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Sono and Sonophotoctalysis for wastewater treatment

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ABSTRACT

In the last two decades, advanced oxidation process (AOP) has been developed to remove low amount of organic compounds from aqueous wastewater. Free radicals involved in the AOP can be produced using several radiation methods, including UV, γ -radiation, electron-beam and ultrasonic waves. Ultrasonication promotes oxidative degradation of organic compounds by hydroxyl radicals. The chemical effect of ultrasound is produced through the phenomenon of cavitation, which is caused by the expansion and contraction of cavitation nuclei due to the compression and rarefaction cycles of ultrasonic waves. Cavitation causes the formation, rapid growth and finally implosive collapse of the bubbles, resulting in unusual reaction environment in the vicinity of the bubble. The temperature inside the cavity can theoretically reach temperatures of about 5,200 K in the collapsing bubbles and 1,900 K in the interfacial region between the solution and the collapsing bubbles. The main objective of this research is to compare the degradation of Eosin B and Rhodamine B by sonochemical degradation, and by the combination of ultrasound with other advanced oxidation process,like sonophotocatalysis and photocatalysis in presence of Na₂S₂O₃, KI to inhibit electron-hole recombination and enhance the degradation. The degradation of the two dyes were analysis under the influence of ultrasound, photocatalysis and sonophotocatalysis under solar irradiation and sun simulator using n-titanium dioxide ae well as bulk titanium dioxide as catalyst. Finally, it was shown that the enhancement of the degradation can be achieved by sonophotocatalysis.

Keywords: Sonophotoctalysis; wastewater treatment; spectroscopic studies.

INTRODUCTION

Mankind has witnessed unprecedented and remarkable flourish in industry during the past few decades. This growth resulted in a prosperous life style for the population of many countries. In many developing countries, there is an explosive industrial growth and the use of fossil fuels has caused environmental pollution as well toxic wastes that find their way into the air and water, leading to serious health problems. To address these problems, a number of advanced oxidation process for waste water treatment have been developed [1-3]. AOP involves various combinations of ozone, hydrogen peroxide, sonolysis, ultraviolet radiation and photocatalytic treatment [4], all these processes are based on the production of hydroxyl (OH) radicals. These species are highly reactive and unselective and attack most organic molecules, with rate constants usually on the order of 10^6 - 10^9 mol L⁻¹ s⁻¹ [5]. Among these processes, we study, the technique where sonolysis with high-frequency ultrasound is used in combination with titanium dioxide TiO₂ under irradiation of UV (US/UV/TiO₂) for the purification of water from persistent organic pollutants in water. A large number of minute bubbles, which are referred to as cavities, are generated by the irradiation of US in water. When the cavities collapse, a liquid jet with energy of a high magnitude pressure pulse is formed to stir the bulk liquid intensely [6]. As result, the inside of the cavity reaches high temperature and pressure instantaneously (5000 K, 1000 atm) [4], thus destroying organic pollutants. In addition, active species such as OH

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[7-9], which contribute to the degradation of organic pollutants, can be generated by sonication of pure water via the following chain reaction:

$H_2O +))) \rightarrow OH + H$	(1)
$OH + H \rightarrow H_2O$	(2)
$OH + OH \rightarrow H_2O_2$	(3)
$2 \text{`OH} \rightarrow \text{H}_2\text{O} + \text{O}$	(4)

When US are used in combination with UV irradiation, OH radical is also readily generated from H_2O_2 via the following reactions [10]:

$$H_2O_2 + \hbar v \to 2^{\circ}OH \tag{5}$$

Further, the product of OH radical is promoted when O_2 is present in water as shown in the following equations [8, 9]: $O_2 +))) \rightarrow O + O$ (6) $O + H_2O \rightarrow 2 \cdot OH$ (7)

In photocatalysis with UV/TiO₂, OH radical is primarily generated from water by UV irradiation as well as US according to the following [11-13]:

However, there is disagreement over the actual mechanisms of photocatalysis. Different possible chemical reactions which produce reactive species during the photocatalytic degradation of organic dyes and can be summarized as follows [14-19];

