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# Photocatalytic removal of Acid Red 88 dye using zinc oxide nanoparticles fixed on glass plates

**Yahya Zandsalimi[1], Pari Teymouri[1], Reza Darvishi Cheshmeh Soltani[2], Reza Rezaee[1], Narmin Abdullahi[1], Mahdi Safari[1]**

1 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
2 Department of Environmental Health, School of Health, Arak University of Medical Sciences, Arak, Iran

**Original Article**

## Abstract

In this study, ZnO nanoparticles fixed on glass plates were employed as photocatalysts for the degradation of Acid Red 88 (AR88) dye in aquatic solution. ZnO nanoparticles were synthesized through coprecipitation method and fixed on glass plates. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used for characterization of nanoparticle samples. A batch reactor equipped to UV lamps was used for photocatalytic experiments. The effect of pH, initial concentrations of AR88, radical scavengers, and enhancers were studied on photocatalytic removal efficiency of AR88. The results showed an increase in AR88 removal at the neutral pH of 7 (79%), but a decreased in acidic and alkaline pH values. It was also found that at lower initial concentration of dye the removal efficiency increases. Among different radical scavengers and enhancers, addition of $CH_4O$ as radical scavenger and ethylenediaminetetraacetic acid (EDTA) as enhancer had the greatest effect on degradation efficiency. The photocatalysis process using fixed ZnO nanoparticles was shown to have good efficiency for removal of AR88 from aqueous solution. Therefore, it can be concluded that the photocatalysis process using fixed catalyst could be a promising method for treating wastewater of dye industries.

**KEYWORDS:** Acid Red 88, Photocatalytic Process, Nanoparticles, Zinc Oxide

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## Introduction

Synthetic dyes are a group of organic pollutants that are widely used in the textile, paper, food, and plastic industries.[1] Wastewater from such industries is discharged into aquatic environments causing water pollution and environmental problems.[2] Among commercial dyes, the azo group is the largest and most important group, comprising up to 70% of dye compounds.[2] Azo dyes have nitrogen–nitrogen double bond (-N = N-) in their chemical structure, along with one or more aromatic system(s).[3] Worldwide production of azo dyes is about 500,000 tons per year, 1-20% of which is estimated to be discharged into the water bodies.[4] Therefore, such dyes are serious threats to the ecosystem.[5] These materials may reduce light penetration into the water, which affects the photosynthetic activity of plants. They may also cause eutrophication, depletion of dissolved oxygen in water, and increase in suspended solids and turbidity.[6] In addition, many dyes are resistant to biodegradation and oxidizing agents and are

**Corresponding Author:**
*Mahdi Safari*
*Email: safari.m.eng@gmail.com*

toxic and carcinogenic for humans and aquatics.[1,7] Therefore, it is essential to remove dyes from wastewater before it entering the environment.[8] Various methods have been used to remove dyes such as adsorption processes, chemical coagulation, chlorination, reverse osmosis, and nano-filtration.[1,9] However, the conventional processes for the purification of wastewater are not effective enough.[10] In such processes, only a change in the phase of dye occurs and the concentrated pollutants and generated secondary pollutants require advanced treatment processes.[11] Therefore, the appropriate option would be the application of processes, which lead to the removal of pollutants or their oxidation to harmless byproducts. Today, the integration of different advanced oxidation processes for the decomposition of organic pollutants has become more widespread.[12] For example, the integration of ultraviolet light and titanium dioxide ($TiO_2$) or zinc oxide (ZnO) catalysts for the removal of organic contaminants is a photocatalytic process with a more effective performance than other processes.[13] In general, advanced oxidation processes are oxidation and decomposition reactions in which free radicals, such as hydroxyl produced by UV light, breakdown organic matters into simpler inorganic compounds such as mineral acids, water, and $CO_2$.[14]

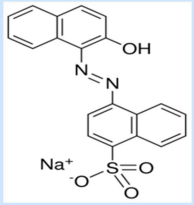
ZnO is a semiconductor photocatalyst with a high light sensitivity, high stability, and non-toxic nature and high efficiency in the production of electrons. Such characteristics make it a good candidate for the photocatalytic process.[15] The principal advantage of ZnO over $TiO_2$ is its capability to absorb a wide range of electromagnetic waves.[16,17] Catalysts in the photocatalytic processes are used in the fixed or suspension forms. The fixed catalysts are economical and functional because they do not need to be removed after large scale processes.[15] Acid Red 88 (AR88), is a mono azo dye and is widely used in the textile and food industries. It is resistant against optical, chemical, and biological decompositions and its byproducts (e.g., aromatic amines) have carcinogenic effects.[7] To the best of our knowledge, the use of ZnO nanoparticle fixed on glass plates as catalyst has not been reported for the removal of AR88 dye from aquatic solution. Therefore, this study investigated the efficiency of ZnO nanoparticles fixed on glass as catalyst in AR88 removal in the presence of UV light on a laboratory scale.

