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Contributing factors on the removal of Azo-dyes from industrial wastewater: A comparison of the efficiency of sonocataysis and photocatalysis process

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Abstract

The influence of the number of operating parameters on photocatalytic and sonocatalytic Acid Red 88 degradation from an aqueous solution was investigated in this paper. The experimental results indicated that the sonocatalytic process with Ni-TiO_2 was far more effective for the degradation of high concentration azo dyes, regardless of the process condition.

In order to achieve a larger surface area of the catalyst, Ni-TiO_2 was suspended in the aqueous solution. The optimum experimental conditions obtained as catalyst dosage of 0.6mg L^{-1}, pH of 7 and dye concentration of 30 mg L^{-1}. The COD value of the solution after photodegradation showed a significant decrease to 59 mg L-1 from 1573 mg L^{-1} while this value decreased to 34 mg L^{-1} after sonocatalytic degradation. The catalyst performance was evaluated by SEM and XRD techniques. Dye removal efficiency of 88% was obtained by sonocatalysis process with a dye concentration of 300 mg L^{-1} and within a pH range of 2-11. However, the efficiency was only 28% after photocatalytic degradation with the same dye concentration and within a more limited pH range of 3-9. Therefore, a specific method was proposed in this article for azo dye degradation.

Keywords: *Sonocatalysis, Photocatalysis, Ni-TiO_2, Acid Red 88, Wastewater.*

Introduction

The application of photocatalytic processes using semiconductors to solve the environmental problems has drawn considerable amount of attention. Previously, many studies have shown that the heterogeneous photocatalysis using a light absorbing semiconductor is a well-known advanced oxidation process (AOP) [1, 2]. When a semiconductor is exposed to UV radiation, it is excited to create electron-hole pairs. The

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generated holes then react with the absorbed hydroxide ions to form hydroxyl radicals while the electrons react with the adsorbed oxygen to produce superoxide ions. These oxidants, which are more reactive than normal oxygen molecules, are capable of removing a wide range of organic pollutants from a wastewater [3-5]. Since the photocatalytic technology seems to have little or no effect on effluents containing appreciable quantities of pollutants and low levels of transparency, the application of sonocatalytic technology has been receiving increasing attention recently [6].

In the present work, an aqueous solution containing an Azo Dye (Acid Red 88) was used with a photocatalyst to investigate the influence of the number of operating parameters on the color degradation process. The experimental parameters were catalyst ($Ni-TiO_2$) dosage, pH and dye concentration. Moreover, in order to evaluate the efficiency of photocatalysis and sonocatalysis processes, the COD measurements were carried out. Finally, the catalyst performance was characterized by SEM and XRD techniques.

Experimental

Materials

The commercial azo-dye Acid Red 88 was obtained from Merck, Germany. Concentrated hydrochloric acid and sodium hydroxide (obtained from Merck) were used for pH adjustment of the solution. Illustrated in Figure 1 is the reactor used for photocatalysis and sonocatalysis processes. As can be seen, the reactor consists of a glass container with dimensions (290 × 70 × 80 mm) and its walls are covered with an aluminum foil. Also, a 1-Watt UV lamp was used as a source for excitation which was placed inside a single-walled quartz tube and was fixed in the middle of the reactor. The UV lamp was purchased from Philips, the Netherlands and the 1600-Watt Ultrasonic generator was obtained from Faran Electronic Industries Co., Iran. The reactivity was 1000 ml after deducing the volume fraction occupied by the quartz tube.

