Kinetic study of sodium dodecylsulfate degradation by solar heterogeneous photocatalysis based on tungsten oxide

Abstract :

Sodium Dodecyl Sulfate or SDS is a chemical compound widely used in detergent and cosmetic formulations. This work describes the application of solar heterogeneous photocatalysis based on tungsten oxide (WO_3) to the kinetic study of the degradation of sodium dodecylsulfate. The experiments were performed at room temperature to study the effect of the initial catalyst mass. The results showed that a small amount of tungsten oxide is sufficient to degrade sodium dodecyl sulfate. The initial concentrations of SDS varied between 5 and 15 $mg.L^{-1}$. According to the results, more than 87% reduction is obtained after 120 min of solar irradiation of the SDS solution for a WO_3/SDS mass ratio of 1/5. The detailed kinetic analysis of the photodegradation of sodium dodecylsulfate showed that the disappearance of the anionic surfactant follows a pseudo-prime model. According to the Langmuir-Hinshelwood model, the kinetics constant calculated from the linear form of this model are : $k = 0.042\ mg.L.min^{-1}$ and $K = 0.060\ L.mg^{-1}$.

Keywords: Sodium dodecyl sulphate, Heterogeneous photocatalysis, Tungsten oxide, Solar radiation.

1. Introduction

Sodium dodecylsulfate with the chemical formula $C_{12}H_{25}SO_4Na$, is a chemical compound widely used in cosmetics [1,2]. It has very powerful detergent and foaming power [3]. Like most anionic surfactants, sodium dodecyl sulfate is a toxic and bio-recalcitrant substance, posing a real problem of water contamination due to the activity of the cosmetic and soap industries [4,5]. SDS is a good indicator of pollution and requires specific treatment.

Many advanced oxidation processes (AOP) have been developed to decontaminate liquid effluents. Photocatalysis is a AOP that can be used in both homogeneous and heterogeneous environments for the oxidation of pollutants while reducing their overall toxicity of the effluent. Solar photocatalysis uses solar light, that is to say the photon from radiation, for the total mineralization of most organic pollutants, both in homogeneous and heterogeneous environments [6,7]. This treatment process uses an inexhaustible and economical source of energy to drive photochemical reactions. It is promising, but still has certain drawbacks such as the shaping of the catalyst or the significant recombination of the photogenerated charges. Previous work [8,9] demonstrated the degradation of anionic surfactants by heterogeneous photocatalysis of semiconductors using natural or artificial light.

Tungsten oxide (WO_3) is used as an anticorrosive, photochromic and electrochromic agent, but also considered as an effective photocatalyst material in the treatment of many pollutants [10,11]. It is non-toxic, easy to manufacture and has many properties like chemical stability during the process. Its band gap energy is 2.6 eV, i.e. exciting radiation with a wavelength equal to 459.26 nm. Its direct band corresponds to an energy of 3.2 eV, i.e. exciting radiation with a wavelength equal to 387.5 nm corresponding to UV radiation [11,12]. Tungsten oxide has good visible light absorption properties [12].

The present study describes the application of heterogeneous photocatalysis based on tungsten oxide under solar radiation in the degradation of sodium dodecyl sulfate. Monitoring the photodegradation of sodium dodecylsulfate makes it possible to systematically evaluate the abatement rates as a function of a few physicochemical parameters such as the initial catalyst concentration and that of the pollutant studied. The photodegradation kinetics of sodium dodecyl sulfate are then examined by determining the reaction order and kinetic constants relative to the classical Langmuir-Hinshelwood model.

2. Material and Methods

2.1. Material

The chemicals and devices that were used for this work are: tungsten oxide powder (WO_3), sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, w 98%) from Fluka, dichloromethane (CH_2Cl_2, $w \geq 99\%$) from J.T.Baker, methylene blue ($C_{16}H_{18}ClN_3S$) from Merck, sodium tetraborate ($Na_2B_4O_7.10H_2O$, w 99%) from Acros, liquid sodium hydroxide (NaOH, $w \geq 98\%$) from Panreac, sulfuric acid (H_2SO_4, w 95 - 98%) from Panreac, HANNA portable pH meter, DR/3900 type UV/Visible spectrophotometer.

