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Removal of patent blue V dye using air bubble-induced oxidation based on small glass balls: intensification studies

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ABSTRACT

Removal of patent blue V dye from aqueous solutions has been investigated in the present work using air bubble-induced oxidation based on the use of glass balls. The dependency of removal of patent blue V on the operating parameters, such as initial concentration and pH has been established and it has been observed that optimum initial concentration of dye exists and also acidic conditions are favourable for enhancing the degradation. The effect of intensifying additives, such as ZnO, TiO_2 and MnO_2 as well as combination with ferrous sulphate has been investigated for the first time for the case of air bubble-induced oxidation. The maximum extent of removal (97%) of patent blue V was observed for the combined approach of air bubble-induced oxidation and ferrous sulphate, which promote the production of $HO^{\cdot}$ through the radical mechanisms. For the different oxides, the order of activity for higher removal of patent blue has been observed as $TiO_2 > MnO_2 > ZnO$. The present work has enabled the development of an intensified process involving use of air bubble oxidation for the treatment of dye containing wastewaters.

Keywords: Air bubble oxidation; Patent blue V; Glass balls; Solid additives; Process intensification

1. Introduction

Industrial revolution has brought numerous advances leading to the development of newer products and processes, but this has also led to a steep increase in the environmental problems. Due to the increasing industrialization, growth of population and economy, the presence of new and toxic molecules in the effluents is increasing at a high rate and the negative impact on the environment is drastic and quite far reaching. A major contribution to this phenomenon has been due to the development of new dyes to meet the aesthetic sense of the consumers. The

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pollution caused by the presence of dyes due to the significant usage in textile and food industries has seriously threatened the concept of greener environment. Due to increase in the awareness of environmental impact, it has become necessary for the industries to develop and apply effective techniques for decolourization of the effluents containing dyes before disposal into the water bodies.

Many physical and chemical methods, such as coagulation, precipitation, floatation, chemical oxidation, solvent extraction, etc. have been tried for the removal of dyes from wastewater, but these have not been very successful, since majority of the dyes are stable to oxidizing agents and also the treatment processes involve high costs, thus reducing the acceptability. Advanced oxidation processes (AOPs) have also been extensively explored for effective degradation of these compounds either individually or in different combinations. AOPs are characterized by the production of $HO^{\cdot}$ radicals as a primary oxidant, which are extremely reactive species and powerful oxidizing agents [1]. Another technique which has been successfully applied for the degradation of dyes is cavitation, which can also be used for the treatment of refractory compounds present in wastewater. Cavitation generally explored, this far, is based on the use of high-frequency sound waves (acoustic cavitation) or the alteration in the liquid flow due to the presence of constrictions, such as orifice and venturi (hydrodynamic cavitation) [2].

The present work is based on the use of a different approach based on the use of glass balls and passage of high-velocity air through the interstitial areas for generating conditions similar to cavitation. Xu et al. [3] have also reported similar approach of air bubble-based oxidation, where the production of oxidants is induced using small marbles and the reported work concentrated on the mechanistic details and understanding the effect of some operating conditions. As per the suggested mechanism, introduction of air bubbles into a pool of liquid containing small glass balls (Fig. 1) results in the formation of oxidants. When the introduced air passes through the glass balls, it induces liquid jets, which cuts the introduced bubbles into many smaller tiny bubbles due to the impact on the glass balls. The bubbles contain some amount of vapour, which will be exposed to severe conditions during the collapse. The formed tiny bubbles can continuously reduce in size due to the impact on layers of glass balls or these tiny bubbles can quickly recombine to form a bigger bubble. In the first case, the continuous impact on the surface of glass balls may create significant shear effects and conditions of higher temperature/pressure locally resulting in the generation of radicals due to the dissociation reactions. In the second case, when the inner wall tension reaches a maximum limit, the bigger bubbles break instantly leading to the intense conditions locally, which induce the formation of $OH^{\cdot}$ and $^{\cdot}O^{2-}$ radicals with strong oxidation ability along with some quantum of hydrogen peroxide. Due to the formation of reactive radicals and the oxidizing species, the organic pollutants can be degraded effectively.

