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RESEARCH ARTICLE

A Kinetics Study on Degradation of An Textile Dye Waste Water with Different Processes

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Abstract

In the present study, the degradation of artificial effluent solution that contains dyestuffs mixture of AR27, disperse red92 and orangeG has been investigated with sonolytic, photocatalytic and sonophotocatalytic methods in the presence of TiO_2*. The effect of parameters such as initial concentration of dyestuff, light intensity, the amplitude of sonolysis and temperature on the degradation processes of artificial effluent solution was studied. The sonophotocatalytic degradation rate followed pseudo-first order kinetics with respect to concentration of dyestuff. It was observed that the reaction rate accelerated in the presence of ultrasound energy in the course of the experiments.*

Keywords: *photocatalysis; sonolysis; sonophotocatalysis; degradation kinetic*

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1 Introduction

Textile dye in high concentration is one of the most difficult constituents of the textile wastewater to treat. The type of dye in the effluent can vary daily, or even hourly, depending upon the variety of recipes, techniques, machinery, raw materials, and fabrics. Discharged dye effluents from the textile industries cause important environmental dangerous. The interest in making the dye effluents colorless has increased in the recently. The traditional physical methods are commonly used for removing the pollutants. But these methods are not very destructive and they forward the organic compounds to another phase [1-4]. This phenomenon causes a secondary pollutant. Therefore the usage of photocatalytic processes has increased in the recent days and different studies have been carried out about this process.

In some studies sonolytic degradation process has been investigated beside photocatalytic process. Selli et al. [5] studied the efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO_2 and sonolysis. They reported that the fastest degradation rate was attained under sonophotocatalytic conditions, with slightly higher energy. Also they investigated the degradation of methyl tert-butyl ether in water with using the combined sonolysis and photocatalysis. They compared the effects of these processes and noticed that the optimal operating condition was afforded by the combined use of ultrasound and photocatalysis (sonophotocatalysis) under intermittent stirring, leading to MTBE degradation in the shortest time with the lowest energy consumption.

The photocatalytic process is an advanced oxidation process (AOP) involving the conversion of organic pollutants to short species and even to their complete mineralization through the generation of highly reactive free radical oxidants. Among destructive photocatalyst, titanium dioxide is one of the most effective and widely used. Titanium dioxide is inexpensive, stable, readily available and the most extensively studied semiconductor photocatalyst for the purification of water and air. For these reasons titanium dioxide has been used commonly for photocatalysis processes. Photoexcitation of TiO_2 requires light with wavelengths of $\leq$ 380 nm. Upon absorption of a photon by TiO_2, an electron is promoted to the conduction band, generating what is commonly referred to as an electron-hole pair [6].

The conduction band election is available for reduction and the valence band hole available for oxidation. The hole can subsequently react by electron transfer with a substrate to form a radical species or hydroxide (water) to form hydroxyl radical. In condensed oxygenated aqueous media the surface of TiO_2 is completely hydroxylated and upon photoexcitation generates hydroxyl radical in an adsorbed state [7-10].

The hydroxyl radical is a powerful oxidizing agent and attacks to organic compounds and intermediates (Int.). These intermediates react with hydroxyl radicals (OH*) to produce final products (P), also hydroxyl radicals could be consumed by inactive species. In some studies the photocatalytic degradation of dyes has been reported as a mechanism; [11-13]

$$TiO_2 + h\nu \xrightarrow{k1} e^- + h^+ \qquad (1)$$

$$e^- + h^+ \xrightarrow{k2} \text{heat} \qquad (2)$$

$$h^+ + (H_2O)_{ads} \xrightarrow{k3} (OH^*)_{ads} + H^+ \qquad (3)$$

$$h^+ + OH^-_{ads} \xrightarrow{k4} (OH^*)_{ads} \qquad (4)$$

$$(OH^*)_{ads} + (C_{Dye})_{ads} \xrightarrow{k5} \text{Int.(Intermediates)} \qquad (5)$$

$$(OH^*)_{ads} + \text{Int.} \xrightarrow{k6} \text{P(final product)} \qquad (6)$$

$$(OH^*)_{ads} + S_{inactive} \xrightarrow{k7} \text{İnactive species} \qquad (7)$$

In the photodegradation of dyes by UV radiation in the presence of TiO_2, the rate-determining step is the reaction (5) between adsorbed OH^* radicals and dye according to this mechanism [13]. The reaction rate follows pseudo-first order kinetics by considering the steady-state conditions and based on several other literature reports [14-16]. The kinetic expression is showed in the following form:

$$\left(\frac{-dC_{Dye}}{dt}\right) = k_P\left(C_{Dye}\right) \qquad (8)$$

In this equation;

$$k_P = k_c I_a \left(\frac{K_D}{1+K_D(C_D)_0}\right) \qquad (9)$$

has been given [17].

