

Photocatalytic degradation of an azo dye, Acid Red 27, in aqueous solution using nano ZnO

M Shanthi* & V Kuzhalosai

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

Email: shanthism@gmail.com

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Photocatalytic degradation of Acid Red 27 by nano ZnO has been investigated under different conditions. Optimum experimental conditions on catalyst amount, pH and dye concentration have been determined. Addition of some inorganic oxidizing species such as H_2O_2 , $K_2S_2O_8$ and $KBrO_3$ up to a certain concentration increases the rate of degradation. The photodecolourisation and degradation kinetics are discussed in terms of Langmuir-Hinshelwood kinetic model.

Keywords: Photocatalysis, Photodegradation, UV light, Dyes, Zinc oxide, Azo dyes

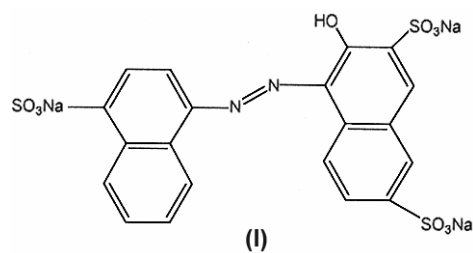
The disposal of a large amount of effluent from textile industry produces severe environmental hazards because this effluent normally contains appreciable quantities of organic compounds that are not easily degraded by conventional waste water treatment methods such as adsorption, biological treatment, coagulation, etc¹. Several efforts have been made to develop efficient and cost-effective methods to solve this environmental problem. Advanced oxidation processes (AOPS) emerge as an attractive alternative for treating waste water containing various organic compounds, especially unsaturated organic compounds²⁻⁷ like azo dyes. In theory, most AOPS are based on the generation of hydroxyl radicals, which are highly reactive and non-selective. Therefore, the AOPS are able to oxidize a wide range of organic compounds. Production of eco-friendly end product is the special feature of these processes.

Heterogenous photocatalysis using non-toxic semiconductor catalyst is one of the promising AOPS. ZnO is a representative of the metal oxide class, which is important for the study of electrochemistry catalysis⁸. Recent developments and technology have proved that the research on nanostructures has rapidly expanded because of their unique and novel applications in optics, catalysis and biological science, particularly, the ZnO nano systems have exciting applications owing to their polymorphological structures⁹.

For photocatalytic degradation studies, nano sized ZnO is preferred compared to large sized ZnO particles. The two most important properties of a nanomaterial, which makes it superior to other

microscopic (or) macroscopic particles for application to catalysis are (i) the high surface to volume ratio and (ii) the quantum confinement at the nano scale. The first property results in catalysts with high surface area and high porosity, which ensures enhanced reaction rates due to the high level of interaction of the reactants with the active sites. The second property governs the transport of electrons and holes from the bulk to the surface of the material, whose length scale is also of the order of a few nanometers. Moreover, for photoapplications, the catalyst should absorb and not block or scatter the incident radiation and generate charge carriers by band gap excitation. This is possible only with nano sized semiconductor materials with suitable band gap energy. Therefore, owing to the enhanced molecular transport properties of the surface, it is evident that nano sized materials are beneficial as photocatalyst¹⁰.

In the present study, we have taken a reactive mono azo dye, Acid Red 27 (I) ($\lambda_{max} = 521$ and 332 nm) and examined the various parameters for the optimum conditions for the removal of aromatic content of the dye.



Materials and Methods

The commercial azo dye Acid Red 27 (AR 27) obtained from Colour Chem, Pondicherry, was used as such. The photocatalyst, nano ZnO purchased from Aldrich Chemical company, had particle size of <100 nm and surface area of 15-45 m²/g. Analar grade reagents, H₂O₂, K₂S₂O₈ and KBrO₃ (E. Merck) were used as received. Doubly distilled water was used to prepare experimental solutions. The pH of the solutions was adjusted using H₂SO₄ and NaOH. The pH of the solution was measured by using Hanna Phep (model H 198107) digital pH meter.

Photoreactor

Heber multilamp photoreactor (Fig. 1) was used for the photoreaction. This model consists of eight medium-pressure mercury vapour lamps (8 W) set in parallel and emitting at 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and a built-in cooling fan at the bottom. It is provided with a magnetic stirrer at the centre. Open borosilicate glass tube of 50 mL capacity (40 cm height and 20 mm dia.) was used as the reaction vessel with total light exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure mercury lamps in open air. The solution with nano ZnO and dye was continuously aerated by a pump to provide oxygen and for complete mixing of the reaction solution.

