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Scientific paper

Exploring a Substitute for Hydrogen Peroxide in Fenton Process – A Case Study on the COD Removal of Acid Orange 8

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Abstract

Hydrogen peroxide (HP) is widely used in advanced oxidation processes (AOPs). This study evaluates the chemical oxygen demand (COD) removal efficiency of Acid Orange 8 (AO 8) at a higher concentration by modified Fenton processes using substituted HP, such as *tert*-butyl hydroperoxide (TBHP), sodium perborate (SPB), and sodium persulphate (SPS) as oxidising agents. Under optimal conditions, COD removal was found to be 72.8 and 58.9% at pH 3.0 and 6.5 in the Fenton process in 300 min. The COD removal efficiency of different systems is in the order: Fe^{2+}/SPB > Fe^{2+}/HP > Fe^{2+}/TBHP > Fe^{2+}/SPS indicating the possibility of using SPB as a substitute for HP and SPS. The order of efficiency is attributed, among other factors, to their ability to produce $HO^\bullet$ radicals. Various anions are shown to exhibit an inhibitory effect in the order: $I^- > Br^- > F^- > Cl^- > SO_4^{2-} > NO_3^-$. The inhibitory effect of Cl^- is observed at higher concentrations than F^- and Br^-, even though I^- displays inhibition at all concentrations. Finally, COD removal kinetics and the degradation mechanism, based on the identified intermediate products, were determined in this study.

Keywords: Fenton and modified Fenton processes; Substitute of hydrogen peroxide; tert-Butyl hydroperoxide; Sodium Perborate; COD removal kinetics; Identification of products and degradation mechanism

1. Introduction

Synthetic dyes are widely used in different industries, such as textile, cosmetic, printing, drug, food processing, tannery, leather etc.[1] Such dyes are stable and resistant to biodegradation causing discoloration of wastewater.[2] The colour tends to persist even after different conventional treatment process such as coagulation,[3] adsorption,[4] membranes processes,[5] biological processes,[6] etc. Among the various AOPs, Fenton (Fe^{2+}/HP) has been proved to be convenient, efficient and cost effective.[7–12] Fenton process utilises highly reactive hydroxyl radicals ($HO^\bullet$), generated by the decomposition of HP by Fe^{2+} (Eq. (1)). Hydroxyl radicals are non-selective and have high oxidation potential of 2.8V *vs.* normal hydrogen electrode (NHE) with rate constant in the order of 10^7 to 10^{10} $M^{-1}s^{-1}$.[13] Therefore, they have excellent ability to mineralize organic compounds including azo dyes to carbon dioxide, water and inorganic salts. However, the effectiveness of this process has been limited by its narrow working pH range.[7] Thus, there is a need for search of alternate oxidant to be used in the Fenton process. Persulphate (PS), e.g. sodium persulphate (SPS) has long been used successfully and efficiently in place of HP in a process, called modified Fenton process (Fe^{2+}/PS).[14–16] This process utilises reactive sulphate radicals ($SO_4^{\bullet-}$), which are generated by the activation of PS by Fe^{2+} (Eq. (2)). The advantage of this process is its ability to work in a broad pH range.[17]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \tag{1}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \tag{2}$$

It has been reported that *tert*-Butyl hydroperoxide (TBHP), an organic peroxide and Sodium perborate (SPB) are potential oxidants to replace HP in the Fenton process.[18–20] The difference among these three oxidants is the presence of different groups adjacent to the peroxo-bond (–O–O–). While it is hydrogen atoms on both sides of the peroxo-bond in HP, *tert*-butyl on one side in TBHP and dihydroxyboranyl on both sides in SPB (Fig. 1).

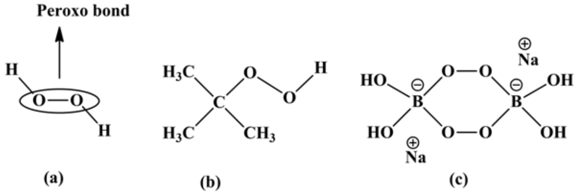

Figure 1. Structure of oxidants: (**a**) HP; (**b**) TBHP; (**c**) SPB (dimer)

TBHP is widely used as a radical initiator in polymerization reaction and as a cross linking agent in unsaturated polyester.[21,22] It is also used as a source of *tert*-butyl derivatives.[21] When used as an oxidant in the modified Fenton process (Fe^{2+}/TBHP), TBHP generates *tert*-butoxyl radical ($(CH_3)_3CO^•$, t-$BuO^•$) as the major species along with *tert*-butylperoxyl radical ($(CH_3)_3COO^•$, t-$BuOO^•$) (Eqs. (3) and (4)).[18,19,23] However, generation of $HO^•$ was not reported in those studies. The generation of t-$BuO^•$ radicals is analogous to the classical Fenton reaction (Eq. (1)).

