RESEARCH ARTICLE

Advanced Oxidations of Tartrazine Azo-dye

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Through this research, the degradation of Tartrazine (TZ) azo-dye in synthetic wastewater solutions, has been examined under the influence of diverse experimental circumstances of ultrasound and ultraviolet irradiation. At small initial concentrations of Tartrazine (TZ) (10ppm), the photochemical process alone was considered efficient for degradation of TZ. However, in the case of sonochemical alone, the degradation continued very gently, resulted in fewer than 53% of Tartrazine (TZ) elimination after 200 min. Whereas, the adding of an oxidant such as H_2O_2 leads to increasing the degradation efficiency to certain extent. Additional increasing of H_2O_2 over the optimum concentration decrease the degradation because of the scavenging consequence of excess H_2O_2.

Overview

Photo-chemical and sono-chemical techniques using specific irradiation are exceedingly effective Recently, wastewater decontamination using the technique of advanced oxidation have emerged as a recommended process due to the destruction of organic pollutant into safe degradation products [**1**]. Advanced oxidation process (AOPs) include ozonation (O_3), photo-degradation ultra-sonication, photo-Fenton and Fenton. The key principle of AOPs is the development of free radical species in the reaction media by using different types of irradiation and/or chemical reaction. These free radicals (principally H• and HO•) have a powerful efficiency for destruct the organic pollutant by oxidation. The oxidation potential of these free radicals in the range of 2.33V, which leads to a faster rate of reactions, compared traditional oxidants such as $KMnO_4$ and H_2O_2 or [**2**]. These radical be able to attack the organic compounds in the wastewater by addition reactions according to the following equations [**3**].

$$TZ + {}^{*}OH \rightarrow ROH \quad (1)$$

$$TZ + {}^{*}OH \rightarrow TZ^{*} + H_2O \quad (2)$$

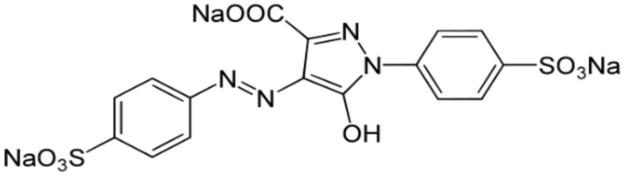
$$TZ^{n} + {}^{*}OH \rightarrow TZ^{n-1} + {}^{-}OH \quad (3)$$

TZ refer to the organic pollutant Tatrazine-azo dye in the water.

Contrasting conservative physicochemical procedures, AOPs offer more rapid reaction rate; [**4-6**]. The traditional ways and means for wastewater treatment, includes; adsorption, condensation, coagulations, membrane separations and so on require secondary treatments and high operating costs [**7-12**]. Tartrazine is poisonous to humans, cancer causing and mutagenic as it performances as hyperactivity and leads to thyroid cancer, migraine, eczema, asthma, and other interactive problems. The allowable daily consumption for labors unprotected occupationally to tartrazine is 0 - 7.5 mg/kg body mass [**10**]. Tartrazine has been categorized as a hazardous azo dye since it catalyzes, asthma, thyroid cancer, migraine, ADHD syndrome and other responses that include carcinogenetic, eczema, blurred vision, itching, and muto-genetics [**11**] **Table 1**. Demonstrate structure of Tartrazine azo dye according to IUPAC [**10**].

Table 1. Tartrazine azo dye chemical structure and molecular weight according to IUPAC.

Structure of Tartrazine



Molecular weight	534.3 g/mol
Percent of purity of Tartrazine	≥ 98%

After comprehensive research in literature reports concerning the safe elimination of Tartrazine dye (TZ) using different degradation practices, we found few papers discusses this problem. Based on the previous thoughts, this work dedicated to study the sonochemical and photochemical decomposition of Tartrazine (TZ) dye in an aqueous medium.

Constituents and procedures

Constituents

Tartrazine azo-dye (TZ) with purity more than 98.0%, delivered by Fluka, was used to make wastewater synthesis solution which is dissolved in deionized water, using an Elga B114 Deionizer (C114 cartridges, TDS = 3.5 ppm, and EC = 5 µS.cm@25ºC). All other chemicals, obtained from Fluka, have been used as supplied.

