaline media can be proven by the results of the substrate adsorption on TiO₂ surface at darkness (the inserted figure in Fig. 5). It shows that...
the substrate can be adsorbed on the catalyst surface only at natural pH conditions.

The natural pH of 5.4 can be chosen as a moderate and optimum pH value and the experiments were followed under this pH, having the advantage of no need to add chemicals into the solution.

It has to be noted that a pH reduction of only 0.3 was detected during the whole 60 min of degradation. This low variation can be attributed to the low concentration of optimum 5 mg/L TiO2.

3.3. Effect of hydrogen peroxide and persulfate dosages

Addition of H2O2 up to concentrations of 68.0 mg/L (2 mM), in the operation of UV/TiO2 process leads to higher reaction efficiency, as shown in Fig. 6. The reason is attributed to the increase in the concentration of •OH radicals, generated by photocatalytic splitting of H2O2. At low concentration of hydrogen peroxide, it inhibits the electron-hole recombination, and it could act as an alternative electron acceptor (Eqs. (1) and (30)).

\[ e_{CB}^- + H_2O_2 \rightarrow \cdot OH + \cdot O^\cdot \] \hspace{2cm} (30)

However, further increase of H2O2, beyond 34.0 mg/L (1 mM), causes the excess H2O2 molecules to scavenge the valuable hydroxyl radicals in the solution and form a much weaker oxidant hydroperoxyl radical (HO2•) (Eq. (12)), which could further scavenge hydroxyl radicals (Eq. (14)). The excessive hydroxyl and hydroperoxyl radicals may also recombine into H2O2 (Eqs. (13) and (15)), which leads to stability in the overall oxidative power of all oxidants in the solution [42,43]. Another aspect is that the amount of adsorbed TX-100 is decreased with increasing H2O2 that competes with the substrate in adsorbing at the sites of the catalyst surface.

The results of experiments with different KPS doses in the presence of UV light and TiO2 particles are also presented in Fig. 6. Adding small amounts of KPS up to 540.7 mg/L (2 mM) has accelerated degradation of TX-100. In this way, the degradation rate is enhanced by several ways such as: (i) generating SO4•− radicals as oxidizing species by interaction with UV light (Eq. (16)), (ii) increasing the •OH radicals concentration (Eqs. (17) and (18)) and (iii) preventing the electron-hole recombination by accepting the conduction band electron:

\[ e_{CB}^- + S_2O_8^{2−} \rightarrow SO_4^{−} + SO_4^{2−} \] \hspace{2cm} (31)

From Fig. 6, the amounts of 34.0 mg/L of H2O2 (1 mM) and 270.3 mg/L (1 mM) of S2O8^{2−} can be introduced as the optimum values. In the case of UV/TiO2/KPS, adding extra amounts of KPS does not provide much improvement in degradation efficiency (the results obtained after 10, 30 and 40 min, also, show rather plateau regions for concentrations more than 1 mM); moreover, using the same concentration of the oxidants has the advantage of easy comparison between the applied processes in temperature and kinetic study sections.

Inserted in Fig. 6 is UV absorption spectrum of H2O2 (34.0 mg/L) and KPS (270.3 mg/L). The oxidant with higher UV absorption (KPS) is more effective in degradation, due to high absorption of UV light leading to higher formation of reactive radical species [29,44].

These results are not adequate to decide about advantage of applying H2O2 and KPS reagents accompanied with UV/TiO2 process. To clarify the role of persulfate, two experiments with 1 mM KPS and 1 mM H2O2 were performed in the presence of UV light irradiation without TiO2 particles. The results have been compared with UV/TiO2 and UV/TiO2/oxidant processes in Fig. 7. The figure shows that when peroxide and persulfate oxidants are added to the UV/TiO2 process, the degradation efficiency have been enhanced from 37.5% to 52.0% for UV/TiO2/H2O2 and to 77.9% for UV/TiO2/KPS, respectively, after 60 min for instance, but adding TiO2 particles to the UV/KPS or UV/H2O2 (UV/oxidant) will cause a reduction in degradation (from 63.3% to 52.0% and from 84.2% to 77.9% for UV/H2O2 and UV/KPS, respectively, after 60 min). This reveals that simultaneous application of UV/H2O2 and UV/KPS processes, each with TiO2 particles, is not desirable due to existence of some retardation effects.