$$Fe^{2+} + t - BuOOH \rightarrow Fe^{3+} + t{-}BuO^{•} + HO^{-} \quad (3)$$

$$Fe^{3+} + t - BuOOH \rightarrow Fe^{2+} + t{-}BuOO^{•} \quad (4)$$

The use of SPB has been widely seen in ophthalmology, dental industry, pulp bleaching, and detergent industry as a bleaching agent.[24] The reagent possesses low toxicity and a longer self-life and has been used as a substitute for HP in organic synthesis.[20] SPB when dissolved in water releases sodium metaborate and H_2O_2 (Eq. (5)).[20,24] Thus, the presence of catalysts like Fe^{2+} in aqueous acidic SPB solution would establish Fenton process, which leads to the generation of $HO^•$.[25] The degradation of cytarabine antineoplastic was studied by the photoactivation of TBHP and SPB[26] and the efficiency of oxidants was established to be: HP>SPB>TBHP. Further, SPS was shown to be most effective among all the oxidants.

$$\begin{aligned}&2Na^{+}[(HO_2)B(-O-O-)_2B(OH)_2]^{2-} + \\ &+\ 2H_2O \rightarrow 2Na^{+} + 2[H_2BO_3]^{-} + 2H_2O_2\end{aligned} \quad (5)$$

A thorough literature survey reveals that the concentration of pollutants used in the degradation process varies in the range 10 to 30 ppm.[10] Further, the degradation and/or COD/TOC removal of organic pollutants using substituted hydrogen peroxides such as TBHP and SPB in a modified Fenton process have not been paid due attention. It is expected that different groups adjacent to the peroxo group as in TBHP, SPB and HP would greatly influence the cleavage of peroxo bond and subsequent generation of $HO^•$ through Fe^{2+} catalysed activation. To augment these two lacunae found in the literature, the present work has been devoted the establish the effect of various oxidants such as SPS, TBHP and SPB on the colour and COD removal of a higher concentration (0.3 mM) of Acid Orange 8 (AO 8) solution, a representative organic pollutant in the modified Fenton processes. This is proposed to be achieved through optimising operational parameters such as concentration of catalyst and oxidant, and pH for the effective decolorization and COD removal of AO 8 in Fenton (Fe^{2+}/HP) and modified Fenton processes (Fe^{2+}/TBHP, Fe^{2+}/SPB and Fe^{2+}/SPS). Kinetics of COD removal and HP consumption has been studied in detail. Effort has made to identify intermediate ions and products formed during the reaction. Based on the identified ions and intermediate products, a mechanism of degradation of AO 8 has been proposed.

2. Materials and Methods

2. 1. Reagents

The anionic water-soluble diazo dye, Acid Orange 8 (AO 8) was procured from sigma aldrich (Germany). The molecular structure, chemical and physical properties of AO 8 are described in Table S1. The other chemicals used in this work, viz. iron (II) sulphate ($FeSO_4.7H_2O$, GR), HP (H_2O_2, 30% w/w purified, GR), methanol (CH_3OH, GR), sodium hydroxide (NaOH, GR), sulphuric acid (H_2SO_4, GR), sodium nitrate ($NaNO_3$, GR), sodium chloride (NaCl, GR), anhydrous sodium sulphate ($NaSO_4$, GR), *tert*-Butanol ($(CH_3)_3COH$, GR), sodium peroxodisulphate ($Na_2S_2O_8$, AR) were procured from Merck. Sodium perborate tetrahydrate ($NaBO_3.4H_2O$, GR), sodium fluoride (NaF, AR), sodium iodide (NaI, AR) were obtained from Himedia (India). Sodium bromide (NaBr, AR) and *tert*-Butyl hydroperoxide ($(CH_3)_3COOH$, 70% aqueous solution, AR) were obtained from Nice and Avra (India), respectively. Solutions of mercuric sulphate and sulphuric acid (Solution 1) and silver sulphate, chromic acid, sulphuric acid and demineralized water (Solution 2) used for the measurement of low range COD was obtained from HACH (USA). Methane sulphonic acid (CH_3SO_3H) and sodium hydroxide (NaOH, 50–52% in water) used in ion chromatographic analyses of intermediate products were procured from Himedia (India) and Sigma (Germany), respectively. All the chemicals were used as received without further purification.

2. 2. Procedure

The procedure for this work is similar to our earlier work published recently.[27] However, for a clear understanding of the readers, we are presenting a brief description here. Aqueous solution of desired concentration of AO 8 was prepared in Millipore water (Elix3 Century, Millipore India, Bengaluru). The reactions were carried out in the presence of air and at room temperature (21 ± 2 °C) by placing required volume of the dye solution of required concentration in amber borosilicate bottles. Each bottle was designated to be used for analysis after a predetermined reaction period. Each bottle was sealed with aluminium foil and three holes were pierced through it to allow free passage of air. The desired pH of the solution was maintained by adding H_2SO_4 or followed by the sequential addition of 0.5 ml of desired Fe^{2+} solution of concentration 60 mM and 0.5 ml of the HP and TBHP was taken from 1400 mM stock solution which corresponds to 7.0 mM in the resulting 100 ml dye solution in Fe^{2+}/HP and Fe^{2+}/TBHP systems. The only change in procedure for Fe^{2+}/SPB system is the concentration of the oxidants, i.e. 5.0 ml of the desired concentration of SPB was added depending upon their required concentration. The pH was measured using a digital pH meter (Eutech instruments, Singapore). In all the reactions the volume was made upto 100 ml by adding water. All the solutions used in this work were freshly prepared except the dye solution, which was stored at 4 °C and used within three days. No adjustment of pH was done during the course of the reaction and any change in pH during the reactions was noted regularly.