## Materials and Methods

All chemicals used in this study were analytical grade and purchased from Merck Company (Germany). AR88 dye was purchased from Alvan Sabet Corporation, Iran. The characteristics of AR88 are presented in table 1.

ZnO nanoparticles have been synthesized through simple coprecipitation method. For the preparation of ZnO nanoparticles, 1.362 g $ZnCl_2$ was added to 50 ml deionized water. Then, 1 M NaOH solution was dropwise added to the abovementioned solution under magnetic stirring until the pH reached 10. The suspension was filtered and washed with absolute deionized water and ethanol and dried in an oven at 80 °C for two days.

**Table 1. Characteristics of Acid Red 88**

| Dye | Chemical Structure | Molecular Formula | λmax (nm) | $M_w$ (g/M) |
|---|---|---|---|---|
| Acid Red 88 |  | $C_{20}H_{13}N_2NaO_4S$ | 505 | 400.38 |

First, glass plates were kept in a solution of 50% NaOH for 24 hours. Then, 3% nanosuspension was prepared and mixed for 1 hour. It was placed in an ultrasonic bath until particles were dispersed. Subsequently, 5 ml of homogeneous solution was poured on the glass plates (3 × 15 cm) and kept for 24 hours at room temperature to dry slowly. Then, the glass plates were placed in an oven with a temperature of 450 °C for 3 hours for stabilization.[15]

A Plexiglas batch reactor with working volume of 500 ml was used for photocatalytic experiments. Moreover, 4 glass plates with fixed catalyst were placed on the inner surfaces of reactor walls. A 9-W low-pressure UVC lamp (Philips, Netherlands) with a quartz cover was used as the UV source. A magnetic stirrer (Heidolph, Germany) was used for mixing the solution (Figure1).

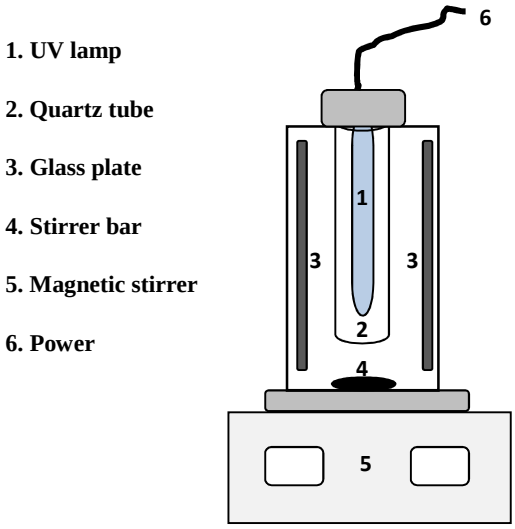



**Figure 1. Photocatalytic reactor**

Initially, AR88 dye stock solution (1000 mg/l) was prepared by dissolving 1 g of dye in 1000 ml of deionized water and the stock solution was kept in the refrigerator. Different concentrations of AR88 were prepared by the dilution of stock solution (1000 mg/l) and added to the reactor. The effect of different pH (3, 5, 7, 9, and 11), initial concentrations of AR88 (10, 25, 50, and 100 mg/l), and contact times (30, 60, 90, and 120 minutes) were studied on photocatalytic removal efficiency of AR88. Furthermore, the effects of radical scavengers ($Na_2CO_3$, NaCl, and $CH_4O$) and enhancers ($H_2O_2$, ethylenediaminetetraacetic acid (EDTA), and $FeSO_4$) were evaluated on the AR88 removal efficiency.

Equation (1) was used to calculate the percentage of dye removal.[18]

$$(1)\ R = [\ C_0 - C_t\ /\ C_0] \times 100$$

where, R is the removal percentage (%), and $C_0$ and $C_t$ are dye concentrations at times of 0 and t, respectively.

