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Research Article

Photo Catalytic Removal of Sodium Dodecyl Sulfate From Aquatic Solutions With Prepared ZnO Nanocrystals and UV Irradiation

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In this study, ZnO Nano catalyst has been synthesized and examined as photo catalyst for UV-induced removal of Sodium Dodecyl Sulfate (SDS) from aquatic solutions. This anionic surfactant was selected based upon its toxicity, wide use in industrial laundry and as a primary pollutant in municipal waste water systems.This study aimed to investigate removal of surfactant, SDS, in a batch photo catalytic reactor under various operating conditions including ZnO suspension concentration, initial surfactant concentration and initial pH of solution to find out the desired condition for removal of surfactant. ZnO Nano crystals were synthesized using the precipitation method and $ZnSO_4.7H_2O$ was used as the starting material and NaOH as precipitant. The removal of SDS reactions by UV/ZnO process was performed into a batch photo reactor. In addition, various operating conditions including ZnO suspension concentration, initial surfactant concentration and initial pH of solution were investigated. In total, 98% of surfactant was removed at 40 minute and removal efficiency of SDS increased with increasing pH up to nine and after that with increase in pH, efficiency decreased. Possible roles of inorganic oxidant on the reaction were discussed. The removal of SDS follows pseudo-first order kinetics. Based on the results of this study, ZnO-UV photo catalytic process can be used as an efficient method for further study in detergents removal.

Keywords: ZnO Nanoparticles; SDS; Photocatalytic Removal; Kinetics

1. Introduction

Surfactant molecules contain both hydrophobic and hydrophilic moieties. This structure of surfactants gives properties that can be used in both industrial applications as well as consumer goods. Surfactants are the active ingredients in personal hygiene products and detergents for industrial and household cleaning (1). The volume size of global surfactant market is about 18 M ton and an increase of 20% is estimated until 2012 (2). There are four classes (cationic, anionic, amphoteric and nonionic) based on the ionic charge (if present) of hydrophilic portion of surfactant in an aqueous solution (3). A large number of surfactants, including the anionic types used in the present study, have relatively low biodegradability (4). Anionic surfactants are the major class of surfactants used in detergent formulations. Sodium dodecyl sulphate (SDS), a member of the linear alkyl benzene sulfonates (LAS) family is used as detergent, dispersant and anionic surfactant (4).

Surfactants removal operations involve processes such as chemical and electrochemical oxidation (5, 6) membrane technology (7-9), chemical precipitation (10, 11), photo catalytic degradation (12, 13), adsorption (14-16) and various biological methods (17-19). Each has its merits and limitation in application.

In recent years, UV-induced Advanced Oxidation Processes (AOPs) have been suggested as one of the practicable technologies for removal of persistent organic pollutants (20, 21). Researchers showed that using UV/TiO_2, UV/ZnO, UV/O_3, UV/H_2O_2 and UV/Fenton were more efficient in organic pollutants degradation (22-24). Among AOPs, semiconductor photo catalyst has emerged an important destructive technology leading to total mineralization of organic pollutants (25). Moreover, this process uses cheaply available nontoxic semiconductor (TiO_2, ZnO) and leads to total mineralization of organic compounds to CO_2, water and mineral acids (26). Though, TiO_2 is the most commonly used photo catalyst for removal of a wide range of organic compounds, ZnO is found to be a suitable alternative to TiO_2 since its photo degradation mechanism has been proven to be similar to that of TiO_2 (27, 28). Besides, according to Kormann et al. and Hoffman et al. the quantum yield of H_2O_2 production in illuminated aqueous suspensions of ZnO was found to be one order of magnitude higher than the corresponding value for TiO_2.(29, 30).

Sodium dodecyl sulphate as an anionic surfactant is a primary pollutant in municipal waste water systems and attracted environmental concerns. To the best of our knowledge, there has not been any report on photo catalytic removal of sodium dodecyl sulphate by UV/ZnO process. Therefore, SDS was chosen as the sample for our investigation.

This study aimed to investigate removal of the surfactant, SDS, in a batch photo catalytic reactor under various operating conditions including ZnO suspension concentration, initial surfactant concentration and initial pH of solution to find out the desired condition for removal of surfactant. We also analyzed the effect of $S_2O_8^{2-}$ on the photo catalytic removal of surfactant with ZnO under UV-C light irradiation. The electrical energy per order for photo catalysis was calculated in the presence and absence of $S_2O_8^{2-}$.

