



Removal of acid 4092 dye from aqueous solution by zinc oxide nanoparticles and ultraviolet irradiation

Mohammad Hadi Dehghani^{a,b,*}, Parvin Mahdavi^a

^aDepartment of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, I.R. Iran, Tel. +98 21 66954914; Fax: +98 21 66915233; email: hdehghani@tums.ac.ir

^bCenter for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, I.R. Iran

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ABSTRACT

One of the most important environmental concerns is that of water contamination from industrial effluent and dyes used in the textile industry are a primary cause of such contamination. Most conventional methods of wastewater treatment are insufficient to remove these pollutants, so tests were done on a method of removing acid red 4092 dye from wastewater. Tests investigated advanced oxidation processes, based on hydroxyl radical production, were used as an effective method to remove this type of pollutant. The purpose of this study was to investigate the removal of acid red 4092 dye by zinc oxide nanoparticles and ultraviolet radiation (UV-150 W). Dye concentration was measured before and after treatment using a spectrophotometer (Perkin–Elmer Lambda 25–UV/vis). Experiments were performed in a batch photo-reactor on synthetic wastewater with concentrations of 0.5, 1.0, 1.5, and 2 mg/L. The study investigated the effects of factors such as initial dye concentration, irradiation time, dose of catalyst, and pH on the removal efficiency of acid red 4092 dye by the photocatalytic process in the presence of zinc oxide nanoparticles. The dye samples were irradiated by ultraviolet radiation for 2–12 min. Experiments showed that the best result was obtained in the treatment with concentration of dye = 0.5 mg/L, radiation time = 12 min, pH 5, and dosage of catalyst = 0.2 g/L. Results of the study showed that with increasing concentration of acid red 4092 dye (2 mg/L), removal percentage was decreased and with increasing radiation time (12–14 min), removal percentage was increased (100%). This research determined that the photocatalytic process of zinc oxide nanoparticles in the UV reactor effectively removed the acid red 4092 dye from an aqueous solution.

Keywords: Acid red 4092 dye; Zinc oxide nanoparticles; Ultraviolet irradiation; Aqueous solution

1. Introduction

Dye is an organic compound that consists of two main groups of compounds, chromophores and auxochromes. Acid dyes are classified according to their

chemical constitution and application. Acid dyes usually consist of sulfonic acid salts, carboxylic or phenol organic acid, and they are used for coloring wool, nylon, and silk textiles [1–5].

Dye pollutants are a major environmental concern. Wastewater effluent containing dye is a significant source of pollution in ecosystems; it affects the esthetic

*Corresponding author.

quality of water sources and aquatic life of ecosystems [1,2]. The presence of dye in wastewater from the textile industry causes interference in biological decontamination operations because dye has very low biological degradation capability. Most dyes are stable against light and heat. However, the technology developed to make dyes resistant to bleach, sunlight, and oxidation, means that as a pollutant, chemicals do not separate in conventional wastewater treatment systems. Also, some dyes and associated raw materials produce toxic aromatic amines that are carcinogen for humans. Dye effluent discharged into an environment can cause the production of dangerous substances from oxidation, hydrolysis, or other chemical reactions. Also, discharge of textile wastewater to a water ecosystem results in decreased penetration of sunlight that causes eutrophication and a decreased rate of photosynthesis by aquatic plants and algae [1–11].

A number of technologies are reported in the related literature for the removal of dyes [1–25]. Conventional biological decomposition is almost impossible for most organic dyes. Methods such as absorption on activated carbon, ultrafiltration and coagulation, reverse osmosis, ion exchange, and oxidation processes usually remove this type of pollutants effectively. Recently, advanced oxidation processes are commonly used for the degradation of resistant compounds. The main advantage of these methods is that they can be accomplished under environmental conditions and result in the complete mineralization of organic carbon. Such processes are based on the formation of highly active species of hydroxyl radicals that are capable of quick and non-selective degradation of a wide range of pollutants. The treatment of dyed wastewater by ultraviolet light and a strong oxidant presents an effective alternative method to remove dye from wastewater. Photocatalysis is used successfully for the oxidation of many organic pollutants, especially for mineralization and discoloration of dyes [1–25].