When Eq. (8) is integrated,

$$\ln\left(\frac{C_{D0}}{C_D}\right) = k_P.t \qquad (10)$$

is obtained.

If,

$$k_c.I_a = k_1 \qquad (11)$$

then,

$$k_P \approx k_1\left(\frac{K_D}{1+K_D(C_D)_0}\right) \qquad (12)$$

It is also explained that the photocatalytic and the sonophotocatalytic degradation of dyestuffs follow pseudo-first order kinetics in other several studies [8, 12, 17].

The exposure of water to ultrasound results in local hot spots (4000–5000 K) as a consequence of the formation, growth and collapse of cavity bubbles containing entrapped gases and vapors of the surrounding water [18]. At collapse, chemical reactivity is initiated through thermolytic decomposition of bubble contents into free radical species, and/or through free radical oxidation of dissolved solutes at the gas–liquid interface or the bulk liquid [19-20]. The chain of reactions occurring during sonication of pure water is as the following [18]:

$$H_2O \xrightarrow{Ultrasound} H^* + OH^* \qquad (13)$$

$$OH^* + OH^* \longrightarrow H_2O_2 \qquad (14)$$

$$H_2O_2 + H^* \longrightarrow H_2O + OH^* \qquad (15)$$

Ultrasonic irradiation has shown promise for the purification of contaminated water (or textile effluents) and involves at least in significant part standard hydroxyl radical mediated chain oxidation processes [20, 21].

The effect of sonolysis is based on the OH^* radicals which are occurred from the homolysis of H_2O. Ultrasonic irradiation has shown promise for the purification of contaminated water and involves at least in significant part standard hydroxyl radical mediated chain oxidation processes. Hydrogen atoms react with oxygen atoms or undergo termination and are generally not considered to be important in the degradation of organic substrates during sonolysis. The sonochemical treatment of a variety of organic pollutants yields low molecular weight carboxylic acids as the final products. [11, 22-23]

Three regions, gas phase, gas-liquid interface and bulk liquid solution are present during cavitation. The most extreme conditions are generated in the gas phase, commonly referred to as the hot-spot. Significantly, high temperature and pressure conditions produced at the gas-liquid interface can accelerate hydrolysis, eliminations, low temperature pyrolysis and supercritical water oxidation processes that are not observed from other AOTs. Changes to the bulk solution are relatively insignificant.

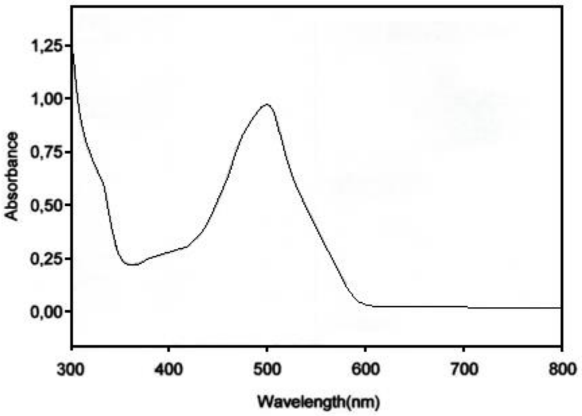
Ultrasonic technology is well advanced and used for a number of industrial applications (for cleaning, pigment dispersion, etc.). Versatility of ultrasonic irradiation should make it adaptable for the removal of problematic contaminants in aqueous phase. Despite the tremendous interest in the ultrasonic irradiation induced degradation of pollutants, much of the fundamental understanding and characterization of these complex processes are still at the preliminary stages [19-21, 24].

In this study, the effect of ultrasound energy (sonolysis) on the photocatalytic degradation of dyestuffs by UV radiation in the presence of TiO_2 was observed. The degradation of artificial effluent solution that contains dyestuffs mixture of *AR27*, *disperse red92* and *orangeG* has been investigated with sonolytic, photocatalytic and sonophotocatalytic methods in the presence of TiO_2. The effect of parameters such as initial concentration of dyestuff, light intensity, the amplitude of ultrasound energy and temperature on sonophotocatalytic degradations kinetics of artificial effluent solution was studied.

