Application of Sonocatalyst and Sonophotocatalyst for Degradation of Acid Red 14 in Aqueous Environment

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A-B-S-T-R-A-C-T

Background & Aims of the Study: Azo dyes are employed in industrial processes such as textile industry to create large quantities of colored sewages that have organic and non-organic materials. So, remediation of them is essential. In this project, degradation and mineralization of Acid red 14 (AR14) that is a mono Azo dye and widely used in the textile industries was investigated by Sonocatalysis and Sono photo catalyst in the presence of homogeneous (Fe^{3+}) photo catalyst.

Materials & Methods: This study is an experimental investigation on a laboratory scale. The study performed on synthetic wastewater that hold Acid red 14. The influence of operational parameters such as initial dye concentration and ultrasonic power on the sonochemical degradation was also studied. The optimization of variables was done by one factor at a time method.

Results: The efficiency of the Sonophotocatalytic process with Fe^{3+} was higher than Sonocatalysis and photo catalyst processes alone. The combination of sonolysis, Fe^{3+} and photo catalyst caused a highly synergistic effect and the synergy index obtained for Fe^{3+} Sono photo catalysis was 2.05. Chemical oxygen demand (COD) analysis was used to study the degree of mineralization. After 180 min of reaction, the removal of COD was 15, 25.4 and 55.5% for UV/Fe^{3+}, US/Fe^{3+} and $UV/US/Fe^{3+}$ process, respectively. The degradation by photocatalysis and sonolysis followed pseudo first-order with respect to the concentration of AR14.

Conclusions: The results showed that the Sono photo catalytic degradation and mineralization of AR14 in the presence of Fe^{3+} was synergistic, most likely because of the participation of Sono-Fenton and photo-Fenton reactions.

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Background

One of the main groups of pollutants in wastewaters is organic dyes that are produced from textile or other industries. The textile industry uses a large amount of water through the dyeing operations. Dyes are widely used and hence wastewaters discharged into rivers or public sewage (1,2). The dye effluent may hold chemicals, which are toxic and carcinogenic in different microbiologic and fish species (3–4). So, it is essential to find an effective method to remove color from textile wastes. The conventional methods such as biological and physical-chemical treatment (coagulation–flocculation, and activated carbon adsorption) are not suitably efficient because dyes are scarcely removable according to their low molecular weight and high water solubility. Furthermore, the conventional methods are not

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destructive but only extract the pollution from one phase to another, thus a secondary pollution is handled and extra treatments are considered necessary (5−7). Several advanced oxidation processes (AOPs) have been suggested and widely used for the degradation of many toxic, non-biodegradable, carcinogenic and mutagenic contaminants (8). Many investigators have used AOP branches such as ozonation, photocatalysis, sonolysis, Fenton and photo Fenton reactions, and so on for the degradation of azo dyes (9–13). In the last decades, much attention has been given to the sonochemical degradation of organic contaminants in aqueous environment (14–17). The Sonochemistry mostly includes the chemical effects created by ultrasound when a sound wave is passed through an aqueous solution. Regularly, as a moment of the homolytic cleavage of water in the cavitation bubbles the production of reactive radical species such as, OH• and H• is happening.

The degradation of azo dyes by Sonochemical process has been studied by many researchers (18–22). Nevertheless, this system does not achieve comprehensive mineralization over short irradiation times, because of the generation of hydrophilic intermediate products, reaction volume and volatility of the pollutants (22,23). Therefore, the arrangement of Sonolysis with other advanced oxidation processes has been employed to solve the limitations of the single sonochemical degradation process (24–26). The Sonophotocatalysis which is the combination of Sonolysis with photo catalysis is often considered to be a suitable choice.

Aims of the study:

The main object of this study is to investigate the possibility of decolorization and mineralization of AR14 by Sonocatalysis and Sonophotocatalysis process. The effect of different operational factors such as power of ultrasonic and concentration of AR14 was also investigated.

Materials & Methods

Materials

Acid red 14 (AR14) was purchased from an Afrand Tuska company of Iran and used without further purification. The chemical properties of AR14 are shown in Table 1. H_2SO_4 and NaOH are all supplied from Merck. Distilled water was used for the entire work. Hydrated iron (III) nitrate ($FeNO_3 \cdot 9H_2O$) purchased from Sigma–Aldrich and it was used for the Fenton-like degradation reactions.