The morphology of fixed ZnO nanoparticles was evaluated using a scanning electron microscope (SEM) (TESCAN, Czech Republic). The X-ray diffraction (XRD) patterns of synthesized ZnO nanoparticles were studied using a Cu anode XRD system (λ: 1.54056 Å) in 2θ range from 10 to 80° and step size of 0.026°/s. A DR-5000 UV-VIS spectrophotometer (HACH, USA) was employed for the measurement of AR88 at 505 nm (Determinate λ max). The pH of the solution was measured using a digital pH meter (Jenway, UK).

## Results and Discussion

### Structural analysis

*SEM results*

Figure 2 shows the SEM image of ZnO nanoparticles on glass plate. The fixed ZnO nanoparticles have relatively uniform spherical shape and uniform size distributions. The average size of ZnO nanoparticles is 20-50 nm with tangible agglomeration. It can be observed that the fixation of ZnO nanoparticles on a glass plate has been accomplished well.

*XRD results*

The crystal structure of synthesized ZnO nanoparticles was examined using XRD analysis and is shown in figure 3. The diffraction peaks analysis of the ZnO nanoparticles revealed peaks at 100, 002, 101,

102, 110, 103, and 112 planes, corresponding to the hexagonal wurtzite phase of ZnO.

Moreover, the sharp and intense peaks display the excellent crystal structure of synthesized ZnO nanoparticles. The crystallite size of ZnO nanoparticles was estimated using the Debye–Scherrer equation.[19] Accordingly, the average crystallite size of the ZnO nanoparticles was about 47.4 nm.

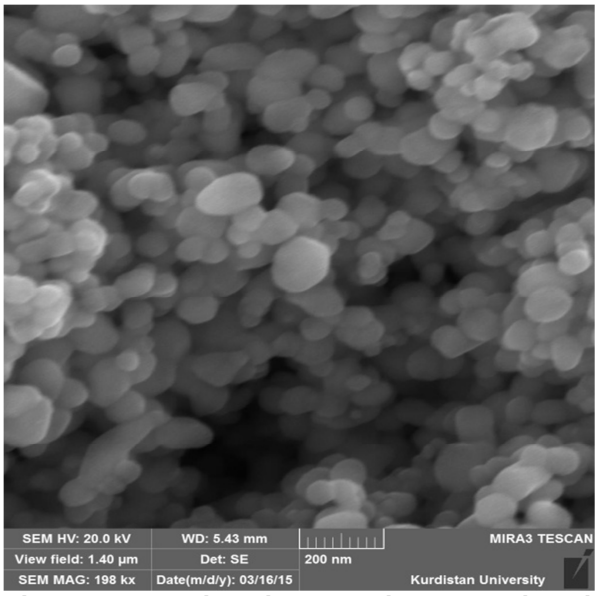



**Figure 2. Scanning electron microscopy (SEM) image of fixed ZnO**

## Photocatalysis efficiency of AR88

### *Effect of pH*

The pH of the solution may affect the surface charge of adsorbent, the degree of ionization of different contaminants, the separation of functional groups on the adsorbent active sites, and also the structure of dye molecules.[20] The effect of pH on the photocatalytic removal of AR88 from aqueous solutions was studied at the pH range of 3 to 11 and dye concentration of 50 mg/l (Figure 4). Samples were taken at 30-, 60-, 90-, and 120-minute time intervals and the removal (%) was calculated using equation 1. The highest removal efficiency (78%) was at neutral pH, and any increase or decrease from pH of 7 reduced the removal efficiency. A similar result was also reported by Daneshvar et al. for Acid Orange 7, in which photocatalytic degradation was higher at neutral and alkaline pH values.[21] The presence of free hydroxyl anions in the solution is necessary for hydroxyl radical production. However, at the acidic pH values, there are no free hydroxyl anions in the solution.[15]