$\text{TiO}_2 + h v \rightarrow h_{vb}^+ + e_{CB}$ ($O_2 + hv \rightarrow$	(1
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OH(ads) ⁻	$+ {h_{vb}}^+$	$\rightarrow OH_{(ads)}$	(2)
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$$H_2O + h_{vb}^{+} \rightarrow OH^{\cdot} + H^{+}$$
(3)

$$2 \text{ OH}^{\cdot} \rightarrow \text{H}_2\text{O}_2 \tag{4}$$

$$2H^+ + O_2 + 2e_{CB} \rightarrow H_2O_2$$
 (5)

$$2 H_2 O + 2 h_{vb}^{+} \rightarrow H_2 O_2 + 2 H^{+}$$
 (6)

$$H_2O_2 + hv \rightarrow 2 OH^{-1}$$
 (7)

$$O_{2(ads)} + e_{CB} \rightarrow O_2^{-}$$
 (8)

$$O_2^- + e_{CB}^- (+2H^+) \rightarrow H_2O_2$$
(9)

$$O_2^{\cdot \cdot} + H_2O_2 \rightarrow OH^{\cdot} + OH^{\cdot} + O_2$$
 (10)

$$O_2^{\cdot \cdot} + H^+ \rightarrow OOH^{\cdot}$$
 (11)

$$O_2 \cdot + h_{vb}^+ \to {}^1O_2 \tag{12}$$

$$OOH' + O2'' \rightarrow O_2 + H_2O_2 \tag{13}$$

$$Dye_{(ads)} + hv \rightarrow Dye^{*}_{(ads)}$$
 (14)

$$\text{Dye}^{*}_{(ads)} + \text{TiO}_{2} \rightarrow \text{Dye}_{(ads)}^{+} + \text{TiO}_{2}(e)$$
 (15)

$$\text{Dye}^*_{(ads)} + \text{O}_2 \rightarrow \text{Dye}_{(ads)} + {}^1\text{O}_2$$
 (16)

$$Dye + TiO_2(e) \rightarrow Dye^{-1}$$
 (17)

 $Dye + h_{vb}^{+} \rightarrow Dye^{+}$

(18)

MATERIALS AND METHODS

2-Experimental

The chemical studied were selected from simple aromatic dyes. They are Eosin B and Rhodamine B they are xanthene dyes, having staining properties. They are freely soluble in water and thus can be found in water from the dye industry. The molecular structure of Eosin B and Rhodamine B are shown in Figure 1.



Figure 1 chemical structure of Rhodamine B and Eosin B

2-1-Experimental conditions

Reagent-grade methanol, Titanium dioxide nanoparticle, diaminopyridine(Aldrich), Silver nitrate, peroxodisulphate (Na₂S₂O₈), Potassium Iodide (KI), and Sodium thiosulphate (Na₂S₂O₃) were analytical grade reagents purchased from Merk. The dyes namely Rhodamine B and Eosin were of analytical grade and used without purification. Unless otherwise specified, all reagents used were of analytical grade and the solutionwere prepared using double distilled water.

Sonolysis experiments were performed at ultrasound bath (Elma D-78224/Htw, Type E 60 H f 50/60 V 220-240 IP 20 P 500 W) a continuous wave mode. Erlenmeyer flask or round bottom flask was used as reaction vessels. The bath temperature was maintained by adding ice. The bottom of the reaction vessel is placed to the bottom of the water bath.. The volume of the solution sonicated was 300mL. Photo-irradiation was carried under solar irradiation or by means of simulator with 300 xenon lamp for solar light with AM 1.5 filters. The solar sonophotocatalytic or photocatalyic degradation of the dye where carried out in 300 ml Elmyer or round bottom flask at the roof of Tail University all the degradation reactions were carried out according to the following procedure: 240 mg of photocatalyst was added to 300ml of 37.6µM aqueous dye solution Rhodamine B and Eosin). Initially the solution mixture was stirred using magnetic stirrer for 60 min in the dark to ensure establishment of the dye's equilibrium adsorption. After 60 min, the sun light or Sun simulator allowed irradiating the reaction mixture, and at 20 min intervals, samples were drawn from the suspension and the change of each dye concentration was measured using UV-Visible spectrophotometer (Perkin Elmer) at fixed wave length of 549 and 515 for Rhodamine B and Eosin respectively. For this purpose, the photocatalyst was removed by centrifuge> Solar experiments were carried out from 10 a.m. to 1 p.m. The intensity of solar radiation was (1050 Wm²) measured by using solar meter. It fluctuates during the reaction even under clear sky. However, we kept the solar experiment of required reaction under identical conditions, by carrying out the experiments simultaneously, side by side, thus making it possible to compare results of photodegradation.