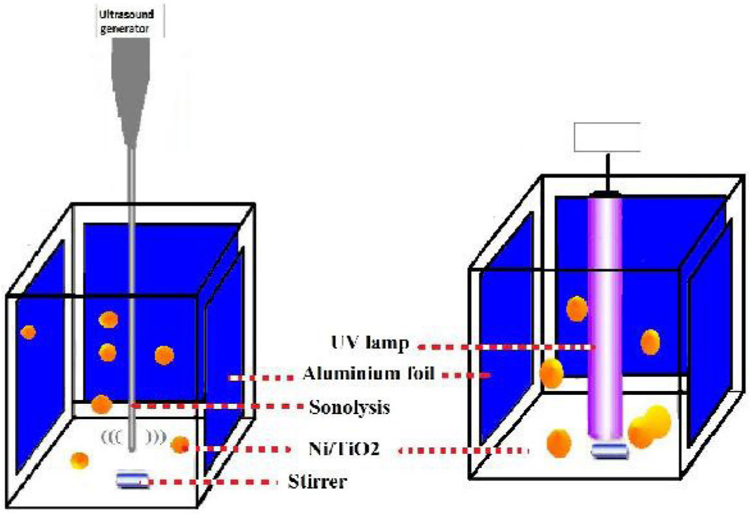

Figure 1. Schematic diagram of the photocatalytic & sonocatalytic reactor used for dye degradation (Dye concentration of 30 mg L^{-1}, pH of 7, Temperature of 25°C and Catalyst dosage of 0.6 mg L^{-1}).

Methodology

The dye stock solution was prepared by dissolving dye in distilled water, Then Ni-TiO_2 was added and the pH of the solution was adjusted by adding NaOH and HCl. The suspension was put under stirring at 200 rpm in the reactor to form a homogeneous mixture. Next, UV light and Ultrasound were housed in the photoreactor separately and irradiation was performed for 30 min to evaluate each operating factor influence on the dye removal rate. As mentioned before, the principal factors affecting dye degradation rate were the catalyst dosage, pH and the dye concentration. The amount of catalyst used in each experiment varied from 0.1 to 0.9 mg L^{-1} (0.1, 0.3, 0.6 and 0.9 mg L^{-1}). The studies were performed at pH 2, 3, 5, 7 and 9. The dye concentration ranged from 30 to 300 mg L^{-1} (30, 50, 100, 150, 200 and 300 mg L^{-1}). Finally, the purified samples were measured for their COD values to investigate the dye removal efficiencies.

The Photocatalysis and Sonocatalysis: SEM and XRD analyses

The surface characteristics and catalytic activity of Ni-TiO_2 were studied by a Scanning Electron Microscope (SEM). The efficiency of nanoparticles were evaluated by X-ray reflectivity technique (XRR) with a reflector from Philips, The Netherland using CuKa radiation operated at 40 kV and 40 mA. In addition, the SEM technique was employed to determine the surface composition of Ni-TiO_2 before and after the degradation process. The initial porous structure of Ni-TiO_2 with small pores and similar edges can clearly be seen in the SEM image in Fig. 2-a. Fig. 2-b presents the structure of the catalyst after photocatalysis process. As can be seen, pores of the catalyst were blocked as a result of the dye adsorption. Moreover, Fig 2-c shows the influence of the sonocatalysis on the catalyst structure after the adsorption of dye molecules on Ni-TiO_2 surface.

Likewise, XRD analysis of TiO2 and Ni-TiO_2 were performed to obtain more information about the catalyst structure. As shown in the X ray diffraction scan (10 to 80 degrees 2-theta) presented in Fig. 2-d, the crystalline structure of TiO_2 changes after its combination with Ni. Also, the XRD patterns of TiO_2 and Ni-TiO_2 seem to have similar intensities but a considerable reduction in relative diffraction intensities of Ni-TiO_2 is obvious from the figure. Part of Ni penetrates into TiO_2, and Ni ions were distributed uniformly in the interstices of semiconductor crystalline structure. In addition, there was no tendency for Ni to combine with oxygen which is due to the low nickel loading (2%).