2.2. Preparation of tungsten oxide

In this work, we used tungsten oxide (WO_3) nanoparticles prepared from tungsten powder by Eroi et al. [13], according to the following method : dispersion of metallic tungsten powder (1.0 g) in demineralized water acidified with glacial acetic acid, followed by the addition of H_2O_2; the mixture is kept in an ice bath before placing it in the reactor and heated to 85°C. The precipitate obtained is centrifuged to recover the hydrated tungsten oxide WO_3-H_2O, then dried at 60°C, then annealed at 600°C to obtain WO_3. WO_3 monoclinic crystal structure obtained by Eroi et al. [13] was characterized by X-ray diffraction, scanning electron microscopy, as well as Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy.

2.3. Characterization

XRD analysis is considered a promising technique, investigating the crystalline structure and size of the synthesized nanoparticles[13]. Figure 1 displays the XRD pattern of the synthesized tungsten oxide nanoparticles before and after calcination. The precipitate obtained showed various diffraction peaks at 2θ = 16, 53; 25, 63; 35, 03 and 49, 64 which are assigned to (020), (111), (131) and (202) reflections according to the JCDPS card N° (84-0886). This crystalline structure is identical to hydrated tungsten oxide WO_3-H_2O of orthorhombic structure. The calcination of WO_3-H_2O at 200 and 600°C respectively showed different XRD patterns. At 200°C diffraction peaks were in agreement with the hexagonal phase of WO_3 (JCDPD card N° 75-2187). The h-WO_3 hexagonal phase was also observed after calcination treatment (Perfecto et al., 2016). The peaks corresponding to (100), (001), (200) and (2011) crystal planes were also identified. Increasing the calcination temperature up to 600°C showed the peaks assigned to WO_3 monoclinic structure (JCDPD card $N^0$71-2141). These peaks appeared at 2θ values of = 23.12; 23.58; 24.38; 26.59; 28.93; 33.26; 34.17; 41.9 having miller indices (002), (020), (200), (123) (112), (022), (220), (222) respectively (JCDPD card $N^0$71-2141).

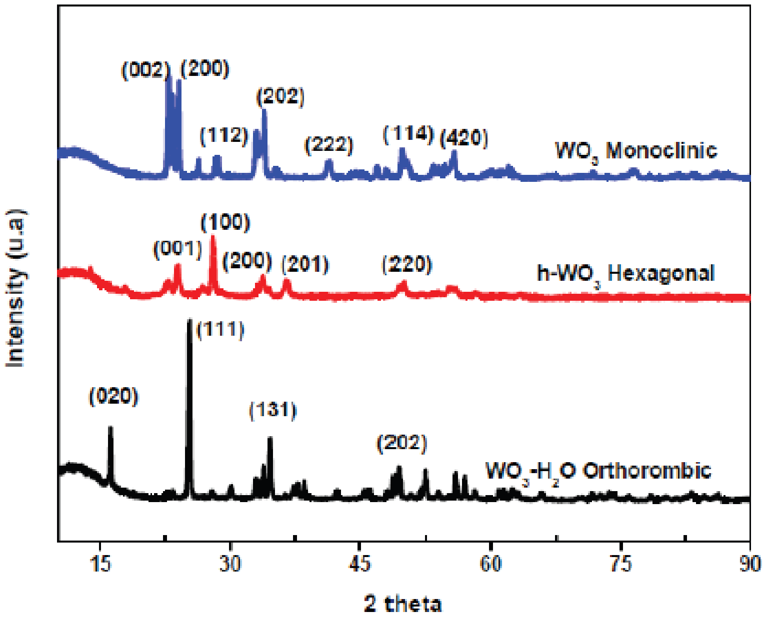

Figure 1. XRD patterns of WO_3-H_2O orthorombic, h-WO_3, hexagonal at 200°C and WO_3 monoclinic at 600°C[13].

2.3. Method of Analysis

Photodegradation of sodium dodecylsulfate was carried out as follows: a volume of 250 mL of a neutral SDS solution at the initial concentration $C_{SDS,0}$ = 15 mg/L is used; a weighed mass of WO_3 is added to the SDS solution to achieve fixed mass ratios r = C_{WO3}/C_{SDS}. The experiment is carried out in a transparent glass reactor, in order to facilitate the absorption of solar radiation by the solution. The mixture contained in the reactor is stirred for 120 min continuously by a magnetic stirrer and subjected to sunlight at a temperature varying between 32 to 34°C. After each time interval, samples of 5 mL of the mixture are taken for analysis.

The residual concentration of sodium dodecyl sulfate in each sample was determined using a UV/Vis spectrophotometer type DR/3900 using the analysis of active substances with methylene blue (MBAS) according to the AFNOR T 73- method. 260. The maximum adsorption wavelength is 635 nm. The SDS reduction rate is calculated as follows :

$$\text{SDS reduction rate } (\%) = \frac{C_0 - C_{SDS}}{C_{SDS,0}} x100$$

Where C_0 and C_{SDS}represent respectively the mass concentrations of sodium dodecylsulfate at the initial time and time t.