RESULTS AND DISCUSSION

The combination of ultrasound and photocatalysis for environmental remediation is an active field of research [20-24]. We found, in our experiments that US + irradiation indeed enhances the photodegradation of Rhodamine B and Eosin compared with sonolysis alone. However, in contrast to our previous work, the presence of $Na_2S_2O_3$ decreases the degradation [25-27]. The effectiveness of sonophotocatalusis can be summarized as follows: [28]

• Ultrasound through acoustic cavitation generates extra source of OH Radicals from cavitation.

• Acoustic cavitation can remove intermediated from the photocatalytic active sites. Acoustic cavitation generates a number of physical effects, such as shear forces, turbulence and microstreaming, that help regenerate the active catalytic surface.

• When the catalytic or the pollutant is in the form of a powder or agglomerate, acoustic cavitation increases the uniformity of the dispersion, thereby increasing the available surface area.

• Acoustic cavitation is able to enhance mass transfer towards the liquid-solid interface.

• Acoustic cavitation is capable of accelerating the adsorption activity of reactant on the photocatalyst.

• Sonolysis is likely to decompose the hydrophobic part of pollutant compound, which is unlikely to occur on the surface of photocatalyst.

3-1- Sonocatlytic (US+TiO₂), photocatalytic (UV+TiO₂) and sonophotocatalytic degradation of Rhodamine B and Eosin B

Table 1 shows the decomposition rate of Rhodamine B under various conditiond in aqueous phase. In aqueous phase soncatalytic, there three potential sites for sonochemical reactions, namely

(i) The gaseous region of the cavitations bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:

$$H_2O +))) \longrightarrow H' + OH'$$
(19)

(ii) The bubble-liquid interface where hydroxyl radicals are located and, therefore radical reactions predominate although pyrolytic reactions may also, to a lesser extent, occur and (iii) the liquid bulk where secondary sonochemical activity may take place mainly due to free radical that have escaped from interface and migrate to the liquid bulk. It should be pointed out that the hydroxyl radical recombine yielding hydrogen peroxide, which may in turn react with hydrogen to regenerate hydroxyl radicals:

OH. + OH.	\longrightarrow H ₂ O ₂	(20)
$H_2O_2 + H^{\cdot}$	\longrightarrow H ₂ O + OH [·]	(21)

In presence of TiO_2 particles in the reaction mixture, the sonochemical degradation should partially be increased. This can be explained on the bases of the adsorption and desorption characteristic of the dye on TiO_2 catalyst.

3-2- Photocatalytic (UV+TiO₂) degradation of Rhodamine B and Eosin

The relative degradation time curves during the photcatalytic degradation of Rhodamine B while the percentage degradation is summarized in Table 1. As clearly seen photocatalytic degradation occurs appreciably slower than sonophotocatalysis but faster than soncatalytic degradation under similar experimental conditions. For instance, in 40 min and at 0.6 g/L catalyst loading, percentage degradation is changed from 4.83% in sonocatalytic to 34.16% in photocatalysis and to 57.26 in sonophotocatalysis respectively.

3-3- Sonophotocatalytic (US+UV+TiO₂) degradation of Rhodamine B

Degradation of Rhodamine B by means of simultaneous ultrasound and ultraviolet irradiation in presence of TiO_2 was studied and changes of degradation reaction during sonophotocatalysis. It is very interesting to see a synergistic effect between ultrasound and ultraviolet irradiation in presence of semiconductor since percentage degradation of the combined process (US + UV +TiO₂) are greater than the sum of the percentage of the individual process (US + TiO_2 + UV + TiO_2). The Synergy can be quantified as the normalized difference between the percentage degradation obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis [29]

$$\% Synergy = \frac{100 \ x \ \% US + UV + TiO2 - (\% US + TiO2 + \% UV + TiO2)}{\% US + UV + TiO2}$$

The beneficial effect of coupling photocatalysis with sonolysis may be attributed to:

- Increase production of hydroxyl radicals in the reaction mixture through reaction $H_2O \rightarrow H^{-} + OH^{-}$ and H_2O_2

- Enhanced mass transfer between the liquid phase and the catalyst surface [30]

- Catalyst excitation by ultrasound-induced luminescence which has a wide wave wavelength range below 375 nm [31, 32]

- Increased catalytic activity due to ultrasound de-aggregating catalyst particles, thus increasing surface area [33].



catalyst



Fig. 1a: Difference in concepts of catalytic and photocatalytic reactions: A catalyst contains active sites of which a substrate is converted into a product, while no active sites are present on a photocatalyst.