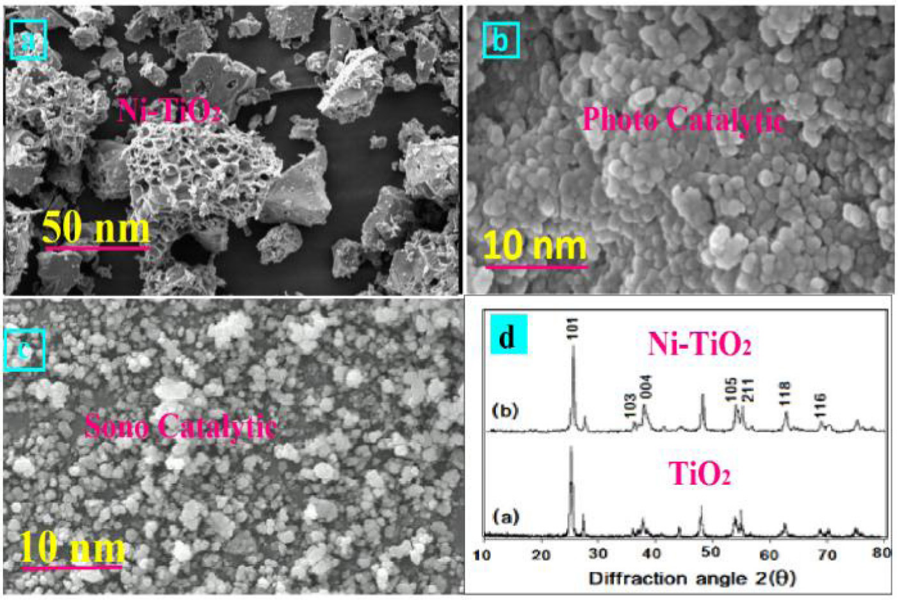

Figure 2. SEM micrographs of (a) The initial Ni-TiO_2 catalyst; (b) Ni-TiO_2 after photocatalysis; (c) Ni-TiO_2 after sonocatalysis; XRD patterns of d(a) Ni-TiO_2; d(b) TiO_2.

Results and discussion

Photodegradation of the Dye

The photocatalytic and sonocatalytic Acid Red 88 degradation from an aqueous solution was investigated in the maximum absorption at lambda max of 505 nm. The optimum experimental conditions were determined to be 0.6 mg L^{-1} catalyst dosage, 30 mg L^{-1} the initial dye concentration and pH of 7.

Effect of Catalyst loading

The influence of catalyst dosage on the dye degradation kinetic energy was studied by using 5 doses of nano-sized Ni-TiO_2 including 0.1, 0.3, 0.6, 0.9 and 1 (mg L^{-1}). It was observed that when catalyst dosage was increased from 0.1 to 1 mg, the photodegradation of azo dye increases. Figure 3-a shows the result of photocatalytic Acid Red 88 degradation with nano Ni-TiO$_2$. However, as can be seen from this figure, the removal coefficient was similar when catalyst dosages of 0.6, 0.9 and 1 mg were applied. Hence, due to economic issues, catalyst loading of 0.6 mg was selected as the optimum dosage. The effect of catalyst dosage can be described by figure 3-b. When the photocatalyst is placed under UV illumination, it is excited to create electron-hole pairs. The number of active sites on Ni-TiO$_2$ surface will increase as the catalyst loading increases and consequently, more hydroxyl and superoxide radicals are formed. Next, these hydroxyl and superoxide radicals react with dye molecules and convert them into nontoxic CO$_2$ and H$_2$O [7].

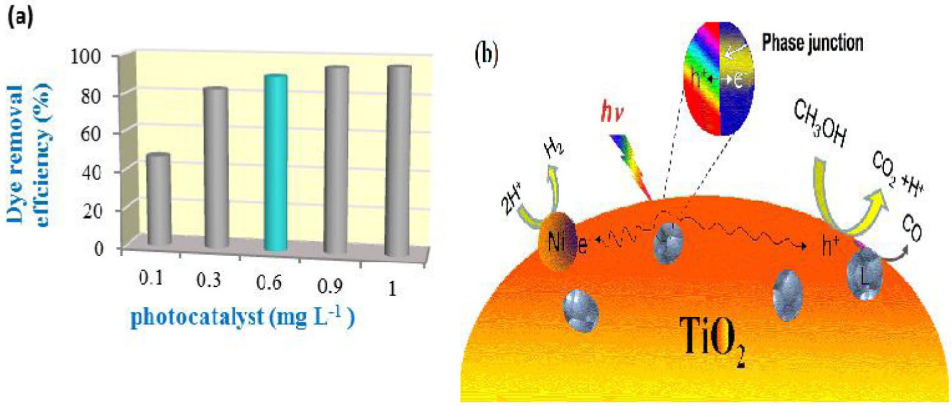

Figure 3. a) The effect of catalyst loading on Acid Red 88 degradation (Experimental conditions: Dye concentration 30 mg L^{-1}, pH=7, Exposure time= 30 min, Temperature=25 ˚C). **b)** Schematic of photocatalytic degradation.