2. Materials and Methods

2.1. Reagents and Materials

SDS used in this research had a purity of 99.9% purchased from Sigma Aldrich (Spain). Its chemical structure and other characteristics are listed in Table 1. This anionic surfactant was selected based upon its toxicity, wide use in industrial laundry and as a primary pollutant in municipal waste water systems. Other chemicals used in this study were obtained from Merck Co. (Germany).

Table 1. Characteristics of Sodium Dodecyl Sulfate

Variables	Values
Molecular formula	$CH_3(CH_2)_{11}OSO_3Na$
Molecular mass	288.38, g/moL
CAS No.	151-21-3
Other names	Lauryl sodium sulfate aquarex methyl
Chemical class	Anionic surfactant
Water solubility	250, g/L at 20 °C
Toxicity	Orl-Rat LD_{50} 1300, mg/kg
Chemical structure	

2.2. Synthesis of ZnO Nano Crystals

ZnO nanocrystals were synthesized using the precipitation method. $ZnSO_4.7H_2O$ was used as the starting material and NaOH as precipitant without further purification. NaOH solution was added dropwise to the vigorously stirred solution to adjust pH to about seven and a large amount of white slurry was formed. The resulting slurry was continuously stirred for 12 hours, and then washed with deionized water. The wet powder was dried at about 100 °C in air to form the precursor of ZnO. Finally, the precursor was calcinated in air at a certain temperature (300 °C for 3 hours) to produce the Nano sized ZnO photo catalyst.

Synthesized sample was examined by X-ray diffraction (XRD) using Siemens D-5000 diffract meter with Cu K^{α} radiation (Germany) to confirm the crystal structure and estimate the average crystallite size. Figure 1 illustrates X-ray diffraction pattern of synthesized ZnO nanoparticles. X-ray diffraction data was recorded using Cu K^{α} radiation (1.54056 °A). The intensity data was collected over a 2θ range of 10-70 °.

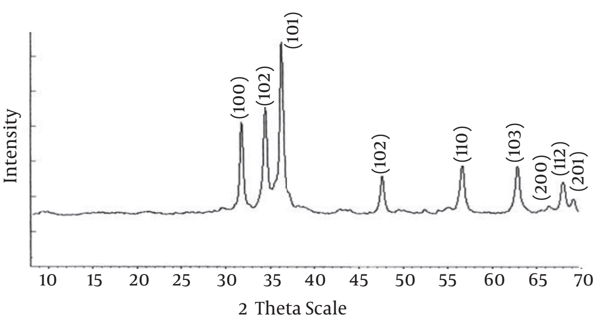


Figure 1. X-ray Diffraction (XRD) Pattern of Synthesized ZnO Nanoparticles

The full width at half maximum of the most intense peak ($\theta = 17.61$) was used to get the average crystallite size of synthesized sample using Scherrer's equation (31). The average crystallite size of synthesized ZnO is about 14 nm. X-ray diffraction studies confirmed that the synthesized material was ZnO of the wurtzite phase and all the crystal structures agreed with the reported Joint Committee on Powder Diffraction Standards data (JCPDS 36 - 1451).

2.3. Photo Reactor Pilot

The removal of anionic surfactant (sodium dodecyl sulfate) reactions during UV/ZnO process was performed into a batch photo reactor. This photo reactor formed from a glass cylindrical reactor with 2.0 L volume immersed in a cooling water jacket with 10.0 L volume of cold water. A low-pressure lamp (ARDA 125 W) (France) with quartz cortex, was used as the UV emitter (UV - C, λ = 247 nm). The UV lamp was immersed centrally in the glass reactor.

2.4. Set-up and Procedures

For the photo degradation of SDS, a solution containing 10 mg/L of anionic surfactant and 150 mg/L ZnO nano powder was prepared and allowed to equilibrate for 30 minutes in the darkness, then 1000 mL of the prepared suspension was transferred to a 2000 mL Pyrex reactor. Irradiation was performed in the photo reactor. The suspension pH values were adjusted at desired level (4 - 10) using dilute NaOH and HCL and then the pH values were measured with pH meter (Suntex sp-701, Taiwan). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous and the suspension was sampled after an appropriate illumination time. Before determination of concentration of anionic surfactant, samples were centrifuged for removal of ZnO particles.

