Novel homogeneous catalyst assisted sonocatalytic degradation of dye Direct Blue 71

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Industrial effluents, particularly from dye industry, is one of the major causes of serious concern as it contaminates the environmental water resources and affect human health. Treatment of such contaminants is a challenging area of interest to researchers. In this context, here, we have explored degradation and mineralization of Direct Blue (DB71) dye in aqueous solution by means of ultrasound irradiation at a frequency of 25 kHz and its combination with a novel homogenous sonocatalyst is investigated. The following experiments have been conducted to achieve complete degradation of the dye molecule. In-situ generation of the radicals under ultrasonic irradiation is measured by EPR technique. The effects of various operational parameters such as the effects of pH, dye concentration, catalyst dosage, electrolytes, energy input and kinetics of oxidation processes on the degradation efficiency are studied. COD measurements are also carried out in order to evaluate the mineralization efficiency of DB71. The effect of electrolytes on dye degradation is studied with different inorganic electrolytes. The rate constant decreases with increasing dye concentration. The degradation increases with increasing catalyst concentration and decreases with increasing dye concentration. Sonocatalytic degradation of the dye molecules are observed by UV-visible absorption and TOC measurements. The by-products formation of the sonocalytically degraded dye samples are analyzed by ESI-MS$^+$ analysis. The catalyst is also tested for its efficiency in the degradation of real dye house effluents.

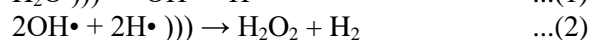Keywords: Advanced oxidation, Dye degradation, Direct Blue, Environmental pollution, Mineralization, Sonocatalysis
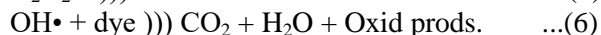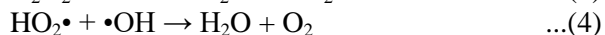
Due to enormous growth of industries, many industries are releasing wastewater that contains toxic organic, inorganic compounds endocrine disruptors mainly dyes etc. These contaminants cause health hazards to the human and other living beings. Hence, the dye house effluents have to be treated before the liberation into the enviornment. Different methods of oxidation and reduction have been reported in the literature[1]. Among all these methods advanced Oxidation Processes (AOP) are most appropriate methods by the generation of the highly reactive radicals for the oxidation of toxic organics into non-toxic substances like CO_2 and H_2O.

AOP's are mainly based on homogeneous and heterogeneous catalysts. In the recent years, heterogeneous semiconductor nano materials have been used for the degradation of organics and inorganics using advanced oxidation technologies, but it has some demerits. Degradation of destructive organics from aqueous phase using homogeneous catalysts such as fenton reagent[2], photofenton[3], and ozonation[4] have been described in the literature. Homogeneous catalysts are in general more effective than heterogeneous catalysts because it is usually water soluble and more reactive[5]. To overcome the disadvantages on the degradation, novel homogeneous catalysts are required for the eco-friendly purposes.

The degradation of organic compounds from aqueous phase by homogeneous catalysts usually through free radical mediated processes. Generally free radicals are generated under UV-visible irradiations, ultrasound and thermal etc., This study focuses on the generation of free radicals by sonochemical methods. Sonication induced cavitation is the formation, growth, and successive collapse of micro cavities producing highly turbulent motion in bulk liquid with pressures and temperatures releasing enormous amount of energy in the reactor instantaneously[6,7]. OH radicals can be generated from the pyrolytic reactions during sonochemical reactions. The sonication of water also produces hydroxyl radicals[8,9]. Generation of OH• is shown in the following chemical reactions (1 to 6).

$$H_2O\ ))) \rightarrow OH\bullet + H\bullet \qquad ...(1)$$
$$2OH\bullet + 2H\bullet\ ))) \rightarrow H_2O_2 + H_2 \qquad ...(2)$$

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet \qquad ...(3)$$
$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \qquad ...(4)$$
$$H_2O_2 +))) \rightarrow 2OH\bullet \qquad ...(5)$$
$$OH\bullet + dye))) CO_2 + H_2O + Oxid \, prods. \qquad ...(6)$$

where,))) refers to the ultrasonic (US) irradiation. The hydroxyl radicals combine with dye molecules upon US irradiation it can mineralize the target molecules to form water and carbon dioxide.