3. Results and Discussion

3.1. Photolysis and photocatalysis

Initially, the study focused on the kinetics of degradation of sodium dodecylsulfate (15 mg.L^{-1}) by solar photolysis and by solar photocatalysis with WO_3 (Figure 2). Under solar radiation for 120 min and in the absence of WO_3, a slight decrease of 6% in the initial quantity of SDS was observed. This low rate of reduction due to photolysis would be the result of low adsorption of solar radiation. On the other hand, under solar radiation and in the presence of WO_3 (15 mg), a reduction of approximately 48% in SDS was observed. This rate of reduction due to photocatalysis would result from good adsorption of visible light [12]. This confirms that the WO_3 particles are at the origin of the activation of the photocatalytic reaction [13,14].

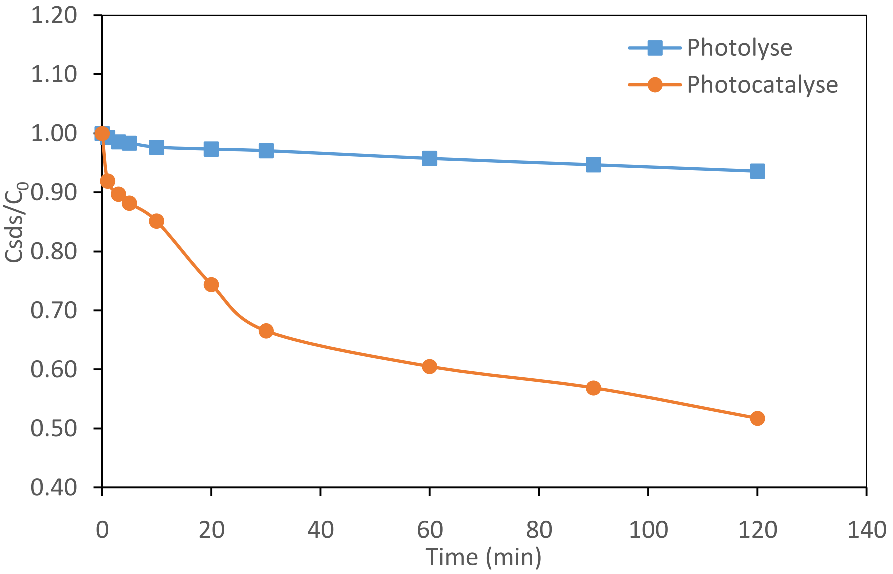

Figure 2: Kinetics of sodium dodecylsulfate degradation by photolysis and solar photocatalysis.

3.2. Effect of tungsten oxide mass

The effect of catalyst mass on the photodegradation of sodiumdodecylsulfate is studied. For an aqueous solution containing SDS 15 mg.L^{-1} (C_{SDS}), the initial mass of WO_3 (C_{WO3}) supplied varies from 3 to 300 mg, thus corresponding to C_{WO3}/C_{SDS} mass ratios equal to r. The results obtained are visible in Figure 3. In the series of experiments for which the mass of WO_3 supplied is greater than or equal to that of SDS ($r \geq 1$), SDS reduction rates of less than 40% have were noted after 120 min of treatment. Under the opposite conditions ($r < 1$), an elimination of more than 50% of SDS was observed. Figure 3 shows that the high elimination rate (87%) of sodium dodecylsulfate is observed when the mass of WO_3 is 3 mg, i.e. r = 0.2. This result indicates that a small quantity of tungsten oxide supplied causes a significant photodegradation of sodium dodecylsulfate, thus confirming that the absorption capacity of photocatalysis increases in the presence of a small quantity of catalyst [14].

By representing the photodegradation efficiency as a function of the mass ratio r, we obtain Figure 4. According to this figure, the SDS elimination rate is close to 90% when the mass ratio is 1/5. The photodegradation efficiency decreases as the mass ratio increases. An equilibrium seems to be reached from ratio 1, that is to say the mass of WO_3 equal to that of SDS. Beyond this ratio, the yield evolves very slowly. Many studies [15,16] have already reported similar results, justifying that a lower quantity of catalyst increases photocatalytic activity.