Ultrasonic reactor setup for the sonochemical process

Ultrasonic bath with capacity 15 L (Honda electronics) was used to conduct the degradation experiments. The bath operates at 40 KHZ and 360 W, while the temperature of the reaction was maintained constant by water recirculation. 100 ml of the dye solution was maintained in Erlenmeyer flask as a reaction vessel. The distance between the reaction flask and the bottom of the bath was maintained constant at about 1 cm, in which ultrasonic intensity was maximum. To avoid errors of the reading of the concentration due to evaporation during experiments the reactor vessel was sealed carefully with aluminum foil.

Photochemical reactor setup for the photochemical process

In these experiments, 250 ml glass photochemical reactor was used and filled with the dye solution. Then the solution is subjected to UV – lamp radiation for the specified time intervals. At regular time's intervals for UV-Vis analysis, a sample of (ca. 5 ml) was withdrawn.

Quantitative analysis experiments

Samples intermittently pulled from the reactor, which irradiated by US or UV, were quantitatively analyzed by UV-visible spectrophotometer by revealing its absorbance.

Outcomes and discussion

Optimization of the operating conditions

Consequence of Tartrazine dye concentration

As the manufacturing wastewater comprises contaminants in variable intensity. **Fig. 1** shows the removal efficiencies of Tartrazine (TZ) vs irradiation time. It is very obvious that the degradation of the TZ dye increases with irradiation time and hence the removal increases. Generally, the degradation process depends upon irradiation time.

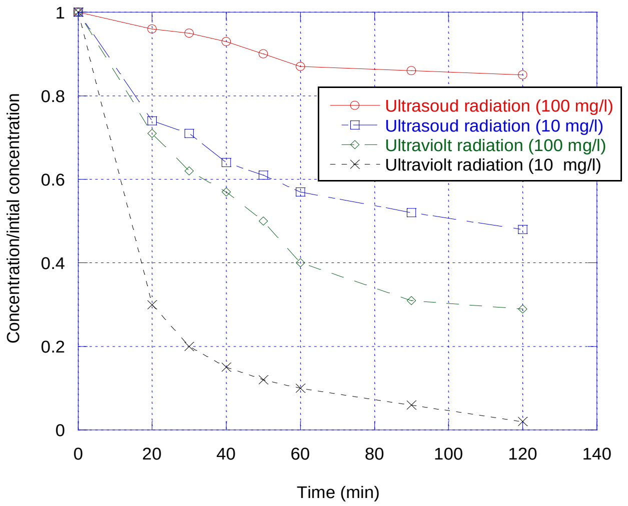


Fig. 1. Effect of Tartrazine (TZ) concentration.

In that case, the removal due to exposure to ultrasound is found to be decreased as presented in **Fig. 2**. This is may be accredited to, any growth of the initial concentration of the solution resulted to the weakening effect of the cavitation reactions [**13**].

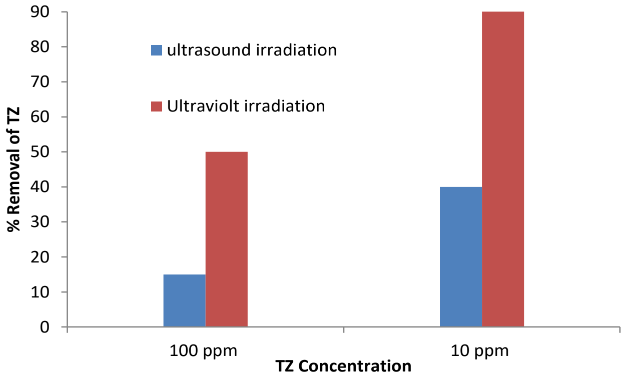


Fig. 2. Comparison of the % removal efficiencies.

In addition, the advanced oxidation of TZ using UV irradiation show better results than ultrasound irradiation, in such experiments the removal of Tartrazine (TZ) reach 90 % for initial concentration 10 mg. While, the process of using US irradiation acquire less efficiency

The results of degradation of Tartrazine (TZ) curves by US and UV treatment were found to be fit to a first-order reaction for describing the kinetic performance. Taking into consideration that, the US and UV radiation are the lone accountable for Tartrazine (TZ) dye degradation in the solution, as described in Equations [**1- 3**].

$$-\frac{dC}{dt} = KC \qquad (4)$$

where, C is the Tartrazine (TZ) concentration k is constant which is the first-order rate, and t is the time where $t > 0$.