Among new oxidation methods or advanced oxidation processes, heterogeneous photo catalysis has been used as a novel technology for the mineralization of many pollutants [1–5,7–11,17–25]. Semiconductor photocatalysis is another commonly applied method used to destroy the dye that is often successful in facilitating the decomposition of a wide range of organic compounds [1–5].

In recent years, heterogeneous metal oxides such as ZnO that have high photocatalytic capability in UV reactors have been developed for use in the removal of environmental pollutants such as dye and other organic compounds. Heterogeneous photolysis using the nano photocatalytic reactor (UV/ZnO) is a very

effective technology for decomposition. The most important advantage of zinc oxide, determined by the results of this study, is its ability to attract a wide spectrum of electromagnetic waves and high photocatalytic efficiency of dye in wastewater [1–4,18,23].

The aim of this study was to evaluate the performance of a nano photocatalytic reactor (UV/ZnO) on the removal of acid red 4092 dye from wastewater discharged from the textile industry. The dye used in this study was an acidic water-soluble dye that was used for dyeing textile fibers and it turns red after dissolving in water. In this study, zinc oxide nanoparticles were used as a catalyst for the removal of acid red 4092 dye. The effect of pH, nanoparticle concentration, and time taken for the process has been studied.

2. Materials and methods

2.1. Materials

Tests in this study applied nanoparticle ZnO (99.8% purity) with light sponge powder, the ZnO had an average size of 6–12 nm, specific surface area 40–150 m²/gr, mass density of 105 kg m⁻³ and hexagonal crystal structure, it was prepared by the Isfahan Nano Spadana Company. The acid red dye used in these tests was obtained from a dye factory in Iran and used without further purification. The acid red dye used in tests had the chemical formula C₂₂H₁₄N₆Na₂O₉S₂. Tests were done on synthetic samples containing 0.5, 1, 1.5, and 2 mg/L of dye. After adjusting the pH level of samples by a pH-meter and adding the determined concentrations of nanoparticles, the samples were placed on a magnetic mixer for 20 min in a dark environment for the mixing process. The test solution was then transferred to a reactor and radiation was applied at the same time as the mixing process. Concentrations of nanoparticles used in this study were 0.1 and 0.2 g/L. Also, due to different acidity conditions of wastewater and the effect of pH on surface charge, properties of the photocatalyst, tests were taken at pH 5 and 10.

2.2. Apparatus

The reactor used in this study was a stainless steel closed bottom cylinder with a volume of 3 L made by the Tehran Steel Company. In the cylinder, a magnetic mixer was used to completely mix samples for reactor irradiation. A cooling method was used to lower high temperatures produced by the radiation lamp and this was done by placing a 4 L container inside the cylinder. The space between the cylinder and the chamber was filled with ice to lower the temperature. The UV

lamp used in this study was a 150 W lamp. Characteristics of the UV lamp are shown below (55130 Mainz/Germany):

Lamp type	TQ 150
Lamp power	150 W
Average lamp lifetime	2.000 h
Lamp lifetime warranty	1.000 h
Material of immersion tube	Quartz glass
Power supply	VG TQ 150

Measurement of dye content in samples was done by spectrophotometer (Perkin–Elmer Lambda 25–UV/vis). Calibration curve for acid dye was obtained at 400–700 nm. The pH level of solution was determined with a pH meter. Zinc oxide nanoparticles were separated from the solution using the centrifuged model (Hettich–Universal) at 10,000 rpm for 10 min.

3. Results and discussion

3.1. Effect of initial dye concentration

The effect of acid red 4092 dye concentration was tested on the removal efficiency. Evaluations were made for dye concentration that varied from 0.5 to 2 mg/L at optimum conditions (pH 5 and ZnO = 0.2 g/L). Results shown in Fig. 1, demonstrate that removal percentage was decreased according to increased concentration of dye (2 mg/L). Time taken for the complete removal (100%) of dye concentrations 0.5, 1.0, 1.5, and 2 mg/L were 6–8, 10, 10, and 12–14 min, respectively.