2. 3. Analytical Techniques

Decolorization studies were carried out by measuring the absorbance at 471 nm with the help of a UV-Vis spectrophotometer (HACH, USA; DR 6000). The COD was measured by following the procedure prescribed by HACH, USA and reported by Kumar et al.[10] In short, a mixture of 2.0 ml of a given sample, 0.25 ml of 'Solution 1' and 2.8 ml of 'Solution 2' (low range) was digested in a COD digester (HACH, USA; DRB 200) at 150 °C for 2 hrs. The digested samples were cooled to room temperature and analysed at 420 nm for COD measurement with the help of a UV-Vis spectrophotometer (HACH, USA; DR 6000). The data presented in the text and figures were analysed by standard deviation using 'Origin 7' (Microcal Inc.) and has been rounded up to significant values.

Decolorization and COD removal efficiency (COD_{eff}) was calculated using (Eqs. (6) and (7)), respectively. The rate constant for COD removal was obtained according to the pseudo-first-order rate law (Eq. (8)).

$$\text{Decolorization (\%)} = \frac{A_0 - A_t}{A_0} \times 100\ \% \tag{6}$$

$$COD_{eff} = \frac{COD_0 - COD_t}{COD_0} \times 100\% \tag{7}$$

$$-\ln(COD_t/COD_0) = k_{COD}.t \tag{8}$$

Where, COD_0 and A_0 are initial COD and absorbance at time 't' = 0 and COD_t and A_t are COD and absorbance at time 't', respectively. The slope of the straight line obtained by plotting –ln (COD_t/COD_0) vs. time is considered as the first order rate constant (k_{COD}) for COD removal. Concentration of residual hydrogen peroxide, organic acids, cations, anions, were analysed with the help of ion chromatography system (ICS) manufactured by Thermo Scientific, USA (Dionex, ICS-1100). The details of ion chromatographic techniques was described in our recent publication[10] and therefore, are not described here.

3. Results and Discussion

3. 1. Spectral Analysis and Decolorization Study

The UV-Vis absorption spectra of aqueous AO 8 shows four absorption bands – three appearing at 241, 263, 312 nm in the UV region and one at 417 nm in the visible region (Fig. 2). The presence of absorption peaks at 241, 263 and 312 nm representing $\pi \rightarrow \pi^*$ transitions indicate the presence of aromatic rings in the AO 8. The 311 nm band represents benzene and/or naphthalene rings attached to the azo bond. The peak at 471 nm, representing $n \rightarrow \pi^*$ transitions of C=O, C=N and N=N chromophore groups is responsible for the color of the AO 8 solution.