Photo reactor

The setup involves a cylindrical Pyrex reactor (1 L), which could be mixed magnetically. The top of the reactor was closed and equipped with several ports. The temperature inside the reactor was adjusted by recirculation of water through a thermostated. The Ultrasonic source was operating at 20 kHz, a W-385 Heat Systems-Ultrasonics apparatus. Its maximum US emission power was 20 W and a tip diameter was 13 mm. Irradiation was performed through the reactor Pyrex walls. The light source was a Jelosil, 250W iron halogenide lamp, equipped with filters and radiating in the wavelength range at 315–400 nm.

The initial pH of the solution was adjusted using a Basic pH Meter PT-10P Sartorius Instrument Germany Company.

Analytical Procedure

All ultrasound experiments, except power variation, were completed at an ultrasound frequency of 20 kHz in a continuous wave mode with a power output of 39 mW mL−1. Hydrated iron (III) nitrate ($FeNO_3 \cdot 9H_2O$) was used for carrying out the Fenton-like degradation reactions. All Sonocatalytic, photo catalytic and Sonophotocatalytic experiments were completed in the same experimental arrangement. A desired concentration of AR14 was prepared by dissolving the appropriate amount in 1 L water. During experiments, 3 ml aliquots were taken at appropriate time intervals.

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Samples were taken, then analyzed by a UV–Vis spectrophotometer (Agilent, 5453, American) at 515 nm. The Calibration plot according to the Beer Lambert's law was applied by concerning the absorbance to the concentration. The decrease in the absorbance at 515 nm is due to the color removal of AR14 solution. The suitable efficiencies were estimated with respect to its initial value and the removal percent for the AR14 and COD was achieved as (Eqs. 1–2):

$$Removal\ of\ AR14(\%) = \left(\frac{(AR14)_0 - (AR14)}{(AR14)_0}\right) \times 100$$

(1)

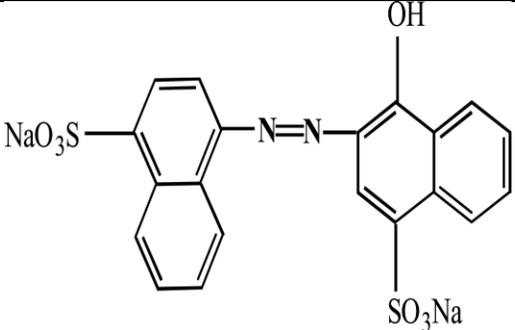$$Removal\ of\ COD(\%) = \left(\frac{(COD)_0 - (COD)}{(COD)_0}\right) \times 100$$

(2)

Where $(AR14)_0$ and $(COD)_0$ are the concentration of the AR14 and amount of COD at the start of the reaction and $(AR14)$ and (COD) are the concentration of AR14 and amount of COD at time t, respectively.

The COD was determined through a HACH-5000 spectrophotometer via a Dichromate solution as an oxidant in strong acidic conditions (27). At the end of the reaction, the solution was settled and then it was filtered to remove the precipitated. A sample was diluted with distillate water, then 1.5 ml of potassium dichromate and 3.5 ml of sulfuric acid as two reagents were mixed with 2.5 ml of the sample in a test tube. The sample was digested into the COD reactor for 2 h at about 150 °C. After acidic digestion, the sample was cooled and measured by the COD meter to estimate the mineralization efficiency of AR14 (28).

Table 1) Chemical structure and maximum absorption of AR14.

Pollutant	Molecular structure	λ_{max}, nm	M_w (g mol^{-1})
Acid Red 14		515	501

Results

Effect of concentration of Acid red 14

The concentration of AR 14 was varied from 10 to 50 mg/l to investigate its effect on the degradation efficiency. It can be seen that the Sonophotocatalytic degradation followed pseudo first-order- kinetics with respect to the concentration of AR14. It is obvious from Fig.1 that, the Plots of $\frac{-d(AR)}{dt}$ versus (AR) were linear and the slope of the plot achieved the first-order rate constants.
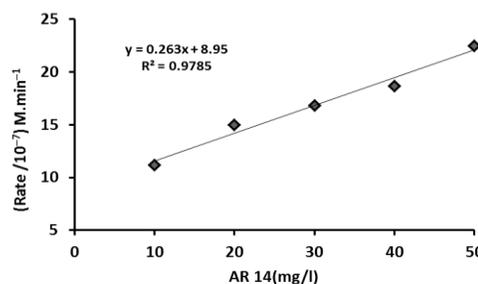

Figure 1) Effect of the concentration of AR14 on its Sonophotocatalytic degradation rate. Acoustic power = 39 mWmL^{-1}.