Similar results were also obtained in other reports on nano photocatalytic processing tests applied to other dyes [1–25]. These studies reported a greater possibility of forming competing intermediates resulting from degradation of the dye molecules under high concentrations of dye that can interfere with the

process and reduce the removal percentages. Also, in tests on samples with high dye concentrations, the active catalyst sites are covered by negatively charged dye molecules. Dye molecules have the capability to absorb ultraviolet irradiation that plays an important role in the rate of discoloration. These factors reduce hydroxyl radical production in the surface of the catalyst. So in this process, dye removal percentage for dilute solutions was more than that for solutions with higher dye concentrations [1–4,18–23].

The results of other researches have determined that an increasing concentration of dye molecules attracts photons and thus prevents them from reaching the surface of the nanophoto catalyst with the effect of reducing efficiency of the nanophotocatalytic process. Reports of other researches indicate that with increasing initial concentration of dye, due to absorption of molecules on the surface of nanoparticles, hydroxyl is not formed well and thus efficiency of the process is reduced. As a result, there is a decrease in O_2^{\bullet} and OH^{\bullet} molecules that available to attack the dye molecules at higher concentrations. Hence, the rate of photo degradation is related to concentration of dye and a higher concentration of dye causes lower rate of degradation [1–4,18–25].

3.2. Effect of irradiation time

Fig. 2 shows the effect of irradiation time on acid red 4092 dye removal percentage at different irradiation periods and optimum catalyst loading and initial dye concentration (pH 5, ZnO = 0.2 g/L, and dye concentration = 0.5 mg/L). Fig. 2 shows that increased irradiation time resulted in increased removal percentage. The removal percentage of acid red 4092 dye increased from 90 to 100% according to an increased irradiation time from 2 to 9 min. However, efficiency of removing acid red 4092 dye at optimum conditions was 100% after

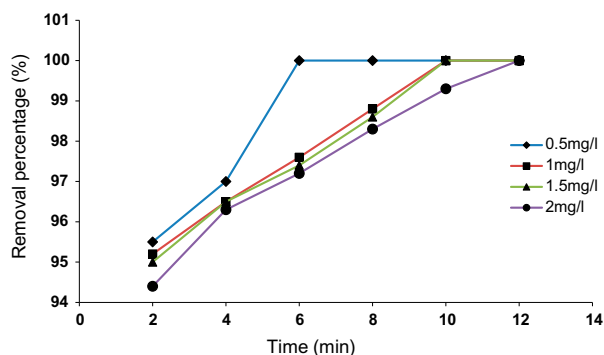


Fig. 1. Comparison of acid red 4092 dye removal percentage by UV/ZnO (pH 5, ZnO = 0.2 g/L).

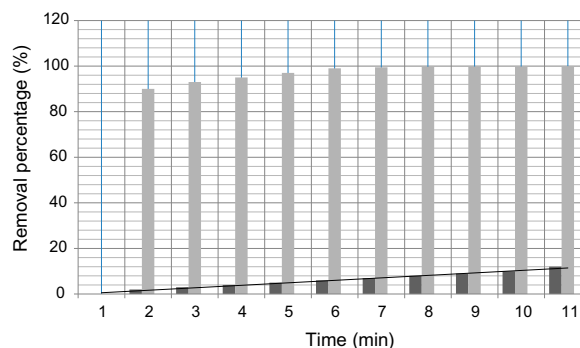


Fig. 2. Acid red 4092 dye removal percentage by UV/ZnO (pH 5, ZnO = 0.2 g/L, and dye concentration 0.5 mg/L).

9 min, and then it remained constant after the equilibrium time had been reached. This can be attributed to the gradual degradation of dye molecules to smaller fragments under optimum conditions, in that, the number of the active radicals ($\cdot\text{OH}$ and O_2) increased under a longer irradiation time [1–4,18–23].

3.3. Effect of pH

To determine the optimum pH, 2 g/L of zinc oxide catalyst with dye concentration 0.5 mg/L was tested in the conditions of acidic (pH 5) and alkaline (pH 10). The pH level of the dye solution was adjusted to within the range of 5 and 10 using HCl and NaOH solutions. The dye samples at different pH values; acidic pH (5), and alkaline pH (10) were analyzed and the removal percentages of acid red 4092 dye were determined as 94, 96.2, 97.5, 100, 100, and 100% at pH 5 and 90, 93, 94.2, 96.5, 98, and 100%, at the times 2, 4, 6, 8, 10, and 12 min, respectively. Results of this study showed the effect of pH on photocatalytic degradation of dye samples as a function of irradiation time.

