Facile approach for synthesis of stable, efficient and recyclable ZnO through pulsed sonication and its application for degradation of recalcitrant azo dyes in wastewater

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Facile approach for synthesis of stable, efficient and recyclable ZnO through pulsed sonication and its application for degradation of recalcitrant azo dyes in wastewater

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Highlights

• Synthesis of ZnO using ultrasound-assisted sol–gel and hydrothermal method.
• ZnO synthesized via ultrasound has large specific surface area and high pore volume.
• ZnO is better for adsorption and sonocatalysis.
• Simultaneous application of sonolysis and photolysis gives highest decolorization.
• 97% decolorization in 20 minutes and 87% COD removal in 17 minutes were achieved.

Abstract

In the present study, the ultrasound in pulsed mode used as a part of advanced oxidation method. The influence of pulsed ultrasound mode for the preparation of zinc oxide wurtzite nanoparticle were synthesized. The catalysts synthesized were analysed using SEM, TEM, EDAX, BET surface area, XRD and DRS to study about their morphological and structural characterizations. The ZnO nanoparticles exhibited highly hexagonal structure from pulsed sonication synthesis route. The efficiency of the decolourization of RR4 were studied under different operation parameters like dye concentration, initial solution pH, antioxidants like H₂O₂ concentration and catalyst loading. The hybrid combined process of pulsed sonolysis, pH (4.0), H₂O₂ (17.64 mmol) and Catalyst (0.35 g/L)) achieved 97% degradation and 87.5% COD removal in about 20 minutes of reaction time. The cyclic degradation studies of RR4 removal with 0.35 g/L of ZnO showed the reusability of catalyst upto 5th removal cycle with negligible loss in the catalytic performance. GC–MS study, used for the detection of the RR4 intermediates revealed the oxidation/reduction reaction by the reactive radicals proceeded via the reductive cleavage of the azo bonds. The studied process based on the pulsed ultrasound is found to be effective for the degradation of RR4 dye.

Keywords: pulsed ultrasound, azo dye, advanced oxidation process, reactive red 4, water treatment, decolourization.
1. Introduction

In the recent decades the disposal of wastewater from the different types of industries like pesticides, cosmetics, paper, textiles and leather has been increasing day by day. Among all textile and dyeing industry are the major contributor of wastewater. The accumulation of toxic compounds in the water resources have been entailed as unsolved puzzle for the environment and more hazardous to human health. In fact, approximately 200 litres of water required to produce 1 kg of textiles [1]. About 20% of the dyes and dye products enter into the water resources through the discharge of textile industries. The azo dyes constitute the major dye used in textile and dyeing industries exceeding over 60% of the dye used [2]. The intermediates of the dye compounds have adverse effects as deplete the dissolved oxygen in aquatic system and endanger to flora and fauna. Hence it is more essential to treat with an efficient method to transform all these dyes and intermediates into toxic free compounds [3]. Moreover, the anaerobic and incomplete degradation of dyes generates aromatic amines and other recalcitrant secondary pollutants which are more toxic and carcinogenic [4]. Hence, there is a need for an efficient oxidation method to treat the dyes and its by-products before being disposed into water resources. For decades advanced oxidation processes have proved to be an efficient and powerful tool to eliminate these dyes from wastewater [5].

Environmental sonochemistry is an example for advanced oxidation process which is widely followed treatment methods for the complete destruction of recalcitrant pollutants in the wastewater [6]. The physical and chemical effects of the ultrasound produced cavitation bubbles in the aqueous solution generates high temperature and pressure within the liquid during the collapse of the bubbles deals with the destruction of complex compounds [7]. The effective treatment is caused by the increased rate of generation of $\cdot$OH radicals and other reactive moieties. The degradation kinetics followed by the sonochemical treatment can be of zero order, first order depend upon the in situ production of $\cdot$OH radicals and their degree of contact with the contaminants present in the wastewater [8]. The limitations of the individual process can be eliminated by the process integration of ultrasound with the addition of catalyst. Further the turbulence in the aqueous solution created by the ultrasound helps in catalyst fragmentation and de-agglomeration thus increasing the activity of the catalyst [9]. Recently the pulsed ultrasound treatment has been studied for improving the efficiency of the degradation kinetics.