DB71 is a tri-azo dye is used to stain membrane-immobilized antibodies, proteins and adsorption studies. DB71 is toxic, mutagenic, carcinogenic and also contaminate water bodies[10]. Therefore, it is necessary to remove these contaminants from water and wastewater. Hence, in the present study, we focused on degradation of DB71 dye from aqueous phase through sonocatalytic process.

Materials and Methods

Chemicals

DB71 dye (1,5-Naphthalenedisulfonicacid,3-[[4-[[4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl) azo]-6-sulfo-1-naphthalenyl]azo]1naphthalenyl]azo]tetra sodium salt was purchased from Sigma-Aldrich (India) Bangalore, India. Magnesium chloride, silver sulfate, were purchased from S.D. Fine Chem., Mumbai, India. 5,5-Dimethyl 1-Pyrroline N-Oxide (DMPO), potassium chloride, sodium bicarbonate, sodium chloride, were supplied by Merck, Mumbai, India. Potassium dichromate and ammonium ferrous sulfate were supplied by Qualigens, Mumbai, India. Dye house effluent was collected from Pilot Tannery, CSIR-Central Leather Research Institute, Chennai, India. All the chemicals are analytical grade and used as received without further purification. DMPO was purified[11] and processed before analysis.

Methods

The pH meter was calibrated using buffer solutions between 4 and 7 at 25°C (Elico pH meter, Hyderabad, India). The degradation of the dye molecule was monitored by UV–visible spectrophotometer (Shimadzu UV-2101PC, Japan). Sonochemical experiments were performed using (Sonics, Vibracell, USA, 20 kHz, 750 W) horn and split type probes. The COD analysis was carried out in the (Thermoreactor Spectroquant TR-320, Merck, Germany) block digester. The TOC analysis was carried out using Multi N/C 2100 S BUTOC analyzer (Analytikjena, AG Germany). The reactive radical production was confirmed by EPR analysis using Bruker, Model EMX X Band, electron paramagnetic resonance spectrometer (Germany). The by-product analysis was carried out by ESI-MS instrument (Model LCQ Advantage MAX, Thermo Finnigan).

Sonocatalytic studies

Sonocatalytic degradation experiments were performed in a sonochemical reactor with horn and split type probes. The sonochemical reactor consists of a 250 ml jacketed glass reactor fitted with accessories for withdrawing samples. The sonotrode is capable of supplying a maximum power output of 750 W. Atmospheric conditions were used in all the experiments. The experimental procedure for the kinetics measurement for e.g., 25 ppm DB71 dye with 1500 ppm of catalyst at neutral pH of 200 ml, was introduced in the sonochemical batch reactor with (35% amplitude energy input). 5 ml of the aliquots were withdrawn at regular time interval. The samples were filtered analysed for the reduction in absorbance by UV-visible spectrophotometer. The calibration graph was drawn against different dye concentrations. The unknown concentrations of the degraded dye samples were computed from the standard graphs. The residual concentration of the dye molecules after the degradation was determined from calibration chart. The efficiency of the dye degradation was calculated using Eqn (7).

$$Degradation \, efficiency \, (\%) = \frac{Co - Ce}{Co} \times 100 \qquad ...(7)$$

Where, C_o and C_e are the initial and final dye concentrations in the aqueous phase, respectively. The sonocatalytic dye degradation was also analyzed for COD reduction by closed reflux method.

Results and Discussion

Analysis of in-situ formation of reactive free radicals by EPR spectroscopy

The in-situ formation of free radicals were analyzed by Electron Paramagnetic Resonance Spectroscopy (EPR) by taking required amount of catalyst and DMPO was taken in an eppendorf tube then irradiated under ultrasound at room temperature for about 30 min at 35% amplitude energy input. Then the mixture was loaded into the EPR flat cell and analysed for the formation of free radical adduct by EPR spectroscopy. The in-situ formation of free radicals upon ultrasonic irradiation of the aqueous phase in the presence and absence of catalyst were

confirmed by EPR spin trapping technique using the radical trapping reagent DMPO. A typical EPR spectrum of the in-situ formation of free radicals was formed and the line shape and the hyperfine splitting are in good agreement with those reported in the literature. Further, the in-situ formation of OH• radicals in the aqueous phase under US irradiation was also evaluated without catalyst as shown in Fig. 1. The EPR spectrum showed a strong and stable four peak spectrum with intensity ratio of 1:2:2:1 which is the characteristics of DMPO spin trapped OH radicals. Distance between the each peak was observed as 15G, and with this it was concluded US irradiation of the aqueous phase OH free radicals. The peaks corresponding to the OH radicals show that the G values matched with the literature values.