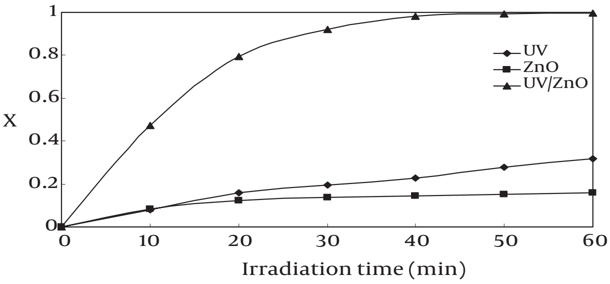
The concentration of anionic surfactant in each degraded sample was determined using Methylene Blue Active Substances (MBAS) and absorbance of the samples and standards at 652 nm against a blank of chloroform by spectrophotometer (Shimatzu, UV-Vis 1700) (32). By this method conversion percent of SDS was obtained in different intervals.

3. Results and Discussion

Photo catalytic experiments were performed under the following conditions:

1) Surfactant solution with the UV in the absence of ZnO; 2) surfactant solution with ZnO in dark and 3) surfactant solution under irradiation of UV with ZnO. The results were presented in Figure 1. Addition of ZnO without irradiation had a negligible effect on photo catalytic removal efficiency. The surfactant was resistant to self-photolysis in UV radiation. It can be seen from Figure 2 that in the presence of ZnO nanoparticles and UV irradiation, 98% of surfactant was removed at 40 minute.

Figure 2. Effect of UV light and ZnO Nanoparticles on Photo Catalytic Removal of SDS



$[SDS]_O = 10$ mg/L; $[ZnO]_O = 150$ mg/L; pH = 7; $X = (C_O - C)/C_O$ = Removal Value

The basic principle of heterogeneous photo catalysis such as ZnO to act as sensitizer and consequently to enhance the photo degradation of surfactant can be summarized shortly as follows. A semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB) and the lowest empty band, called conduction band (CB), are separated by a band gap, i.e. a region of forbidden energies in a perfect crystal. When a photon of energy higher or equal to the band gap energy is absorbed by ZnO particles, an electron from the VB is promoted to the CB e^-_{CB} with simultaneous generation of a hole (h^+_{VB}) in the VB (Equation 1).

$$\text{ZnO} + h\nu \rightarrow \text{ZnO}\left(e^-_{CB} + h^+_{VB}\right) \tag{1}$$

These generated species can either recombine and dissipate the energy as heat or react with adsorbed water or oxygen molecules and/or adsorbed hydroxyl anions, to produce strong oxidizing hydroxyl radicals or super oxide anions, which can promote the oxidation of surfactant molecule. Furthermore, the surfactant molecules might be decomposed to form organic acids as the intermediate products (Equations 2-6) (26).

$$H^+_{VB} + H_2O_{(ads)} \rightarrow H^+ + OH_{(ads)} \tag{2}$$

$$H^+_{VB} + OH^-_{(ads)} \rightarrow OH_{(ads)} \tag{3}$$

$$e^- + O_{2(ads)} \rightarrow O_2^- \tag{4}$$

$$OH_{(ads)} + \text{surfactant} \rightarrow \text{intermediateproduction} \rightarrow \text{degradationproduct} \tag{5}$$

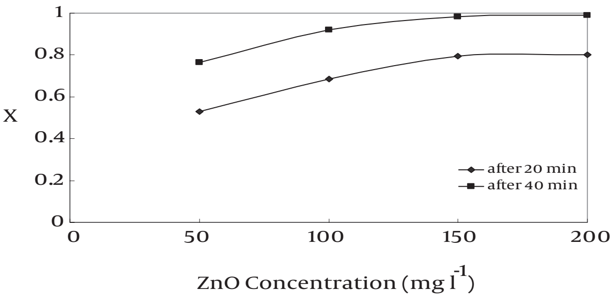
$$h^+_{VB} + \text{surfactant} \rightarrow \text{intermediateproduct} \rightarrow \text{degradationproduct} \tag{6}$$

3.1. Effect of Photo Catalyst Dosage

The desired amount of ZnO has to be added to avoid excess catalyst and to ensure total absorption of radiation photons for efficient photo catalytic removal. It depends on the type of photo catalyst, pollutant concentration, characteristics of UV radiation (power, wavelength), photo reactor geometry, etc. (33).

The influence of ZnO concentration from 50 to 200 mg/L on the photo catalytic removal efficiency of SDS was investigated. Figure 3 reveals that photo catalytic removal efficiency increases with increased ZnO concentration from 50 to 150 mg/L and after that, increase in amount catalyst does not affect the efficiency significantly.