The working principle of air bubble-induced oxidation is somewhat similar to hydrodynamic cavitation, where cavitation is generated by the passage of liquid through a constriction, such as throttling valve, orifice plate, venturi, etc. [4] Several authors have studied degradation of dyes, pesticides and other chemicals [5–10] using hydrodynamic cavitation and it has been demonstrated that hydrodynamic cavitation is also

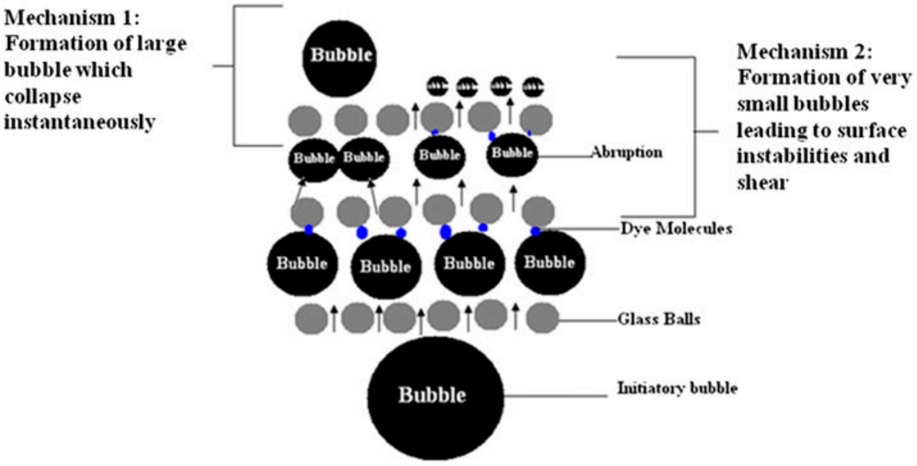

Fig. 1. Possible mechanism of air bubble induced oxidation phenomenon.

efficient in the degradation of toxic chemicals and effective intensification can be obtained based on the use of different additives. The present work reports a novel study of intensification of degradation using air bubble-based oxidation, which has been investigated for the first time to the best of our knowledge.

Patent blue V has been used as a specific pollutant which is an acidic dye, also called as Food Blue 5, having a molecular formula of $C_{27}H_{31}N_2O_7S_2$. The dye has dark bluish colour and is used in cosmetics, textile industries and detergents [11]. Though patent blue is used in many applications, its occurrence in water can create significant problems including the adverse effects on micro-organisms and serious allergic reactions to human beings, such as anaphylaxis. The typical range of concentration of patent blue V in the waste water from the processing industries is about 10–100 mg/L, depending on the type of application. Considering these attributes, developing efficient treatment strategies for the removal of patent blue V is very important and hence, has been investigated using an approach based on the use of air bubble oxidation. The development of intensified process based on the use of different additives for process intensification, such as titanium oxide (TiO_2), manganese oxide (MnO_2), zinc oxide (ZnO) and sodium chloride (NaCl) as well as ferrous sulphate giving Fenton like mechanism has also been attempted.

2. Materials and methods

2.1. Materials

Patent blue V, a synthetic dye, is basically a sodium or calcium salt of [4-(α-(4-diethylaminophenyl)-5-hydroxy-2,4-disulfophenylmethyli-dene)-2,5-cyclohexa-dien-1-ylidene] diethylammonium hydroxide. The colour index number of patent blue V is 42045. It has the appearance of a violet powder in the solid form. In aqueous solution, the colour varies depending on the pH with deep blue color under basic conditions and yellowish-green colour under acidic conditions. The dye was obtained from Loba Chem. Pvt. Ltd, Mumbai, India. The chemicals required for adjustment of pH, such as NaOH and H_2SO_4 as well as the additives, such as TiO_2, ZnO, $FeSO_4{\cdot}7H_2O$, MnO_2 and NaCl were obtained from Merck Specialties Pvt. Ltd, Mumbai, India.

2.2. Equipment and procedure

A schematic representation of air bubble oxidation reactor set-up has been depicted in Fig. 2. The reactor consists of four compartments with a total height of 35 cm filled with a number of glass marbles with diameter of 6 mm. The first compartment of reactor is 20 cm in height and 10 cm in diameter, while the other three compartments of the reactor have a height of 5 cm. The top compartment is conical in shape with maximum diameter at the top being 25% larger than the base and other compartments. The reactor was completely leak proof and also the joints used for input and output ports were carefully sealed. The flow of air into the column was distributed through the sieve plate attached to the first and second compartment. A constant glass ball size has been used throughout the experiments and the height of the packed section containing the glass balls was about 75% of the reactor height. An air compressor obtained from Renault Professional Air Compressor Private Ltd., Pune, operating at a maximum power rating of 7 HP and with an air tank capacity of 36 L was used to introduce air into the reactor. The flow rate of air was kept constant at 4.5 L/min.