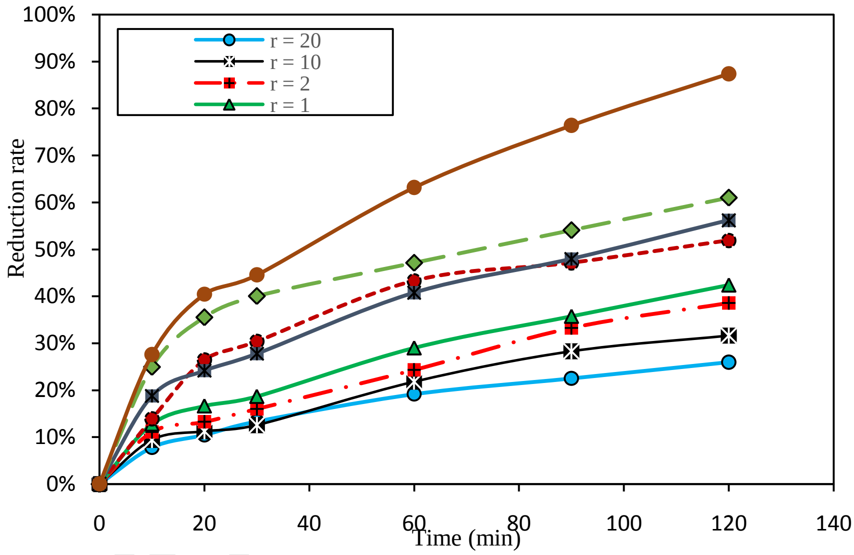

Figure 3: Effect of WO_3 mass on solar photodegradation of SDS 15 mg.L^{-1}.

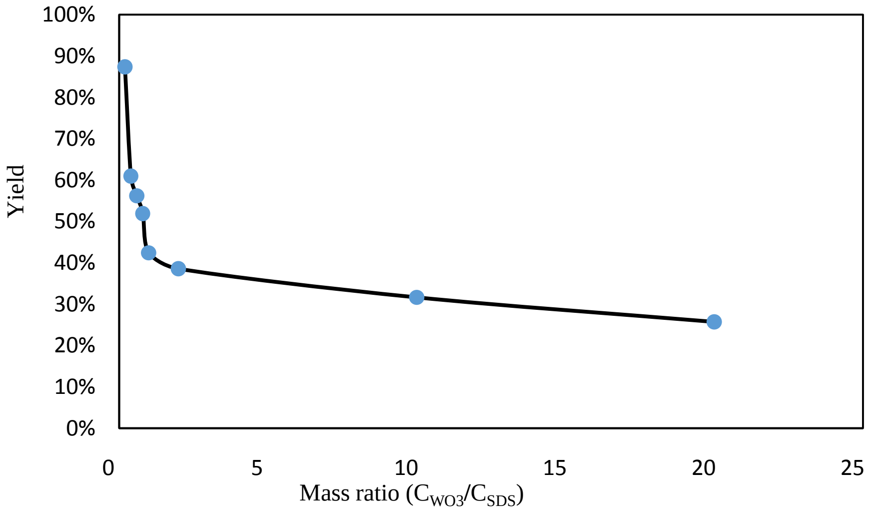

Figure 4: Evolution of the photodegradation yield of sodium dodecylsulfate as a function of the mass ratio r. $C_{SDS,0}$ = 15 mg.L^{-1}.

Tests on the reuse of tungsten oxide (WO_3) nanoparticles were carried out. After four consecutive trials, a slight loss in the effectiveness of WO_3 was observed. These tests have shown that it is easy to recover these particles. Despite good stability, the reuse of WO_3 nanoparticlesrelatively decreases its effectiveness on the photodegradationof sodium dodecylsulfatein aqueous solution.

3.3. Experimental determination of the reaction order

The photodegradation of solar sodium dodecylsulfate follows the reaction scheme :

Step 1:$\boldsymbol{WO_3}$**+ hν→** $\boldsymbol{WO_3(e^- + h^+)}$

$$\boldsymbol{H_2O_{(ad)} + (h^+) \rightarrow H^+ + OH^-_{ad}}$$

$\boldsymbol{WO_3\ (h^+) + OH^-_{ad} \rightarrow WO_3 + OH^*_{ad}}$

Step 2 : SDS + $\boldsymbol{OH^*_{ad}}$ **→ Pox**

Reaction balance:**SDS+**$\boldsymbol{WO_3(h^+) + H_2O_{(ad)} \rightarrow Pox + H^+ + WO_3}$(1)

Where Pox corresponds to the oxidation products of sodium dodecylsulfate.The speed of this reaction process is expressed as:

$$v = -\frac{dC_{SDS}}{dt} = k.\,C_{SDS}^{p}.\,C_{WO3}^{q}$$

C_{WO3} is the mass concentration of tungsten oxide, C_{SDS} the solution concentration of sodium dodecylsulfate and p+q = n is the overall order of the reaction.