Figure 3. Effect of Catalyst Loading on the Removal Efficiency of SDS



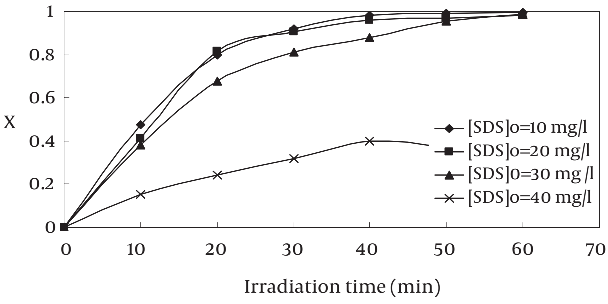
$[SDS]_O = 10$ mg/L; pH = 7; $X = (C_O - C)/C_O$ = Removal Value

This can be explained for availability of active sites on the catalyst surface and penetration of UV light into the suspension (34). The total active surface area increases with increasing catalyst dosage. However, deviation from linearity at higher concentration is probably due to aggregation of free catalyst particle and screening effect resulting from excessive opacity of the solution (35).

3.2. Effect of Initial pH

pH is an important parameter for photo catalytic degradation. It is related to the ionization state of the surface of photo catalyst as well as pollutants. The change of pH values can influence the adsorption of pollutants on the photo catalyst surface, which is an important step for the photo catalytic process. The effect of pH on the photo catalytic removal of SDS was studied in the pH range of 3-11. Figure 4 indicates that photo catalytic removal efficiency of SDS increased with increasing pH up to 9 and after that with increase in pH, efficiency decreased. The surface of photo catalyst was changed positively under pH < $pH_{IEP.}$ The isoelectric point of pH (pH_{IEP}) corresponds to the zeta potential equal to zero. The zero point charge for ZnO is 9.2 (36). The surfactant used in this study was anionic surfactant and negatively charged under experimental conditions because of the sulfate group.

Figure 4. Effect of Initial pH on Photo Catalytic Removal of SDS



$[SDS]_O$ = 10 mg/L; ZnO = 150 mg/L; X = $(C_O\text{-}C)/C_O$ = Removal Value

Accordingly, electrostatic interaction between photo catalyst surface and surfactant anions leads to adsorption at pH < 9.2. Unfortunately, the mere electrostatic argument is unable to exhaustively account for the relative photo catalytic behavior as a function of pH. Other concomitant effects can come into play. For example, ZnO can undergo photo corrosion through self-oxidation (Equation 7) (37, 38).

(7) $$ZnO + 2h^+ \rightarrow Zn^{2+} + \frac{1}{2}O_2$$

In particular, ZnO powder exhibits tendency to dissolve with decreasing pH (Equation 8) (39).

(8) $$ZnO + 2H^+ \rightarrow ZN^{2+} + H_2O$$

In a strongly alkaline environment, ZnO can undergo dissolution according to Equation 9.

(9) $$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$$

Moreover, possible formation of photo catalytically inert Zn $(OH)_2$ surface layers upon UV irradiation (Equation 10) has also to be considered in aqueous media (40).

(10) $$2ZnO + 4H_2O + 4h^+ \rightarrow 2Zn(OH)_2 + O_2 + 4H^+$$

Therefore, reduction of photo catalytic activity of ZnO at exceedingly low and high pH values can originate from either acidic/photochemical corrosion of the catalyst (Equation 7 and Equation 8), from alkaline dissolution (Equation 9) and/or surface passivation with $Zn(OH)_2$ (Equation 10). In addition, reactions (7) and (9) can compete with the formation of hydroxyl radicals by decreasing the availability of holes for water or surface OH^- oxidation.

3.3. Effect of Substrate Concentration

It is important both from the mechanistic and application points of view, to study the dependence of photo catalytic reaction on the substrate concentration. The effect of various initial surfactant concentrations on the photo catalytic removal has been investigated from 10 to 40 mg/L. Figure 5 shows the effect of initial SDS concentration on photo catalytic removal efficiency. It can be seen that anionic surfactant removal efficiency decreased as initial SDS concentration increased. The presumed reason is that when the initial concentration of SDS is increased, more and more organic substance molecules are adsorbed on the surface of ZnO Nano powder. Therefore, there are only fewer active sites for adsorption of hydroxyl ions, so the generation of hydroxyl radicals would be reduced (41).