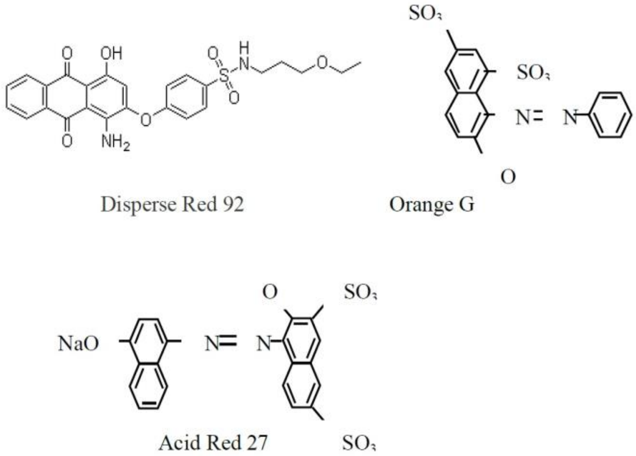
2 Experimental

The processes were performed in a Pyrex glass reactor. For sonolytic experiments an ultrasonic generator (Cole Parmer, Ultrasonic homogenizer, 750 W, 20 kHz) with a cup horn probe was used. Pen-Ray UV lamps (Cole Parmer, 44 W/m^2) were used as the radiation source for photocatalytic experiments. The water was circulated continuously within the water jacket reactor by the constant temperature water circulator to keep the temperature stability. The required O_2 for system was procured from a vacuum pump.

The commercial titanium dioxide supplied by Degussa (P25) was used as photocatalyst. According to the manufacturer's specifications, P25 has an elementary particle size of 30 nm, a BET specific surface area of 50 m^2/g and its crystalline mode was 80 % anatase and 20 % rutile. The artificial effluent solution was prepared with the dyestuffs mixture of *AR27, disperse red 92 and orange G*. These dyestuffs were used without further purification. Molecular formulas of these constants and the absorbance spectrums of the artificial effluent solution in different dye concentrations are shown in Fig. 1.



(a)



(b)

Fig. 1 (a) Absorbance spectrum of artificial effluent solution.
(b) Molecular formula of the dyes in artificial effluent solution.

The experiments were carried out with 300 ml dye solutions prepared in appropriate concentrations by using deionized water. 30, 40, 50, 60 % (32.36-43.03-49.03 and 55.03 W) amplitude of ultrasound energy and 20, 30, 40, 50 °C (± 0.4 °C) temperatures were used for the experiments. The light intensities of 44, 88 and 132 W/m^2 were chosen. The reactor was isolated from the outside light. Different concentrations of dye solutions (20, 30, 35 and 40 ppm) and 200 mg TiO_2 were introduced in this reactor. Solutions were stirred in the dark for 30 min. after the addition of the catalyst to equilibrate the system. 5 ml. samples of suspension were withdrawn at regular intervals and were immediately centrifuged at 6000 rpm for 10 min. to completely remove catalyst particles. Dye concentrations were analyzed by measuring the absorbance of the solution samples with UV-Vis spectrophotometer (Thermo Electron Evolution 500 spectrophotometer) at $\lambda_{max.}$= 499 nm for determining the degradation. Sonolytic, photocatalytic and sonophotocatalytic experiments were studied for displaying the effect of ultrasound.

3 Results and Discussion

In this study, the initial dye concentration (30 ppm), temperature (30°C), amplitude of sonolysis (30 %) and light intensity (44 W/m^2) parameters were selected constant parameters for comparing the experimental data of sonolytic, photocatalytic and sonophotocatalytic processes.

The degradation data of the experiments for constant parameters were graphed in Fig.2. After 80 min. the degradation values were approximately 19, 68 and 82% for sonolytic, photocatalytic and sonophotocatalytic processes respectively. From the results it can be said that the purely sonolysis has an inconsiderable effect for the degradation of dyes.