Methodology

In all experiments, 50 mL of reaction mixture was irradiated. The suspension was stirred for 30 min in dark for attainment of adsorption equilibrium. At specific time intervals, 2 mL of the sample was withdrawn and centrifuged to separate the nano zinc oxide. The sample (1 mL) was suitably diluted and its

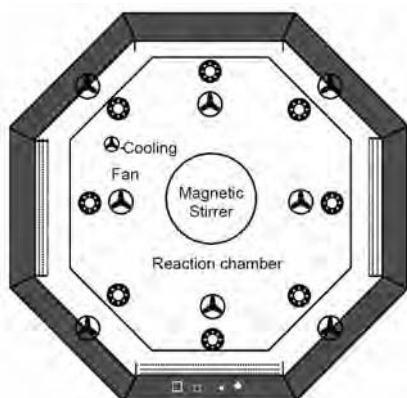


Fig. 1—Schematic diagram of photoreactor.

absorbances at 521 and 332 nm were measured immediately. Absorbance at 521 nm was due to the colour of the dye solutions and was used to monitor the decolourisation of dye. The absorbance at 332 nm represents the aromatic content of dye and the decrease of absorbance at 332 nm indicated the degradation of aromatic part of dye. UV spectral measurements were made using Shimadzu UV 1650 PC UV-visible spectrophotometer.

Results and Discussion

Photodegradation of the dye

Figure 2 shows the results of photodegradation with and without nano ZnO-UV light. In the absence of photocatalyst, the dye solution on irradiation with the UV light has been found to be stable. In the presence of nano ZnO and in the absence of UV light, there is a small decrease in dye concentration initially and the dye solution is stable till the end of the experiment. The initial decrease is due to the adsorption of the dye molecule on the surface of nano ZnO. Simultaneous irradiation and aeration with the catalyst caused 68.6 % decolourisation and 49.5 % degradation after 60 minutes. The changes in UV-visible spectra was shown in Fig. 3.

Effect of catalyst loading

The amount of catalyst is one of the main parameters for the degradation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. To determine the optimal dosage of the catalyst,

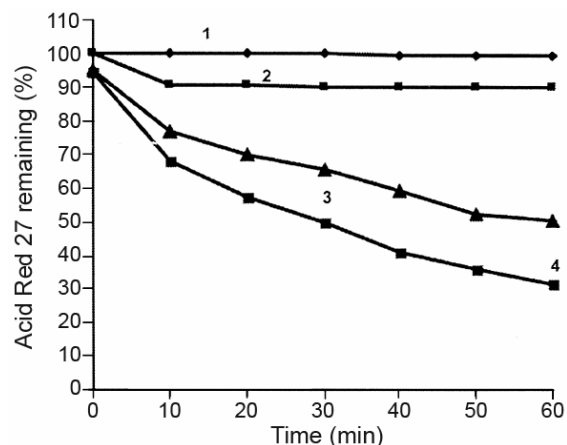


Fig. 2—Photodegradability of Acid Red 27 dye using UV light/nano ZnO. [1, Dye solution irradiated with UV light in the absence of nano ZnO. 2, Dye solution treated with nano ZnO in dark; 3, Degradation of dye solution with UV light in the presence of nano ZnO; 4, Decolourisation of dye solution with UV light in the presence of nano ZnO].