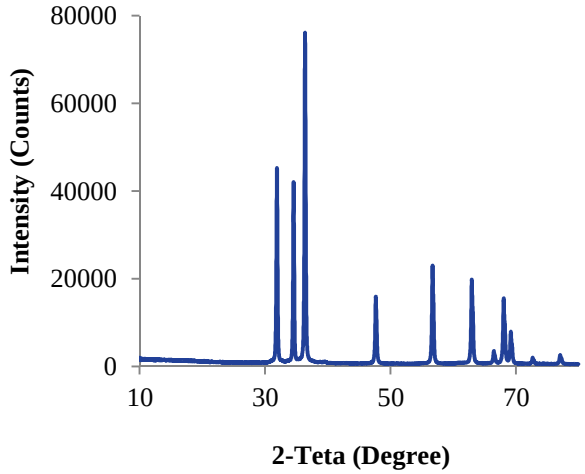



**Figure 3. X-ray diffraction (XRD) pattern of ZnO nanostructures**

### *Effect of initial dye concentration*

The effect of initial dye concentration on the photocatalytic removal of AR88 in aqueous solutions is shown in figure 5. Samples with 10, 25, 50, and 100 mg/l of dye concentration and pH of 7 were provided and exposed to UV light for 120 minutes. The results showed that when the dye concentration increases from 10 to 100 mg/l, the removal efficiency decreases from 92% to 45% (Figure 5), meaning that their access to the catalyst surface is reduced. An important part of dye removal is performed by active hydroxyl radicals, generated by UV radiation on the catalyst surface. High concentration of dye molecules may act as an inhibitor of hydroxyl radical generation by absorbing light photons, which results in decreased dye removal efficiency.[21]

Grzechulska and Morawski studied the removal of azo acid black using a photocatalytic

process.[22] They reported that higher concentrations of dye cause the formation of multiple layers of dye molecules on the catalyst surface and prevent the direct contact of other molecules with the hydroxyl radicals, and thus, reduce the efficiency of the process. In addition, the increased numbers of dye molecules absorb light photons and inhibit them from reaching the catalyst surface and producing hydroxyl radicals.[22]

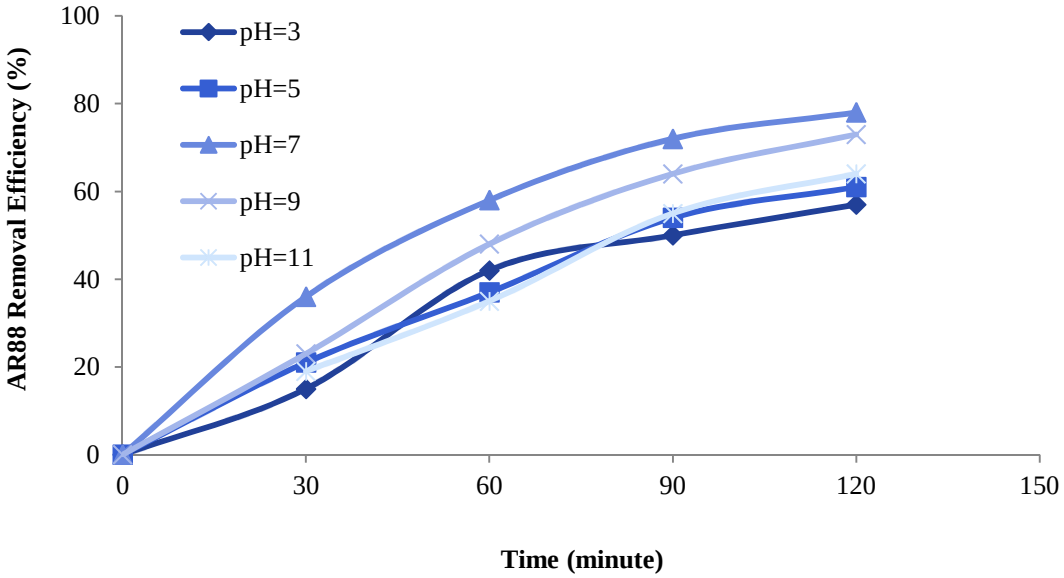



**Figure 4. Effect of pH on the photocatalytic removal of Acid Red 88 (AR88) from aqueous solutions (initial dye concentration: 50 mg/l, time: 120 minutes)**

