

Synthesis of $ZnAl_2O_4$ Nano-Particles and Its Application for Photo-Catalytic Decolourization of Model Azo Dye Acid Red 88 in Presence of Natural Sunlight

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Abstract: We describe the synthesis of $ZnAl_2O_4$ nanoparticles by simple and cost-effective solution combustion method. The prepared $ZnAl_2O_4$ nanoparticles were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV spectrophotometer and FT-IR spectra studies. It was calculated that the corresponding band gap was found to be 3.07eV for $ZnAl_2O_4$. The photocatalytic activity of $ZnAl_2O_4$ was determined against Acid red 88 (AR 88) dye. The experiments were carried out at different catalyst dosage, oxidant concentrations and pH variation with respect to identical dye concentration. The decolourisation was strongly enhanced in addition of proper amount of electron acceptor such as H_2O_2 . Thus, the results revealed that the AR 88 decolourisation efficiency increases with the increase in catalyst loading, oxidant concentrations and pH up to the optimal level. The maximum of 98.44% decolourisation was achieved in addition of H_2O_2 (1-4ml/0.4g/100ml) in 90 minutes with 98.02% of pH 11 (0.4g/100ml) in 90 min and 94.07% of decolourisation was reported in 0.4g/100ml of catalyst load. Hence, the efficiency of $ZnAl_2O_4$ nanoparticles and its influencing parameters in the decolourisation of AR 88 was ascertained.

Keywords: Acid red 88, azo dye, decolourisation, photo-catalyst, $ZnAl_2O_4$ nano particle.

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I. Introduction

Azo dyes used in textile industry are considered as a major source of environmental contamination and effluents from textile industry are toxic, non-biodegradable and resistant to destruction by physico-chemical treatment methods. Since the presence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably, the color removal from wastewaters is often more crucial than other colorless organic substances [1][2][3][4][5]. Various chemical and physical processes, such as chemical precipitation and separation of pollutants, electro-coagulation [6] elimination by adsorption on activated carbon etc., are currently used. Most of these methods are not ineffective and these methods only transfer the contamination from one phase to another and hence further treatments are deemed necessary [7][8]. In recent years, Advanced Oxidation Processes (AOPs) based on the generation of highly reactive species such as hydroxyl radicals that quickly and non-selectively oxidizes a broad range of organic pollutants, are reported as more effective and an alternate to conventional methods [9]. The present work was aimed to explore simple and cost-effective method to synthesize solar light active $ZnAl_2O_4$ nanoparticles and to investigate the influence of parameters such as catalyst dosage, oxidant concentrations and pH on photo-catalytic decolourisation of azo dye. One of the widely used textile azo dyes, Acid Red 88 (AR88) was selected as a model azo dye for photo-decolourisation experiments (Fig. 1), in the presence of the natural sunlight.

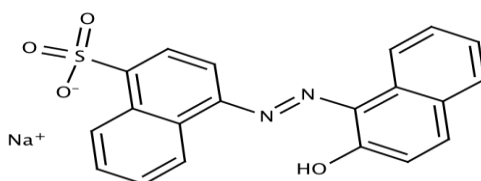


Figure 1: Structure of Acid Red 88 dye.

II. Experimental

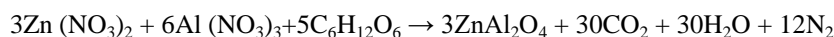
2.1 Materials

Zinc Nitrate (Zn(NO₃)₂ · 6H₂O), AR and Aluminum Nitrate (Al(NO₃)₃ · 9H₂O) for the synthesis of ZnAl₂O₄ nanoparticle were procured from Loba Chemicals, Mumbai and Dextrose (anhydrous) (C₆H₁₂O₆) was procured from SD Fine chemicals limited, Mumbai. Hydrochloric acid (LR, 35.0%) and Sodium hydroxide (LR, ≥ 97%), which are used for adjusting the pH of the dye solution, were procured from RFCL Limited, New Delhi and MERCK, Mumbai respectively. Model Dye Acid Red 88 (azo dye) was procured from Panam Biochemicals, Bangalore and used without further purification. Its structure is given in Fig. 1.