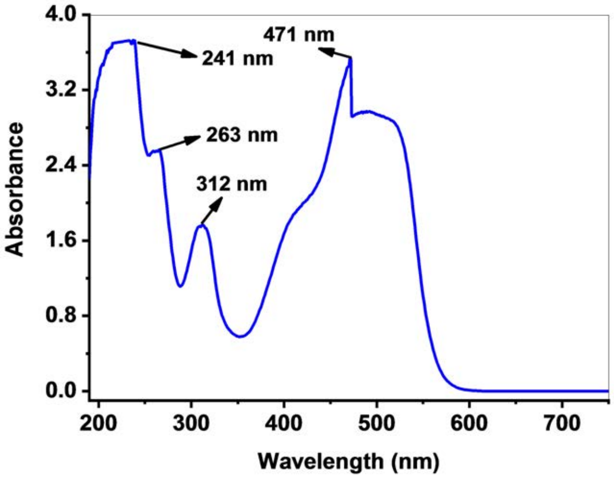

Figure 2. UV-Vis absorption spectrum of pure AO 8: [AO 8] = 0.3 mM

The decolorization was measured by monitoring the decrease in absorbance at 471 nm. The cleavage of –N=N– bonds with a probability of 60% is considered as the initial step in the degradation of azo dyes.[28] The gradual cleavage of –N=N– bond decreases the intensity of color in the dye solution. It was observed that absorption maxima of the peak at 471 nm decreased to 89.6% in 5 min and 97.3% in 10 min in Fe^{2+}/HP system (Fig. 3a). Needless to mention here that although 97.3% decolorization was achieved in only 10 min, it takes further 20 min for the rest 2.7% decolorization. In other words, complete decolorization was achieved in 30 min. Thus, there is a rapid cleavage of the azo bond during the first 10 min of the reaction followed by slow cleavage during the next 20 min. On the other hand the peak at 311 nm decreases very slowly as compared to the peak at 471 nm. This may be due to the formation and accumulation of intermediate aromatic products in the system.[27] However, in the case of Fe^{2+}/SPB system, the decolorization at 5 min was a mere 20.0% which increased to 64.9% at 10 min and 97.3% in 90 min (Fig. 3b). No further change in decolorization was observed till 300 min of the reaction. Thus, the decolorization is faster in the initial stages in Fe^{2+}/HP system than in Fe^{2+}/SPB system, although at the end of the reaction not much difference was observed in both the processes. The decolorization in Fe^{2+}/TBHP system was found to be slower than in other two systems yielding only 5.5% in 5 min, which increased to 7.6 and 70.4% in 10 min and 300 min, respectively (Fig. 3c). Fe^{2+}/SPS system has been earlier proved to be the most efficient process due to the higher oxidation potential of persulphate (2.5 to 3.1 V *Vs.* normal hydrogen electrode (NHE)) and its ability to operate at all pH values.[14,29,30] Under optimum conditions, the decolorization in Fe^{2+}/SPS system at pH 3.0 reached up to 75.3 and 93.5%, respectively, in 90 and 300 min. Thus, the degree of decolorization in all the systems studied is in the order: Fe^{2+}/HP ≈ Fe^{2+}/SPB > Fe^{2+}/SPS > Fe^{2+}/TBHP (Fig. 3d).

3. 2. Optimization of Operational Parameters and COD Removal Study

3. 2. 1. Fe^{2+}/HP System

The optimization of operational parameters such as Fe^{2+} dosage, concentration of HP and pH for a 0.3 mM solution of AO 8 was done by determining the COD_{eff} at 90 min of treatment. The COD was measured by varying one parameter while maintaining the other two constant.[27]