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Effect of power

The influence of the ultrasonic power on the degradation of AR14 is shown in Fig. 2. It can be clearly seen that the degradation rate was enhanced from 10^{-7} to 46.5×10^{-7} M. min^{-1} with increase in the ultrasonic power from 19 to 69 mW mL^{-1}. This phenomenon can be described by this fact that, the number of active bubbles was enhanced with increasing the delivered power. So, the formation of hydroxyl radicals was increased (29).
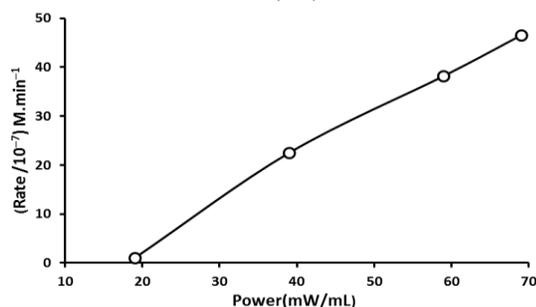

Figure 2) Effect of ultrasound power on the degradation of AR14 ((AR)= 50 mg/l).

Effect of Fe^{3+} on the Sonocatalytic, photo catalytic and Sonophotocatalytic degradation

The removal of AR14 by Sonocatalysis (US + Fe^{3+}), photo catalysis (UV+Fe^{3+}) and Sonophotocatalysis (US+UV+Fe^{3+}) was studied with an initial dye concentration of 50 mg/l, (Fe^{3+}) =0.04 mM and pH of 3 in all experiments. It can be seen from Fig. 3 that the degradation rates of photolysis and Sonolysis in the existence of Fe^{3+} were similar. A greater amount of degradation was achieved for Sonophotocatalysis (US + UV+ Fe^{3+}) compared with the individual processes. The photolytic degradation of AR14 in UV/Fe^{3+} process may be related to the absorbance of light by complex and produces AR14$^{.+}$, Fe^{3+} and organics (29). According to the Eq.3, the Fe^{3+} changes to Fe^{2+} which initiates the Fenton reaction for the degradation of the dye. With continuous irradiation of the Fe^{3+} solution, the regeneration of the catalyst with the production of an additional hydroxyl radical is obtained. Nevertheless, on one occasion that all the H_2O_2 is spent by Fe^{2+}, then the reaction is stopped.

As it can be seen from Fig.3, the degradation rate was 6.3×10^{-7} , 7.5×10^{-7} and 28.5×10^{-7} M. min^{-1} for UV/Fe^{3+}, US/Fe^{3+} and UV/US/Fe^{3+} process, respectively.

$$Synergy\ Index = \frac{R_{(UV+Fe^{+3}+US)}}{R_{(UV+Fe^{+3})}+R_{(US+Fe^{+3})}}$$
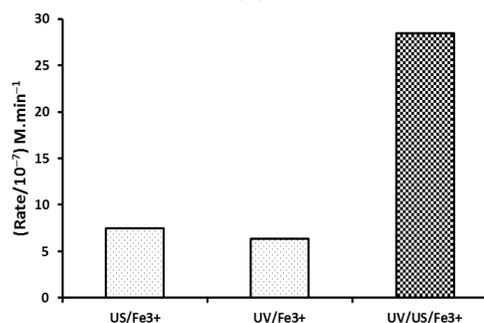(3)

Figure 3) Degradation rates of AR14 in different processes ((AR)= 50 mg/l, (Fe^{3+})= 0.04 mM, pH at 3).