Fig. 1b: Contributions to photocatalysis from various sub-disciplines of chemistry.



Frequency ranges of sound and its application. Source: T. J. Mason



Fig. 2a:











Fig. 3a: Schematic model illustrating the seven fundamental processes occurring with TiO₂ photocatalysis



Fig. 3b: Correct electron energy band diagrams of TiO_{2:} electron energy E plotted upwards as a function of the distance from the surface to the bulk of the solid



Fig. 3c: Photodegradation of Rhodamine B in US, US+Sun, US+KI, US+Na₂S₂O₃



Fig. 4: Sonolysis of Rhodamine B in bulk TiO₂ for 180 min.



Fig. 5: Sonolysis of Rhodamine B in n-TiO₂ for 180 min



Fig. 6: Degradation of Rhodamine B US+SUN in bulk TiO₂ for 180 min



Fig. 7: Degradation of Rhodamine B US+SUN in n-TiO₂ for 180 min



Fig. 8: photoderadation of Rhodamine B in bulk TiO₂ + Sun



Fig. 9: photoderadation of Rhodamine B in n-TiO₂ + Sun



Fig. 10: Sonodegradation of Rhodamine B in $n-TiO_2 + Na2S_2O_3$



Fig. 11: Sonodegradation of Rhodamine B in $n-TiO_2 + K$



Fig. 12: Sonophotocatalysis (Eosin + TiO₂+Na2S2O3 + Simulator)



Fig. 13: EOSIN + SIMULATOR (no catalyst)



Fig. 14: Eosin + TiO2 + Simulator



Fig. 15: Eosin + TiO2 + Simulator without sonication







Fig. 17: FT-IR spectrum of Eosin (a) and Rhodamine B (b) in the absence (i) and presence (ii) of n-TiO₂



Fig. 18: Cost of AOP involving ultrasound for dye degradation

		А	В	С	D	Е	F	G	Н
No.	Min.	Nano Sono dark	Bulk Sono dark	Nano +Sono Sun	Bulk Sun + sono	Nano Sun	Bulk Sun	NanoSono Dark+ Na ₂ S ₂ O ₃	NanoSono Dark+ KI
-	T ₀	3.0522	3.0522	3.0522	3.0522	3.0522	3.0522	2.0146	1.9798
1	20	2.9242	3.0473	2.3714	1.6855	2.6844	2.0581	2.0969	1.5921
C	40	2.9048	3.0578	2.0095	1.3045	2.0525	1.7849	2.0916	1.5663
2 40	40	40 4.8%	0%	34%	57%	32%	41%	0%	10.5%
3	60	2.9149	3.0769	1.4296	-	-	1.3696	2.0169	1.5574
4	80	2.9399	3.0704	0.9873	0.9538	-	1.0941	2.0159	1.6442
5	100	2.888	3.0335	0.5956	0.4514	1.0147	0.9052	2.0434	1.5964
6	120	2.9349	3.0449	0.3489	0.2972	0.9464	0.7189	2.0308	1.4692
7	140	2.9037	3.0627	0.1481	0.1989	0.6207	0.5671	2.0402	1.5673
8	160	2.5487	2.8855	0.0478	0.1548	0.477	0.4385	2.0500	-
9	180	2.2605	2.5909	0.0342	0.1257	-	0.4131	2.1076	-

Table 1. Photodegradation of Rhodamine I	3 in n-TiO ₂ and bulk T	iO ₂ by US, sun	US+sun
Table 1. I notouegradation of Knoualinne I	\mathbf{J} III II-11O ₂ and Durk 1	10 ₂ by 0.8, suit,	USTSUI

$Dye + TiO_2 + Na_2S_2O_3$					
Time	Absorbance				
0 min.	0.5249				
20 min.	0.5158				
40 min.	0.4029				
60 min.	0.3362				
80 min.	0.3064				
100 min.	0.2684				