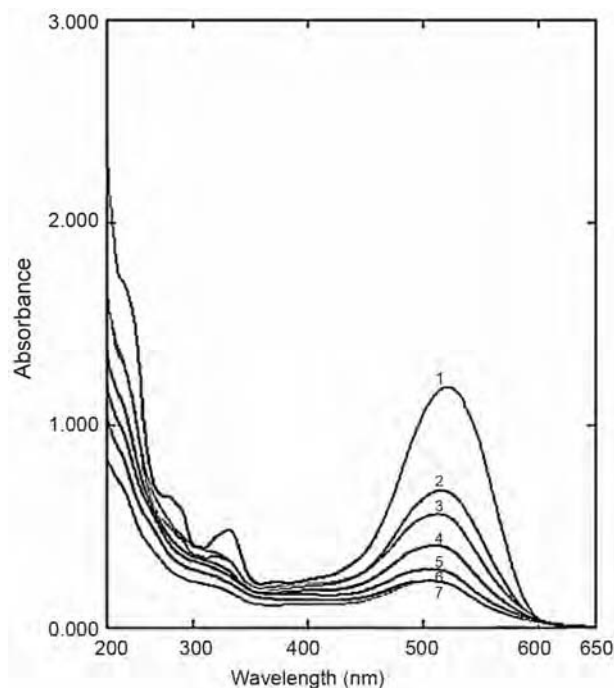


Fig. 3—UV-visible spectra of Acid Red 27 on irradiation in presence of nano ZnO. {ZnO = 100 mg/ 50 mL; [AR 27] = 5×10^{-4} mol/L; pH = 7 ± 0.1 . 1, 0 min; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 50 min; 7, 60 min}.

varying 50–150 mg were mixed with 50 mL of the dye solution. Studies show that when catalyst dosage was increased from 50 to 100 mg, the decolourisation increases from 42.7 to 58.9 % and degradation from 30.5 to 41.2 %. However, on further increase in the dosage of the catalyst beyond 100 mg, there is a slight decrease in the dye removal rate. Increase of the catalyst loading beyond the optimal dosage may cause screening effect. This effect reduces the specific activity of the catalyst¹¹. At higher dosage of the catalyst, particle aggregation may also reduce the catalytic activity. The optimum concentration of the catalyst for efficient UV photodecolourisation and degradation is found to be 100 mg/50 mL. Hence, 100 mg/50 mL was used as the catalyst dosage for the photocatalytic degradation of Acid Red 27 dye.

Effect of pH

An important parameter that influences the photocatalytic degradation is solution pH. The effect of pH from 3–11 on the decolourisation and degradation was studied. Increase of pH of the dye solution from 3 to 7 increases the decolourisation from 30.4 to 58.9 % and degradation from 24.9 to 41.2 % at 40 min. irradiation time. A slight increase in

the degradation rate 48.5 % was observed on further rise in pH from 7–11 while decolourisation increased to 66.1 %. The photocatalytic removal of colour and degradation were observed to be faster in slightly alkaline pH than in acidic pH range^{12–15}. Similar results were reported in literature for acidic dyes bearing sulfonate group. At high acidic condition, the removal efficiency is minimum. This is due to two reasons: (i) at low pH, ZnO particle agglomeration reduces the dye adsorption as well as photon absorption, and, (ii) in AR 27, the azo linkage (-N=N-) is particularly susceptible to electrophilic attack by hydroxyl radical. However, in low pH, the concentration of H⁺ ions is in excess and H⁺ ions interact with azo linkage decreasing the electron densities at azo group. Consequently the reactivity of hydroxyl radical by electrophilic mechanism is also decreased. Hence, at acidic pH range, degradation efficiency is minimum. The increased efficiency in the alkaline pH range may be explained on the basis of increase in the formation of OH radicals with increase in pH. In our earlier work for the degradation of O-cresol using AOP we observed similar efficiencies¹⁶. In acid and neutral solution the formation of OH radical can be given by the equation, $\text{H}_2\text{O} + \text{h}^+_{(\text{VB})} \rightarrow \cdot\text{OH} + \text{H}^+$. In alkaline solution the OH radical is also formed from hydroxide ion $\text{OH}^- + \text{h}^+_{(\text{VB})} \rightarrow \cdot\text{OH}$.

Effect of dye concentration

The effect of various initial dye concentrations on the photocatalytic decolourisation and degradation has been investigated from 1×10^{-4} to 9×10^{-4} mol/L.

It is found that increase in the dye concentration decreases the removal rate. Similar results have been reported for the photocatalytic oxidation of other dyes. Increase in the concentration of dye from 1×10^{-4} to 9×10^{-4} mol/L decreases the decolourisation rate constant from 0.069–0.008 min⁻¹ and degradation rate constant from 0.040–0.001 min⁻¹. When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases, which affects the catalytic activity of nano ZnO. The increase in dye concentration also decreases the path length of photon entering the dye solution. At high dye concentration a significant amount of UV light may be absorbed by the dye molecules rather than by the catalyst which may also reduce the catalytic efficiency^{17,18}.