3.4. Kinetics of Photo Catalytic Removal of SDS

Photo catalytic removal of SDS by UV/ZnO process exhibited pseudo first-order kinetics with respect to the concentration of organic compound. In which kobs is the pseudo first-order rate constant. Figure 6 shows a plot of ln ($[SDS]_0$/[SDS]) versus time for all the experiments with different initial concentrations of SDS (Equation 11).

(11) $$-\frac{d[SDS]}{dt} = k_{obs}[SDS]$$

Whose integration gives, for $[SDS] = [SDS]_o$ at $t = 0$ (Equation 12).

(12) $$\mathrm{Ln}\left(\frac{[SDS]_0}{[SDS]}\right) = k_{obs}t$$

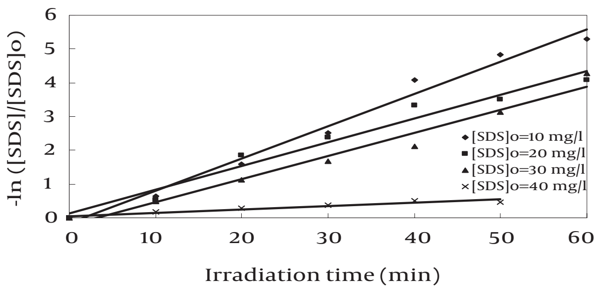


Figure 5. Removal Efficiency for UV-Induced Photo Catalytic Removal of SDS in the Presence of ZnO (150 mg/L) and Different Concentrations of SDS; X = $(C_O\text{-}C)/C_O$ = Removal Value

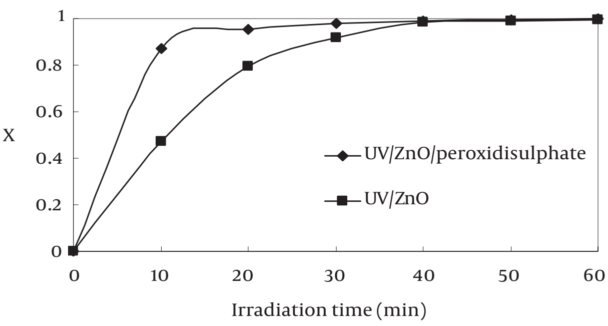


Figure 6. Determination of Pseudo-First-Order Kinetic Rate Constant, k_{obs}

By applying a least square regression analysis, k_{obs} values were obtained. Table 2 reports the values of $k_{obs}$and R (liner correlation coefficient) squared for all performed experiments. The reaction rate proceeds according to pseudo first-order kinetics with a kinetic constant, which decreases as the initial reactant concentration increases. This can be ascribed to the decrease in the number of active sites on the catalyst surface due to covering the surface with SDS molecules, which is directly proportional with the initial concentration of SDS.

Table 2. Rate Constants for Photo Catalytic Removal of SDS With Different Initial Concentration

$[SDS]_0$, mg/L^1	k ,min^{-1}	R_2	$t_{1/2}$, min
10	0.0955	0.98	7.26
20	0.0702	0.98	9.87
30	0.0682	0.97	10.16
40	0.0099	0.96	70

3.5. Effect of S2O82-

Major energy wasting step in the photo catalytic reaction is the electron-hole recombination, which leads to low quantum yield. Hence, the prevention of electron-hole recombination becomes very important. This can be achieved by adding a proper electron acceptor to the system. In heterogeneous photo, catalytic reaction molecular oxygen is usually used as an electron acceptor for the prevention of electron-hole recombination. Besides, adding molecular oxygen, the electron-hole recombination can be reduced by the addition of irreversible electron acceptors such as $S_2O_8^{2-}$. Addition of these electron acceptors enhances the photo catalytic removal efficiency by several ways: (i) preventing the electron-hole recombination by accepting the conduction band electron (ii) increasing the hydroxyl radicals concentration and (iii) generating other oxidizing species to accelerate compound oxidation rate. The photo catalytic removal of SDS in the presence of 100 mg/L $S_2O_8^{2-}$ has been studied. The results are shown in Figure 7.

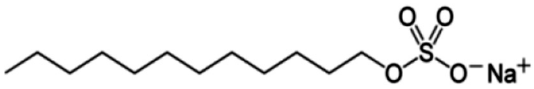


Figure 7. Effect of Adding Inorganic Oxidant on Photo Catalytic Removal of SDS. $[SDS]_0$ = 10 mg/L; ZnO = 150 mg/L; pH = 7

From Figure 7, it is clear that addition of peroxidisulphate to photo catalytic process enhances the removal efficiency. The enhancement of the reaction is due to the following reasons:

(i) $S_2O_8^{2-}$ can generate sulphate radical anion SO_4^- photolytically in aqueous solution. SO_4^- then reacts with H_2O to produce OH (Equation 13 and Equation 14).