Preliminary sonocatalytic studies

Homogeneous catalyst assisted sonocatalytic degradation of DB71 was optimized by various experimental parameters, such as effect of aqueous phase pH, catalyst dosage and initial concentration of dye molecules under atmospheric conditions.
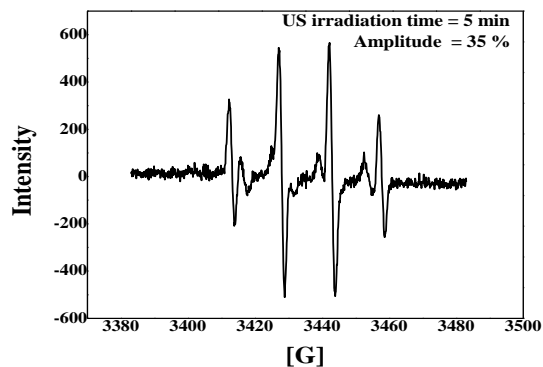

Fig. 1 — EPR spectrum of DMPO-OH adducts at 35% amplitude in 5 min irradiation

Effect of aqueous phase pH on the degradation of DB71 dye

The effect of pH was conducted in a batch reactor to determine the optimum pH for maximum degradation of the DB71 dye with PS as a catalyst. The experiments were performed at the pH range between 1.70 and 11.75, and irradiated under ultrasound with 35% amplitude energy input at room temperature (27°C). The initial dye concentration was fixed as 10 ppm/10 mL and 100 ppm and the experimental results are shown in Fig. 2.

Maximum degradation of dye molecule was observed in neutral pH. The percentage of degradation increased from acidic to neutral pH after which a decrease was observed in the alkaline pH for DB71 dye molecule. Hence, the neutral pH was chosen for further degradation experiments under US irradiations with PS.

The influence of ultrasound on the degradation of dyes with different pH without the catalyst have also been carried out experimental results are given in Fig. 2A. It is observed that in the presence of catalyst, passage of ultrasound irradiation has enhanced the percentage of degradation processes. However, in the absence of the catalyst, percentage of degradation is not appreciable. This minimal percentage of degradation could be due to the cavitation of aqueous phase that produces OH• which is responsible for the degradation.

Variation of initial catalyst dosage on degradation of DB71 dye

Effect of catalyst concentrations on dye degradation was studied in order to determine the optimum concentration of catalyst required for the maximum degradation of DB71 under ultrasonic irradiation at 35% amplitude energy input. The amount of catalyst was varied from 25 to 3000 ppm
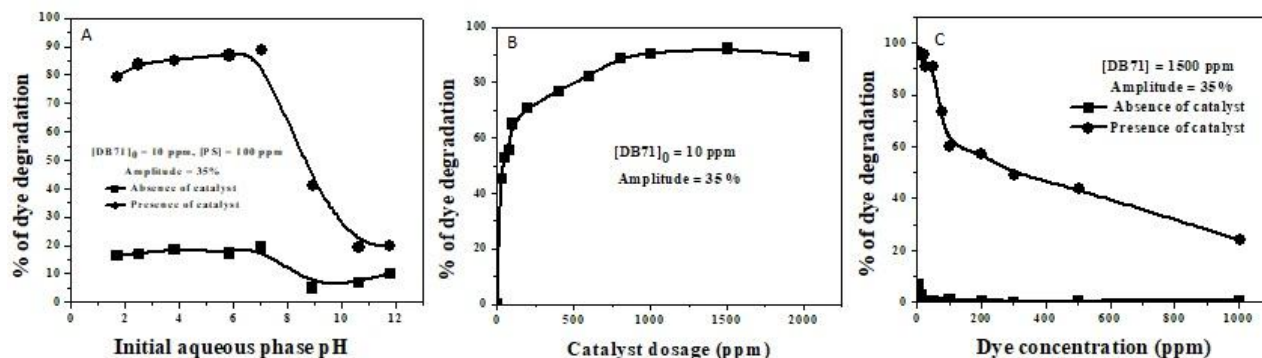