The λ_{max} of the dye solution was determined by UV-VIS Spectrophotometer 169 (Systronics, India) and relative absorbance with respect to time was determined by UV-VIS Spectrophotometer 119 (Systronics, India).

2.2 Synthesis of ZnAl₂O₄ nanoparticles:

The ZnAl₂O₄ nano-particle was prepared by solution combustion method using Zn(NO₃)₂ · 6H₂O, Al(NO₃)₃ · 9H₂O and C₆H₁₂O₆ (as fuel). Initially, Zn(NO₃)₂ · 6H₂O (3.3mol), Al(NO₃)₃ · 9H₂O (4.164mol) and C₆H₁₂O₆ (5mol) were dissolved in minimum quantity of water at 2:2:5 molar ratio in a silica crucible. The crucible was introduced to the muffle furnace and then muffle furnace was heated from room temperature to 600° C. The solution boils and undergoes dehydration followed by decomposition along with the release of the certain amount of gases, it swells forming foam which ruptures with a flame. The product formed after combustion is a voluminous and foamy ZnAl₂O₄. After the complete combustion, the crucible was taken out and allowed to cool. According to the propellant chemistry, the following reaction takes place during combustion [10]



2.3 Characterization of ZnAl₂O₄ nanoparticles:

2.3.1 X-Ray Diffraction:

The average crystallite size (D in nm) of synthesized ZnAl₂O₄ particle was determined from XRD pattern of the ZnAl₂O₄ nano-particles (figure.2) according to the Scherrer's equation, i.e., $D = k (\lambda / \beta \cos \theta)$ where k is a constant equal to 0.9, λ the X-ray wavelength equal to 0.154 nm, β the full width at half maximum and θ the half diffraction angle [11]. The average crystallite size of ZnAl₂O₄ nanoparticles was 37nm

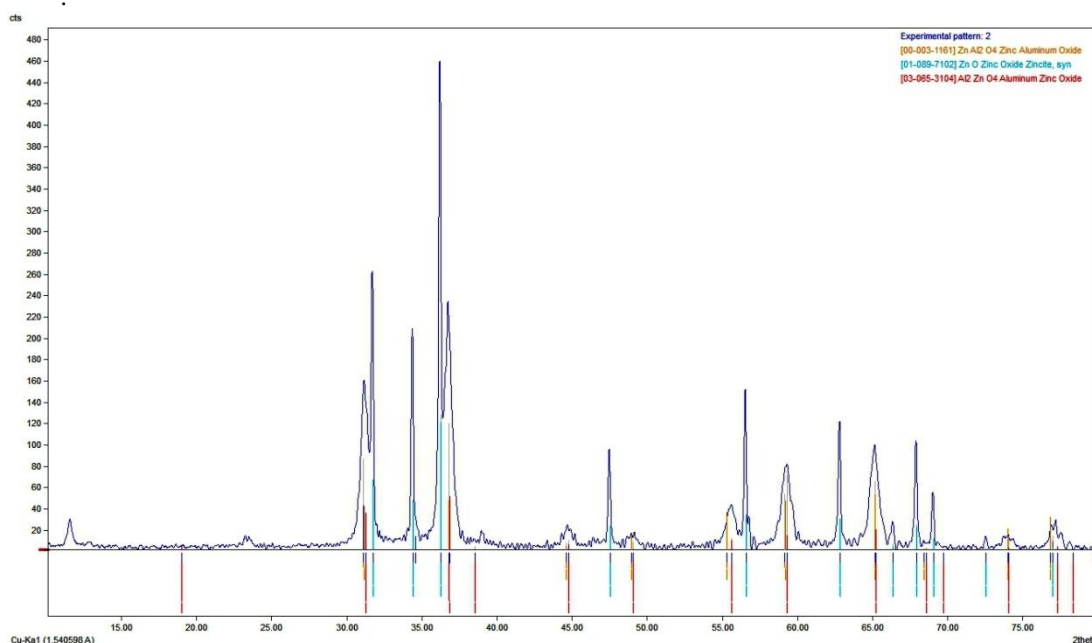


Figure 2: X-Ray Diffraction pattern of synthesized ZnAl₂O₄ nanoparticles.