Ultrasound has a uniqueness as the chemical free treatment method utilizing the generated $\cdot$OH radicals i.e., short lived oxidants [10]. Major hinderance is the high
operational energy being wasted in the continuous mode. The shielding effect of the bubbles created when these bubble accumulate near the irradiating source [11]. This energy wastage can be reduced by the several ways like modification of the reactor, integrating the ultrasound with other techniques and the pulsed mode ultrasound. The pulsed mode ultrasound is usually operating ultrasonic equipment in cyclic repetition such as ON and OFF mode repeatedly. This process has been developed to deliver more rapid effects both in time and life cycle of the generated cavitation bubbles [12]. In recent years the highlights of the ultrasound performance in degradation of pollutants has been reported as the effective method among advanced oxidation process.

The technologies employed in degradation studies still produces incomplete intermediates after the oxidation process [13]. The usage of catalyst helps in transforming these complex intermediates into harmless compounds [14]. Recently the piezoelectric and electronic properties of wurtzite ZnO crystals showed the generation of electric dipole where the wonderful cation-anion displacement occurs promoting the formation of oxidative radicals very rapidly [15]. When these semiconductor catalysts coupled with the pulsed ultrasound in the degradation of azo dyes showed a beneficial synergetic effects. This strategy helped inducing a high efficiency technology to remove the organic pollutant from wastewater. The aim of this work was to assess the performance of pulsed ultrasound with ZnO semiconductor catalyst as a part of advanced oxidation process for degradation of azo dyes, studying the effects of various other parameters like pH, anti-oxidants, dye concentration and volume on the rate of decolourization. Moreover, the synergetic efficiency of the combined parameters with pulsed ultrasound process was evaluated.

2. Experimental procedure

2.1. Chemicals

Reactive Red 4 was obtained from Sigma Aldrich (Colour Index No. 18105, EC No. 241-663-8, molecular weight: 995.21) and was used as supplied. High purity reagents, sulphuric acid (Merck), sodium hydroxide (Merck), zinc acetate (Merck), ethanol and hydrogen peroxide solution (30% w/w, Merck) were used for the solution. All the solutions were prepared using Millipore water. All chemicals and reagents used were of analytical grade and used without any further purification. Ultrasonic processor (Sonics & Materials, VCX 500) was used for the experimental study.
2.2 Synthesis of catalyst

The ZnO particles are prepared in an ultrasonic processor using zinc acetate and sodium hydroxide as precursors. 0.005 M zinc acetate and 0.02 M sodium hydroxide in the stoichiometric ratio of 1:2 were dissolved in water [16]. Following the hydrothermal process, the solution was sonicated for 30 min with an ultrasonic probe. The milky white precipitate was filtered and washed with ethanol 5 times to remove the impurities. The obtained ZnO nanoparticle was dried in a vacuum oven at 105°C for 24 hours to remove the moisture.

2.3 Catalyst characterization

The morphology of synthesized catalysts ZnO was investigated using scanning electron microscopy (SEM) images (JEOL, Hitachi Corporation, Japan). The elemental composition of the prepared catalyst by the energy-dispersive analysis of X-rays (EDAX) conjugating with SEM confirms the formation of ZnO. The surface area and pore volume of the synthesized catalyst were measured using BET (Brunauer–Emmett–Teller) surface area and particle analyser (ASAP 2020, Micromeritics, USA). The phase purity and composition of the synthesized catalyst were studied using X-ray diffraction (XRD) (Cu Kα radiation, D8 advance Bruker, Germany). XRD patterns were recorded in the 2θ range between 20° and 80°. By using the Scherrer formula the average crystallite size (D) of the catalyst was calculated (Eqn. 1).

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}, \quad \text{Eqn. 1}
\]

where k is the X-ray wavelength and b is the full width at half maximum (FWHM) obtained at a corresponding 2θ angle. UV–visible diffuse reflectance spectra (DRS) were recorded to determine the absorption capacity of the catalysts prepared. Specord (Analytikjena) S-600 UV–visible spectrophotometer was used in the wavelength range of 200–800 nm to obtain the DRS spectra [17].