The photocatalytic decolourisation and degradation of AR 27 dye containing nano ZnO obeys pseudo-first

order kinetics. At low initial dye concentration the rate expression is given by $\frac{-d[C]}{dt} = k'[C]$, where k' is the pseudo first order rate constant. The dye is adsorbed on to the ZnO surface and the adsorption-desorption equilibrium is reached in 30 min. After adsorption the equilibrium concentration of the dye solution was determined and taken as the initial dye concentration for kinetic analysis. On integration, (with the limit of $c = c_0$ at $t = 0$) with c_0 being the equilibrium concentration of the bulk solution, $\ln\left[\frac{C_0}{C}\right] = k't$, where c_0 is the equilibrium concentration of dye and c is the concentration at time t .

A plot of $\ln C_0/C$ versus t for photodecolourisation and degradation is shown in Fig. 4. A linear relationship between dye concentration and irradiation time has been observed.

The Langmuir-Hinshelwood (C-H) kinetic expression has been used to analyse the heterogeneous photocatalytic reaction successfully. The experimental

data have been rationalised in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction successfully¹⁹. The rate of oxidation of AR 27 dye at the surface is proportional to the surface coverage of dye on nano ZnO assuming that the adsorption of the dye on the catalyst surface is stronger than that of the intermediate products²⁰. The effect of the dye concentration on the rate of degradation is given in the following form²¹, $r = K_1K_2C/l + K_1C$ and $1/r = 1/K_1K_2C + 1/K_2$ where C is the concentration of the dye at time t , K_1 is the constant related to adsorption and K_2 is related to the reaction properties of the dye.

The applicability of L-H equation for the decolourisation and degradation has been confirmed by the linear plot obtained by plotting the reciprocal of initial rate ($1/r$) against reciprocal of initial concentration ($1/C$). The values K_1 and K_2 are found to be $1.57 \times 10^3 M^{-1}$ and $3.38 \times 10^{-5} M \text{ min}^{-1}$ for decolourisation and $0.97 \times 10^3 M^{-1}$ and $4.32 \times 10^{-5} M \text{ min}^{-1}$ for degradation respectively.

Effect of electron acceptors

In the photocatalytic reaction of nano ZnO, the major energy wasting step is electron-hole recombination which leads to low quantum yield. Hence, the prevention of electron-hole recombination becomes very important. This can be achieved by adding a proper electron donor (or) acceptor to the system. Usually molecular oxygen is used as an electron acceptor in a heterogeneous photocatalysed reaction. Besides the addition of molecular oxygen, the electron-hole recombination can be reduced by the addition of irreversible electron acceptors such as H_2O_2 , $K_2S_2O_8$ and $KBrO_3$. The addition of these electron acceptors enhanced the degradation rate in several ways, i.e., (i) preventing the electron-hole recombination by accepting the conduction band electron, (ii) increasing the hydroxyl radical concentration, and, (iii) generating other oxidizing species namely, sulphate radical anion to accelerate the intermediate compound oxidation rate.

Effect of addition of H_2O_2

The effect of three electron acceptors, viz., H_2O_2 , $K_2S_2O_8$ and $KBrO_3$ was studied. In order to maintain the efficiency of the added H_2O_2 , it is necessary to choose the optimum concentration of H_2O_2 (Table 1). The addition of H_2O_2 (5–10 mmol) increases the decolourisation from 65.5 to 70.6 % and degradation 48.4 to 55.9 % in 40 min. Further increase of H_2O_2

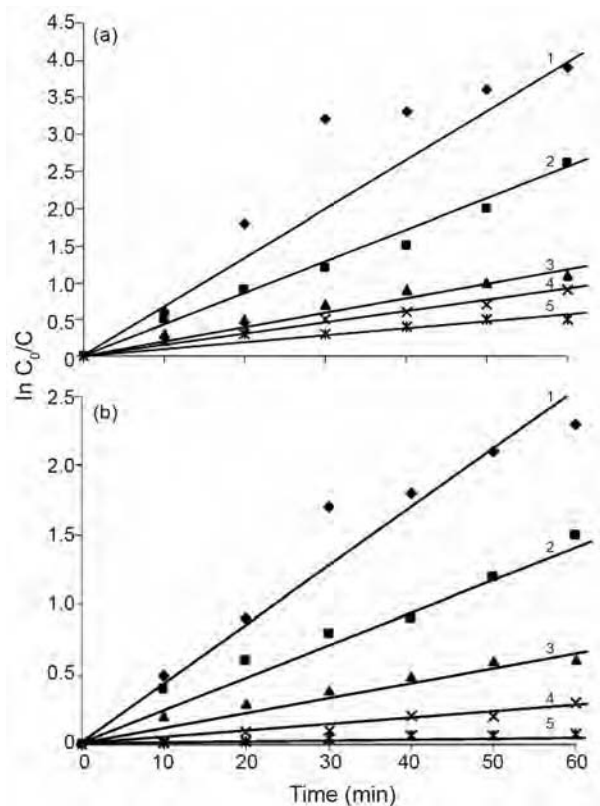
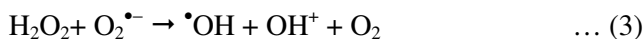