2.3.2 Scanning Electron Microscopy (SEM):

The sample precursors of ZnAl₂O₄ were examined by SEM to study the structure of the synthesized nanoparticles. The SEM images of prepared ZnAl₂O₄ compound exhibited irregular, dense crystals like appearance and non-uniform flakes like structure (Fig. 3).

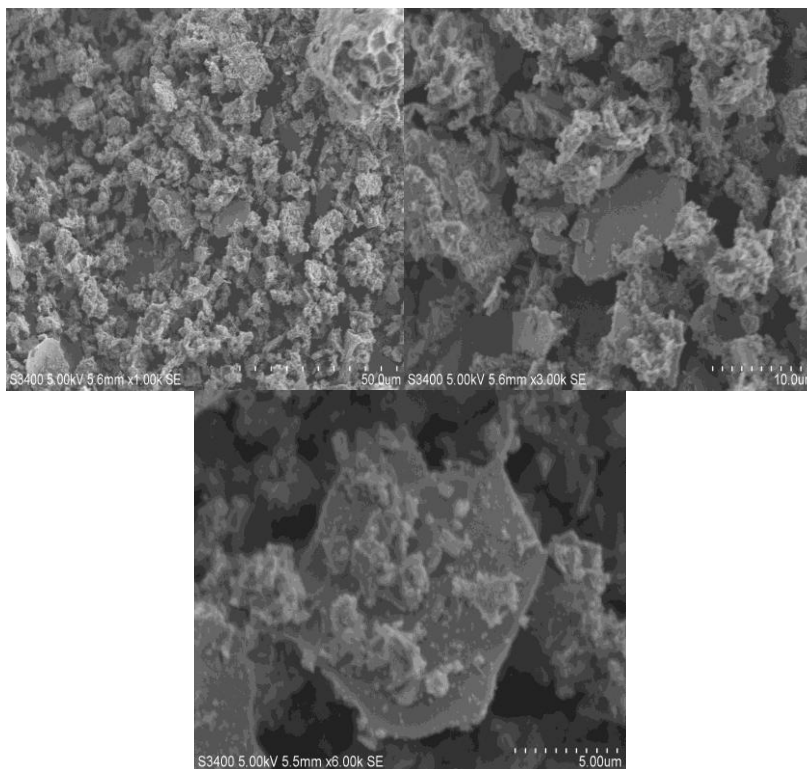


Figure 3: SEM photograph of ZnAl₂O₄

2.3.3 UV-Vis Spectroscopy:

The UV-Vis absorption spectra of ZnAl₂O₄ nano particles were recorded by taking its powder form directly as shown in fig.4. For recording UV-Vis spectra the sample of ZnAl₂O₄ was recorded over the wavelength range 200- 1000nm and the spectral data showed the strong cut off appears at 402.32nm [12]. The band gap energy of ZnAl₂O₄ nanoparticle was calculated by using the formula $E_g = hc/\lambda$, where h =Planck's constant, c =velocity of light and λ =wavelength. It was noticed that the corresponding band gap was found to be 3.07eV.

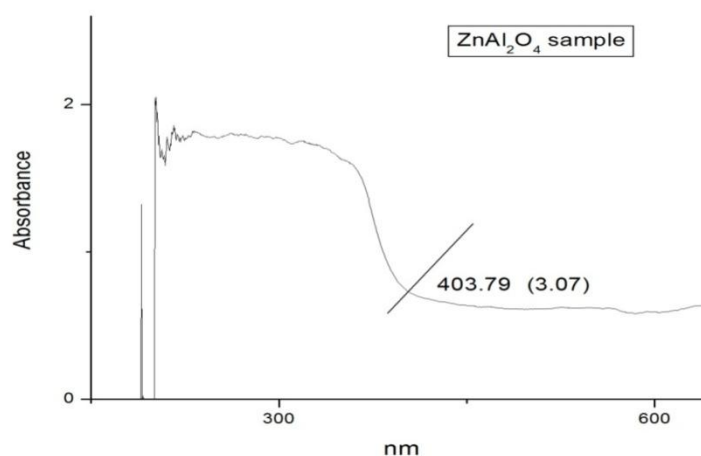


Figure 4: UV-Vis spectra of ZnAl₂O₄nanoparticle

2.3.4 FT-IR Spectroscopy

Fig:5 illustrates the infrared spectrum of the prepared nanoparticle ignited at 600°C. When ignited at 600°C the absorption peaks are centered at 3406.59 cm⁻¹ was attributed to the O-H stretching band and the band 1364.31 cm⁻¹ was O-H bending band. These bands are the evidence for the presence of water in prepared nanoparticle. However, the strong peak observed at 505.17 cm⁻¹ was assigned to Zn-Al-O stretching band, which indicating the presence of ZnAl₂O₄nanoparticle in ignited compound [13].