The shading or scattering of UV light with TiO2 particles turbidity can reduce direct photolysis of H2O2 and S2O8^{2−} molecules (Eqs. (11) and (16)) and also absorption of UV light with H2O2 and S2O8^{2−} species leads less doses of UV light to reach TiO2 particles. On the other hand, H2O2 molecules can scavenge generated hydroxyl radicals with UV/TiO2 process (Eqs. (12) and (14)) where hydroperoxyl radical is significantly less reactive than •OH radical with respect to...
organic oxidation. In addition, the peroxide oxidants can react with TiO₂ and form surface peroxytitanium complexes that irreversibly block the active sites of the catalyst [45]. These inhibition mechanisms may account for most of the negative effect of the inorganic peroxides on TiO₂ photoactivity. Also, in the case of KPS addition to the UV/TiO₂ process, SO₄²⁻ ions produced by S₂O₈²⁻ reactions can be adsorbed on TiO₂ surface (which has positive charge) and lead to decrease in active surface of catalyst or react with •OH radicals which totally provides a negative effect on the operation of UV/TiO₂ process.

Considering the above discussion, it can be deduced that UV/KPS is the most promising process for degradation of TX-100 molecules in aqueous media and is more studied here in comparison with UV/TiO₂ process.

3.4. Effect of temperature

Temperature influence on the used processes was tested in the range of 15–45 °C and the results for the UV/TiO₂ and UV/KPS are shown in Fig. 8, for instance. A 71.9% and 80.9% degradation after 60 min for UV/TiO₂ and UV/H₂O₂ processes, and hence a perfect degradation after 30 min for UV/KPS, all at 45 °C, can be achieved.

Thirty degrees of centigrade increase in temperature will cause 42.8%, 50% and 66.0% enhancements in degradation efficiency.
for UV/TiO₂, UV/H₂O₂ and UV/KPS processes, respectively, after 30 min. In a research by Perkowski et al. [4] for the aim of TX-100 degradation, using titania photocatalytic process; a near perfect degradation is achieved after 5 h under the corresponding optimum conditions. Lower rising effect of temperature with UV/TiO₂ degradation is achieved after 5 h under the corresponding optimum conditions. Lower rising effect of temperature with UV/TiO₂ degradation, using titania photocatalytic process; a near perfect degradation was achieved after 5 h under the corresponding optimum conditions.

3.5. Mineralization

Mineralization can be defined as reaching to the final degradation step of organic substances and their intermediates under destructive treatment process. Organics due to the mineralization will be converted to CO₂ and H₂O. COD values have been related to the total concentration of organics in the solutions [46]. Using this criterion, the mineralization of TX-100 by UV/TiO₂ and UV/KPS processes was investigated under optimum amount of the reagents, natural pH and 45°C. The results are presented in Fig. 9, showing the substrate conversion based on COD values with respect to its initial value, after times of 30 and 60 min.

The COD removal reaches to 44.9% and 61.2% for the case of UV/KPS and 4.1% and 20.4% for the case of UV/TiO₂ process after 30 and 60 min, respectively. It shows that UV/KPS can operate about 3 folds more effective than UV/TiO₂ process with the aim of mineralization. Meantime, degradation efficiency with the mentioned used processes under the same conditions (natural pH and 45°C) was 98.5% and 51.7%, respectively, after 30 min. The ratio of degradation and mineralization efficiencies of, 2.2 and 12.6, respectively, indicates the presence of significantly more organic content in the media for the case of UV/TiO₂ process. A number of works are previously concerned on identifying relevant intermediates [47,48].

3.6. Kinetic study

Due to the practical applications, the kinetic degradation of TX-100 was investigated under UV/KPS, UV/H₂O₂ and UV/TiO₂ under the conditions of 270.3 mg/L (1 mM) S₂O₈²⁻, 34.0 mg/L (1 mM) H₂O₂ and 5 mg/L TiO₂ under initial natural pH, up to 30 min of the degradation process for the temperature range of 15–45°C.

Here, a preliminary power law kinetic model was chosen for modeling the experimental data, as:

\[ r = -\frac{dC}{dt} = kC^n \]  (32)

where \( r \), \( C \) and \( t \) represents the rate of degradation, concentration of TX-100 and time respectively. Also \( k \) and \( n \) are the rate constant and reaction order. As well known, according to the Arrhenius equation, the rate constant of reaction is related to temperature by equation:

\[ k = k_0 e^{-\frac{E_a}{RT}} \]  (33)

where \( k_0 \), \( E_a \) and \( R \) are frequency factor, activation energy and the universal constant of gasses, respectively.