As the WO_3 catalyst is in solid form its concentration therefore remains unchanged over time. Thus SDS is the only reagent to have an effect on the rate of the reaction. Hence the speed of photodegradation studied is expressed by the relation :

$$v = -\frac{dC_{SDS}}{dt} = k_{app}\, C_{SDS}^{p}$$

$k_{app} = k.\,C_{WO3}^{q} \approx k.\,C_{0,WO3}^{q}$ represents the apparent rate constant and the order p with respect to the SDS becomes that of the photodegradation reaction studied. Integrating the previous relationship will determine the p-value :

$$\frac{1}{C_{SDS}^{p-1}} = \frac{1}{C_{SDS,0}^{p-1}} + (p-1).\,k.\,t$$

Figure 5 represents the photodegradation kinetics of sodium dodecylsulfate (15 mg.L^{-}1) as a function of time for different mass ratios.

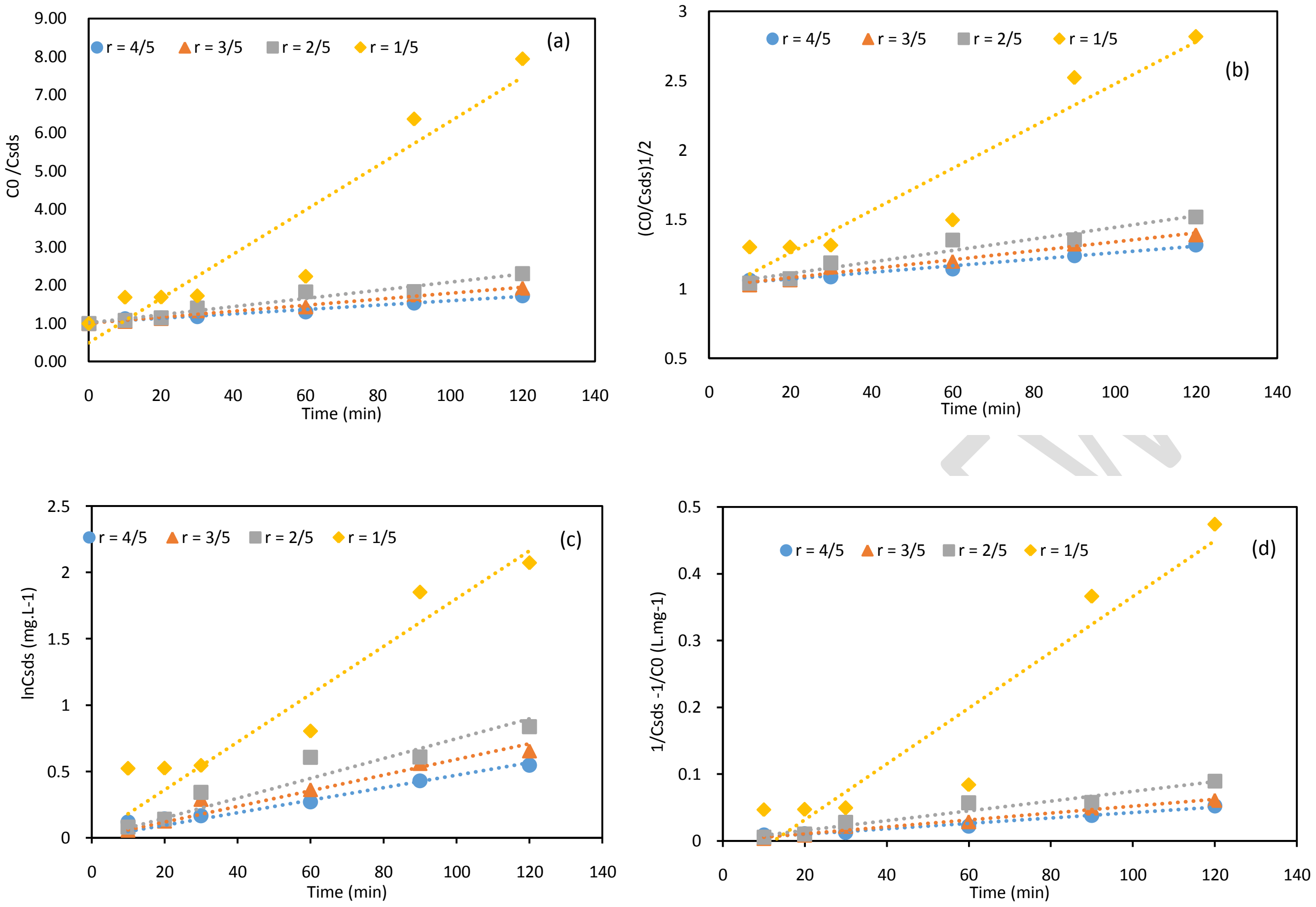

Figure 5: Photodegradation kinetics of sodium dodecylsulfate for different mass ratios. $C_{SDS.0}$ = 15 mg.L^{-1} at 32°C. With p-order equal to 0 (a), 1/2 (b), 1 (c) and 2 (d).

Table 1 brings together the k_{app}rate constants and correlation coefficients determined according to the kinetic models used.

Table 1 : Kinetic constants observed for different mass ratios r.

r / *p*	1/5	2/5	3/5	4/5
0	0.9164	0.9234	0.9569	0.9624
1/2	0.9217	0.9483	0.9614	0.9751
1	0.9287	0.9814	0.9835	0.9898
2	0.8984	0.9436	0.9557	0.9762

The correlation coefficients deduced from the linear trend curves in Figure 4 vary between 0.89 and 0.99 for all of the kinetic models. The highest coefficient is obtained in the case of the pseudo-first order kinetic model. This indicates that the photodegradation of sodium dodecylsulfate in the presence of tungsten oxide follows kinetics of order 1, for a solar irradiation time of 120 min. This result is similar to those of previous studies [16,17] which reported that the degradation of pollutants by photocatalysis follows kinetics of order 1.