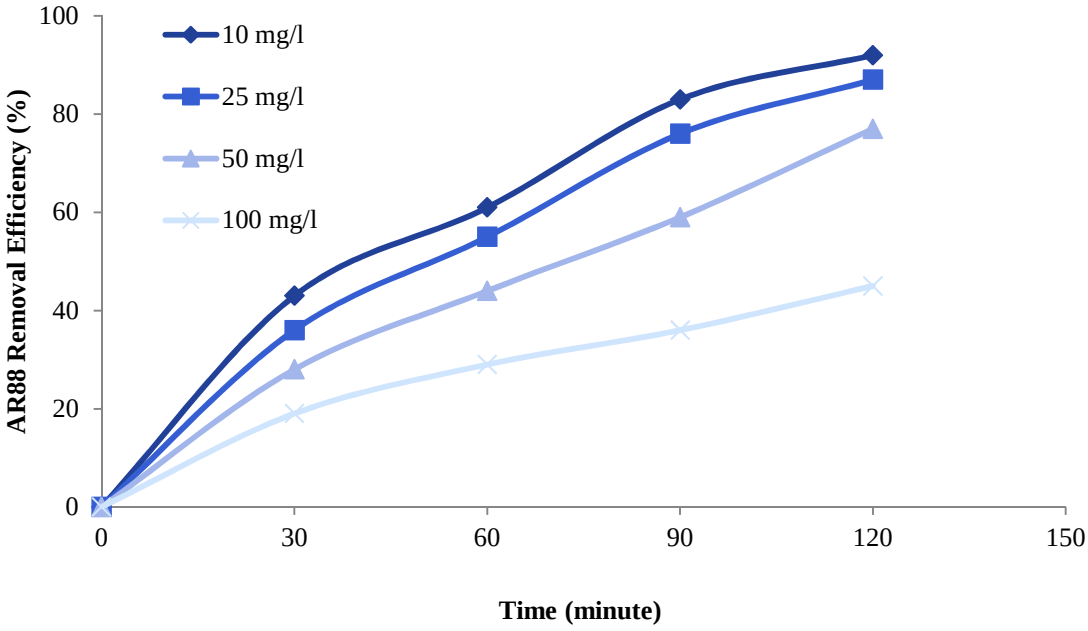



**Figure 5. Effect of initial dye concentration on the photocatalytic removal of Acid Red 88 (AR88) from aqueous solutions (pH: 7, time: 120 minutes)**

### *Effect of radical Scavengers*

To evaluate the effect of interferences on the photocatalytic removal efficiency of dye, 1 mM of NaCl, $Na_2CO_3$, and $CH_4O$ were separately added to the samples with a dye concentration of 50 mg/l and at neutral pH. Figure 6 shows the effect of radical scavengers on the photocatalytic removal of AR88 from aqueous solutions. After 120 minutes of contact time, the results showed that such interferences reduce the removal efficiency of the studied dye (Figure 6). The reaction of ions such as $Cl^-$ and $CO_3^{2-}$ with the hydroxyl free radicals reduces the free radicals, and thus, removal efficiency. Daneshvar et al. investigated the effect of operational parameters of Rhodamine B treatment.[23] They showed that Rhodamine B degradation decreased in the presence of $Cl^-$, $HCO^{3-}$, and $CO_3^{2-}$, which was due to the scavenging of hydroxyl radicals.[23]

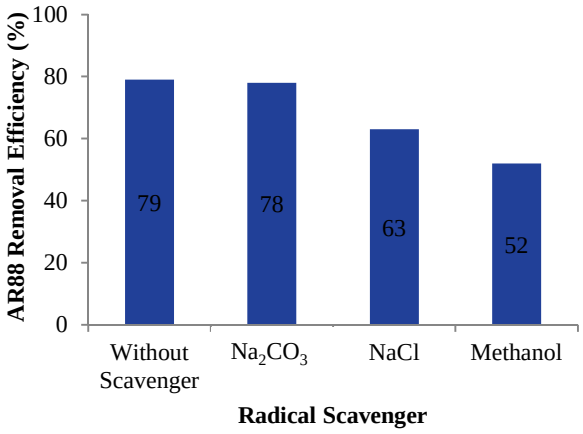



**Figure 6. Effect of radical scavengers on the photocatalytic removal of Acid Red 88 (AR88) from aqueous solutions (initial dye concentration: 50 mg/l, pH: 7, time: 120 minutes)**