2.4 Experimental procedure

0.01004 mmol (1000 ppm) concentration of Reactive Red 4 stock solution was prepared with Millipore water and used for the experimental study. The degradation studies were carried out using 1000 mL dye solution placed in water cooled jacketed beaker at room temperature 25°C. Fig 1a. represents the scheme of the experimental setup. The pH of the Reactive Red 4 solution was adjusted either by adding drops of 0.05N sulphuric acid solution or 0.05N
sodium hydroxide solution. A small dosage in steps of H₂O₂ concentrations (8.82, 17.64, 26.46, 35.28, 44.1, 52.62, 61.74, 70.56, 79.38, 88.2, 97.02 and 105.84 mmol) was added to study its effect of anti-oxidants on RR4 dye colour removal. For all the experiments, the ultrasound was irradiated for an hour and the decolourization of RR4 was monitored using UV–vis spectrophotometer for every 15 min with intermittent sampling.

2.5 Analytical Procedure

The optical absorption spectra of the Reactive Red 4 dye solutions were determined by JASCO UV–Visible spectrophotometer equipped with a photoelectric detector at the maximum absorption wavelength of 517 nm. The UV–vis spectrum and the chemical structure of RR4 are shown in Fig. 1b. The aromatic intermediates after degradation studies were analysed using GC-MS (Perkin Elmer). The GC was equipped with Elite-5 (5% Diphenyl) Dimethylpolysiloxane series capillary columns of length 30m, inner diameter 0.53mm, film thickness 1.50mm and interfaced directly to the MS. The GC column was operated at a temperature of 80 °C for 2 minutes then increased to 250 °C at the rate of 15 °C min⁻¹. The other experimental conditions were: Electron ionization voltage 70 eV, helium as carrier gas, injection temperature 280 °C and source temperature 80 °C.

3. Results and Discussions

3.1 Effect of pulsed sonication treatment

The experiments were conducted in continuous sonication and pulsed sonication system, respectively to illustrate the degradation potential of the individual processes. As shown in Fig.2, the colour hardly decreased when both the processes were applied to 0.01004 mmol concentration of reactive red 4 solution. It is due to the fact that only a small amount of •OH radicals were formed in the presence of only sonolysis [18]. It was also confirmed that little colour removal was achieved when pulsed sonication was applied such that during the ON and OFF time interval (5 seconds) the dye molecules have been decomposed at the bubble water surface. Therefore, the decolorization efficiency was also increased from 29% to 36%. Similarly, the produced •OH radicals were not enough for complete degradation RR4 as mere ultrasound was inefficient for the complete removal of the recalcitrant pollutant molecules [19].

Fig 1a and Fig 1b

Fig 2
3.2 Effect of pH

The effect of pH on decolourization of RR4 was also performed. Fig. 3 shows that the low pH favors high decolourization with small differences in the range 2.0-4.0, and lower rate at alkaline pH [20, 21]. The natural pH of the solution is 6.71, during acidification the dye would become hydrophobic and easily available for ultrasound treatment. Similar studies reveal that the degradation kinetics increased for RR4 dye molecules in the acidic medium. Also at acidic condition the H$^+$ ions will be readily activated, generates more 'OH radicals during ultrasound treatment. Under alkaline condition there is a gradual decrease in the degradation rate. This is due to the formation of conjugate base of the dye molecule which makes the dye molecule more hydrophilic and deactivates the formation of 'OH radicals resulting in lesser degradation. The colour removal rate of the dye is maximum of 42.19% when the pH is 4 [22]. The colour removal rate was increased little from natural pH to pH 7.0 due to the availability of more 'OH radicals than normal solution pH. When compared with ultrasound (US) treatment alone, the solution pH shows high colour removal rate.