3.4. Verification of consistency of experimental results

We propose to verify the consistency of the experimental results with the theoretical results ; for this the reaction percentage method was used. Assuming the reaction order of 1, the experimental data were used for SDS 15 mg.L^{-1} and a mass ratio of 1/5. What determined : the speed constant k_1 = 1.65x10^{-2} min^{-1}, the time ratios$\frac{t_{1/2}}{t_{1/4}}$ = 2.5and$\frac{t_{3/4}}{t_{1/2}}$ = 2.1.

By the calculation method,ln $\left(\frac{C_0}{C_{SDS}}\right) = k_1.t$, we deduced:$k_1$ = 1.72x10^{-2} min^{-1} et $t_{1/2}$ = 40.3 min, then the time ratios $\frac{t_{1/2}}{t_{1/4}}$ = 2.4and$\frac{t_{3/4}}{t_{1/2}}$ = 2.

The results indicate a very good consistency between the experimental values and the theoretical values. Therefore the hypothesis according to which the degradation of sodium dodecyl sulfate by photocatalysis follows a first order kinetic law is valid. This is confirmed by work carried out with numerous pollutants [17,18]. We can then write the equation:

$$v = -\frac{dC_{SDS}}{dt} = k_{app}\,.C_{SDS}$$

The highest kapp constant for order 1 is obtained with a mass ratio 1/5 and is worth $k_{app} = k.C^{q}_{WO3} \approx k.C^{q}_{0,WO3} = 1.58\times10^{-2}\ \text{min}^{-1}$;this corresponds to a half-reaction time of 42 min.

The evolution of the speed constant k_{app} as a function of the mass ratio is represented by the curve in Figure 6.

The observed results show that the rate constant decreases with the mass ratio between the catalyst WO_3 and the anionic surfactant SDS. This indicates that the rate of photodegradation decreases with the initial quantity of catalyst and requires a longer time for the degradation of the pollutant.