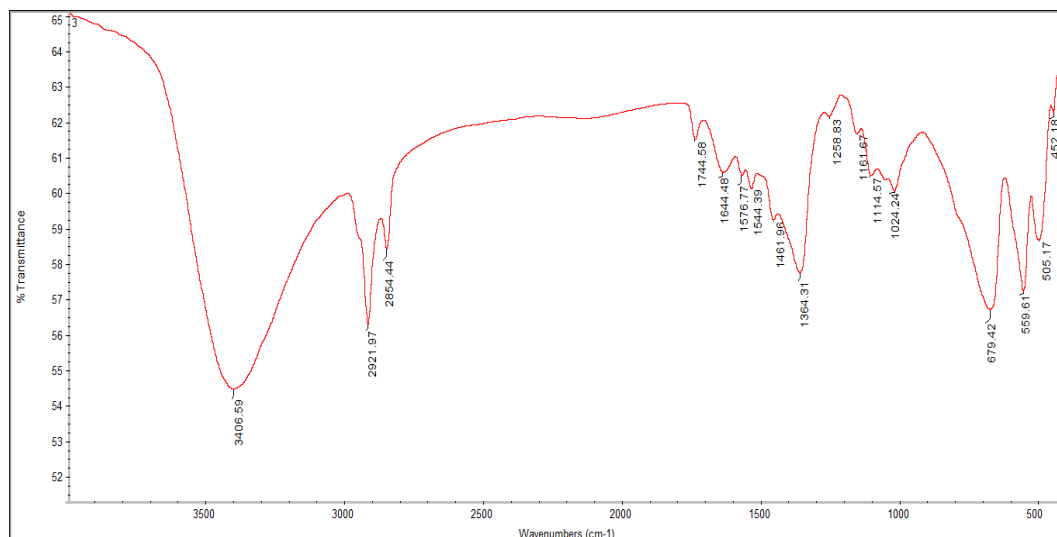


Figure 5: FT-IR Spectra of prepared ZnAl₂O₄ nanoparticles

2.4 Experimental procedure:

The series of photo-catalytic experiments were carried out in batch mode using glass reactors of 100ml capacity. The reactors were ensured with enough supply of oxygen in the reaction solution. Initially, 500ppm dye solution was prepared by dissolving 0.5g of Acid Red 88 in 1000 ml distilled water and transferred to 7 glass reactors including control sample. The solution containing photocatalyst at different catalyst dosages (0.1g to 0.6g) was magnetically stirred in darkness for 2 to 3 min to establish adsorption equilibrium prior to photoreaction. After each 30-minute interval of irradiation time, a 5-ml aliquot of the reaction volume was taken, centrifuged and concentration of Acid Red 88 was monitored spectrophotometrically by recording absorbance of the supernatant at a wavelength of 504nm (λ_{max}). The reaction mixture was regularly stirred after each sampling time throughout the reaction to keep the mixture in suspension. To study the effect of pH the experiments were conducted at different pH levels (pH 3 to pH 12) at optimum catalyst dosage. Further, the experiments were repeated at optimum catalyst dosage and for the standard 500ppm dye solution to study the effect of the addition of H₂O₂ (2ml/100ml of reaction volume). The percentage of decolourization was calculated by using the following formula.

The percentage of decolourization = $[(A_0 - A_t) \div A_0] \times 100$

Where, A₀ is the initial absorbance of the dye solution, A_t is the absorbance at time interval 't'.