Fig 3

3.3 Effect of H$_2$O$_2$ concentration

The effect of ultrasound with oxidants were evaluated using hydrogen peroxide addition at different concentration to the RR4 aqueous dye sample at solution pH. In the presence of ultrasonication the generation of 'OH radicals increases according to the concentration of H$_2$O$_2$ added [23]. Fig. 4 illustrate the decolourization efficiency at different H$_2$O$_2$ concentration. The increase in 'OH radicals generation was because the dispersed H$_2$O$_2$ tended to act as additional nuclei available at the cavitation hot spot for the pyrolysis of water molecules and formation of 'OH radicals and can thus be used to quantify the effectiveness in generating the desired reactive radicals [24]. Therefore 66% colour removal due to higher oxidation activities when 8.82 mmol of H$_2$O$_2$ was added. The higher colour removal of 68% was achieved with the increase of concentration to 17.64 mmol of H$_2$O$_2$ than with the ultrasound alone. This ensures the formation of the powerful oxidizers like HO$_2$/O$_2^−$, 'OH whose oxidation–reduction potentials are +1.5 and +2.8 eV respectively. Moreover, the scavenging reaction takes place when the concentration of H$_2$O$_2$ increased further [25] where the large of number of 'OH radicals interact and form H$_2$O and H$_2$O$_2$ where the extinction of 'OH happen resulting in low colour removal rate.
3.4 Effect of dye concentration

The influence of initial dye RR4 concentration of the sample solution was investigated with different concentration ranging from 10ppm to 1000ppm on colour removal rate. As illustrated in Fig. 5, the dye colour removal changed inversely to the initial dye concentration of RR4 [26]. Higher colour removal rate was obtained for the process study where the initial dye concentration of 10ppm solution relative lower initial concentration while the dye concentration was increased 10 times further. For an instance, in 60 min, the simple pulsed sonication achieved 26% decolorization, while 24% decolorization could be achieved in the process when the dye solution concentration increased by 10 folds. The possible explanation might be that the ratio of \( \cdot \mathrm{OH} \) radicals to dye molecules in the solution decreased when the concentration of the dye molecules increased 10 folds [27], resulting in an excess of dye molecules regarding to \( \cdot \mathrm{OH} \) radicals generated during the sonication process. As a result, the decolorization rate lowered for the high initial dye concentration than the lower dye concentration.

3.5 Catalyst Characterization

SEM images were recorded on catalysts synthesized by both continuous, pulsed mode sonication and shown in Fig.6a and Fig. 6b. We can see the smooth, uniform texture and agglomerated pseudo spherical structure of ZnO [28, 29]. The agglomeration observed was due to the van der Waals forces among the gap energy between the particles. The transformation of surface morphology is from agglomeration to wurtzite relatively due to the shock wave applied during the sonication [30]. During the pulsed sonication ZnO was subjected to some changes in its crystallinity [31]. These changes are significant in pulsed sonication when compared to continuous mode. After the drying in the hot air oven for 24 hours the different structure evolves from both the continuous and pulsed mode of sonication. TEM and EDAX characterization also confirms the formation of ZnO nanoparticles using sonication Fig. 6c and Fig. 6d.

Fig. 7 shows the XRD pattern of the synthesized ZnO catalyst having average diameters. The structure was subjected to sonication with continuous or pulsed mode yielding agglomerated
or wurtzite crystal structure. XRD patterns are shown for ZnO samples in Fig. 6. Diffraction peaks appeared in the pattern are enumerated and listed. The peaks are in accordance with the standard diffraction pattern of ZnO (JCPDS: 036-1451). To understand the crystallinity, the peaks at 20 angles of 31.6, 34.2 and 36.2 were selected. The angular location of these peaks suggests that the planes of (100), (002) and (101) correspond to the hexagonal crystal lattice existing along with a slight residual tensile stress [32]. Also the lattice parameters showing sharp reflections where the presence of Zn(OH)$_2$ has been identified along with the ZnO amorphous nanoflakes [29, 30]. When the ZnO particles subjected to pulsed sonication the lattice during the nucleation and growth gains thermal energy for entropic configuration thus increasing its crystallinity.