Fig. 2 — Effects of (A) aqueous phase pH, (B) catalyst dosage and (C) dye concentration on degradation of DB71 dye molecule under ultrasonic irradiation

with optimum pH of 6.34, dye concentration of DB71 dye the catalyst concentration was varied from 25 to 2000 ppm and the degradation increased from 45.38 to 92.41 up to 1500 ppm. Maximum % degradation was noticed with 1500 ppm of catalyst dosage for DB71 molecule and the results are shown in Fig. 2B. At 1500, ppm DB71 shows 92.41% degradation. For DB71 above 1500 ppm of PS the % degradation decreased which may be due to the fact that at the higher concentrations of the catalyst it tends to prevent proper cavitational effects and thus may be masking the catalytic activity[12].

Variation of initial dye concentration on DB71degradation

The experiment with varied dye concentrations was carried out to optimize the greater degree of degradation of dye molecules with optimized dosage of catalyst and results are illustrated in Fig. 2C. The dye concentrations were varied from 3 to 800 ppm dye with fixed concentration of 1500 ppm of catalyst 10 mL of dye and pH 6.34 (neutral pH) at 35% amplitude energy input. It was observed that under the present experimental conditions, the % degradation decreased from 99.38 to 8.07% with increase in dye concentration. It can be noticed that lower % degradation (i.e., 18.53 was observed for DB71) in the absence of catalyst. Hence, PS catalyst plays major role in the degradation of dye molecules under US irradiations.

Effect of energy input on degradation of DB71 dye under ultrasonic irradiation

An increase in ultrasonic power density would increase the mixing intensity. This increases the cavitation process which leads to the generation of enormous amount of reactive free radicals and these are used for degradation of dye molecule[13].

In order to find out the optimum energy density, the kinetics of DB71 dye degradation was studied in detail. The results of are shown in Table 1 & Fig. 3 (A-C) with different energy densities such as 25, 35 and 45% amp energy inputs under batch reactor conditions with 200 mL of 25 ppm of the dye and 1500 ppm catalyst under ultrasonic irradiation with optimized experimental conditions.

The results were analysed from the experimental data it was found that for DB71 dye 480 min (85.26%), 300 (81.04%), 180 min (79.41%) degradation was attained for all the 25%, 35% and 45% amplitude energy inputs respectively with corresponding time and %degradation (Fig. 3A). The reduction of COD (Fig. 3B) and TOC level was progressed at a faster rate below 30 min of reaction time and followed by the rate of oxidation dropped. From the results it was found that, the rate (pseudo first order rate constants) of dye degradation was increased from 20×10^{-3} to 69×10^{-3} min^{-1} for DB71 (Table 1) dye molecules for 25, 35 and 45 % of energy input respectively is given in Fig. 3C.

The kinetics for the energy input showed that the degradation rate is faster at 45% amp when compared to the degradation occurred in 25% and 35% amplitude energy densities. Though the higher US energy input (i.e., 45% amplitude) enhances the rate

Table 1 — Pseudo first order rate constants for the ultrasonic energy input on kinetics on sonocatalytic degradation of DB71 dye molecule

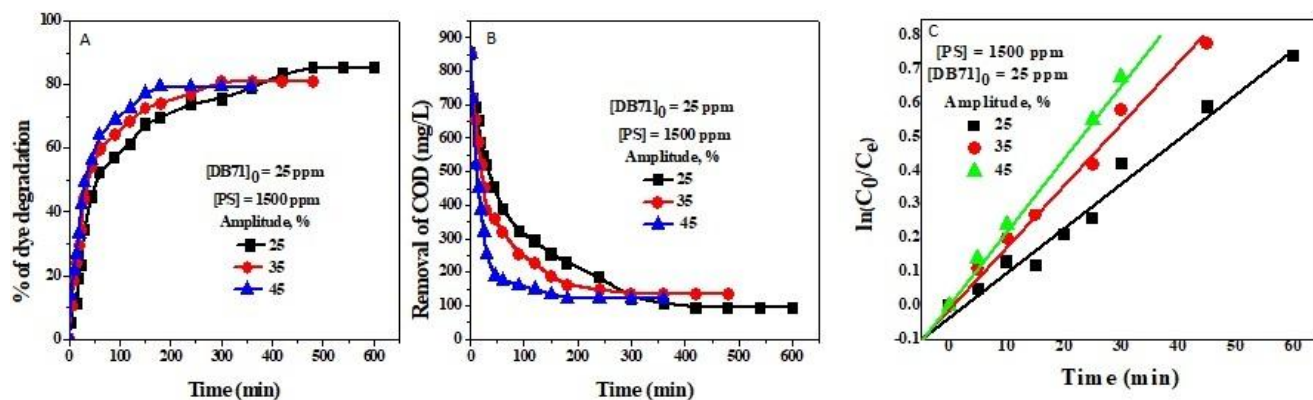| Concentration of the DB71dye (ppm)	Energy input (Amplitude %)	Rate constant $\times 10^{-3}$ (min^{-1})	R^2
25	25	20.29	0.9972
25	35	28.35	0.9872
25	45	69.32	0.9924