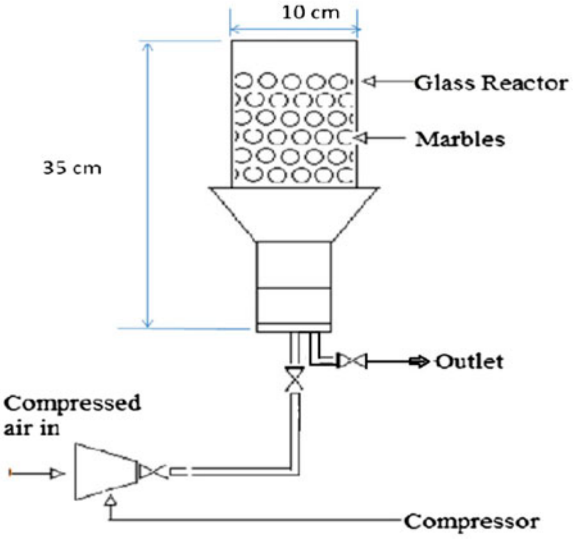

Fig. 2. Experimental set-up for the degradation of patent blue V using air bubble oxidation.

An aqueous stock solution was prepared initially, which was used for the preparation of the solutions of required concentrations for the experimental runs using demineralized water. The volume of solution taken in the reactor was 700 ml. Samples (20 ml volume) were withdrawn from the solution at regular intervals of 10 min. The withdrawn samples were subjected for the separation of solid particles using Whatmann's filter paper (two times to ensure the complete removal of solids). UV–vis spectrophotometer (Chemito Spectrascan UV 2600 double beam) was used to quantify the dye concentration and hence, the extent of removal during the process. The samples were analysed at a wavelength of 675 nm. The extent of removal was calculated comparing the concentrations at zero time and at the actual time (*t*, min).

The experimental runs for understanding the effect of pH on the patent blue V removal were performed at different pH over the range of 2.2–11.2 adjusted using 1 N NaOH and conc. H_2SO_4 as required. The effect of different catalysts was investigated over the concentration range of 0.2–0.6 g/L. The size of TiO_2 used in the work was in the range of 1–1.5 μm and it was in rutile form with tetragonal structure. The particle size of other additives was in the range of 1–3 μm.

All the experiments were repeated at least two times to check the reproducibility and average values have been reported in the discussion. Error bars have also been shown in the figures to depict the variation, which was within 2% of the reported average value.

2.3. *Adsorption study*

The possible adsorption of patent blue V on glass balls was also investigated as a preliminary study. In a typical experimental run, 100 ml of aqueous solution of dye at a fixed initial concentration was mixed with glass balls and the mixture was kept overnight in a dark room. The change in dye concentration was measured by UV–vis spectrophotometer. It was observed that the adsorption of dye on glass surface was negligible, possibly attributed to its finishing or polished surface [12].

2.4. *Detection of formation of hydrogen peroxide*

For the degradation of pollutant species, it is important to know whether free radicals or, in general, the oxidizing agents are generated in the reactor based on the concept of air bubble oxidation induced by glass balls. Thus, experiments have been carried out to investigate the generation of H_2O_2 as in the absence of any pollutants the formed hydroxyl radicals would recombine to give hydrogen peroxide. Measurement of H_2O_2 was performed using a simple method based on the monitoring absorbance using a UV–vis spectrophotometer at a wavelength of 192 nm [13]. Demineralized water was taken to investigate the generation of H_2O_2 in the absence of patent blue dye and the obtained spectra (after 60 min) have been depicted in Fig. 3. The observed peak clearly confirms the generation of H_2O_2, which can be possibly attributed to the formation of $OH^{\cdot}$ and $HO_2^{\cdot}$ radicals which undergo a series of reactions resulting in the formation of H_2O_2 as depicted below:

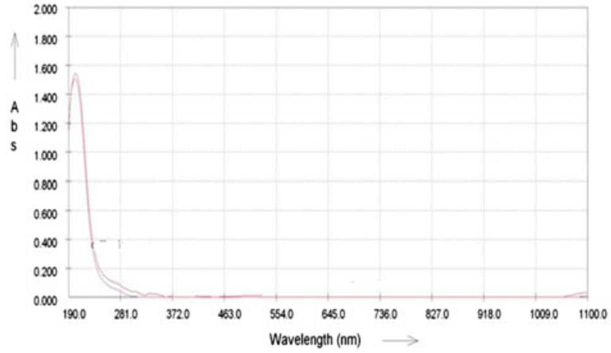

Fig. 3. Generation of hydrogen peroxide using air bubble oxidation induced by glass balls (treatment time of 60 min).