Diffuse reflectance spectra (DRS) shows the absorption properties of the catalyst depends upon the angle of incidence, the refractive index and surface roughness. DRS obtained were analysed using the (Kubelka–Munk theory) Kubelka–Munk equation at any wavelength Eqn 2

$$F(R) = \frac{(1-R)^2}{2R}$$

Eqn 2

where R represents the absolute reflectance and F(R) as Kubelka–Munk function. Fig. 8 shows the diffused reflectance for ZnO nanopowders [33]. It is clearly seen that the diffused reflectance increased with increasing wavelengths. The optical transitions in semiconductor catalyst occurs due to direct and indirect transitions. The optical band gap $E_g$ was calculated by using the fundamental absorption, such that the electron excitation from the valance band to the conduction band. The optical band gap was calculated by using the following equation Eqn 3

$$(au) = \frac{F(R)hu}{t} = A(hu-E_g)^n$$

Eqn 3

where A represents an energy-independent constant and $E_g$ as the optical band gap, n - constant determines the type of optical transitions and for indirect allowed transition, n=2; and indirect forbidden transition, n=3, for direct allowed transition, n=1/2; for direct forbidden transition, n=3/2. The optical band gap of the samples was calculated from the plots of $(F(R)hu/t)^2$ as a function of photo energy $hu$. The optical band gap of ZnO nanoparticles were found to be 3.19eV further in good agreement with the band gap from diffused reflectance previously calculated by other researchers equals to 3.22eV [34].
The variation in the thickness and density of the synthesized catalyst were shown by the BET adsorption-desorption curve. The obtained curve corresponds to type IV hysteresis loop the characteristics of mesoporous particles. The surface area of the synthesized ZnO particles were found to be 3.93 m$^2$/g (Fig. 8), approximately equals to the surface area of ZnO nanoparticles reported earlier [35]. The ZnO agglomerated assemblies with sufficient surface area and more mesoporous structures also acts as adsorbents while used for the treatment of dye pollutants.

3.6 Effect of catalyst loading

ZnO catalyst upon sonication produce electrons from the conduction band or generate holes in the valence band (Eqns. 4 and 5) thereby splitting the water molecule as H$^+$ and $\bullet$OH radicals (Eqn. 6). Amount of ZnO concentration plays an essential role in influencing the generation of $\bullet$OH radicals for the degradation processes [36]. In this treatment process, various concentrations of ZnO were studied to obtain its optimal concentration for the higher colour removal rate. The results for effect of catalyst concentration on degradation of RR4 are shown in Fig. 9. From the experimental results it reveals that decolorization rate of RR4 increases up to the catalyst concentration 0.3 g/L. Addition of ZnO above 0.35 g/L did not affect the decolorization kinetics. The decolorization percentage of RR4 started to decrease slowly when the concentration of ZnO was increased above 0.40 g/L. The reduction in the colour removal rate was due to the catalytic decomposition effect of ZnO. It is known that the scavenging of $\bullet$OH radical happens when its concentration is increased, they recombine to form less oxidative OH$^-$ ions. The catalytic effect also accordingly decreases as its concentration was higher. ZnO also undergoes a reaction with hydroxyl ions to form Zn(OH)$_2$ [37] which has lower catalytic activity (lesser redox potential of conduction and valence band) (Eqn. 7).

\[
\begin{align*}
\text{US} & \quad \text{ZnO} \xrightarrow{\text{US}} \text{Zn}^{2+} + \text{O}_2^+ \quad \text{Eqn 4} \\
\text{US} & \quad \text{ZnO} \xrightarrow{\text{US}} \text{ZnO(e}^-_{CB} + \text{h}^+_{VB}) \quad \text{Eqn 5} \\
\text{US} & \quad \text{Zn}^{2+} + \text{H}_2\text{O} \xrightarrow{\text{H}^+ + \text{Zn}^{2+} - \text{OH}^-} \quad \text{Eqn 6} \\
\text{US} & \quad \text{Zn}^{2+} + 2\text{OH}^- \xrightarrow{\text{Zn(OH)}_2} \quad \text{Eqn 7}
\end{align*}
\]
3.7 Combined effect of pulsed sonolysis, pH, H$_2$O$_2$ and Catalyst