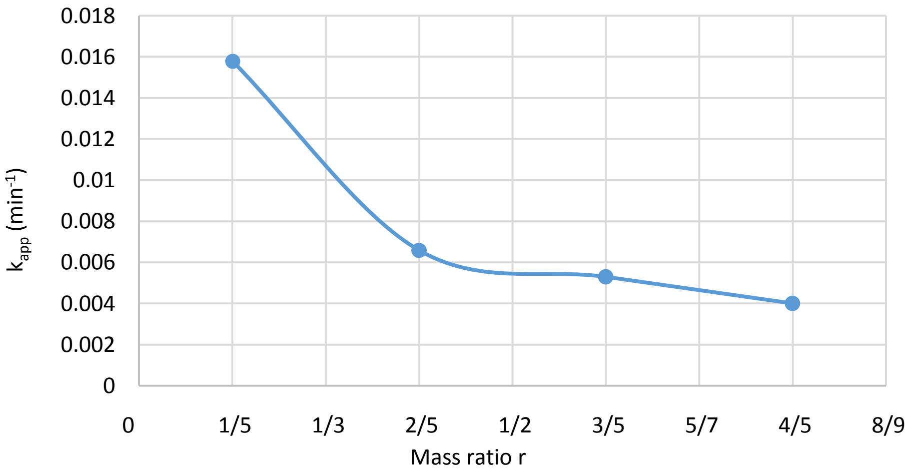

Figure 6: Evolution of the apparent reaction rate constant for different mass ratios r. $C_{SDS,0}$ = 15 mg.L^{-1} at 32°C.

3.5. Effect of initial concentration of sodium dodecylsulfate

It is demonstrated that the photodegradation reaction of sodium dodecylsulfate follows a pseudo-first order kinetic law, in the presence of WO_3 under sunlight radiation for 120 minutes. If C_{SDS} and Co respectively represent the remaining concentration and the initial concentration of the compound studied, the ln(CSDS/Co) curve as a function of time is linear for different initial concentrations (Figure 7). It makes it possible to calculate the apparent rate constant k_{app} and the reaction rate v.

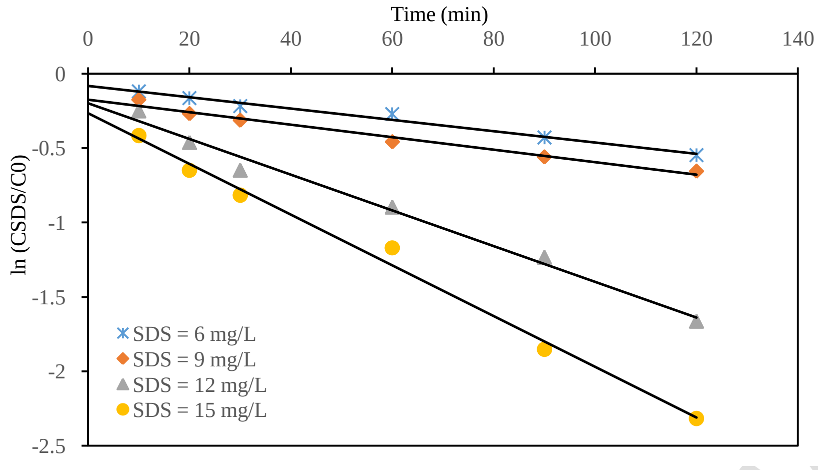

Figure 7: Pseudo-first order apparent kinetics of sodium dodecylsulfate degradation.

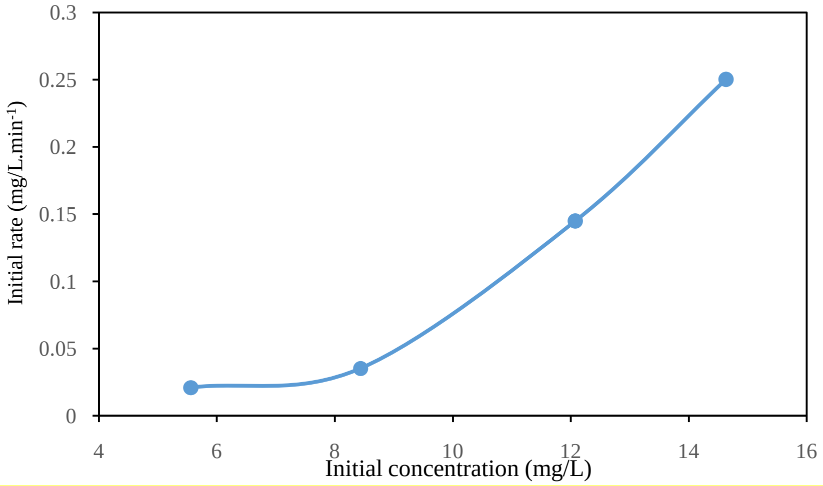

Figure 8: Evolution of the initial rate of degradation as a function of the initial concentration of sodium dodecylsulfate.