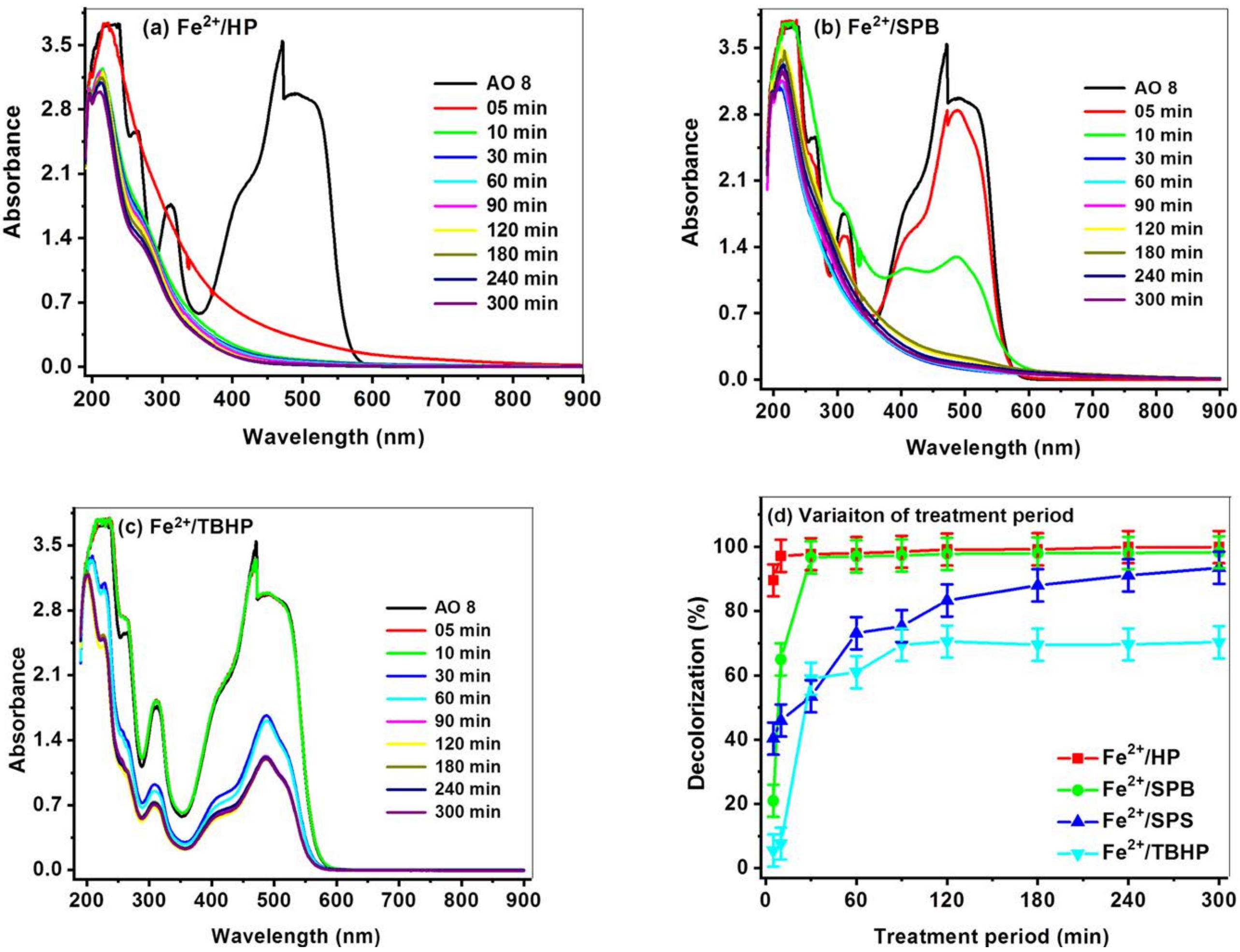

Figure 3. (**a–c**): UV-Vis absorption spectra of AO 8 in different systems (**d**) decolorization in different systems. [AO 8] = 0.3 mM; [Fe^{2+}] = 0.3, 0.2, 0.3 and 0.3 mM for Fe^{2+}/HP, Fe^{2+}/TBHP, Fe^{2+}/SPB and Fe^{2+}/SPS systems respectively; [HP] = 7.0 mM; [TBHP] = 7.0 mM; [SPB] = 2.0 mM; [SPS] = 7.0 mM; pH = 3.0.

The [Fe^{2+}] was varied from 0.05 to 0.7 mM, [HP] from 1.0 to 10.0 mM and pH from 3.0 to 11.0. Using this strategy, the optimum parameters were established as [Fe^{2+}] = 0.3 mM; [HP] = 7.0 mM; pH = 3.0. It is observed that both decolorization and COD_{eff} show a decreasing trend once the operational parameters exceed the optimized values (Fig. 4a–4c).

These inhibiting effects at higher [Fe^{2+}] on the removal efficiency is due to scavenging of $HO^{\bullet}$ by Fe^{2+}. Further the higher concentration of Fe^{2+} leads to a higher generation of Fe^{3+} which scavenges $HO^{\bullet}$ to form monohydroxy complex (Eqs. (9) and (10)).[31,32]

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

$$Fe^{3+} + HO^{-} \rightarrow [FeOH]^{2+} \leftrightarrow Fe^{2+} + HO^{\bullet} \tag{10}$$