Fig. 3 — Effect of ultrasonic energy input on degradation of DB71 dye molecules (A) % of dye degradation, (B) Removal of COD and (C) Pseudo-first order kinetic plots

of the dye degradation many fold, 35% amplitude was chosen for further kinetic experiments considering cost and energy.

Kinetics of sonocatalytic degradation of DB71

Kinetics of sonocatalytic degradation of dye molecules has been done with different initial concentrations of DB71 with optimized experimental conditions from 10, 25, 50, 75 and 100 ppm under batch reactor conditions with 200 mL of the dye solution with catalyst under ultrasonic irradiation at 35% amplitude energy input.

The progress of the kinetics of dye degradation was monitored by measuring absorbance of the degraded samples using UV-visible spectrophotometer and COD analyses. The experimental results were shown in Table 2 and Fig. 4(A-C). It has been observed that 99.81%: (180 min), 81.04%: (300 min), 73.89%: (360 min), 69.04%: (480 min) and 62.86%: (720 min) of degradation was attained for all the 10, 25, 50, 75 and 100 ppm of the initial dye concentrations under US irradiations is shown in Fig. 4A. The experimental results reveal that the removal of COD decreased from 573.58 to 75.47, 853.30 to 133.33, 906.66 to 270.97, 1109.68 to335.48, 1324.14 to 386.21mg/L (for 10, 25, 50, 75 and 100 ppm), respectively Fig. 4B.

Table 2 — Pseudo-first order kinetic rate constants for the sonocatalytic degradation of DB71 dye molecule under ultrasonic irradiation

Concentration of the DB71dye molecules (ppm)	Rate constant 10^{-3} min^{-1}	R^2
10	22.07	0.9969
25	17.93	0.9930
50	12.17	0.9948
75	8.11	0.9977
100	7.07	0.9931

The kinetic data has also been analyzed by pseudo first order rate equation psuedo-first order kinetic plots of $\ln(D_0/D_e)$ *vs*. time for the representative kinetic reactions for various concentrations of dye solution were shown in Fig. 4C. The calculated pseudo first order rate constant (k) and R^2 values are illustrated in the Table 2. It is noted that the rate of reaction decreases with increasing dye concentrations or the rate of reaction is inversely proportional to the initial concentration of dye molecules.

Total Organic Carbon (TOC) analysis for DB71 dye

The degree of mineralization was monitored by TOC measurement of the degraded dye samples of DB71 as a function of time and calculated by the following Eqn (8).

$$\text{Total Organic Carbon} = \frac{TOC_{(ori)} - TOC_{(deg)}}{TOC_{(ori)}} \times 100 \quad (8)$$

From the kinetic studies, TOC level decreases from 107.01 to 26.11 mg/L 180 min for DB71 dye molecule as shown in (Fig. 5). From the results it was observed that the TOC level reduced to less than