Fig. 4—Kinetics of Acid Red 27 dye (a) decolourisation and (b) degradation by UV/nano ZnO for different initial concentrations of the dye. {pH = 7 ± 0.1 ; nano ZnO = 100 mg/50 mL. 1, 1×10^{-4} ; 2, 3×10^{-4} ; 3, 5×10^{-4} ; 4, 7×10^{-4} ; 5, 9×10^{-4} mol/L}.

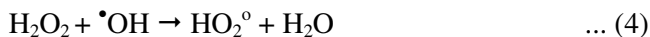
concentration from 10 to 20 mmol decreases the decolourisation from 70.6 to 61.8 % and degradation from 55.9 to 46.8 %. Hence, 10 mmol H₂O₂ concentration appears to be optimal for the degradation. A similar observation (an increase in H₂O₂ level enhanced the degradation rate up to optimal load beyond which inhibition occurs) has been reported earlier in dye degradation²² and organic pollutant degradation²³. The enhancement of decolourisation and degradation by addition of H₂O₂ is due to an increase in the hydroxyl radical concentration as shown by the following equation:



H₂O₂ also reacts with superoxide anion to form OH radical



At high H₂O₂ dosage (>10 mmol) the removal rate decreases due to its hydroxyl radical scavenging effect.



Effect of addition of K₂S₂O₈

The effect of addition of K₂S₂O₈ on the photocatalytic oxidation of AR 27 has been investigated by varying the amount of K₂S₂O₈ from 10 – 25 mg/50 mL. The results are given in Table 2. Addition up to 20 mg increases the

Table 1—Effect of H₂O₂ on the photocatalytic decolourisation and degradation of AR 27 dye

Amount of H ₂ O ₂ (mmol)	AR 27 removal (%)	
	Decolourisation	Degradation
0	58.9	41.2
5	65.5	48.4
10	70.6	55.9
15	64.7	52.7
20	61.8	46.8

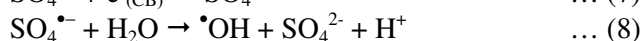
Table 2—Effect of K₂S₂O₈ and KBrO₃ on the photocatalytic decolourisation and degradation of AR 27 dye

Amount of K ₂ S ₂ O ₈ / KBrO ₃ (mg)	AR 27 removal (%)			
	With K ₂ S ₂ O ₈		With KBrO ₃	
	Decolour.	Degrad.	Decolour.	Degrad.
0	58.9	41.2	58.9	41.2
10	65.1	49.4	75.3	65.4
15	70.3	59.9	84.9	76.8
20	74.1	62.4	91.0	82.3
25	77.3	65.1	93.4	84.2

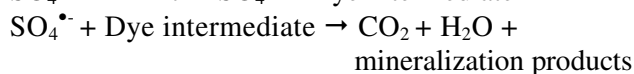
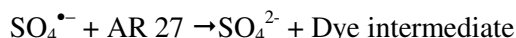
decolourisation from 58.9 to 74.1 % and degradation 41.2 to 62.4 % in 40 minutes. Our results are in good agreement with earlier results²⁴⁻²⁷. Further increase in the addition (25 mg/50 mL) increases the decolourisation by 3.2 % and degradation by 2.7 %. The enhancement of the reaction rate is due to the inhibition of electron-hole recombination and production of other oxidizing species sulphate radical anion.



The sulphate radical anion may react with photogenerated electron and with water molecule producing hydroxyl radical.

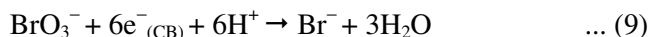


The sulphate radical anion (SO₄^{•-}) is a very strong oxidant (E⁰ = 2.6 eV). This radical anion also participates in the degradation process in the following ways.