$$H_2O \rightarrow OH^{\cdot} + H^{\cdot} \tag{1}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{2}$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \tag{3}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{4}$$

$$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \tag{5}$$

3. Results and discussion

3.1. *Effect of initial dye concentration*

In order to investigate the effect of initial concentration of patent blue V on the extent of degradation, experiments were performed over a range of initial concentration as 10–30 mg/L. The variation in the percentage removal of patent blue with respect to the reaction time at different initial concentrations has been depicted in Fig. 4. It can be seen from the figure that the extent of removal of patent blue dye increases with an increase in the initial concentration from 10 to 20 mg/L, beyond which increase in the initial concentration of patent blue V results in a reduced extent of degradation. It can also be seen from the figure that during the initial period of treatment, the rate of removal of patent blue at 20 mg/L loading was twice than that obtained for the case of 10 mg/L loading. The maximum removal of patent blue as 57% was obtained at an optimum dye concentration as 20 mg/L after 180 min of treatment. The observed optimum can be attributed to the fact that initially the

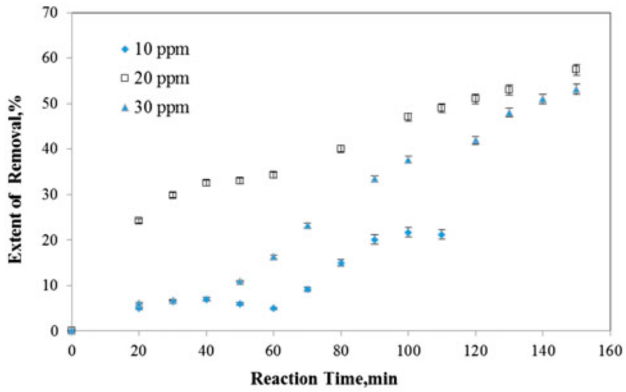

Fig. 4. Effect of initial concentration on the removal of patent blue V using air bubble oxidation (pH 4.2; concentration = 20 mg/L; catalyst loading 1.5–4.5 g/L).

oxidizing species are in excess and with an increase in concentration, these are able to oxidize higher quantum of dye present in the solution giving higher rates till the optimum loading. It is also important to understand that the generation of OH· radicals remains constant based on the operating conditions [14] giving a plausible steady state between the dye molecules that can be utilized for degradation and hydroxyl radicals generated in the solution. Beyond the optimum dye concentration, limited availability of the oxidizing radicals reduces the probability of reaction between dye molecules present in excess and the available oxidizing species, leading to a decrease in the degradation rate. At this point, rate of generation of hydroxyl radicals becomes a limiting factor giving the overall lower extents of degradation.

Another plausible mechanism to explain the existence of optimum dye concentration is based on the fact that the degradation rate is dependent on the relative availability of HO· radicals and dye molecules at the site of reaction. At the surface of the bubble, the availability of OH· is remarkably high [15]. At very low dye concentrations, the possibility of recombination of OH· forming H_2O_2 is dominant at the surface where there is a high concentration of radicals. On the other hand, the oxidation reaction for the removal of dye occurs in the bulk of the solution, where there is a lower concentration of OH· radicals attributed to the fact that only about 10% of the OH· radicals generated in the bubble can diffuse into the bulk. With an increase in the dye concentration, the probability of radical attack on the patent blue molecule increases, thus leading to an increase in the extent of removal. At significantly higher concentration, there is a limiting generation of OH· radicals as compared to the excess dye molecules present in the solution and hence, the extent of removal of dye decreases. The obtained results are consistent with the results reported by Xu et al. [3], who reported that at very high initial concentrations, degradation is not complete and significantly higher treatment times are required. In the work of Xu et al. [3], the initial concentration of methyl orange (MO) was varied over the range of 5.0–25 mg/L and it was reported that maximum degradation of MO was obtained at 10 ppm concentration.

The obtained results for the kinetic fitting are shown in Fig. 5 and it can be seen that patent blue V dye fitted the pseudo-first-order reaction kinetics model. The kinetic rate constant for the removal of patent blue V dye at an optimum concentration of 20 ppm has been observed to be equal to 7.2×10^{-3} min^{-1} with $R^2 = 0.99$ confirming an excellent fitting.