Fig. 5 — Time dependence analysis of TOC level of the degraded DB71 dye molecule
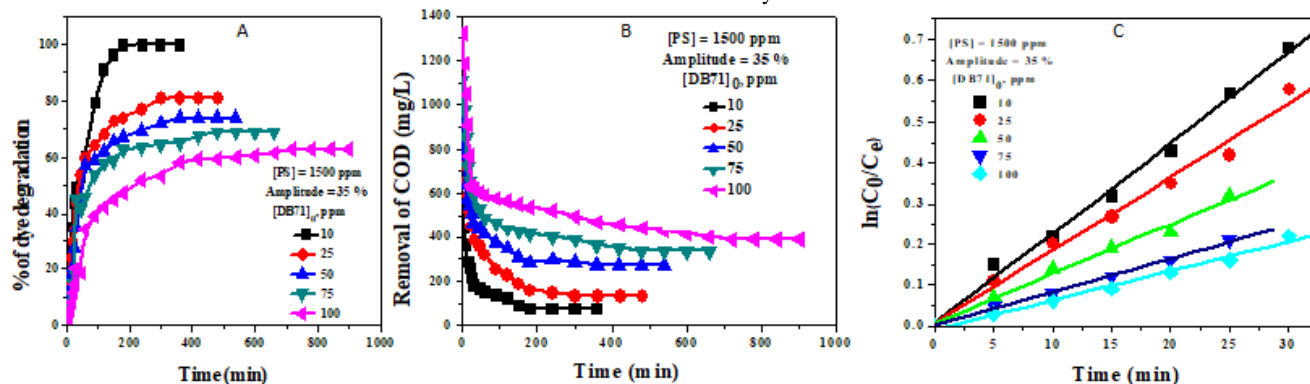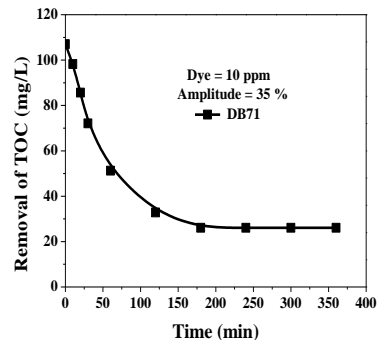
Fig. 4 — Kinetics of degradation of DB71 dye molecules using catalyst under ultrasonic irradiation (A) % of degradation, (B) Removal of COD and (C) Pseudo-first order kinetic plots

26 mg/L for DB71dye molecule. The TOC results clearly show that dye molecules are almost completely degraded and may be mineralized.

Effect of electrolyte concentration on degradation of DB71 dye

Industrial wastewater might have a number of electrolytes. The interference of electrolytes on the degradation of DB71 dye molecule has been studied with NaCl, KCl, NaCO$_3$, NaHCO$_3$, and MgSO$_4$ and the results are shown in Fig. 6. The concentration of electrolytes was varied from 0.5-5 wt % for 25 ppm of dye molecule.

The effect of MgSO$_4$ in DB71 dye shows marginal decrease of % degradation. It was also observed that in the presence of bicarbonate ions, the % degradation of the dye molecule decreased. This is because of bicarbonate halide ions are scavengers for radicals like hydroxyl ions in the oxidation process. DB71 dye shows the % of degradation was from 39.86 to 86.15 for NaCl and 54.16 to 61.41% for KCl.

By-product analysis

It is important to study the formation of by-products of the sonoctalytically degraded dye samples to check the efficacy of the PS catalyst in degradation of dye molecules under US irradiations. Different techniques such as UV-visible absorption spectroscopy, ESI-MS analyses have been used for the by-products analysis of the US degraded samples. Accordingly, plausible degradation mechanism is proposed for the dye molecule.

UV-visible Absorbance measurement for the sonocatalytic degradation

UV-visible absorption spectrum would generally provide valuable information on the formation of probable reaction intermediates and by-products during the course of sonocatalytic reaction. The by-product analysis 25 ppm of the degraded DB71 dye sample under US irradiations were performed in a UV-visible spectrophotometer in the range from 200 to 800 nm. The results are shown in Fig. 7. It is clearly observed that the absorption maximum at 587 nm diminishes very fast and nearly disappeared at 300 min for DB71 dye. This shows that complete decolourisation of the dye molecule can be attained in the presence of 1500 ppm of catalyst with 81.04%.