In the same way as in the photocatalytic process, 5 doses of Ni-TiO$_2$ were employed to investigate the effect of sonocatalysis on Acid Red 88 degradation. It is clear from Figure 4 (a) that the sonocatalytic degradation was nearly the same when 0.3, 0.6, 0.9 and 1 mg L-1 of Ni-TiO$_2$ were used.

In order to have a similar experimental condition, catalyst dosage of 0.6 mg L^{-1} was selected as the optimum value for adequate Acid Red 88 degradation. As represented in Figure 4 (b), the ultrasonic method applied with catalytic activity is able to produce •OH and •O2 species for degradation of different organic contaminants. In fact, the sonocatlytic degradation is based on the cavitation in which ultrasonic waves create small bubbles in the liquid and reflection of ultrasonic waves expands in these small bubbles.

When the bubbles reach the catalyst surface, they collapse violently. During the implosion very high temperatures (approx. 5000-10000 ^{o}C) and pressures are reached locally. This energy can activate the semi-conductors used in the aqueous solutions [8,9] and excitation with these hot spots enhances the sono-photodegradation with Ni/TiO_2 as a result of active surface area of the catalyst and fast electron-hole creation [10].

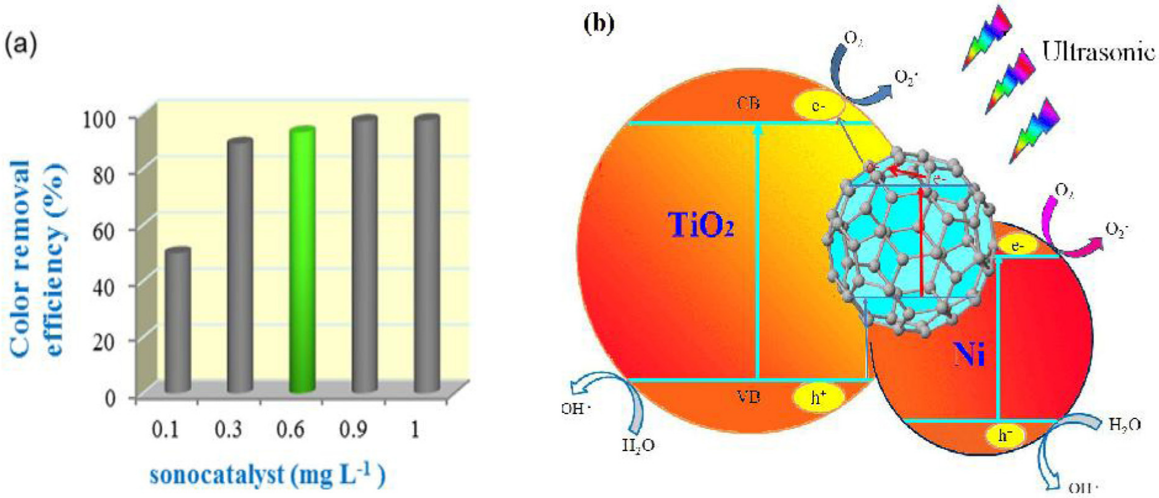

Figure 4. a) The effect of catalyst loading on Acid Red 88 degradation (Experimental conditions: Dye concentration: 30 mg L^{-1}, pH=7, Exposure time= 30 min, Temperature=25 °C). **b)** Schematic of sonocatalysis mechanism.

Effect of pH in Photocatalysis & Sonocatalysis

The rate of degradation of Acid Red 88 by photocatalysis was studied at different pH levels (3, 5, 7 and 9) and the results are shown in Figure 5 (a). It can be seen that dye removal efficiency of 88% was obtained after 30 min at pH 5 and 7. This can be explained by the fact that an increase in pH increases the concentration of OH ions and consequently formation rates of OH• and $•O_2$ increase by Ni/TiO_2. However, when pH value was higher than 7, the degradation rate decreased; this was because when pH was greater than 7, the photocatalyst activity reduced due to generation of ions from the negatively charged surface of photocatalyst [11].