### *Effect of Enhancers*

In the present study, the effect of different enhancers, including $H_2O_2$, EDTA, and $FeSO_4$, on the photocatalytic removal of AR88 from aqueous solutions was investigated and the results are shown in figure 7. The results revealed that the addition of 1 mM $H_2O_2$, EDTA, and $FeSO_4$ into the dye solution (50 mg/l), at neutral pH and for 120 minutes, increases the removal efficiency of the dye by 97%, 99%, and 83%, respectively, from the constant removal of 79%. Subramonian and Wu, in their study on the effectiveness of enhancers on the photocatalytic process, showed that the addition of enhancers ($H_2O_2$ and $S_2O_8^{2-}$) results in the degradation of more dye molecules through the production of more hydroxyl radicals.[24] Similar results have been reported by other researchers.[25] A study on the removal and mineralization of reactive Yellow 86 dye showed that the presence of ferrous ions ($Fe^{+2}$) in the photo-Fenton process causes an increase in $OH^0$ generation, and therefore, increase in the photocatalytic decomposition of dye molecules.[26] In photocatalytic processes, EDTA acts as electron donor and scavenger of valence band holes and provides more radicals by delaying the electron-hole recombination on the particles and also enough time for photoactinic processes. The results of the study by Asgari and Ayati showed that photocatalytic removal of dye is faster in the presence of EDTA compared with its absence, which corresponds with the results of the present study.[27]

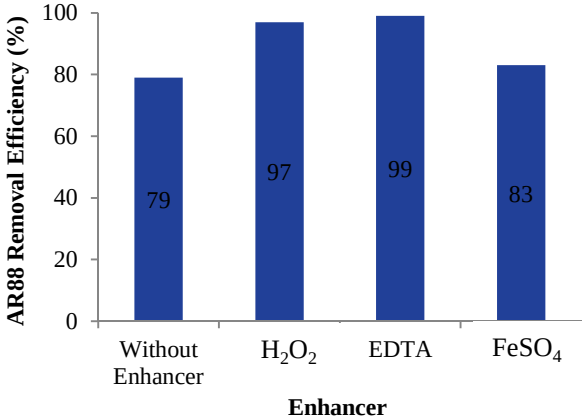



**Figure 7. Effect of enhancers on the photocatalytic removal of Acid Red 88 (AR88) from aqueous solutions (initial dye concentration: 50 mg/l, pH: 7, time: 120 minutes)**
EDTA: Ethylenediaminetetraacetic acid

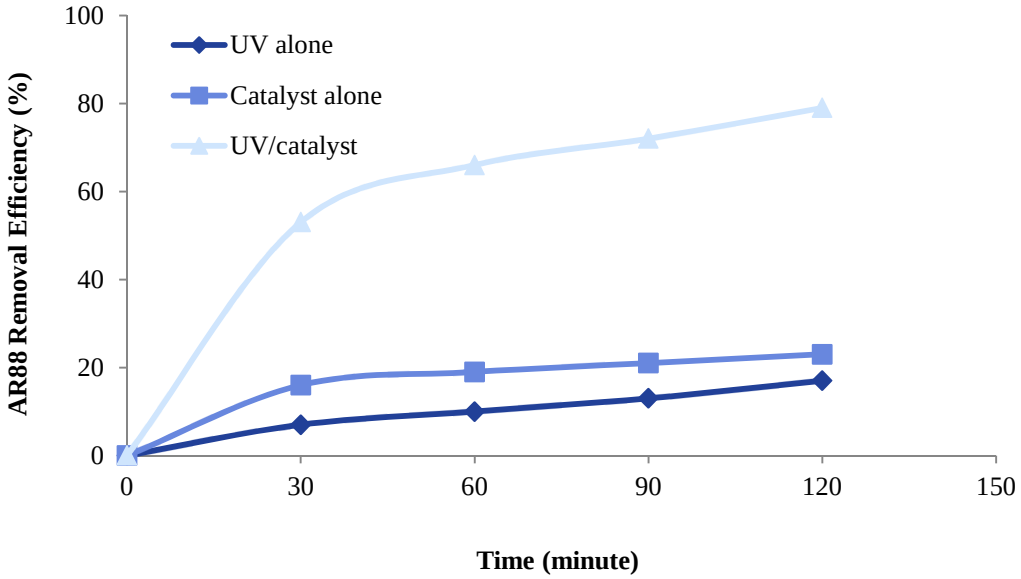



**Figure 8. Comparison of photolysis, nanocatalyst alone, and photocatalysis processes in the removal of Acid Red 88 (AR88) from aqueous solutions (initial dye concentration: 50 mg/l, pH: 7, time: 120 minute)**