(13) $$S_2O_8^{2-} \rightarrow 2SO_4^{-}$$

(14) $$SO_4^- + H_2O \rightarrow \mathrm{OH} + SO_4^{2-} + H^+$$

SO_4^{2-} is a strong oxidant (E^o = 2.6 eV) and can directly react with SDS in the following way (Equation 15 and Equation 16).

(15) $$SO_4^- + \mathrm{SDS} \rightarrow SO_4^{2-} + \mathrm{surfactantintermediate}$$

(16) $$SO_4^- + \mathrm{surfactantintermediate} \rightarrow CO_2 + H_2O + \mathrm{mineralizationproducts}$$

(ii) Peroxidisulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidizing species namely sulphate radical anion (Equation 17).

(17) $$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^- + SO_4^{2-}$$

From the thermodynamic point of view, peroxidisulphate should be more efficient electron acceptor than molecular oxygen as indicated by one electron reduction potential of different species formed from peroxidisulphate and oxygen: E (O_2/)= -155 mV, E($S_2O_8^{2-}$/SO_4^-) = 1100 mV (42).

At high dosage of $S_2O_8^{2-}$, small enhancement of reaction occurs due to the increase of concentration of $S_2O_8^{2-}$ ion. The excess of $S_2O_8^{2-}$ ion is adsorbed on the ZnO surface and reduces the catalytic activity. The adsorbed $S_2O_8^{2-}$ ion also reacts with photogenerated holes and with hydroxyl radicals (Equation 18 and Equation 19) (43, 44).

(18) $$SO_4^{2-} + h_{VB}^+ \rightarrow SO_4^-$$

(19) $$SO_4^{2-} + \mathrm{OH} \rightarrow SO_4^- + OH^-$$

3.6. Electrical energy determination

Although several reports are available in the literature on electrical energy determination of various AOPs, it is necessary to study the electrical consumption of AOPs under experimental conditions. Generally, electrical energy consumption of AOPs depends on the number of experimental factors (type of pollutant being treated, configuration of the reactor, and type of light source used, etc.) and hence, electrical energy determination becomes important for the processes studied. A number of important factors such as economic, effluent quality, cost, etc., play a vital role in selecting a waste treatment technology. Since photo degradation of aqueous organic pollutant is an electrical energy-related process, electrical energy represents a major fraction of operating cost. The figures of merit E_{EO} allow for a rapid determination of electrical energy cost and they indicate the total power required. For comparative study, the treatment efficiencies for different processes are evaluated through the E_{EO} values. The E_{EO} is the electrical energy in kilowatt-hours (kWh) required to degrade a contaminant by one order of magnitude in a unit volume (e. g. 1 m^3 (1000 L)) of contaminated water or air. E_{EO} values can be calculated using the following formula, Bach operation (Equation 20) (45).

$$E_{\mathrm{EO}} = \frac{\mathrm{Lamppower(kW)} \times \mathrm{Time(min)} \times 1000}{\mathrm{Treatedvolume}(L) \times 60 \times \log\left(\frac{C_0}{C}\right)} = \frac{18.4 \times P}{V \times k} \tag{20}$$

The E_{EO} values for photo catalytic removal of SDS by UV/ZnO and UV/ZnO/ $S_2O_8^{2}$ processes were 52.28 and 40.99, respectively. The E_{EO} values reveal that in the presence of $S_2O_8^{2}$ as electron acceptor, the electrical energy consumption decreases.

4. Conclusion

From this experimental study, several conclusions can be made:

1) The surfactant was resistant to direct photolysis and in the absence of UV irradiation, the surfactant cannot be removed by the synthesized ZnO nanoparticles.

2) The optimum amount of photo catalyst for the efficient photo catalytic removal of 10 mg/L surfactant solution at room temperature and pH 7 was 150 mg/L.

3) Adding $S_2O_8^{2}$ with initial concentration of 100 mg/L, to the surfactant solution increases the first-order kinetic constant in the UV/ZnO process from 0.0955 minute^{-1} to 0.1038 minute^{-1}.

4) The electrical energy consumption was in the following order: UV/ZnO > UV/ZnO/ $S_2O_8^{2}$.

5) Based on the results of this study, ZnO- UV photo catalytic process can be used as an efficient method for further studies in detergents removal.

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