3.2. *Effect of pH*

Operating pH is one of the important parameters in deciding the physicochemical properties of the solution, which in turn affects the ease of generation of hydroxyl radicals as well as the nature of pollutants. The effect of pH was investigated over the range of 2.2–11.2 at an optimal loading of dye as 20 mg/L. Concentrated H_2SO_4 and 1 N NaOH solutions were used to adjust the pH of the solution at the required value. The solubility data confirmed that the changes in pH did not affect the concentration as the solubility 25℃ was 40 g/L at a pH of 4.2 and 50 g/L at a pH of 9.2.

Fig. 6 depicts the obtained results for the effect of pH on the removal of patent blue V. It can be seen that the extent of degradation decreases with an

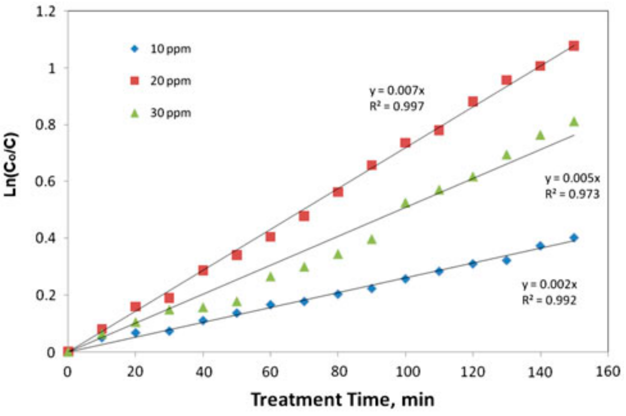

Fig. 5. Kinetic rate constant at optimal concentration of patent blue V using air bubble oxidation (pH 4.2; concentration = 20 mg/L).

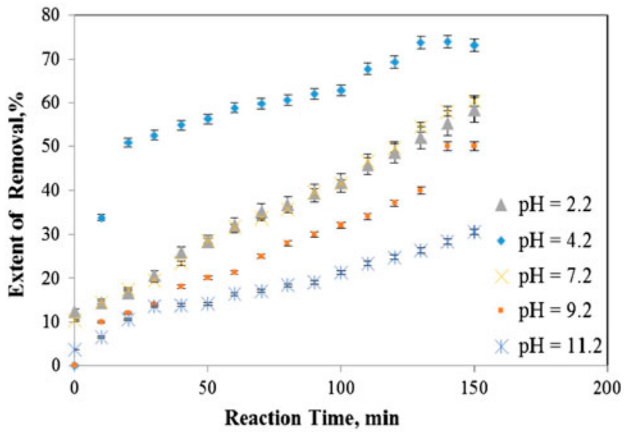

Fig. 6. Effect of pH on the removal of patent blue V using air bubble oxidation (concentration = 20 mg/L).

increase in the pH. The maximum removal (73%) was obtained at a pH of 4.2 and the extent of degradation was significantly lower under alkaline conditions. The enhancement in the degradation at lower pH can be attributed to the fact that dye molecule is present in the molecular state at lower pH and due to the hydrophobic nature; it can easily locate or prefer to be at the gas–water interface, where the maximum concentration of oxidizing species is expected. At a higher pH, the dye molecules are ionized, which are more hydrophilic in nature and this ionic form remains in the bulk liquid. Only a small fraction of the generated $OH^{\cdot}$ radicals can diffuse into the bulk, which results in a lower availability for the oxidation of dye giving a lower extent of removal.

Similar results of higher extent of degradation under acidic conditions can be observed in the literature though for the case of ultrasonically induced cavitation. Shriwas and Gogate [16] reported that sonodegradation of methyl parathion was favoured at a lower pH. Zhang et al. [17] also reported that the optimum pH for the maximum degradation of C.I. acid orange was in the range of 2–4, whereas Sun et al. [18] reported that the extent of decolourization of acid black 1 was increased from 5 to 98% with a decrease in the operating pH from 6 to 3.

3.3. Effect of the presence of solid additives

Many efforts have been directed in the past to intensify the degradation of pollutants using different additives that can have a catalytic action or can increase the generation of oxidants, however, no such study has been reported for air bubble oxidation. With this background, the use of additives to enhance the removal efficiency of air bubble oxidation has been investigated. The presence of solids in the liquid continuum provides an additional heterogenecity due to the presence of surface that represents weak points resulting in an enhanced nucleation leading to the enhanced formation of oxidants [19]. In addition, the solids can have catalytic action on the reactions leading to the formation of different oxidizing species.