Fig. 3 Shows the Tartrazine (TZ) degradation first order Kinetic fitting. While **Table 2** shows the half-life and the rate constant. The results shows that the rate constants reduced with accumulative TZ concentration [**14-17**].

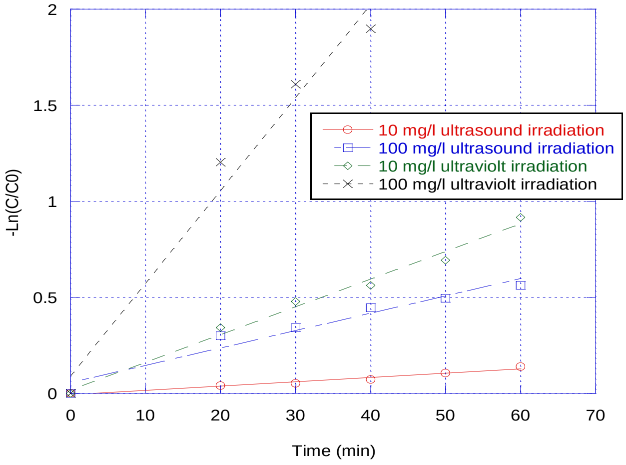


Fig. 3. Tartrazine (TZ) degradation first order Kinetic fitting.

Table 2. The rate constants and half-life for the degradation procedures.

Type of irradiation	Concentrations	Rate constant K (min^{-1})	Half life time (min)	R^2
Ultrasound	10 mg/1	0.012	91	0.932
Ultrasound	100 mg/1	0.0023	>180	0.975
Ultraviolet	10 mg/1	0.0510	15	0.956
Ultraviolet	100 mg/1	0.0143	45	0.981

For sonochemical degradation experiment of TZ, the increase in the primary concentration of the Tartrazine (TZ) dye by 10-fold leads to decrease in the rate constant by 5-fold. Although, in the photo-chemical degradation experiment, the increase in the primary concentration of the Tartrazine (TZ) dye by 10-fold leads to decrease in the rate constant by 4-fold.

The low degradation of TZ by ultrasound irradiation unaccompanied with oxidant might be due to the small rate of recurrence of ultrasound, which hinder the formation of hydroxyl radicals [**18**]. TZ dye which is a highly soluble and volatile substance trapped in the cavitation bubble [**19**]. However, UV irradiation method has the advantages of producing the extremely reactive HO radicals [**20-22**].

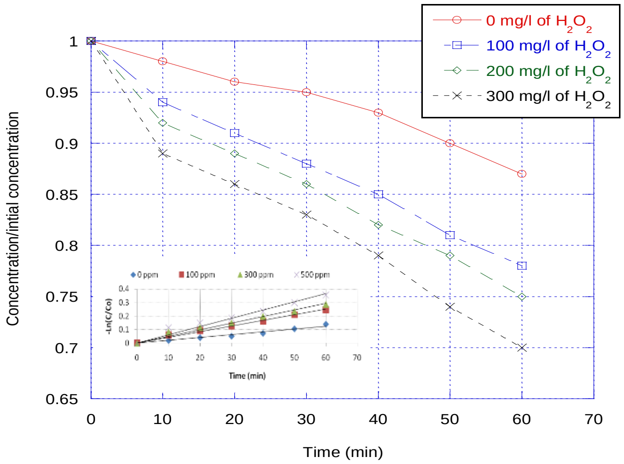


Fig. 4. The sonochemical degradation of Tartrazine dye (TZ) with and without of H_2O_2 (at $C_0 = 100$ ppm initial concentration of Tartrazine (TZ). Inserted curve displays the first order kinetic degradation of Tartrazine (TZ).

Effect of addition of H_2O_2

To investigate the synergistic effect of additional hydrogen peroxide on the total degradation of TZ, some experiments were repeated. In this part of the research, sonochemical and photochemical degradation experiments were conducted with Tartrazine (TZ) dye solutions containing H_2O_2. The hydrogen peroxide concentrations were in the range of 100 to 300mg/l. **Fig. 4** indications the consequence of the accumulation of H_2O_2 on the sonochemical decomposition of Tartrazine (TZ), whereas the inserted Figure displays the reaction kinetics of the degradation. The results revealed that, all degradation reactions kinetic stick to first-order rate laws ($R^2 > 93$). As per understood from Figure 4, the addition of H_2O_2 leads to enhance the degradation effect. However, increasing the concentration to 500 ppm (not showed) has an undesirable influence on the degradation process. Therefore, it can be concluded that, there may be an optimal amount of H_2O_2 to improve the degradation in the range of 300 to 500 ppm.