The initial velocity corresponding to the pseudo-first order kinetic model can be written:

$$v_0 = -\frac{dC_{SDS}}{dt} = k_{app} \, . C_0$$

The effect of the initial concentration C_0on the initial rate v_0 of photocatalysis degradation of sodium dodecylsulfate in aqueous solution is represented by the curve in Figure 8. This figure shows that the initial rate of degradation increases with the initial concentration. In the literature, the photocatalytic degradation kinetics of many pollutants follow a pseudo-first order [16-18]. The Langmuir-Hinshelwood model seems appropriate to describe this degradation kinetics.

$$v_o = -\frac{dC}{dt} = \frac{k.K.Co}{1 + K.Co}$$

With, v_o: Initial degradation rate (mg/L.min^{-1}), K: Adsorption equilibrium constant (L/mg), k: Photocatalytic degradation constant (mg/L.min^{-1}).

The linearization of the previous equation allows to write:

$$\frac{1}{v_o} = \frac{1}{k} + \frac{1}{k.K.Co}$$

and to determine graphically constants k and K, considering the slope line 1/(k.K) and ordinate originally 1/k.

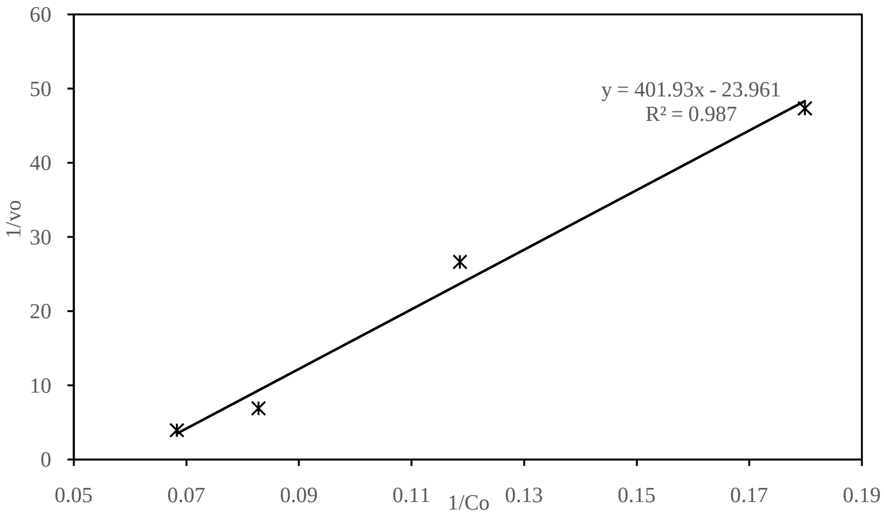

Figure 9: Linearization of the Langmuir-Hinshlwood model

The plot of $1/v_0$ as a function of $1/C_0$ (Figure 9) shows a correlation coefficient $R^2 = 0.987$. This linear correlation coefficient very close to 1 confirms the hypothesis of the Langmuir-Hinshelowood model and highlights a single type of adsorption sites. The shape of the curve is similar to that obtained in many works [18-20]. As a result, the degradation by photocatalysis in sunlight of sodium dodecylsulfate in aqueous solution occurs essentially on the surface of tungsten oxide. The Langmuir-Hinshelowood kinetic constants obtained from the slope and ordinate values are : k = 0.042 mg.L.min^{-1} et K = 0.060 L/mg.

The product $K.C_0$ is less than 1, this shows that the reaction rate becomes directly proportional to the concentration of sodium dodecylsulfate. Since the reaction is pseudo-first order, it can be written according to the equation : $v = K'.C_e = k.K.C_e$

4. Conclusion

This present study is carried out on the photodegradation of sodium dodecylsulfate by tungsten oxide with solar light sources at 32°C for 120 minutes. The experimental results showed that the degradation of SDS is better ensured by solar photocatalysis (48%) than by direct photolysis (6%). These results also demonstrated a high efficiency of the WO_3 catalyst when it is in small quantity compared to the SDS in the reaction medium. On the other hand, this efficiency decreases in the reaction medium where the catalyst is in large excess. The maximum SDS reduction rate (87%) is obtained with a lower mass ratio of catalyst and SDS.

The kinetic analysis of the photodegradation of SDS reveals that, in the presence of WO_3, the reaction follows a first-order kinetic law. The initial degradation rate of SDS increases as its concentration in solution increases, and the reaction rate follows the Langmuir-Hinshelwood model. The kinetic constants calculated from the linear form of this model are k = 0.042 mg.L.min^{-1} and K = 0.060 L.mg^{-1}.

The reusability of monoclinic tungsten oxide (WO_3) nanoparticles showed good stability, but a relative decline in its effectiveness on SDS degradation. Solar photocatalysis using tungsten oxide has shown its great capacity to effectively remove anionic surfactants such as sodium dodecylsulfate, present in aqueous solution.

5. References

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