Experiments have been performed with the addition of different solid particles, such as ZnO, TiO_2 and MnO_2 to investigate the effect on the extent of degradation using air bubble oxidation. Different loadings of ZnO, TiO_2 and MnO_2 particles over a range of 0.2–0.6 g/L have been used for the investigations. It has been observed that all the solid particles show the same trend of enhanced removal in the presence of particles and also the extent of removal increases with an increase in the loading of additive till an optimum magnitude. For example, the removal of patent blue dye increased with an increase in the loading of ZnO till an optimum of 0.3 g/L and further addition of ZnO particles resulted in decreased effects. The maximum extent of removal of patent blue V was 77% at the loading of ZnO as 0.3 g/L. The initial increase in the removal with an increase in the solid loading can be attributed to the fact that the total active surface area increases resulting in an increased production of oxidants. The lower extent of the removal of patent blue dye with the addition of ZnO particles beyond an optimum loading can be attributed to the turbidity of the suspension with high dose of ZnO giving aggregation of particles, resulting in lower number of active sites or an effective surface being available for the desired benefits.

The obtained results are consistent with the reported results of Kaur and Singh [20], where the influence of three different photocatalysts as TiO_2-P25, ZnO and Hombikat UV-100 on the degradation of Reactive Red 198 has been investigated and an existence of optimum catalyst loading for maximum benefits has been demonstrated. Kansal et al. [21] also investigated the degradation of MO and Rhodamine 6G using various solid catalysts, such as TiO_2, ZnO, SnO_2, ZnS and CdS. The results for decolourization efficiency at various catalyst loadings confirmed that initial rates of degradation increased greatly with an increase in the catalyst loading from 0.25 to 1.0 g/L and subsequently the rate of decolourization decreased with a further increase in the catalyst loading.

For the case of TiO_2, similar range of loading has been used to evaluate the optimal amount for the efficient removal of patent blue V. The observed results confirmed that the maximum removal of patent blue V was obtained at the loading of TiO_2 as 0.6 g/L and the extent of removal showed a continuous increase with an increase in the TiO_2 loading over the entire range. The continuous increase in the removal of patent blue V till 0.6 g/L is attributed to the fact that the presence of TiO_2 can enhance the production of free radicals thereby increasing the rate of removal of dye. The difference in the surface characteristics and activity gives different trends for the variation in the extent of degradation with the additive loadings.

The results are consistent with the earlier results of Kubo et al. [22], who have shown that the degradation efficiency of sonochemical reactors increases in the presence of TiO_2 particles and, furthermore, the rate constant for degradation of phenol increased with an increase in the loading of TiO_2 particles. Similar observations have also been reported in an earlier work [23], where degradation of formic acid has been investigated in a multiple frequency sonochemical reactor. The use of TiO_2 particles for intensification of the production of $OH^{\cdot}$ radicals is recommended particularly in the case of wastewater treatment applications, where synergistic effects of sonochemistry and photocatalytic oxidation can be utilized for the intensification of oxidation [24,25].

In the case of MnO_2 solid particles, it has been established that the extent of removal of patent blue V also continuously increases with an increase in the loading of MnO_2. The maximum extent of removal as 81% was obtained at 0.6 g/L of MnO_2, which can be attributed to the presence of additional nuclei for the formation of oxidants.

It is interesting to compare the extent of degradation obtained for different solid additives used in the work. The obtained results at 0.6 g/L catalyst loading have been depicted in Fig. 7 for comparing the efficacy of different solids. It has been observed that the order of activities for higher removal of patent blue V is $TiO_2 > MnO_2 > ZnO$. The higher removal of patent blue V using TiO_2 is based on the enhanced catalytic activity of TiO_2 giving an enhanced generation of hydroxyl radicals and also additional surface area offered by TiO_2 as compared to the other particles. The use of MnO_2 also gives similar mechanism in terms of the formation of superoxide anion and hydroxyl radicals [26] though to a lower extent as compared to TiO_2. The extent of degradation is dictated by the size of the solid particles, which affects the specific surface area and hence the extent of heterogeneity present in the system. The detailed characterization including the SEM images for the specific case of TiO_2 has been presented in the earlier work [27], where it has been observed that TiO_2 particles are extremely fine without forming any agglomerates and more crystalline which can possibly give a higher extent of heterogeneity resulting in higher extents of degradation. The use of TiO_2 particles also gives catalytic effect for the production of oxidizing species which is higher as compared to the ZnO and MnO_2 particles giving higher extents of degradation.