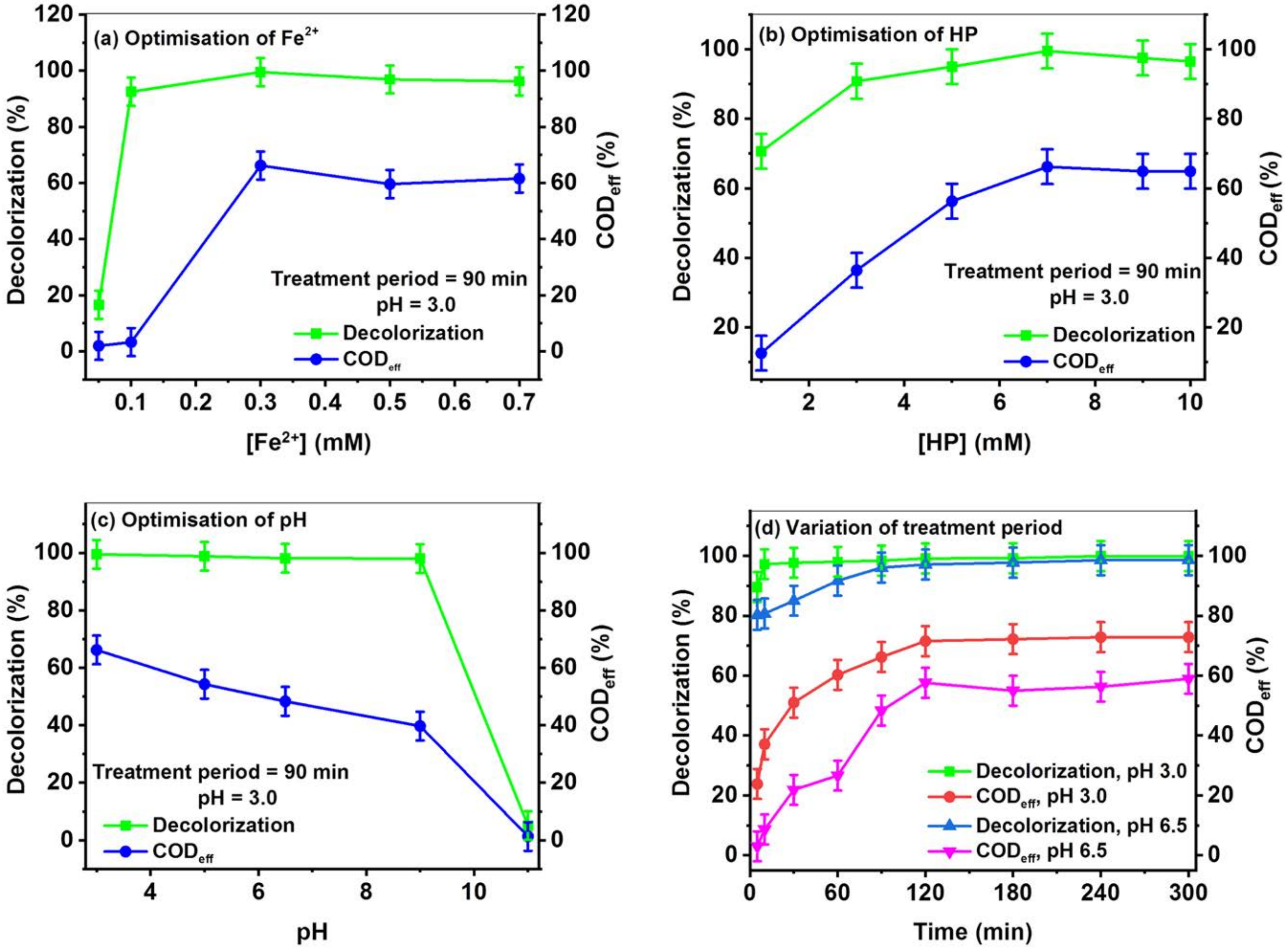

Figure 4. (**a**–**c**) Optimization of operational parameters in Fe^{2+}/HP system (**d**) Variation of COD_{eff} and decolorization with treatment period in Fe^{2+}/HP system: [AO 8] = 0.3 mM

At higher [HP], $HO^{\bullet}$ radicals are scavenged to form hydroperoxyl radicals ($HO_2^{\bullet}$) in accordance to Eqs. (11) and (12), which are less reactive and do not contribute to the degradation of organic molecules and recombination of $HO^{\bullet}$ takes place (Eq. (13)).[7]

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{11}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{12}$$

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{13}$$

The maximum efficiency at pH 3.0 is attributed to the high oxidation potential (2.8 V *vs.* NHE) of $HO^{\bullet}$ radicals[13,33,34] and the lower efficiency at pH > 3.0 is due to the formation of $Fe(OH)_3$, which leads to a decrease in the generation of $HO^{\bullet}$ due to the unavailability of Fe^{2+} ions.[35] Additionally at higher pH, the formation of $HO^{\bullet}$ also retards due to the decomposition of HP to O_2 gas.[36]

Under the optimized parameters, a maximum COD^{eff} of 66.2% was achieved in 90 min. This is attributed to the degradation of dye solutions by $HO^{\bullet}$ radicals and the formation of intermediates. To further increase the magnitude of COD_{eff}, the treatment period was increased up to 300 min. But a mere 6.6% additional increase in COD_{eff} was observed at the end of 300 min. Nevertheless, the COD_{eff} remained constant from 120 min onwards (Fig. 4d). The COD_{eff} consists of 2 stages: the initial fast stage (0 to 60 min) with a COD_{eff} of 60.3% is followed by a slow step (120 to 300 min) with a COD_{eff} of 72.8% (Fig. 5). The fast stage is due to the rapid consumption of HP (97.3% in 5 min and 100% in 10 min). The minor increase in COD_{eff} (12.5%) in the 2nd stage probably is due to the presence of negligible amount of reactive species after the first stage (Fig. 5). As established earlier, the presence of residual HP leads to over estimation of COD of a given solution.[37,38] This effect of excess HP on COD has also been verified by us recently.[10,27] Therefore, the excess use of HP is not recommended for the degradation process. Since 97.3% HP is consumed in 5 min and 100% in 10 min, it may be concluded that presence of HP has no visible effect in the COD value.

In an attempt to provide a cost effective method for COD removal, the experiment was carried out at the natural pH (where no external reagent is required to adjust the pH to desired value) of the dye, i.e. at pH 6.5 under optimal parameters (Fig. 4d). The COD_{eff} progressively increased from 6.0% at 10 min to 58.9% at 300 min. A comparison of COD_{eff} at both pH reveals that COD removal is more effective at pH 3.0 than at 6.5. Colour removal studies under similar parameters indicate that almost complete decolorization was achieved from 30 min onwards at pH 3.0. On the contrary only 85.0% decolorization was achieved in 30 min and almost complete decolorization in 90 min of treatment at pH 6.5 (Fig. 4d).

3. 2. 2. Fe^{2+}/SPS System

For a better comparison of the efficiency of oxidants, we have employed similar parameters ($[Fe^{2+}] = 0.3$ mM; [SPS] = 7.0 mM; pH = 3.0; [AO 8] = 0.3 mM) for COD removal study in Fe^{2+}/SPS system. As described earlier (Sec 3.1), near complete decolorization was achieved in this system. Further, to our disbelief COD removal was completely inhibited at pH ≥ 3.0. Thus, our finding is in good agreement with the earlier report from our laboratory.[39] Thus, it may be concluded that persulphate system inhibit COD removal of the target molecule at higher concentration. It is for this reason that further study on this system was abandoned.