Replacing Eq. (33) into Eq. (32), one can write the logarithmic form of Eq. (33).

\[ \ln r = \ln k_0 - \frac{E_a}{RT} + n \ln C \]  (34)

The differential method of analysis, based on the data of concentration versus time was employed for finding the rate at each appropriate time. The goodness of fitting in agreement with Eq. (34) is shown in Fig. 10 for the UV/KPS process, for instance. In this figure experimental data has been marked with bold dots and the fitted 3D equation with a meshed plane. Variables \( z \), \( x \) and \( y \) are attributed to the \( ln r \), \( 1/T \) and \( ln C \) respectively and from the coefficients of \( a \), \( b \) and \( c \), kinetic parameters can be obtained. Activation energy and kinetic parameters of the used three degradation processes along with the coefficient of determination \( (R^2) \) are given in Table 1.

As the obtained values of \( n \) indicate a pseudo first order reaction rate can be attributed to the degradation of TX-100 with UV/KPS and UV/TiO₂ processes under optimum conditions, while order of degradation with UV/H₂O₂ process is 2.27, close to a second order reaction. The case of pseudo first order reaction is in agreement with the results of other related researches [23,29,49].

Fig. 8. TX-100 conversion versus time for UV/TiO₂ and UV/KPS processes at different temperatures; \( C_{TiO2} = 5 \text{mg/L}; C_{KPS} = 270.3 \text{mg/L} \) and natural pH.
Fig. 9. TX-100 conversion based on mineralization versus time for the UV/TiO\textsubscript{2} and UV/KPS processes; C\textsubscript{0} = 20 mg/L, C\textsubscript{TiO\textsubscript{2}} = 5 mg/L; C\textsubscript{KPS} = 270.3 mg/L; 45 °C and natural pH.

Fig. 10. Correlation diagram for experimental kinetic data; z, x and y are ln \( r \), \( 1/T \) and ln C respectively.

Paying attention to the very close pseudo first order reaction, obtained for UV/TiO\textsubscript{2} process, the kinetic of degradation on the surface of catalyst may also be described with the Langmuir–Hinshelwood (L–H) model, according to [47]:

\[
r = k_r C \frac{K}{1 + KC} = k_{app} C
\]

where \( k_r \) (mg/L min) corresponds to the limiting degradation rate at maximum coverage of the adsorbed Triton and \( K \) (L/mg) the proportion of Triton molecules which adhere to the surface of TiO\textsubscript{2} particles. With refer to different initial rates, corresponding to different initial concentrations, it can be concluded that [6,47]:

\[
k_{app} = \frac{k_r K}{1 + KC}
\]

In fact, if the degradation with UV/TiO\textsubscript{2} be in accordance with the L–H model, the variation of \( 1/k_{app} \) versus \( C_0 \) should be linear. The values of \( k_{app} \) can be obtained from variation of ln C\textsubscript{o}/C versus time reaction for different TX-100 initial concentrations. The results based on obtained \( k_{app} \) values (Table 2) are depicted in Figs. 11 and 12, which reveal a good fit of initial degradation kinetic with L–H model too. The L–H parameters of \( k_r \) and \( K \) are accordingly obtained as 0.199 (mg/L min) and 0.138 (L/mg) respectively.

### 3.7. Effect of temperature on the UV/KPS energy consumption

Since photochemical treatment of aqueous organic pollutants is an electrical energy-related process, the electrical energy can represent a major fraction of the operating costs; simple figures-of-merit based on electric energy consumption can be very useful and informative. The Photochemistry Commission of the Interna-

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**Table 2**

| \( C_0 \) (mg/L) | \( k_{app} \times 10^2 \) (1/min) | \( R^2 \) |
|-------------------|----------------------------------|---------|
| 10                | 1.14                             | 0.9888  |
| 15                | 1.07                             | 0.9858  |
| 20                | 0.72                             | 0.9903  |
| 25                | 0.61                             | 0.9675  |
| 30                | 0.54                             | 0.9436  |