The sonocatalytic degradation was performed at pH 2, 3, 5, 7 and 9. From Figure 5 (b), it can be seen that one of the advantages of sonocatalysis is that pH has no significant influence in the degradation rate of dye. In this process, as a result of the high temperature and pressure attained, electrons are excited from the valence band (VB) to the conduction band (CB), generating electron-hole pairs on the surface of Ni/TiO_2. The generated electrons and holes then react with the dissolved oxygen molecules and H_2O molecules on the catalyst surface to produce superoxide and hydroxide radicals. Subsequently, these free radicals undergo secondary reactions to oxidize dye to CO_2, H_2O and non-organic micromolecules [12].

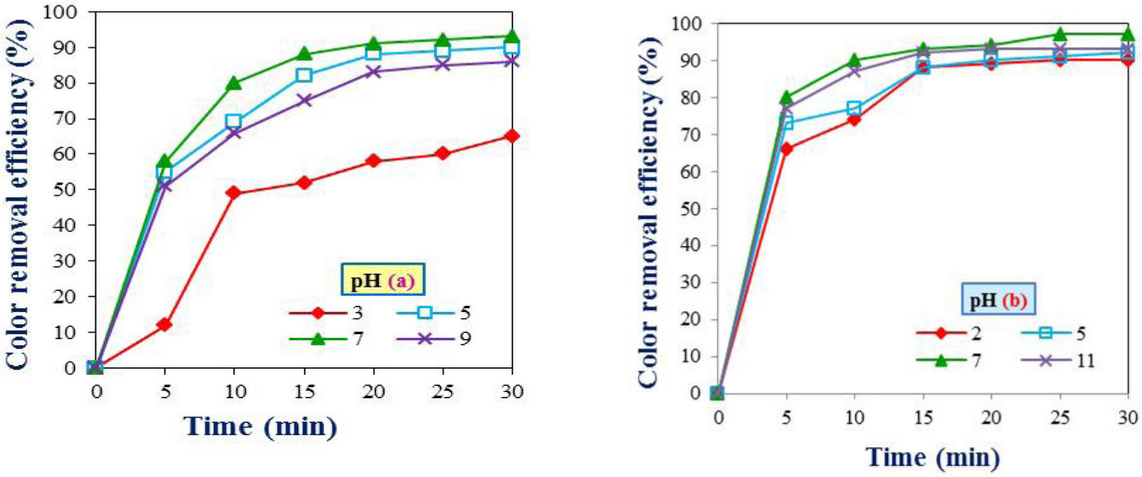

Figure 5. a) The effect of pH on Acid Red 88 degradation in photocatalysis. **b)** The effect of pH on Acid Red 88 degradation in sonocatalysis (Experimental conditions: Dye concentration: 30 mg L^{-1}, Exposure time= 30 min, Temperature=25 ˚C, catalyst dosage= 0.6 mg L^{-1}).

Effect of Acid Red 88 concentration in Photocatalysis & Sonocatalysis

Effect of variation of initial dye concentration on the degradation rate was also studied by taking different concentrations of Acid Red 88: 30, 50, 100, 150, 200 and 300 mg L^{-1}. The results of photocatalytic degradation rate are given in Figure 6 (a). As shown, dye removal efficiency was 91% for the dosage of 30 mg L^{-1} after 30 min. The rate of degradation of the dye was found to decrease with further increase in dye concentration. This may be due to the fact that increased dye concentrations in the solution will prevent optical photons to get absorbed on the photocatalyst surface and stops superoxide and hydroxyl radicals' formation responsible for the absorption of dye molecules [13]. The variation of dye concentration was the same for both sonocatalysis and photocatalysis. More satisfactory results are achieved by sonocatalytic degradation and are presented in Figure 6 (b). The dye removal efficiency was 88% for the dosage of 300 mg L^{-1} and greater than 90% for dye concentrations of 30 to 150 mg L^{-1}.