The complete degradation of dyes into CO$_2$ and H$_2$O were studied in this treatment process and analysed by the COD. The COD values can be related to the concentration of organics present in the dye. The colour removal from the wastewater cannot be considered as complete oxidation [38]. Many researchers have reported that there were reaction intermediates present in the solution after the decolourization studies [39]. In our studies, the intermediates from RR4 which will form aromatic ring structure intermediates were long lived and more carcinogenic to the aquatic life. Thus, the optimum operating conditions of pH, initial concentration of the dye, ZnO catalyst concentration, H$_2$O$_2$ concentration and pulsed sonication, applied for the degradation of aromatic contents and mineralisation of dye were analysed. Fig 10 shows that the decolourization percentage of RR4 in the hybrid process (Combined effect of pulsed sonolysis, pH (4.0), H$_2$O$_2$ (17.64 mmol) and Catalyst (0.35 g/L)) achieved 97% degradation in about 20 minutes of reaction time. Furthermore, it also shows that 87.5% reduction of COD occurring at a faster reaction rate than colour removal achieving with in the time interval of 17 minutes. Thus the combined effect prevails to be more beneficial in COD removal rather than simple decolourization.

3.8 Degradation Pathway of RR4

The formation of intermediates as the chromophores of RR4 evolved as the degradation of dye proceeds reflect in the UV-vis spectra. The spectral changes are attributed to the change in the $\pi \rightarrow \pi^*$ transition related to the –N=N– group, C–C group, C–N group, benzene and naphthalene rings of the RR4 molecule [40]. The absorption peak of RR4 decreases rapidly when the degradation reaction proceeds. After the reaction time when there was no peak in the absorption peak indicating that the azo bonds and the conjugated molecules of the dye molecule were completely destroyed and converted into simpler molecules. The intermediates formed during the degradation after the reaction time 60 minutes were analysed by GC/MS. During the degradation process the byproducts like sulfonic acid, heneicosane, 3-Hexadecene, 1-Octadecene etc were detected. Moreover, there were several pathways through the degradation process followed [41]. The cleavage of –
N=N– group, C–C group, C–N group, benzene and naphthalene rings of the RR4 molecule follow several concurrent pathways by the oxidation of mainly *OH radicals have been indicated and the corresponding plausible pathway have been proposed in Fig.11. Eventually the destruction of RR4 aromatic rings were formed and all the complex molecules were degraded into smaller molecules.

Fig 11

3.9 Reusability of catalyst for RR4 removal

The reusability and stability of the catalyst material for the degradation reveals the cost effectiveness. The catalyst effect on degradation of RR4 was carried out with ZnO (0.30 g/L) for 10 ppm concentration at the solution pH 6.71. After the pulsed sonication for the removal of RR4, the COD was reduced 37%. The catalyst was filtered and treated with 1 M NaOH and 1 M ethanol then washed repeated 3 times with Millipore water and dried at 120°C successively to regenerate for the next cycle of degradation studies. The degradation studies were experimented with 4 cycles. Fig. 12 shows the COD values of the repeated degradation studies using the regenerated catalyst. It revealed that after 3 cycles the catalyst showed 30% COD reduction as there was a slight decrease in the catalytic activity due to the lesser number of active sites in the catalyst [42]. The decrease in sites may be due to the subsequent attack by the dye molecules and reducing the catalytic efficiency. Moreover, the catalyst stands effective after regeneration and further indicating that the catalyst potential for wastewater treatment applications.

Fig 12

Conclusion

The ultrasound in pulsed mode alone have negligible effect on the decolourization of RR4. However, when ultrasound combined with other parameters like pH variation, catalyst loading, dye concentration and H₂O₂ addition gave faster decolourization rate. The synergetic effect of AOP can be explained by the formation of hydroxyl radicals helps in the faster decolourization kinetics. When the concentration of H₂O₂ increased there was an increase of decolourization reaching a maximum (asymptotic value). Moreover, the increase in antioxidant intuitively describes that the excessive addition can favour the radical scavenging resulting in decrease in the removal kinetics. Under the hybrid combined experimental conditions, the dye solution could be completely decolorized within 20 minutes a very short
reaction time. The rate for colour removal is much faster and similar that of COD removal.
All the aromatic ring, azo bond were cleavaged within 20 min, and ended in simpler compounds. Finally, the plausible degradation path of RR4 was predicted.

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Graphical abstract

Facile approach for synthesis of stable, efficient and recyclable ZnO through pulsed sonication and its application for degradation of recalcitrant azo dyes in wastewater

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On the hybrid process of pulsed sonolysis combined with ZnO catalyst produced more *OH radicals for attacking the pollutants thus decolorization of 97% achieved in short time.