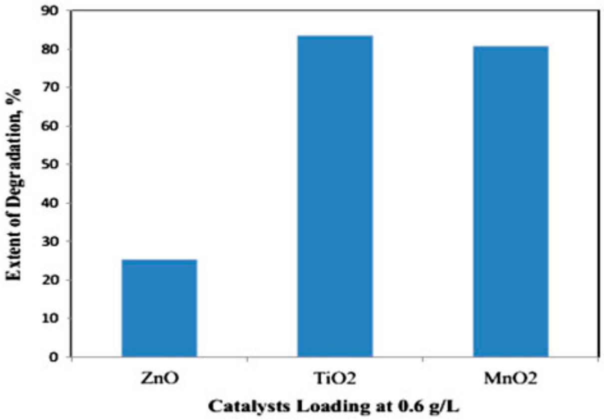

Fig. 7. Effect of catalysts on the removal of patent blue V using air bubble oxidation (pH 4.2; concentration = 20 mg/L; additive loading 0.6 g/L).

3.4. Effect of NaCl

Generally, the presence of salts, such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4), etc. can alter the distribution of compounds in the solution by changing the partition coefficient. Consequently, it can change the distribution of organic pollutants at gas–liquid interface favourably leading to an increase in the rate of degradation. Considering this fact, the removal of patent blue V was investigated at different concentrations of sodium chloride ranging from 0.2 to 0.6 g/L and the obtained results are given in Fig. 8. The extent of removal of patent blue V was significantly higher in the presence of NaCl at a concentration of 0.4 g/L of NaCl, beyond which the removal of patent blue V remained almost constant with a further increase in the concentration of NaCl in the solution.

The maximum removal of 95% was obtained at 0.4 g/L concentration of NaCl, which can be attributed to the fact that addition of salt alters the physicochemical properties of the solution in terms of density, vapour pressure, hydrophilicity of organic pollutant, surface tension and ionic strength of the aqueous phase [28–30]. These changes facilitate the generation of oxidation events in terms of bubble formation and breakage as well as favourable distribution of the pollutant at the site of collapse. All these effects lead to an increase in the rate of removal.

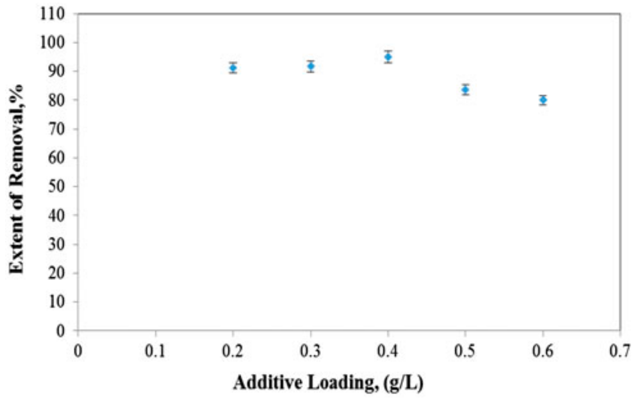

Fig. 8. Effect of NaCl on the removal of patent blue V using air bubble oxidation (pH 4.2; concentration = 20 mg/L).

Mahamuni and Pandit [31] studied the effect of NaCl on the sonochemical degradation of phenol. It has been reported that, compared to the experimental runs without NaCl, addition of NaCl at 2 and 8% loadings increased the reaction rate by 1.1 and 1.5 times, respectively. Ghodbane and Hamdaoui [32] also reported that the presence of salts, such as NaCl, $CaCl_2$, $NaHCO_3$ and KI increased the degradation rate of organic pollutants.

3.5. Effect of addition of ferrous sulphate

The obtained results for the effect of addition of ferrous sulphate ($FeSO_4{\cdot}7H_2O$) on the patent blue dye removal are given in Fig. 9. It can be seen from the figure that the extent of removal of patent blue V increases with an increase in the concentration of ferrous sulphate. The maximum extent of removal as 97% was obtained at a concentration of 0.3 g/L $FeSO_4{\cdot}7H_2O$. The observed intensification can be attributed to the presence of Fe^{2+} that promotes the production of oxidizing species. Under the conditions induced by passage of air bubbles in the system, $FeSO_4$ splits into ferrous ion (Fe^{2+}) and sulphate ion (SO_4^{2-}). Sulphate ions can subsequently react with water molecules to produce $HO^{\bullet}$ which result in an enhanced destruction of patent blue V. Hydrogen peroxide formed during the treatment also reacts with ferrous ions to generate additional active $HO^{\bullet}$ radicals, which may accelerate the destruction of dye via the usual fenton chemistry mechanism. The different reactions constituting the enhanced generation of oxidizing species can be given as follows:

$$FeSO_4 \rightarrow Fe^{2+} + SO_4^{-\bullet} \tag{6}$$

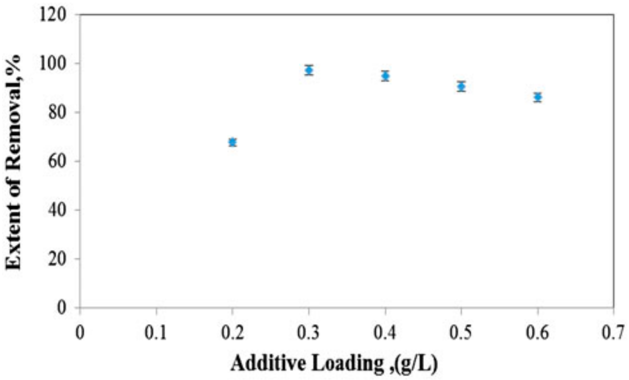

Fig. 9. Effect of ferrous sulphate on the removal of patent blue V using air bubble oxidation (pH 4.2; concentration = 20 mg/L).

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet} \tag{7}$$

$$HSO_4^{-} + HO^{\bullet} \rightarrow H_2O_2 + SO_3^{-\bullet} \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\bullet} \tag{9}$$

Merouani et al. [28] reported that the addition of bivalent iron (Fe^{2+}) accelerates the degradation of Rhodamine B to a higher extent as compared to trivalent iron (Fe^{3+}). An optimum concentration of Fe^{2+} when used in conjunction with ultrasonic irradiation was also reported to be beneficial for intensification [28,33]. When the $FeSO_4$ concentration was higher than the optimum concentration, the solution became saturated with Fe^{2+} ions and resulted in self-quenching of $HO^{\bullet}$ radicals. Therefore, no further improvement in the generation of $HO^{\bullet}$ radicals occurred. In general terms, it can be established that the beneficial effect of the combined techniques can only be achieved if the optimum level is not exceeded.

3.6. COD analysis

The COD values can be related to the total concentration of organics in the solution that can be oxidized chemically and the decrease in COD reflects the degree of mineralization. COD measurements have been done for the specific case of operation involving the use of optimized parameters only and the obtained results are given in Table 1. As it can be seen from the table, the initial COD value for patent blue V solution was 2,465.6 mg/l. After air bubble-induced oxidation treatment, the maximum reduction in the COD value was observed for the case of treatment

Table 1
Percentage reduction of COD for the treatment of solutions containing patent blue V dye using air bubble-induced oxidation

S. no.	Parameters with extent of degradation	Initial COD (mg/l)	Final COD (mg/l)	Percentage removal (%)
1	20 ppm without catalyst, pH 7.2 (73.1%)	2,465.6	1,564.0	36.6
2	0.3 g/L of ZnO (77.1%)	2,465.6	1,245.1	49.5
3	0.6 g/L of TiO_2 (83.4%)	2,465.6	974.2	60.5
4	0.4 g/L of NaCl (95.6%)	2,465.6	800.0	67.6
5	0.6 g/L of MnO (80.7%)	2,465.6	946.8	61.6
6	0.3 g/L of $FeSO_4 \cdot 7H_2O$ (97%)	2,465.6	786.1	68.1

scheme involving the use of $FeSO_4 \cdot 7H_2O$ at a loading of 0.3 g/L under optimized conditions of pH and concentration after 180 min of treatment. The extent of COD reduction varied over the range of 36–68% as demonstrated in Table 1 and this was in correspondence with the extent of removal patent blue V dye.

4. Conclusions

The present work has clearly established that patent blue V dye can be effectively removed from water using air bubble oxidation and the efficiency can be intensified using different additives. Operating process parameters, such as initial concentration and pH of patent blue V significantly affect the rate of removal and it was confirmed that the optimum initial concentration and acidic conditions are suitable giving higher extent of removal. It has been also established that the presence of solid particles intensified the removal of patent blue V dye. Among the different solid particles used, viz. TiO_2, MnO_2 and ZnO over a range of catalyst loadings as 0.2–0.6 g/L, the order of activities for the higher removal of patent blue V was $TiO_2 > MnO_2 > ZnO$. The use of NaCl and $FeSO_4 \cdot 7H_2O$ as additives also resulted in a higher extent of removal of dye i.e. more than 90%. The maximum extent of removal of patent blue dye was obtained as 97% for the approach involving an optimum addition of $FeSO_4 \cdot 7H_2O$ at a loading of 0.3 g/L. Based on the results, it has been clearly established that the air bubble oxidation-based treatment strategies intensified using different additives give a feasible option for degradation of dyes.

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