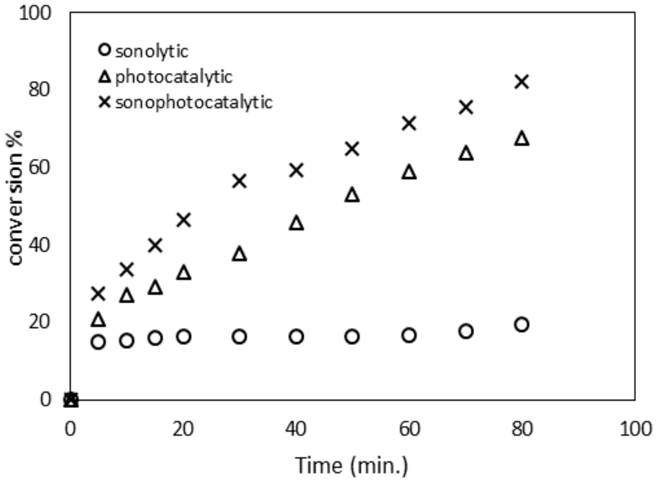


Fig. 2 Degradation conversion of different processes

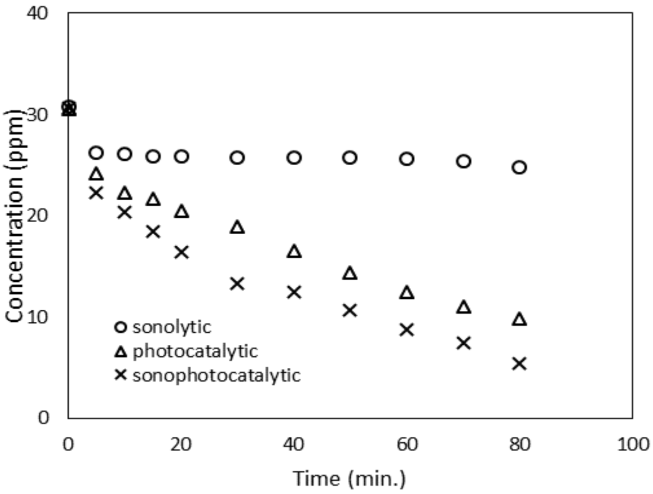


Fig.3 The degradation of the constant parameters

All of the parameters selected for this study (initial dye concentration, temperature, amplitude of ultrasound energy and light intensity) were studied with ultrasound energy (sonophotocatalytic) and without ultrasound energy (photocatalytic).

3.1 Effect of Concentration

The effect of initial dye concentration is an important parameter for degradation processes. The initial concentration values were 20, 30, 35 and 40 ppm. The constant parameters were temperature (30°C), amplitude of sonolysis (30 %) and light intensity (44 W/m^2). It was seen that the degradation rates decreased with increasing the initial concentration for all processes and the highest degradation rate was obtained from the sonophotocatalytic process as seen in Fig. 3. It is the reason of placing the more dye molecule on the catalyst surface by increasing the dye concentration. This state causes reducing the active sites for adsorbing the hydroxyl radicals. Thus the degradation ratio of dye reduces because of the less hydroxyl radicals.

Equation (10) shows a pseudo-first order reaction with respect to the concentration. The graphs of the concentration versus time in the processes yield straight lines indicating pseudo-first order reaction. k_p values were calculated from experimental data using a regression analysis.

The Langmuir adsorption model used for rate constant k_p is seen from the Eq. (9) [13]. k_p is inversely proportional with the initial dye concentration when the other parameters are constant.

The adsorption equilibrium constants (K_D) were calculated from the Fig. 4. For sonophotocatalytic and photocatalytic processes, these values were 0,155 and 0,157 L/mg respectively. Also, k_1 values were determined as 0,44 and 0,45 mg/(L.min.) for sonophotocatalytic and photocatalytic processes, respectively. The equilibrium constants remained the same. It was thought that the sonolysis didn't have any effect on changing the structure of dye.

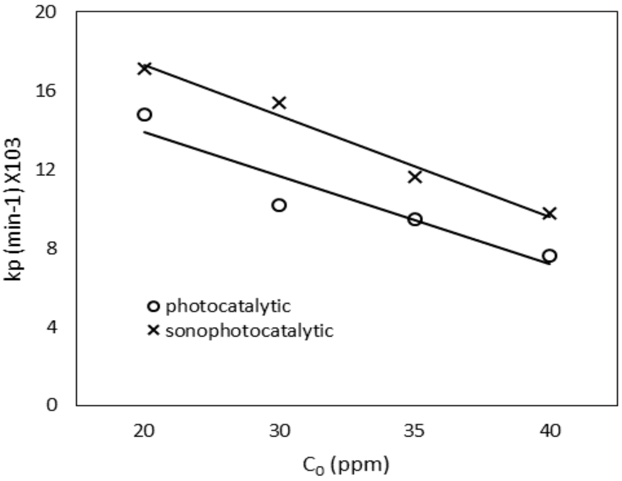


Fig. 4 k_p versus AES concentration plot is for the photocatalytic and sonophotocatalytic processes