As shown in Fig. 3, efficiency of the process in acidic conditions (pH 5) was more than that in alkaline conditions (pH 10). However, under decreased pH level of 5, there was increased efficiency of photocatalytic degradation of the acid red 4092 dye. As a result, dye removal efficiency was determined as a function of pH.

A review of the related literature indicated that one of the most important parameters for the process of dye degradation is pH of the solution. Under acidic conditions, surface of the catalyst is positively charged so it attracts the negatively charged dye molecules. Also, many of the hydroxyl radicals are produced in acidic conditions and this is caused by a lower rate of photo degradation of dye in alkaline conditions [1–4,18–25].

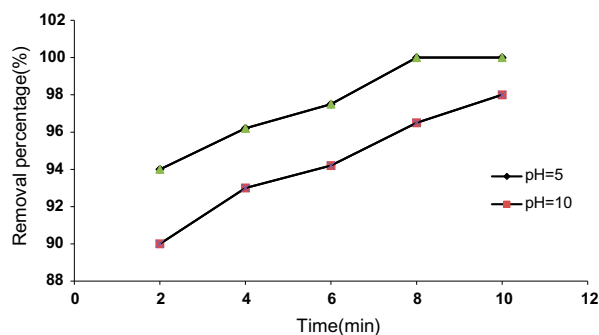


Fig. 3. Comparison of acid red 4092 dye removal percentage by UV/ZnO (ZnO=0.2 g/L and dye concentration 0.5 mg/L).

3.4. Effect of nanoparticle concentration

In this study, the effect of zinc oxide nanoparticles at concentration levels of 0.1 and 0.2 g/L was investigated on the efficiency of the nanophotocatalyst process. Dye solutions were tested at different zinc oxide nanoparticle concentrations of 0.1 and 0.2 g/L, (at optimum conditions of pH 5 and initial dye concentration = 0.5 mg/L), and evaluations were made for the removal percentage of dyes, and these were determined as 94, 97, 99, 100, and 100% and 89.5, 94, 95.5, 98, and 100% at the tested times 2, 4, 6, 8, and 10 min, respectively. Comparisons of dye removal percentages for the two concentrations are given in Fig. 4. As shown in Fig. 4, dye removal percentages at the concentration 0.2 g/L were more than that at 0.1 g/L (from 94 to 100% after 8 min).

This can be attributed to the presence of more active sites on the catalyst surface and the possible effect of radiation on such surfaces that contributed to maximum absorption of photons by the catalyst [4,13–15]. Other studies have indicated that an increased dose of adsorbent resulted in increased level of photon absorption [1–4,18–23].

3.5. Separate and combined process efficiency of ZnO and UV in acid red 4092 dye removal

The acid red 4092 dye solutions at various times as separate (UV) and combined (UV/ZnO) processes at optimum conditions of pH 5 and initial dye concentration = 0.5 mg/L, were evaluated. Removal percentages for samples were determined as 94, 97, 100, 100, 100, 100, 100, 100% (only UV), and 55, 70, 74.5, 85, 89.5, 94, 97, 99, and 100% (UV/ZnO) at irradiation times 2, 4, 6, 8, 10, 12, 14, 16, and 18 min, respectively. Comparison of dye removal percentages in the presence of UV alone and UV/ZnO process is shown in

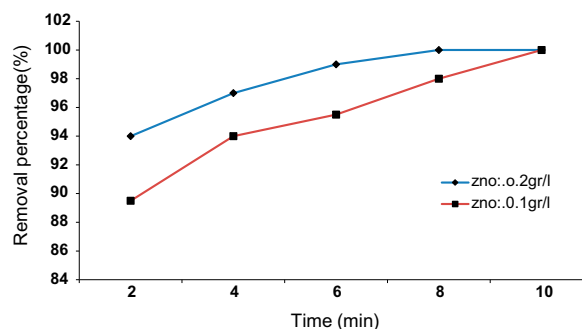
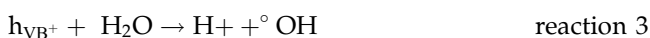
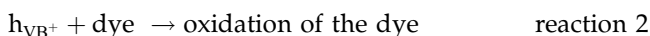
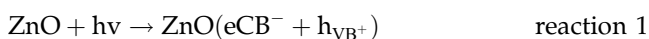


Fig. 4. Comparison of acid red 4092 dye removal percentage by UV/ZnO (pH 5 and dye concentration 0.5 mg/L).