Effect of addition of KBrO₃

KBrO₃ is an efficient electron acceptor and is used as an additive to enhance photocatalytic degradation rate^{28,29}. Addition of KBrO₃ from 10 to 20 mg/50 mL increases the decolourisation from 75.3 to 91.0 and the degradation from 65.4 to 82.3 (40 min). The results are given in Table 2. The enhancement of the removal rate is due to the reaction between BrO₃⁻ ion and conduction band electron (Eq. 9) which reduces the recombination of electron-hole.



Further increase of KBrO₃ from 20 to 25 mg/50 mL increases the decolourisation only by 2.5 % and degradation by 1.9 %. This is due to adsorption effect of Br⁻ ion on nano ZnO surface which affects the catalytic activity of ZnO.

Chemical oxygen demand (COD)

In order to study the toxicity of the photocatalysed solution, the COD values were determined. The COD measurements were carried out for a representative run. Solutions obtained after photodegradation show a significant decrease in COD from 1920 to 320 mg/L after 120 min. In this process, 83.3 % of COD removal was observed after 120 minutes of irradiation. The substantially lower toxicity of the

photodegraded products clearly indicates the high potential of the nano ZnO catalysed photodegradation process for the removal of pollutant (AR 27 dye) from waste water.

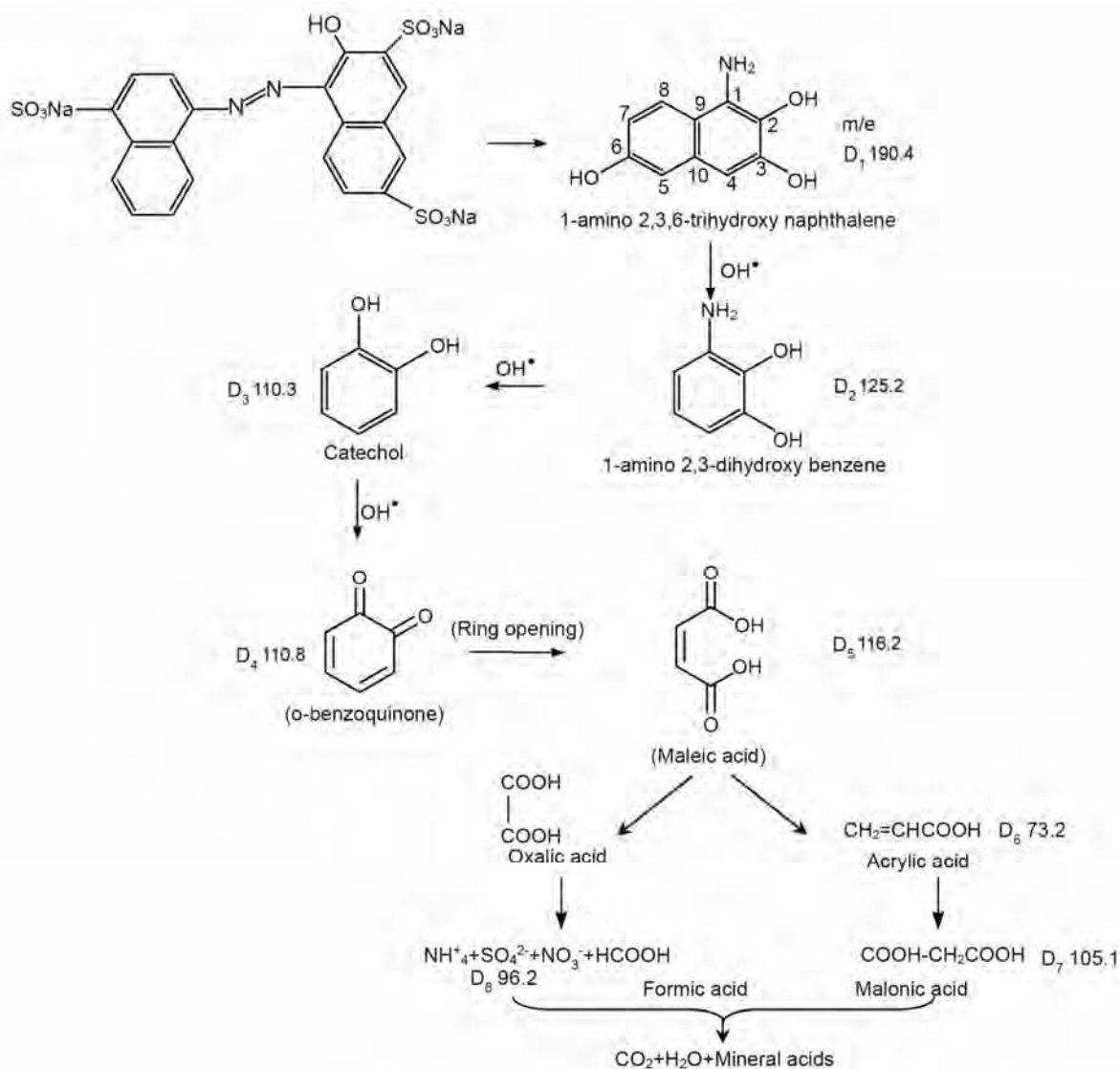
GC-MS analysis

Since the decolourisation is very fast, the attack of hydroxyl radical takes place first at the carbon atoms bearing the chromophoric azo linkage. The fragments produced by the cleavage of the azo bond of the dye molecule must be the primary reaction intermediates. In order to identify the intermediates formed in the photocatalytic reaction, we have carried out GC-MS analysis of the dichloromethane extract of the

partially decolourised solutions (50–60 %) that have undergone 2–4 h photolysis.

The GC-MS analysis of the solution obtained after decolourisation showed the formation of eight main products with the following retention times: 24.230 (D_1 & D_5), 18.882 (D_2), 22.070 (D_3), 20.087 (D_4), 13.709 (D_6), 19.469 (D_7) and 21.782 (D_8) minutes. These eight products were identified based on their molecular ions and mass spectrometric fragmentation peaks. The formation of eight compounds from the photoreaction of dye molecule is shown in the Scheme 1.

The proposed photochemical degradation mechanism of AR 27 includes the reductive cleavage



Scheme 1