Dye only				
Time	Absorbance			
0 min.	0.5249			
30 min.	0.5214			
60 min.	0.5018			

$Dye + TiO_2$					
Time	Absorbance				
0 min.	0.4883				
20 min.	0.2865				
40 min.	0.1985				
60 min.	0.1079				
80 min.	0.0779				
100 min.	0.0474				

Dye $+$ TiO ₂ without sonication					
Time	Absorbance				
0 min.	0.5651				
20 min.	0.4970				
40 min.	0.4939				
60 min.	0.4894				
80 min.	0.4816				
100 min.	0.4811				
120 min.	0.4722				
140 min.	0.4597				

Percentage photodegradation									
		Α	В	С	D	Е	F	G	Н
No	Min	Nano	Bulk	Nano	Bulk	Nano	Bulk	NanoSono	NanoSono
140.	IVIIII.	Sono	Sono	Sup	Sun	Sono	Sono	Dorte No S O	Dorle KI
		dark	dark	Sun	Sun	Sun	Sun	$Dark + Na_2S_2O_3$	Dark+ KI
-	T ₀	3.0522	3.0522	3.0522	3.0522	3.0522	3.0522	2.0146	1.9798
1	20	2.9242	3.0473	2.3714	1.6855	2.6844	2.0581	2.0969	1.5921
2	40	4.83%	0%	34.16%	57.26%	32.75%	41.52	0%	20.89%
3	60	2.9149	3.0769	1.4296	-	-	1.3696	2.0169	1.5574
4	80	2.9399	3.0704	0.9873	0.9538	-	1.0941	2.0159	1.6442
5	100	2.888	3.0335	0.5956	0.4514	1.0147	0.9052	2.0434	1.5964
6	120	2.9349	3.0449	0.3489	0.2972	0.9464	0.7189	2.0308	1.4692
7	140	2.9037	3.0627	0.1481	0.1989	0.6207	0.5671	2.0402	1.5673
8	160	2.5487	2.8855	0.0478	0.1548	0.477	0.4385	2.0500	-
9	180	2.2605	2.5909	0.0342	0.1257	-	0.4131	2.1076	-

Table 2: photodegradation of Rhodamine B in n-TiO₂ and bulk TiO₂ by US, sun, US+sun

Table 3: photodegradation of Eosin in n-TiO₂ by simulator + US

No.	Min.	TiO ₂ +Na ₂ S2O ₃	TiO ₂ +Simulator+sonication	TiO ₂ ,No sonicationc.
-	T ₀	0.5249	0.4883	0.5651
1	20	0.5158	0.2865	0.4970
2	40	23.24%	54.35%	12.60%
3	60	0.3362	0.1079	0.4894
4	80	0.3064	0.0779	0.4816
5	100	0.2684	0.0474	0.4811
6	120			0.4722
7	140			0.4597

CONCLUSION

The sonochemical effect of ultrasound is highly exciting and versatile field. Its operation is simple, convenience. Ultrasonic irradiation can be used in *environmental decontamination* due to the production of high concentration of oxidizing species such as 'OH and H_2O_2 in the solution and localized high transient high temperature and pressures. In this research paper, a comparative study of sonochemical, photocatalysis, sonophotocatalysis of two dyes i.e. Rhodamine B and Eosin B were conducted. Significant enhancement was observed for the combination of ultrasound light and TiO₂.

The following important conclusion can be drawn from the following study:

- The addition of external inorganic anions like $Na_2S_2O_3$, KI decreases the degradation significantly in the presence of ultrasound sonication.

- The addition of external inorganic anions like $Na_2S_2O_3$, KI has a significant effect on the degradation of the dyes in photocatalysis.

Recommendations

- The research has shown that it is technically feasible to remove organic dyes by sonolysis. However, from the degradation of Eosin B and Rhodamine B, using other advanced oxidation process, complete degradation of pollutants is difficult to obtain at reasonable rate with ultrasound alone.

- The research on water detoxification requires a research group from different disciplines (chemistry, biology, chemical engineering) to develop it into a plant scale.

- There a plant for water decontamination in Spain, platoforma Solar de Almeria (CIEMATA), Carretera Senes, Km 4, 04200 Taberna (America). It will be agood idea to collaboration with them so that some of our ph. D. can do their dissertation at this plant.

- Equipment for this research should be purchased by the university since they are expensive.

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