*Comparison of processes*

To determine the effect of important parameters in photocatalytic decomposition of dye removal, adsorption, photolysis, and photocatalytic processes were studied using nanoparticles, UV light, and a combination of nanoparticles and UV light. Therefore, the experiments were performed on dye concentration of 50 mg/l, at pH of 7 and time intervals of 30, 60, 90, and 120 minutes. Figure 8 shows the comparison of photolysis, nanocatalyst alone, and photocatalysis processes in the removal of AR88 from aqueous solutions. The results indicate that the dye removal efficiency using photolysis process (without catalyst), catalyst alone, and the simultaneous use of both was 17, 23, and 79%, respectively. This finding could be attributed to the fact that the UV light or catalyst, separately, cannot produce enough hydroxyl radicals as the main dye degradation factor.[28] Shanthi and Kuzhalosai reported the same result for the removal of azo dye.[29] They reported that the use of photolysis, or the catalyst alone had little effect on the dye degradation, but the simultaneous application of both resulted in a high removal of dye.[29]

## Conclusion

The removal of AR88 from aqueous solution using fixed ZnO photocatalysis under UV light irradiation was studied in the present research. The results showed that the highest removal efficiency was achieved at the neutral pH of 7 (79%). In acidic and alkaline pH, the removal efficiency decreased. By increasing the initial concentration of dye from 10 to 100 mg/l, the removal efficiency decreased from 92 to 45%. The addition of radical scavengers at optimum condition resulted in the decreasing of the removal efficiency, but with the addition of the enhancer the removal efficiency of AR88 was improved. The results of this study confirmed that photocatalysis using fixed ZnO nanoparticles is an efficient method for the removal of textile dyes from aqueous solution.

## Conflict of Interests

Authors have no conflict of interests.

## Acknowledgements

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## References

1. Darvishi Cheshmeh Soltani R, Khataee AR, Safari M, Joo SW. Preparation of bio-silica/chitosan nanocomposite for adsorption of a textile dye in aqueous solutions. International Biodeterioration & Biodegradation 2013; 85: 383-91.
2. Darvishi Cheshmeh Soltani R, Khataee AR, Safari M, Ghanadzadeh MJ, Rajaei MS. Response surface methodological evaluation of the adsorption of textile dye onto biosilica/alginate nanobiocomposite: thermodynamic, kinetic, and isotherm studies. Desalination and Water Treatment 2014; 1-14.
3. Behnajady MA, Modirshahla N, Hamzavi R. Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. J Hazard Mater 2006; 133(1-3): 226-32.
4. Sun JH, Shi SH, Lee YF, Sun SP. Fenton oxidative decolorization of the azo dye Direct Blue 15 in aqueous solution. Chemical Engineering Journal 2009; 155(3): 680-3.
5. Madhavan J, Sathish Kumar PS, Anandan S, Grieser F, Ashokkumar M. Degradation of acid red 88 by the combination of sonolysis and photocatalysis. Separation and Purification Technology 2010; 74(3): 336-41.
6. Noori Motlagh Z, Darvishi R, Shams Khoramabadi G, Godini H, Foroughi M. Study of Methylene Blue Using UV radiation in Study of the Effective Parameters on Decolorizationof Methylene Blue Using UV radiation in the Presence of Immobilized Catalyst. J Ilam Univ Med Sci 2013; 21(1): 36-46. [In Persian].
7. Konicki W, Pelech I, Mijowska E, Jasinska I. Adsorption Kinetics of Acid Dye Acid Red 88 onto Magnetic Multi-Walled Carbon Nanotubes-Fe3C Nanocomposite. CLEAN - Soil, Air, Water 2014; 42(3): 284-94.
8. Batool S, Akib Sh, Ahmad M, Balkhair KS, Ashraf MA. Study of modern nanoenhanced techniques for removal of dyes and water. Journal of Nanomaterials 2014; 2014: 20.
9. Masombaigi H, Rezaee A, Nasiri A. Photocatalytic Degradation of Methylene Blue using ZnO Nano-Particles. Iran J Health Environ 2009; 2(3): 188-95.
10. Mozia S, Tomaszewska M, Morawski AW. Photocatalytic degradation of azo-dye Acid Red 18. Desalination 2005; 185(1–3): 449-56.
11. Alqaragully MB. Removal of Textile Dyes (Maxilon Blue, and Methyl Orange) by Date Stones Activated Carbon. International Journal of Advanced Research in Chemical Science 2014; 1(1): 48-59.
12. Darvishi Cheshmeh Soltani R, Rezaee A, Rezaee R, Safari M, Hashemi H. Photocatalytic degradation of methylene blue dye over immobilized ZnO nanoparticles: Optimization of calcination conditions. J Adv Environ Health Res 2015; 3(1): 8-14.
13. Kamat PS, Huehn R, Nicolaescu R. Semiconductor Nanostructures for Simultaneous Detection and Degradation of Organic Contaminants in Water. J Photochem Photobiol A: Chem 2008; 42(573): 577.
14. Bayat Beed Koupeh R, Ebrahimi M, Keyvani B. Removal of Acid red 206 Dye in Pollutant Water by ZnFe2O4/Bentonite as a Nanophotocatalyst in Batch Reactor Using Taguachi Method. Journal of water and wastewater 2013; 24(3): 128-35. [In Persian].
15. Darvishi Cheshmeh Soltani R, Rezaee A, Safari M, Khataee AR, Karimi B. Photocatalytic degradation of formaldehyde in aqueous solution using ZnO nanoparticles immobilized on glass plates. Desalination and Water Treatment 2015; 53(6): 1613-20.
16. Behnajady MA, Modirshahla N, Daneshvar N, Rabbani M. Photocatalytic degradation of C.I. Acid Red 27 by immobilized ZnO on glass plates in continuous-mode. J Hazard Mater 2007; 140(1-2): 257-63.
17. Mekasuwandumrong O, Pawinrat P, Praserthdam P, Panpranot J. Effects of synthesis conditions and annealing post-treatment on the photocatalytic activities of ZnO nanoparticles in the degradation of methylene blue dye. Chemical Engineering Journal 2010; 164(1): 77-84.
18. Al-Ghouti MA, Khraisheh MA, Allen SJ, Ahmad MN. The removal of dyes from textile wastewater: a study of the physical