By-product analysis of DB71 dye degradation using ESI-MS$^+$ analysis
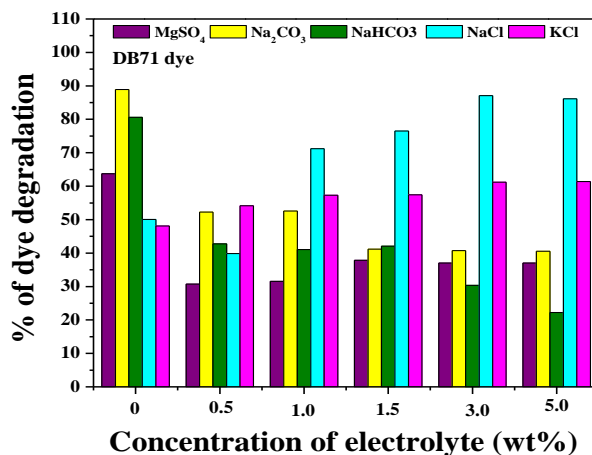
By-products formation of DB71 dye degradation

Fig. 6 — Effect of electrolytes concentration on degradation of DB71 dye molecule using catalyst under ultrasonic irradiation
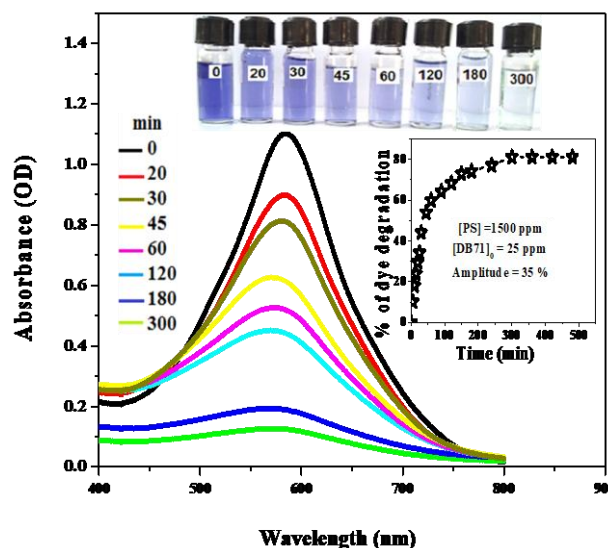

Fig. 7 — UV-visible absorbance spectra of DB71 dye (25 ppm) molecules using catalyst under ultrasonic irradiation (Inset) Kinetics of dye degradation and digital photograph of the degraded samples.

under US irradiations with catalyst was analyzed by ESI-MS$^+$ technique. The mass spectral data were analyzed in order to identify the degradation products for the neat and degraded samples which are illustrated in Fig. 8. The plausible mechanism for the fragmentation pattern of the dye with respect to ESI-MS$^+$ spectrum is given in Scheme 1.

The peak observed at m/z 965.15 is present in the starting mixture as given in Fig. 8A which is not present in the degraded intermediates as shown in
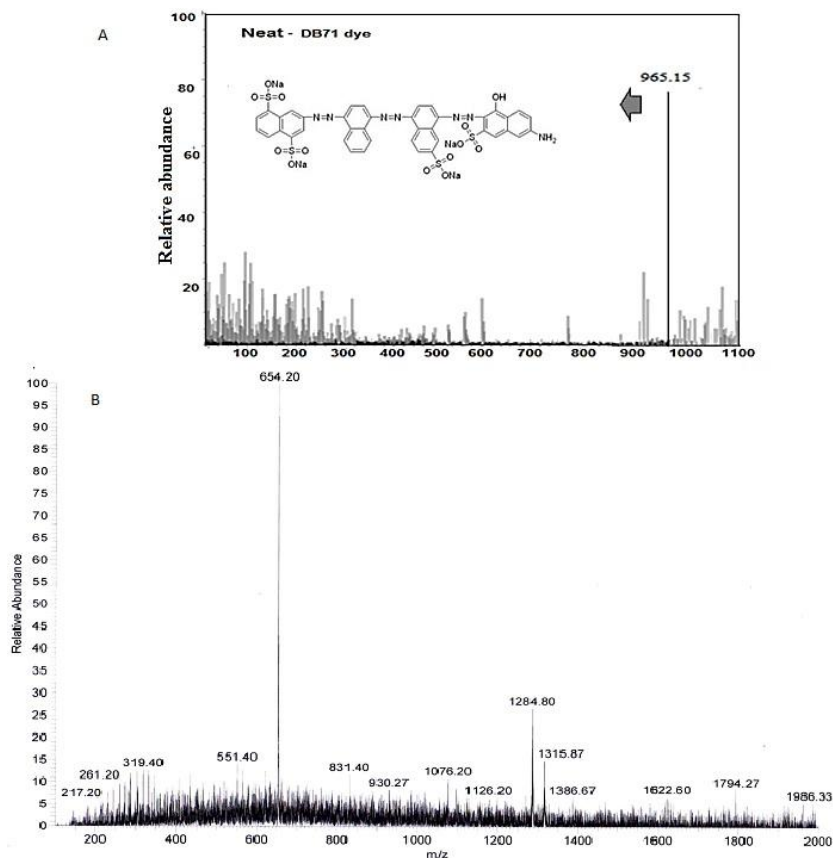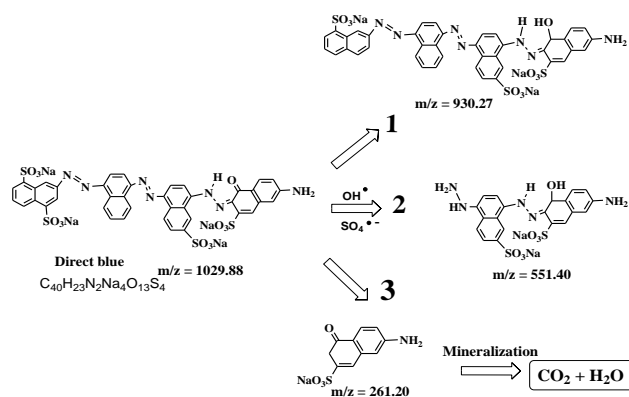
Fig. 8 — (A) ESI-MS$^+$ spectrum of 25 ppm of neat DB71 dye molecules; and (B) Degraded DB71 dye molecule with catalyst under ultrasonic irradiations