Dependable on the philosophy of hot spot, in the ultrasonic cavitation, the pressure and temperature of confined hot spots formed can markedly reach 1500 atm and 6000 K, respectively. Where H_2O_2 decompose into radicals according to (5) and (6) [**25**].

$$H_2O_2 + \text{us} \rightarrow 2\ {}^{*}OH \quad \text{free radicals} \qquad (5)$$

$${}^{*}H \text{ free radicals} + H_2O_2 \rightarrow {}^{*}OH \text{ free radicals} + H_2O \qquad (6)$$

The quantity of H_2O_2 that be able to created by ultrasound themself is excessively minor to disassociate to a great quantity of •OH. Consequently, the extra quantity of H_2O_2 is wanted to considerably speed up the decomposition process. H_2O_2 will intensification the creation of •OH in two ways. By the self-decomposition mechanism by ultrasound irradiation or by the decline of H_2O_2 [**26**].

The effect of addition of oxidant H_2O_2 are revealed in **Fig. 5**. The outcomes revealed that, the photo-degradation improved with addition of oxidant. However, at certain limit of addition the degradation decreased again. This can be attributed to the scavenger effect of H_2O_2 to the HO radical. So, best value of oxidant should be added to obtain maximum efficiency.

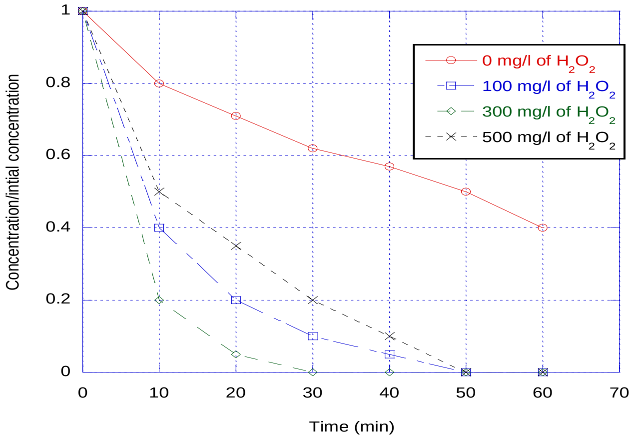


Fig. 5. Consequence of H_2O_2 addition on the photochemical removal of Tartrazine dye (TZ) ($C_0 = 100$ ppm).

The effect of the addition of hydrogen peroxide on the rate of photochemical degradation of Tartrazine dye (TZ) revealed in **Fig. 6**. The result revealed that the addition of 100 ppm and 300 ppm H_2O_2 can lead to improving the degradation when compared with the lack of H_2O_2. On the other hand, 500 ppm H_2O_2 has an undesirable influence on the degradation process. Therefore, it can be concluded that, there may be an optimal amount of H_2O_2 to improve the degradation.

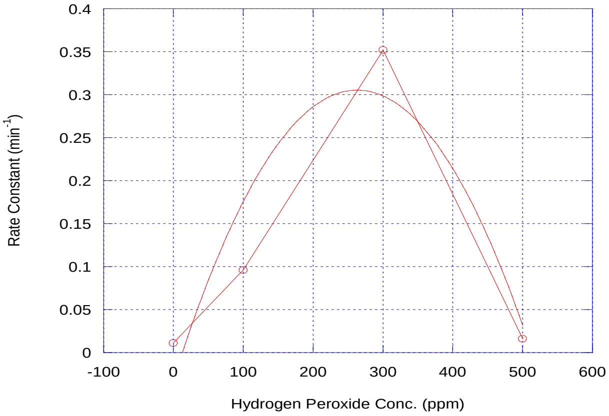


Fig. 6. Consequence of hydrogen peroxide addition on the rate of photochemical removal of Tartrazine (TZ) at $C_0 = 100$ ppm.