3. 2. 3. Fe^{2+}/TBHP System

It was our curiosity to understand the effect of replacing one hydrogen of HP with *tert*-butyl group (as in TBHP) on the COD removal process by a modified Fenton process (Fe^{2+}/TBHP). Since TBHP contains one OH-group, it is expected that hydroxyl radicals are generated when activated by Fe^{2+}. The evidence for the formation of hydroxyl radical by TBHP has been discussed briefly in Sec. 3.3. In this system, the optimization of the catalyst, $[Fe^{2+}]$ and the oxidant, TBHP was done pH = 3.0 for 0.3 mM of AO 8 (Fig. S1). Thus the optimized parameters for this system was established as: $[Fe^{2+}] = 0.2$ mM; [TBHP] = 7.0 mM; pH = 3.0. Under the optimized parameters, a maximum COD_{eff} of 56.3% was achieved in 90 min at pH 3.0 and decolorization of 69.5 and 70.4% in 90 and 300 min, respectively. As in Fe^{2+}/HP system, the COD_{eff} in Fe^{2+}/TBHP system follows a two stage process. The first stage lasts up to 60 min yielding a COD_{eff} of 45.6%. The COD_{eff} value was 69.5% at the end of 300 min in the second stage (Fig. 5).

As already discussed, *t*-BuO• is a major radical species in this system[26] and it contributes to the degradation of cytarabine antineoplastic. Thus, the decrease in COD_{eff} at higher $[Fe^{2+}]$ may be due to the mutual scavenging of $[Fe^{2+}]$ and *t*-BuO• (Eq. (14)).[19] At higher [TBHP], excess generation of *t*-BuO• would lead to its fragmentation and form acetone and ethane (Eqs. (15) and (16)).[18] In addition, presence of excess of *t*-BuO• may lead to the formation of *t*-BuOO• (Eq. (4)), which ultimately leads to unreactive non-radical species (Eq. (17)). However, there is a concurrent opposing factor to this retarding effect, whereby Fe^{3+} is reduced to regenerate Fe^{2+} and accelerate the degradation process (Eq. (4)). Thus, it is expected that COD_{eff} would be higher in HP than in TBHP. This has been verified in Sec. 3.3.

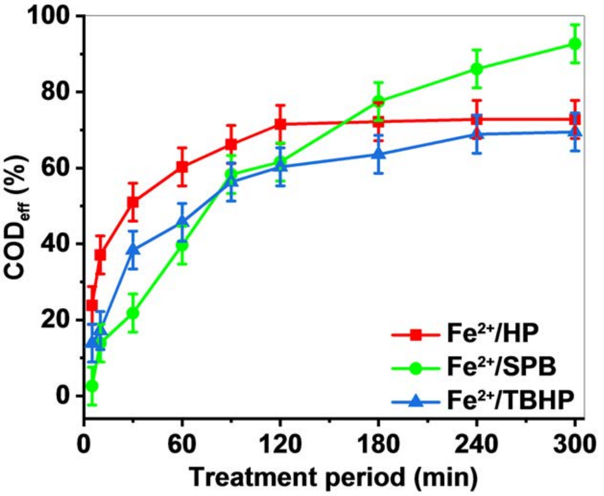

Figure 5. COD_{eff} in different systems at pH 3.0: [AO 8] = 0.3 mM; $[Fe^{2+}] = 0.3$ mM (for Fe^{2+}/HP and Fe^{2+}/SPB systems) and 0.2 mM (for Fe^{2+}/TBHP system); [HP] = 7.0 mM; [SPB] = 2.0 mM; [TBHP] = 7.0 mM

$$Fe^{2+} + t\text{–}BuO^{\bullet} + H^{+} \rightarrow Fe^{3+} + t\text{–}BuO^{-} \quad (14)$$

$$t\text{–}BuO^{\bullet} \rightarrow (CH_3)_2CO + H_3C^{\bullet} \quad (15)$$

$$2H_3C^{\bullet} \rightarrow C_2H_6 \quad (16)$$

$$t\text{–}BuOO^{\bullet} + H_3C^{\bullet} \rightarrow (CH_3)_3COOCH_3 \quad (17)$$

In acidic condition the rapid fragmentation of *t*-BuO• (Eq. (15)) prevents the subsequent oxidation of Fe^{2+} as in (Eq. (14)). Regardless of that *t*-BuOO• will be generated as given in (Eq. (15)).[19] As already discussed in Sec. 1, some authors have not reported the generation of $HO^•$ in Fe^{2+}/TBHP system. However, Pérez et al.[26] in their study have of course reported the role played by $HO^•$ in the degradation of cytarabine antineoplastic. In order to verify the role played by $HO^•$ in the decolorization of AO 8, we have carried out the reaction with *t*-BuOH which is an efficient scavenger of $HO^•$. The decolorization decreases from 69.4 to 51.2 and 14.4% in the presence of 0.1 and 0.7 $molL^{-1}$ of *t*-BuOH, respectively. The generation of $HO^•$ is well established and hence need not be verified again. It is expected that HP and TBHP will generate two and one equivalents of $HO^•$, respectively. Hence the degradation efficiency of HP is expected to be higher than TBHP. This is supported by the COD removal studies involving these two systems as discussed in Sec. 3.3.