**Table 1**

| Process       | \( k_0 \) (mg/L\textsuperscript{-0.02}/min) | \( E_a \) (kJ/mol) | \( n \) | \( k \) at 25 °C (mg/L\textsuperscript{-0.02}/min) | \( R^2 \) |
|---------------|---------------------------------|----------------|--------|---------------------------------|---------|
| UV/KPS       | \( 5.65 \times 10^7 \)          | 52.70          | 0.98   | \( 3.29 \times 10^{-2} \)          | 0.9511  |
| UV/TiO\textsubscript{2} | \( 6.90 \times 10^6 \)          | 52.52          | 1.14   | \( 4.37 \times 10^{-3} \)          | 0.9919  |
| UV/H\textsubscript{2}O\textsubscript{2} | \( 8.90 \times 10^8 \)          | 63.42          | 2.27   | \( 7.75 \times 10^{-5} \)          | 0.9115  |
The International Union of Pure and Applied Chemistry (IUPAC) proposed a figure-of-merit (or more appropriately, an efficiency index, as it compares electrical efficiency of different AOPs) for UV-based AOPs. In the case of low pollutant concentration which is the case here, the appropriate figure-of-merit is the electrical energy per order \( (E_{EO}) \), defined as the number of kWh of electrical energy required for reducing the concentration of a pollutant by 1 order of magnitude, and proposed in reference [50] as 90% degradation, in 1 m\(^3\) of contaminated water. \( E_{EO} \) (kWh/m\(^3\)) can be calculated from the following equations [51,52]:

\[
E_{EO} = \frac{1000 \times P \times t}{60 \times V \times \log(C_i/C_f)}
\]  

where \( P \) is the lamp power (kW) used in the AOP system, \( t \) is the irradiation time (min), \( V \) is the volume (L) of the contaminated water in the reactor and \( C_i \) and \( C_f \) are the initial and final pollutant concentrations.

Considering the first-order degradation kinetic for the decay of TX-100 concentration, the constant ratio of \( \ln(C_i/C_f)/t \) represents the rate constant, \( k \) (in unit of 1/min), the above equation can be written as:

\[
E_{EO} = \frac{38.4 \times P}{V \times k}
\]

The thermal energy \( (E_Q = mC_p \Delta T, m \) the mass of 1 m\(^3\) of contaminated water and \( C_p \) specific heat capacity at constant pressure),
required for heating the medium to a desired temperature, should also be considered in this analysis.

The electric energy (\(E_e\), kWh/m\(^3\)) and thermal energy (\(E_t\), MJ/m\(^3\)) for degradation of 20 mg/L of TX-100 in the UV/KPS process at different temperatures are presented in Table 3. A reduction in the required electrical energy for treating 1 m\(^3\) of the substrate solution is appropriate, when temperature is increased. Considering the natural gas as the most common industrial used fuel for supplying thermal energy and its average heat of combustion which is about 29.7 MJ/kg (corresponding to 0°C and 101.3 kPa) and also its cost in U.S. (about 5.07 US$/28 m\(^3\)) [53]; meanwhile, the cost for supplying 1 kWh industrial electricity in U.S. (about 0.065 US$) [53]; therefore, total cost of treatment process (\(E_t + E_e\)) can be calculated at various temperatures (15°C is considered as the base temperature). The results are given in Fig. 13. It can be seen that by increasing in temperature, the total treatment cost is decreased considerably (despite significant increase in thermal energy cost). This matter is due to the significant enhancement in degradation efficiency with temperature, as discussed in Section 3.4. Temperature can facilitate the dissociation of persulfate to sulfate radicals and also improve the activity of generated radicals.

4. Conclusions

The most important conclusions are: (i) using heterogeneous UV/nano TiO\(_2\) process, a 71.9% degradation of TX-100 under the optimum conditions (5 mg/L of TiO\(_2\), natural pH of 5.4 and temperature of 45°C) can be achieved during about 60 min. (ii) Applying homogenous AOPs, UV/H\(_2\)O\(_2\) and UV/KPS under the optimum conditions of pH and temperature in addition to 270.3 mg/L of KPS or 34.0 mg/L of H\(_2\)O\(_2\) results a 80.9% degradation of TX-100 in 60 min and a perfect degradation of it in only 30 min, respectively. (iv) Homogenous AOPs are more effective than heterogeneous one and UV/KPS process can be introduced as the best. (v) Simultaneous application of homogeneous oxidants with UV/TiO\(_2\) process cannot be desirable due to some retarding physico-chemical phenomena. (vi) A pseudo first order kinetic model, including temperature parameter, can adequately describe the degradation rate for the processes of UV/KPS and UV/TiO\(_2\), but an order of 2.27 for UV/H\(_2\)O\(_2\) process. (vii) The Langmuir–Hinshelwood kinetic model showed a good agreement for the initial rates of degradation for UV/TiO\(_2\) process. (viii) The COD removal in the case of UV/KPS reaches to 61.2% after 60 min. (ix) Economic analysis indicates that in the scale of used set-up and applied operating conditions, increasing temperature is an effective way for reducing the total energy cost of the treatment with the preferred UV/KPS process.