Throughout this course, UV radioactivity is consumed on split the O-O link in H_2O_2 and create the hydroxyl radical. Hypothetically, when using UV irradiation coupled with H_2O_2, the hydroxyl radical concentration increased with the initial hydrogen peroxide concentration. Accordingly, this leads to further decomposition of Tartrazine (TZ). Nevertheless, an optimum hydrogen peroxide concentration needed because excess of H_2O_2 would lead to reaction with HO• and form HO_2• . Therefore, the arrangement of UV with H_2O_2 was essential for the creation of HO• for the higher Tartrazine (TZ) degradation at high solution concentrations [**30**].

In general, from the previous discussion, it can be concluded that in case of H_2O_2 were present in excess in the reaction medium, the degradations of TZ due to US/H_2O_2, UV/H_2O_2 process were mainly due to hydroxyl radicals attack, and the degradations were sturdily depended on initial concentrations

Fig. 5 demonstrate that the addition of oxidant to ultraviolet procedure is more effective. Assessment of sono-degradation and photo-degradation rate constant **Table 3** presented that photolysis of (TZ) was more effective than sono-chemical degradation.

Table 3. The half-life and first-order rate coefficients for the sonochemical and photo-chemical measures at diverse circumstances of Tartrazine (TZ).

Type of irradiation	Concentration	Rate constant K (min^{-1})	$T_{1/2}$ (min)	R^2
Ultrasound	-	0.003	>190	0.98
Ultrasound/H_2O_2	100 ppm	0.005	>130	0.99
Ultrasound/H_2O_2	300 ppm	0.006	>80	0.96
Ultrasound/H_2O_2	500 ppm	0.007	>55	0.94
Ultraviolet	-	0.015	60	0.99
Ultraviolet/H_2O_2	100 ppm	0.086	<15	0.99
Ultraviolet/H_2O_2	300 ppm	0.162	<6	0.99
Ultraviolet/H_2O_2	500 ppm	0.066	15	0.99

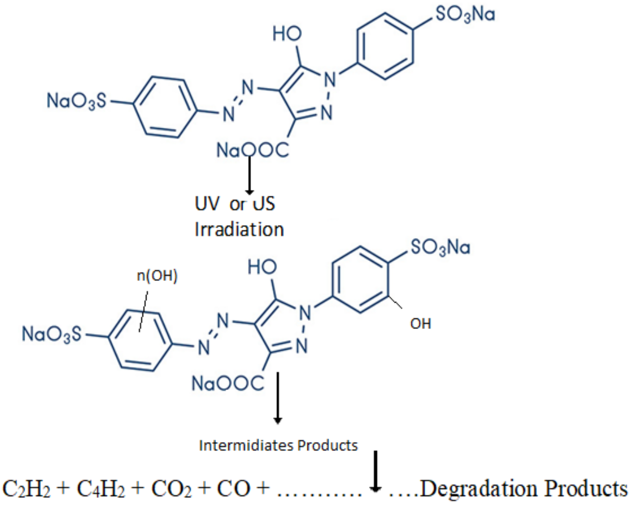


Fig. 8. Proposal of degradation passageway suggested for US and UV degradation of Tartrazine (TZ).

Proposal of degradation mechanism

By literature survey on the degradation of Tartrazine (TZ) mechanisms, there is contradiction regarding the reaction mechanism over hydroxyl radicals or holes. Thus, Agrios and Pichat [31] propose that Tartrazine (TZ) degradation over TiO_2 principally through the formation of radicals on the ring. **Fig. 8** shows the proposed degradation mechanism by applying ultrasound and/or ultraviolet irradiation.

Under these conditions, volatile compounds are directly produced through degradation of Tartrazine (TZ). Generally, degradation products from photolysis and/or sonolyses of Tartrazine (TZ) should be further examined carefully [**32**].

Conclusion

In this investigation, advanced oxidation procedures were used to completely remove Tartrazine (TZ) from wastewater. Various experimental operating conditions including UV, UV / H_2O_2, and the US, US/H_2O_2 have been investigated. Optimal effective conditions for each process were determined, which could be shortened as follows; the degradation of TZ proceed very slowly in case of the sonochemical course without the addition of H_2O_2. UV/H_2O_2 process showed better results and considered more appropriate treatment procedure for complete removal of TZ within a minor time. The addition of H_2O_2 to the reaction leads to increasing the reaction rate constant. However, the excess of H_2O_2 is not favorable due to its scavenging effect. Pseudo-first order kinetics model as regards to TZ concentrations was realized to fitting all the consequences.

Keywords

Tartrazine (TZ), advanced oxidation, rate of reaction, degradation mechanisms.

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