characteristics and adsorption mechanisms of diatomaceous earth. J Environ Manage 2003; 69(3): 229-38.
19. Patterson AL. The Scherrer Formula for X-Ray Particle Size Determination. Phys Rev 1939; 56(10): 978-82.
20. Uzun I. Kinetics of the Adsorption of Reactive Dyes by Chitosan. Dyes and Pigments 2006; 70(2): 76-83.
21. Daneshvar N, Rasoulifard MH, Khataee AR, Hosseinzadeh F. Removal of C.I. Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder. J Hazard Mater 2007; 143(1-2): 95-101.
22. Grzechulska J, Morawski AW. Photocatalytic decomposition of azo-dye acid black 1 in water over modified titanium dioxide. Applied Catalysis B: Environmental 2002; 36(1): 45-51.
23. Daneshvar N, Behnajady MA, Mohammadi MKA, Dorraji MSS. UV/H2O2 treatment of Rhodamine B in aqueous solution: Influence of operational parameters and kinetic modeling. Desalination 2008; 230(1–3): 16-26.
24. Subramonian W, Wu TY. Effect of Enhancers and Inhibitors on Photocatalytic Sunlight Treatment of Methylene Blue. Water, Air, & Soil Pollution 2014; 225(4): 1922.
25. Abo-Farha SA. Photocatalytic Degradation of Monoazo and Diazo Dyes in Wastewater on Nanometer-Sized TiO2. Journal of American Science 2010; 6(11): 130-42.
26. Surana M, Mehta P, Pamecha K, Kabra BV. The decolourization and mineralization of azo dye reactive yellow 86 in aqueous solution by photo-Fenton Reagent, D. Pharma Chemica 2011; 3(2): 39-47.
27. Asgari R, Ayati B. Using the EDTA Hole Scavenger to Accelerate Decolorization in the Immobilized Photocatalytic Process. Journal of Water & Wastewater 2015; 26(97): 19-27. [In Persian].
28. Rahmani Z, Kermani M, Mohammad Mahmoudi N. Performance Evaluation of advanced Photochemical Oxidation (UV/H2O2) and UV in BV16 and RR120 Dye Removal from aqueous solution. The Journal of Toloo-e-Behdasht 2014; 12(4): 135-49. [In Persian].
29. Shanthi M, Kuzhalosai V. Photocatalytic degradation of an azo dye, Acid Red 27, in aqueous solution using nano ZnO. Indian Journal of Chemistry-Section A 2012; 51(3): 428-34.