of the azo bond. The fragments produced by the cleavage of the azo bond of the dye molecule appear to be the primary reaction intermediates. These reactions occur as initial steps at the beginning of the process and are followed by further oxidation, reduction and partial mineralization resulting in water, CO₂ and inorganic salts (sulphates, nitrates, etc.) Two hetero-atoms (S and N atoms) are present in the dye. Generally sulphur is transformed into sulphate (SO₄²⁻) ion, whereas nitrogen atom produces ammonium (NH₄⁺) and nitrate (NO₃⁻) ions^{30,31}. These final products were identified in the treated sample when the treatment time was adequately long, which were confirmed by the decrease in COD.

The intermediates formed by cleavage of azo bonds were adsorbed on the surface of the catalyst and then rearranged. Subsequently, naphthalene derivative such as compound (D₁) was generated primarily by the *hν*_b+ mechanism and [•]OH_{ads} reactions. Repetitive attack of [•]OH towards D₁ generated the benzene derivative such as compound D₂. Then the [•]OH could easily attack the compound D₂ at the carbon carrying NH₂ groups, forming the hydroxyl derivative (D₃), with the NH₂ group released by the radical addition-elimination reaction. Simultaneously, the [•]OH radical attacked the hydroxyl derivative D₃, generating benzoquinone (D₄). Then D₄ is directly oxidized to smaller organic acids such as maleic acid (D₅), acrylic acid (D₆), malonic acid (D₇), oxalic acid and formic acid. Finally, these aliphatic byproducts are mineralized to CO₂ and H₂O. Furthermore, sulphate (D₈) ion was obtained from sulphonic groups on AR 27 molecules mainly via two pathways, namely, the substitution by hydroxyl groups and the reaction with *hν*_b+.

Conclusions

Acid Red 27 is successfully degraded by nano ZnO assisted photocatalysis in aqueous dispersion under irradiation by UV light. The optimum physico-chemical conditions for the degradation of 5×10⁻⁴ M solution at room temperature is found to be nano ZnO concentration 100 mg/50 mL and initial pH 7. The photocatalytic degradation obeys pseudo first order kinetics at low initial concentration. Addition of electron acceptors such as H₂O₂, K₂S₂O₈ and KBrO₃ enhances the degradation. The total degradation of

dye has been shown by chemical oxygen demand method and the intermediate products separated and confirmed by GC-MS analysis.

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