3.2 Effect of Light Intensity

The effect of light intensity was examined at constant initial concentration (30 ppm), temperature (30°C), amplitude of sonolysis (30 %). k_p and light intensity (I_a) were linear as seen from Eq. (9). The various light intensities (44, 88, 132 W/m^2) versus k_p values is plotted (Fig.5) for the photocatalytic and sonophotocatlytic processes. The linear curves prove the kinetic model. The photodegradation increased with the increasing light intensity. UV irradiation generates the required photons for the electron transfer from the valence to the conduction band of a photocatalyst. If more radiations are used, more hydroxyl radicals will be produced on the catalyst surface. In this case, degradation will increase [6]. When two processes are used together the degradation rate increases because of the cavitation are formed with sonolysis. When the cavitation collapses on the catalyst surface, they transfer their energy to the surface and more hydroxyl radicals are generated. As a result, the degradation rate increases by using sonolysis with increasing light intensity [25-26].

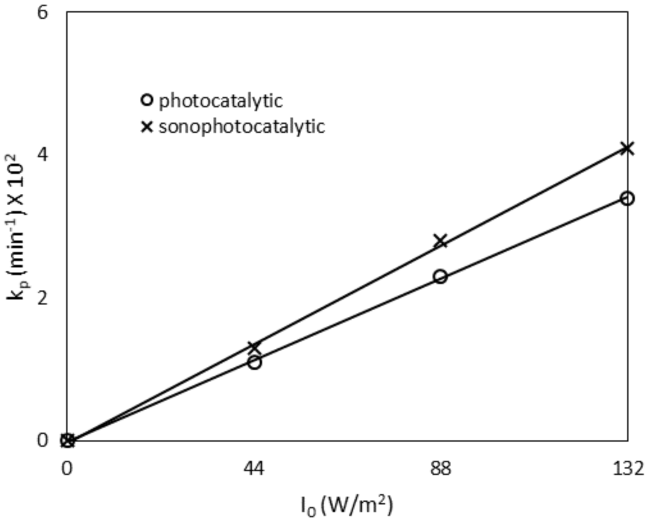


Fig. 5 k_p values versus light intensities for photocatalytic and sonophotocatalytic processes

3.3 Effect of Temperature

The temperature was studied at a constant concentration of 30 ppm, sonolysis amplitude of 30 % and light intensity of 44 W/m^2. The temperature values were 20, 30, 40 and 50°C ± 0,4 °C. The degradation rate increased with the increase of temperature. It can be explained as the quantity of cavitation bubbles increase by the increase of the temperature [27]. When these bubbles collapse strongly on the catalytic surface, they can occur more holes and pores. The surface area of catalyst can increase through these holes and pores. Thus more OH* radicals can occur on the catalyst surface.

The activation energy of the reaction is estimated from the Arrhenius plot (Fig.6) as 65,4 kJ/mol from photocatalytic experiments and 65,6 kJ/mol from sonophotocatalytic experiments. It was thought that sonolysis didn't have an effect on the activation energy.