Fig. 5. As shown in this figure, the dye removal percentages for the combined process (from 94 to 100% after 8 min) were more than that of the UV process alone (from 55 to 100% after 18 min).

This difference is due to the excitation of the zinc oxide nanoparticles, which led to the formation of paired electron-holes in the surface of these particles (reaction 1). Direct oxidation of organic matter (color) in the solution was caused by high-level oxidation ability of h_{VB}^+ (reaction 2). In fact, degradation of organic chemicals can be attributed to the activity of hydroxyl radicals produced through the breakup of water molecules (reaction 3) and the reaction between h_{VB}^+ and hydroxide (reaction 4) [1–4,18,23]:



Hydroxyl radicals are super strong, non-selective oxidants for the degradation of organic chemicals. Electrons in the conduction band of the catalyst surface ($e\text{CB}^-$) reduce molecular oxygen to superoxide anions (five responses). These radicals, in the presence of organic compounds, may lead to the formation of organic peroxide (reaction 6) or hydrogen peroxide (reaction 7) [1–4,18,23]:

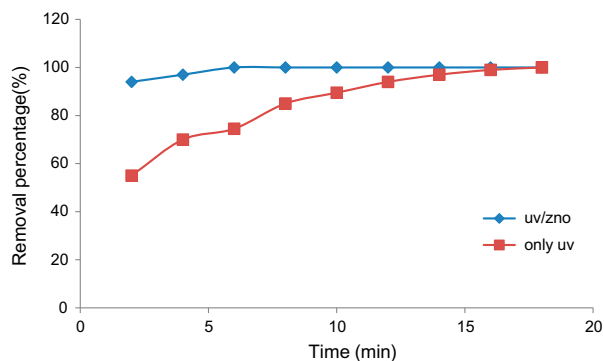
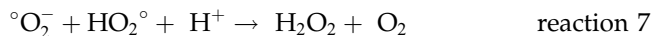


Fig. 5. Comparison between acid red 4092 dye removal efficiency by UV irradiation alone and UV/ZnO process (pH 5 and dye concentration 0.5 mg/L).

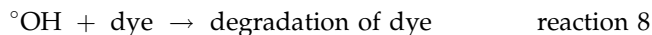
Table 1

Effect of nanoparticle concentration on acid red 4092 dye removal efficiency (ZnO=0.2 g/L)

Dye concentration (mg/L)	pH 10	pH 5
0.5	8	11
1	7.7	10.5
1.5	7	9.8
2	6.5	9



Also, electrons in the conduction band are responsible for the production of hydroxyl radicals that can cause mineralization of organic matter (reaction 8) [1–4,18,23]:



3.6. Dye removal by zinc oxide nanoparticles alone at various pH values

The effect of concentration of nanoparticles alone on acid red 4092 dye removal efficiency (ZnO=0.2 g/L and dye concentration 0.5 mg/L) was determined in the conditions of acidic (pH 5) and alkaline (pH 10). Results shown in Table 1, determine that the highest removal efficiency was observed at the concentration of 0.5 mg/L of dye, by mixing the solution with nanoparticles in a dark environment in acidic condition (11%) and the lowest removal efficiency was observed in alkaline conditions (8%) after 18 min. It can be concluded from the results of these tests that in acidic conditions (pH 5), the removal of dye by zinc oxide nanoparticles was higher than that in alkaline conditions (pH 10).

4. Conclusion

The results of this study showed that the removal efficiency for acid red 4092 dye removal was dependent on the following conditions; irradiation time, concentration of nanoparticles, acidity level, and dye concentration. In the nano photocatalytic process, the removal efficiency with increasing process was constant and was higher under initial time and acidic conditions. According to the results of this study, it can be concluded that the photocatalytic process with zinc oxide nanoparticles under UV irradiation presents an effective technology to remove acidic and other organic dyes from wastewater produced by the textile industry.

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