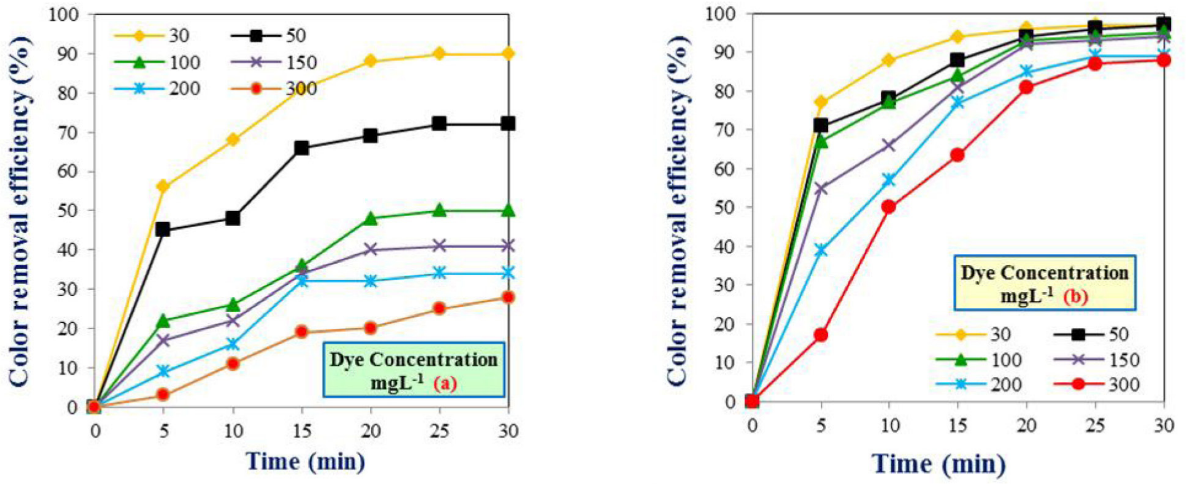

Figure 6. a) The effect of Acid Red 88 concentration on dye degradation rate in photocatalysis. **b)** The effect of Acid Red 88 concentration on dye degradation rate in sonocatalysis (Experimental conditions: pH= 7, exposure time= 30 min, Temperature=25 ˚C, catalyst dosage= 0.6 mg L^{-1}).

The COD measurements

The COD test is widely used for evaluation of different dye removal methods by measuring the total amount of oxygen required for the oxidation of organic compounds to CO_2 and water [14]. In this work, the COD value at optimized condition (pH = 7, dye concentration = 30 mg L^{-1} and catalyst dosage = 0.6 mg L^{-1}) for the initial dye solution and the purified solutions were compared. It was observed that the initial COD value (1573 mg L^{-1}) decreased steadily to 59 mg L^{-1} and 34 mg L^{-1}after 30 min of photocatalytic and sonocatalytic treatments, respectively.

Conclusion

The UV-irradiated photocatalytic and sonocatalytic degradations of azo dye (Acid Red 88) in an aqueous solution using Ni/TiO_2 as the photocatalyst were studied and optimized.The conclusions can be drawn as follows:

(1) The principal factors affecting dye degradation rate were the catalyst dosage, pH and the dye concentration.

(2) Catalyst dosage of 0.6 mg L^{-1} was selected as the optimum value for adequate dye removal.

(3) The photocatalytic degradation rate of Acid Red 88 increased with increasing pH value whereas in sonocatalysis, pH had no significant influence in the degradation rate of dye.

(4) Dye removal efficiency was 98% for the Acid Red 88 initial concentration of 30 mg L^{-1} after sonocatalytic degradation and 90% after photocatalytic degradation. However, by using higher concentrations of dye (300 mg L^{-1}) the removal efficiency reached to 88% after sonocatalysis and to 28% after photocatalysis, respectively.

(5) The significant decrease in the COD value of dye solutions depended mainly on the type

of treatment.

(6) The sonocatalytic degradation is an effective technology for the treatment of wastewaters with different pH and high concentrations of organic pollutants.

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