III. Results And Discussions:

2.5 Effect of photo-catalyst loading:

The effect of the ZnAl₂O₄ photocatalyst weight on the percentage removal of AR 88 was studied from 0 to 0.6g/100ml photocatalyst, at 500ppm dye concentration and pH 7. The results are shown in Fig.6. The amount of catalyst is one of the main parameters for the decolourisation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. Most of the authors have investigated that the reaction rate as a function of catalyst loading in photocatalytic oxidation process [14][15][16]. The results clearly depict that the increase of catalyst weight from 0.1 to 0.4g/100ml increases the dye decolourization sharply from 37.22% to 94.07% at 90 min. The enhancement of removal rate is due to (i) the increase in the amount of catalyst weight which increases the number of dye molecule adsorbed (ii) the increase in the density of particles in the area of illumination [17]. But at concentrations from 0.4 to 0.6g/100ml the decolourization efficiencies are slightly decreased and remain as almost constant. This may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration. The optimum concentration of the catalyst for efficient solar photo-decolourization is found to be 0.4g/100ml. Hence 0.4g/100ml was used as the catalyst dosage for the photocatalytic reaction.

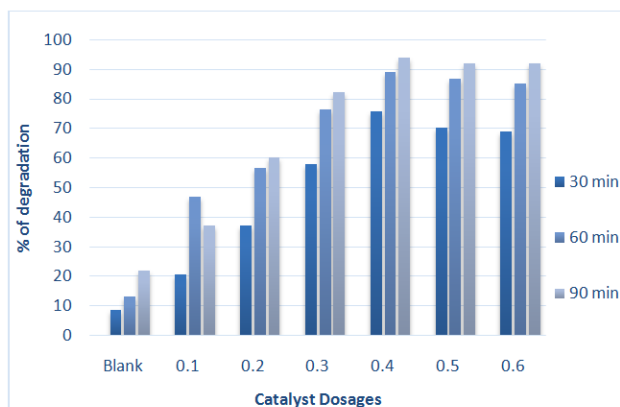


Figure 6: Effect of catalyst dosage ZnAl₂O₄ on the photo-decolourization efficiency of Acid Red 88 dye under solar irradiation time of 90 min. Dye concentration: 500ppm; pH 7.0.

2.6 Addition of Hydrogen peroxide:

To study the effect of addition of hydrogen peroxide (2-5ml) in 100ml each on photocatalytic decolourisation of AR88, experiments were conducted in solar irradiation at optimal catalyst dosages with neutral pH level which are given in Fig. 7.

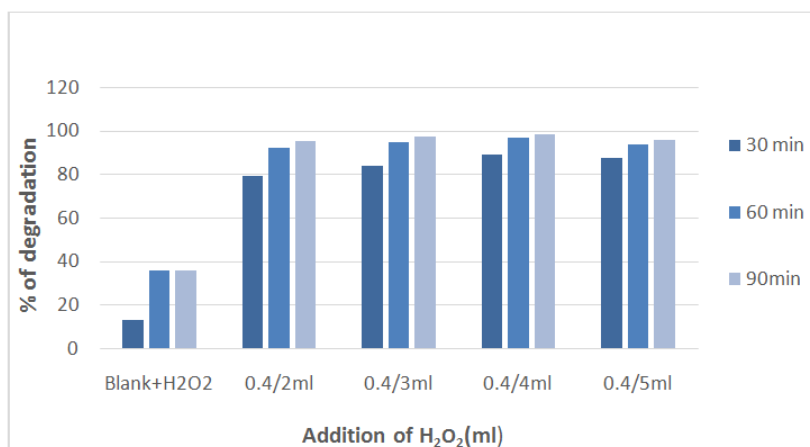
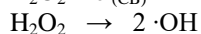
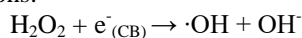
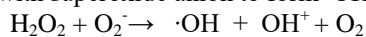


Figure 7: Effect of addition of H₂O₂(2-5ml) with optimal catalyst dosage (0.4g/100ml) on decolourization efficiency of AR 88 dye under solar irradiation time of 30, 60 and 90 min. pH 7; Dye concentration: 500ppm.