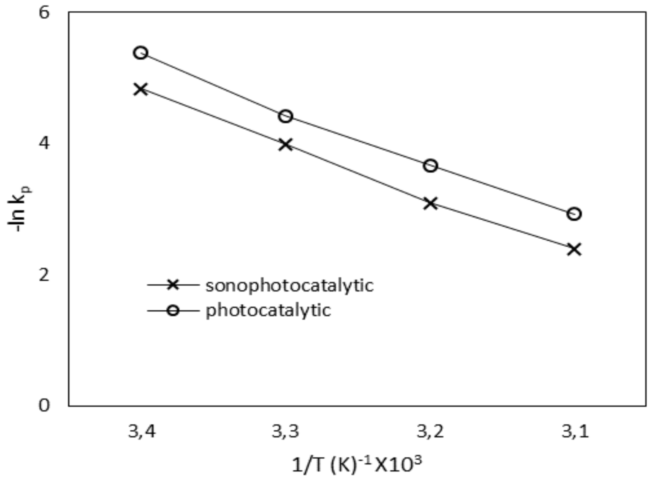


Fig. 6 ln k_p versus 1/T graph

3.4 Effect of amplitude

The effect of amplitude experiments were performed at a constant concentration of 30 ppm, temperature of 30°C and light intensity of 44 W/m^2. The sonolysis powers are detected as 32.36; 43.03; 49.03 and 55.03 W for 20, 30, 40 and 50 % amplitude values respectively, by testing calorimetric method [28]. It can be seen from Fig.7 that the degradation rate increased with the increment of amplitude. This can be explained with increasing the power of sonolysis and rising the amount of OH* radicals. These radicals effect the degradation positively. Also, catalyst surfaces can be more cleaned at the higher powers of sonolysis. Thus, the surface area of catalyst can increase for forming more OH* radicals.

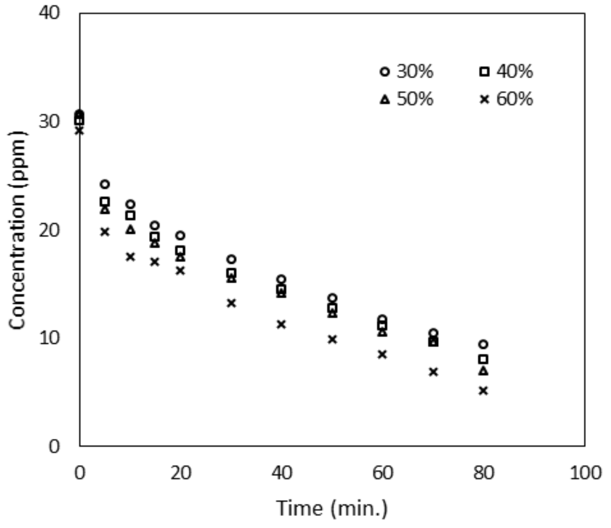


Fig. 7 Concentration change with amplitude of sonolysis

The dependence of reaction rate constant (k_p) on sonolysis power is usually expressed with the following relation [16, 29];

$$k = A_o(1+bW_U)^C \exp(-E/RT) \qquad (16)$$

Sonolysis does not affect the activation energy. If the Eq. (16) and Eq. (9) are combined, the reaction rate constant (k_p) will be as follows;

$$k_P = A_o(1+bW_U)^C.\exp(-E/RT).I_a\left(\frac{K_D}{1+K_D(C_D)_0}\right)$$

(17)

k_p values of different sonolysis powers, concentrations, light intensities and temperatures are used for calculating A_o= 2.13 10^9 , b= 0.015 and c= 0.045 values by nonlinear regression analysis.

In this study the most effective process was sonophotocatalytic on the degradation. This can be attributed to the sonolysis as increment of catalytic performance by cleaning the catalyst surface. Thus, the chemical reactions can occur easily on the catalyst surface. Also, collapse of cavitation generated by sonolysis produced at high temperatures and pressures. They cause the forming of OH^* radicals by homolysis of water. Hence, much more OH^* radicals (generated from photocatalysis and sonolysis) are found in the medium, are required for degradation.

4 Conclusions

In this study, the degradation kinetics of an artificial effluent solution was studied by comparing the sonocatalytic, photocatalytic and sonophotocatalytic processes. The effects of some process parameters on the kinetics, the fastest process and an equation including the effect of sonolysis were investigated. The obtained results from this study can be summarized as follows:

- The sonocatalytic, photocatalytic and sonophotocatalytic processes were used for degradation of the artificial effluent solution. Concentration, temperature, light intensity and amplitude of sonolysis were used as parameters. These processes followed Langmuir-Hinshelwood as pseudo-first order kinetics.
- It was obtained that the most effective process was sonophotocatalytic on the degradation due to generating the much more OH^* radicals in this process.
- Sonolysis didn't affect the activation energy of the degradation reaction. It was efficient on the reaction rate constant (k_p).
- An equation including the effect of sonolysis was determined for sonophotocatalytic degradation kinetics as:

$$\left(\frac{-dC_{Dye}}{dt}\right) =$$

$$3{,}19x10^7(1+0.029W_U)^{0{,}153}.\exp(-7880/T).I_a\left(\frac{0{,}156}{1+0{,}156(C_D)_0}\right)$$

(18)

Acknowledgements

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