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References

[1] H.J. Chen, D.H. Tseng, S.L. Huang, Biodegradation of octylphenol polyethoxylate surfactant Triton X-100 by selected microorganisms, J. Bioresource Technol. 96 (2005) 1483–1491.
[2] J. Perkowska, J. Mayer, L. Kos, Reactions of non-ionic surfactants, Triton X-type, with OH radicals. A review, Fibers Text. East. Eur. 13 (2005) 81–85.
[3] M.A. Manzano, J.A. Derales, D. Sales, J.M. Quirou, The effect of temperature on the biodegradation of a nonylphenol polyethoxylate in river water, Water Res. 33 (1999) 2593–2600.
[4] J. Perkowska, A. Bluska, W.K. Jozwiak, Titania assisted photocatalytic decomposition of Triton X-100 detergent in aqueous solution, Environ. Prot. Eng. 31 (2005) 61–75.
[5] M.J. Rosen, Surfactants and Interfacial Phenomena, 3rd ed., Wiley, New Jersey, 2004.
[6] J. Saien, S. Khezrijjoo, Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO\(_2\) process: optimization, kinetics and toxicity studies, J. Hazard. Mater. 157 (2008) 269–276.
[7] J. Saien, A.R. Soleymann, Degradation and mineralization of direct blue 71 in a circulating upflow reactor by UV/TiO\(_2\) process and employing a new method in kinetic study, J. Hazard. Mater. 144 (2007) 506–512.
[8] D. Salari, A. Niaei, S. Aher, M.H. Rasoulifard, The photooxidative destruction of C.I. Basic Yellow 2 using UV/S\(_2\)O\(_8\)\(_2\)\(^2\) process in a rectangular continuous photoreactor, J. Hazard. Mater. 166 (2009) 61–66.
[9] J. Zhao, Y. Zhang, X. Quan, S. Chen, Enhanced oxidation of 4-chlorophenol using sulfite radicals generated from zero-valent iron and peroxysulfide at ambient temperature, Sep. Purif. Technol. 71 (2010) 302–307.
[10] Y.F. Huang, Y.H. Huang, Identification of produced powerful radicals involved in the mineralization of biphenyl A using a novel UV-Na\(_2\)S\(_2\)O\(_3\)/H\(_2\)O\(_2\)-Fe(III) two-stage oxidation process, J. Hazard. Mater. 162 (2009) 1211–1216.
[11] A. Syoufh, K. Nakashima, Degradation of methylene blue in aqueous dispersion of hollow titania photocatalyst: optimization of reaction by peroxysulfide electron scavenger, J. Colloid. Interfaces Sci. 313 (2007) 213–218.
[12] H. Nishikiori, N. Tanaka, T. Kitsu, T. Fujii, Photocurrent observed in doped titania gel, J. Photochem. Photobiol. A: Chem. 179 (2006) 125–129.
[13] H. Shibata, T. Ohkubo, H. Kohno, P. Rangsunvijit, H. Saka, M. Abe, Preparation and photocatalytic activity of titania particulate film with mesostructured silica as binder, J. Photochem. Photobiol. A: Chem. 181 (2006) 357–362.
[14] L.K. Konstantinou, T.A. Albanis, TiO\(_2\)-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, Appl. Catal. B: Environ. 49 (2004) 1–14.
[15] N. San, A. Hatipoglu, G. Kocturk, Z. Cynar, Photocatalytic degradation of 4-nitrophenol in aqueous TiO\(_2\) suspensions: theoretical prediction of the intermediates, J. Photochem. Photobiol. A: Chem. 146 (2002) 189–197.
[16] C. Gomes da Silva, J.L. Faria, Photochemical and photocatalytic degradation of an azo dye in aqueous solution by irradiation, J. Photochem. Photobiol. A: Chem. 155 (2003) 133–143.
[17] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.
[18] M.N. Chong, S. Le, B. Jin, C. Saint, C.W.K. Chow, Optimisation of an annular photoreactor process for degradation of Congo red using a newly synthesized titania impregnated kaolinite nano–photocatalyst, Sep. Purif. Technol. 67 (2009) 355–363.
[19] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.
[20] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res. 44 (2010) 2975–3072.
[21] A. Kunz, P. Peralta-Zamora, N. Duran, Hydrogen peroxide assisted photocatalytic degradation of ethylenediaminetetraacetic acid, Adv. Environ. Res. 7 (2002) 197–202.
[22] D. Salari, N. Daneshvar, F. Aghazadeh, A.R. Khataee, Application of artificial neural networks for modeling of the treatment of wastewater contaminated with methyl tert-butyl ether (MTBE) by UV/H\(_2\)O\(_2\) process, J. Hazard. Mater. B125 (2005) 205–210.