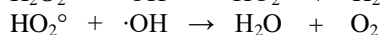
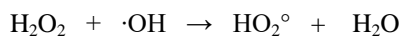
The decolourisation rate of AR88 increased with increasing addition of H₂O₂(2-4ml) from 79.13% to 88.78% in 30 min, 92.06% to 96.73% in 60 min and 95.23% to 98.44% in 90 min. Further increase of H₂O₂ concentration from 4 to 5ml which shows the decreases in the decolourization from 88.78% to 87.18 in 30 min, 96.73% to 93.48% in 60 min and 98.44% to 95.48% in 90 min of time interval. Hence 4ml H₂O₂ concentration in 100ml of dye solution appears to be optimal for decolourization. Decolorization was increased around by 2.36% in addition of H₂O₂ when compare to normal catalyst loading. A similar kind of observation (an increase in H₂O₂ level enhanced the decolourisation rate up to optimal load beyond which inhibition occur) had been reported in dye decolourisation [18]. The probable reason is that the addition of H₂O₂ increases the OH concentration which in turn increases OH radical population. The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radical as shown by the following equations:



H₂O₂ also reacts with superoxide anion to form ·OH radical.



At high H₂O₂ dosage (5ml/100ml) the removal rate of colour decreases due to its hydroxyl radical scavenging effect.



2.7 Effect of pH

The pH value is one of the factors influencing the rate of decolourisation of some of the organic compounds in the photo-catalytic process. The amphoteric nature of most metal oxide nanoparticle influences the surface charge of the photocatalyst. The influence of pH on adsorption capacity of AR88 onto ZnAl₂O₄ was investigated in the range of pH values from 3 to 12 at a fixed dye concentration of 500ppm with optimum catalyst amount (0.4g/100ml). The effect of pH on the decolourisation of AR88 is illustrated in the fig.8.

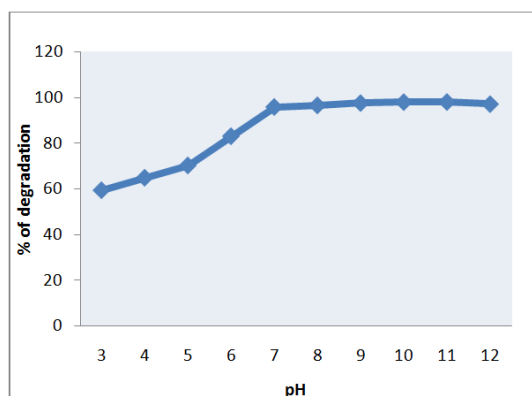


Figure 8: Effect of pH (3 to 12/0.4gm/100ml) on photo-catalytic decolourisation of Acid Red 88 at irradiation time of 90 min. Dye concentration: 500ppm

Increases in pH of a dye solution from 3 to 11 increases the decolourisation rate from 59.36% to 98.02% at 90 min and which slightly get decreases in photo-decolourisation rate from 98.02% to 97.08% at 90 min of dye solution pH ranges from 11 to 12. This clearly shows that the best results were obtained in alkaline conditions than in acidic range. The optimum decolourisation was achieved at pH 11, *i.e.*, almost 98% in just 90 minutes at 0.4g/100ml of catalyst load. Similar kind of observations reported in earlier studies [19][20][21][22]. At acidic pH range the removal efficiency is minimum, this may be due to the ZnAl₂O₄ nanoparticle agglomeration reduces the dye adsorption as well as photon absorption.

IV. Conclusion

The present study showed that in the presence of natural sunlight synthesized ZnAl₂O₄ nanoparticle were highly active, it could be more efficiently photo-degrade the AR 88 red azo dye. Direct exposure of dye solution to solar light leads to its decolourisation at minimal level when photolysis was carried out in the absence of ZnAl₂O₄. The presence of small amount of ZnAl₂O₄ nanoparticle which accelerates the dye decolourisation. The obtained results indicated that the degree of degradation of AR88 were normally effected by the amount of ZnAl₂O₄, H₂O₂ concentration and pH variations. As we observed that optimal catalyst dosage was found to be 0.4g/100ml with dye concentration of 500ppm. The addition of appropriate amount of hydrogen peroxide has improved the photo-decolourisation rate. However, at high concentration, H₂O₂ would quench the hydroxyl radicals. Furthermore, the rate of decolourisation of Acid red 88 linearly depends on the illumination of solar light with different time periods. Since it can be proved that ZnAl₂O₄ nanoparticles can be efficiently used for the photocatalysis of dyes in aqueous environment. These techniques could implement to ensure more problem of cleaning large volume of wastewater to a certain extent in short time.

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