Mineralization studies

The mineralization studies were also performed for the Sonocalytic, photo catalytic and Sonophotocatalytic degradation using Fe^{3+}. It is shown in Fig. 4, that there is no significant COD removal in the presence of Fe^{3+} during the Sono catalytic and photo catalytic processes. Also, the COD removal was not significant for the photo catalysis (15%) and Sonocatalytic (25.4%) after 3 h of treatment process. After 180 min, a synergistic enhancement (55.5 %) in the mineralization for Sonophotocatalysis in the presence of Fe^{3+} was achieved (Fig. 4). The synergistic mineralization may be due to the coincident operation of photo-Fenton and Sono-Fenton reactions (Reactions (3) and (4)).
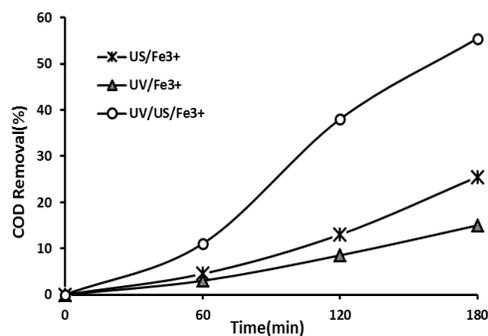

Figure 4) The removal of COD as a function of time for the degradation of AR14 for different processes ((AR)= 50 mg/l, (Fe^{3+})= 0.04 mM, pH at 3).

Discussion

During degradation process, the generated OH radical is affected by the variations in bubble temperatures as a result of volatile products that are made and enter the cavitation bubbles (30). With an increase in the concentration of AR14, the reaction between the dye and hydroxyl radicals was increased, So the rate of reaction was improved.

This phenomenon can be described by this fact that, the number of active bubbles was enhanced According to the Eq.3, a synergy value of 2.05 was achieved for the Sono photocatalytic degradation of AR14 in the presence of Fe^{3+} showing that the combination of photolysis and sonolysis improves the degradation of dye. The synergistic improvement in the Sono photo catalytic degradation may be originated from the additional production of hydroxyl radicals over photo-Fenton and Sono-Fenton reactions (Eqs. 4–5):

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^\bullet + H^+ \qquad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + H_2O \qquad (5)$$
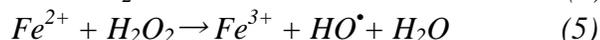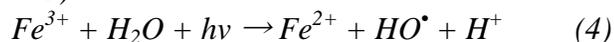
As it can be seen from the above equations, the continuity in the formation of hydroxyl radicals was not probable in the absence of light with increasing the delivered power. So, the formation of hydroxyl radicals was increased (29).

The chemical oxygen demand (COD) analysis was performed to determine the amount of mineralization of AR14 into CO_2 and water. The structures of AR14 were characterized on the UV−vis absorption spectra of their aqueous environment. AR14 has three absorbance peaks at 515, 317 and 218 nm. AR14 was considered by one main band in the visible region, with its maximum wavelength at 515 nm, and two bands in the ultraviolet region placed at 218 and 317 nm. The peaks at 218 nm and 317 nm were attributed to the absorption of the p–p* transition related to the naphthalene rings bonded to the N N group in the dye molecules (31). The band at 515 nm was ascribed to the chromophore-containing azolinkage of the dye molecules (32).

Conclusions

The Sonocatalytic, photo catalytic and Sonophotocatalytic degradation of AR14 in the presence of the photo catalyst and Fe3+ were investigated. When the low ultrasound frequency (20 kHz) is applied, the Photocatalysis and Sonocatalysis processes reveal synergistic effects. A synergy value of 2.05 was achieved for the Sonophotocatalytic degradation of AR14 showing that the combination of photo catalysis and Sonocatalysis improved dye degradation. The Sonophotocatalytic degradation followed pseudo first-order kinetics with respect to the concentration of AR14 and the degradation rate improved with an increase in the ultrasonic power. The Sono photo catalytic degradation and mineralization of AR14 in the presence of Fe3+ was synergistic, most likely because of the participation of Sono-Fenton and photo-Fenton reactions. The COD removal was not significant for the photo catalysis (15%) and Sonocatalytic (25.4%) after 3 h of treatment process. After 180 min, a synergistic enhancement (55.5 %) in the mineralization for Sonophotocatalysis in the presence of Fe3+ was achieved.

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Footnotes

Conflict of Interest:

The authors declare no conflict of interest.

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