Scheme 1 — Plausible degradative reaction mechanism for DB71 dye molecule

Fig. 9 — Reduction in COD in mg/L for the real dye house effluent

Fig. 8B. This indicates that the neat DB71 dye molecule has degraded and formed a major fragmented species[14] (m/z 930.27, 551.40, 261.20 etc.). The ESI-MS analysis of the sonocatalytically degraded samples of DB71 clearly demonstrated that the dye molecules are readily degraded under present experimental conditions.
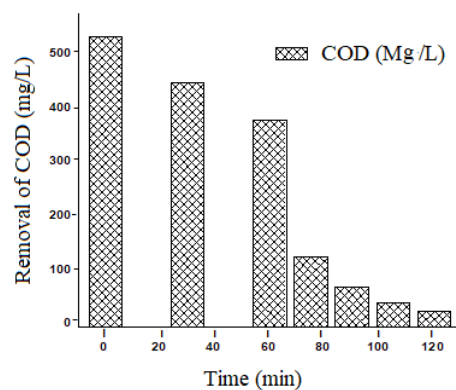
Sonocatalytic degradation of real dye house effluent under ultrasonic irradiation

The catalytic efficiency of the catalyst under US irradiations has also been tested with real dye house effluents. The composite dye house effluent was appropriately diluted and used for the further experiments. For a typical experiment, 100 mL of effluent mixed with 1500 ppm of catalyst and

irradiated under US irradiations with 35% energy input. The progress of the dye degradation was monitored simultaneously measuring the colour intensity and COD analyses. The results are shown in Fig. 9. It is noticed that the complete removal dye was observed at 120 min of US irradiations with PS and the reduction of COD level from 550 to less than 50 mg/L. Hence, the experimental results clearly demonstrated that toxic organics could be removed from dye house effluents with catalyst under US irradiations which can be used for different applications[15-17].

Conclusions

It is observed from the above results that DB71 dye showed 99% degradation at lower dye concentration and with higher concentrations up to 62%. The sonocatalytic reactions followed pseudo-first order kinetics and reaction rate increased many folds when increasing energy input and decreases with increasing initial dye concentration. The concentration of COD levels are remarkably decreased under US irradiation of the degraded dye samples with catalyst. This confirms that the US assisted homogeneous catalytic process could be effectively used for the oxidation of organics from the aqueous media. The effect of electrolytes was minimal on the degradation process. ESI-MS$^+$ analysis showed the additional support for the degradation. The catalyst was proved to be having improved sonocatalytic activity as observed from the kinetic experimental observations. Finally, the fragmented by-products may undergo further degradation in the mineralization process. The dye molecules are not only decolourized but may also be oxidized into water and carbon dioxide without the formation of toxic by-products. Hence, the catalyst may be exploited further for large scale industrial applications.

Conflict of interest

The authors declare no conflict of interests in this study.

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