3. 2 .4. Fe^{2+}/SPB System

The optimization process was similar to those described in Fe^{2+}/HP system (Sec. 3.2.1). The optimized parameters were found to be $[Fe^{2+}]$ = 0.3 mM; [SPB] = 2.0 mM; pH = 3.0 for 0.3 mM of AO 8. The effect of pH was established in the pH range from 3.0 to 11.0 at the treatment period of 90 min. Very interestingly it was found that it works only in pH 3.0 with 97.3 and 58.3% decolorization and COD_{eff} respectively. At higher pH, decolorization was found to be in the range of 6.5 to 11.5% due to which no COD_{eff} was observed. The observed COD_{eff} at pH 3.0 is due to the *in situ* establishment of Fenton reaction as already described in Sec. 1. It was also reported by Kurin-Csörgei et al.[25] that in acidic medium the perborate species (H_3BO_3) is in equilibrium with H_2O_2 in the ratio 1:1 (Eqs. (18) and (19)). At higher pH range, the species $(HO)_3B(OOH)^-$ and $(HO)_2B(OOH)_2^-$ exist in relatively higher ratio (Eqs. (19) and (20)).[25] In other words, HP is scavenged at higher pH leading to a retardation of COD_{eff}.

$$[H_2BO_3]^- + H^+ \rightarrow H_3BO_3 \tag{18}$$

$$H_3BO_3 + H_2O_2 \leftrightarrow (HO)_3BOOH^- + H^+ \tag{19}$$

$$(HO)_3BOOH^- + H_2O_2 \leftrightarrow (HO)_2B(OOH)_2^- + H_2O \tag{20}$$

The COD_{eff} was found to be 0.7 and 58.3% at 0.05 and 0.3 mM of Fe^{2+}, respectively, and shows a decreasing trend on further increasing the dosage to 0.7 mM (Fig. S2 (a)). As for COD_{eff} it was found to increase from 20.5 to 58.3% when the [SPB] was increased from 0.5 to 2.0 mM, respectively (Fig. S2 (b)). The retarding effect of higher concentration of Fe^{2+} and SPB is due to the fact that the reaction is governed by the *in situ* established Fenton process in the system and the effect of different parameters are also applicable here (Sec. 3.2.1). It is pertinent to note that 92.7% COD removal was observed in 300 min (Fig. 5). The corresponding decolorization was 98.3%. We assume it as 100% decolorization as it falls within ±5% error.

A closure look at Fig. 5 reveals that the COD removal efficiency of different systems is in the order: Fe^{2+}/SPB > Fe^{2+}/HP > Fe^{2+}/TBHP > Fe^{2+}/SPS. The higher efficiency of Fe^{2+}/HP system than Fe^{2+}/TBHP has already been discussed in Sec. 3.2.3. The other important factor lies in their ability to generate hydroxyl radicals. While HP system generates two equivalents of $HO^•$ radicals, TBHP only one. SPB system, on the other hand, generates four equivalents of HP, which generates four equivalents of $HO^•$ radicals in the *in situ* established Fenton process.

3. 3. COD Removal Kinetics

As discuss in the above section, the COD removal in all the processes consists of two steps except in Fe^{2+}/SPB where a single step removal process (5 to 240 min) was observed. The rate constant in Fe^{2+}/HP system was found to be 11.67 and 00.39 ($10^{-3}min^{-1}$) for first and second step, respectively (Fig. S3). The initial rate in Fe^{2+}/HP system is higher than that in Fe^{2+}/TBHP system and overall rate in Fe^{2+}/SPB system. However, the rate is reversed in the second step. In Fe^{2+}/TBHP system, 45.6% COD removal was obtained in the first step and 23.9% in the second step with a rate constant of 8.24 and 2.03 ($10^{-3}min^{-1}$), respectively (Fig. S4 and Table S2). The reaction in Fe^{2+}/SPB system is a one step process, proceeds linearly and rapidly rapid by following pseudo-first order kinetics with a rate constant of 08.24 ($10^{-3}min^{-1}$) (Fig. S5). The COD removal increases from 2.6 to 92.7% when the treatment period is increased from 5 to 300 min. The linear progress in the COD removal may be due to the constant production of $HO^•$ in the system.

A comparison of rate constant (Table S2) and the COD removal data (Fig. 5) reveals that compared to Fe^{2+}/HP system, the reacting species in Fe^{2+}/TBHP system reacts slowly in the first step. As evident from the rate constant, $HO^•$ in Fe^{2+}/HP system is generated abundantly in the first 60 min of the reaction (first stage with higher rate constant). As for Fe^{2+}/TBHP system, apart from the active radicals i.e., $HO^•$, *t*-$BuO^•$ radicals act as a subsidiary radical which maybe produced in the second phase of the reaction due to which the rate is higher than Fe^{2+}/HP system.

3. 4. Effect of Presence of Anions on the COD Removal Processes

Dye wastewater released from dye and textile industries mostly contains inorganic anions such as Cl^-, NO_3^-, and SO_4^{2-}.[26] Hence, there is a possibility that these ions might affect the colour and COD removal processes. We have, therefore, undertaken the study of effect of such ions on the colour and COD removal processes. Apart from inorganic anions, halide ions are also predominant in the effluent.[26] They scavenge the $HO^•$ radicals and adversely affect the treatment process by forming radical and non-radical Reactive Halogen Species (RHS). The concentration of various inorganic ions such as Cl^-, NO_3^-, and SO_4^{2-} was varied from 1.0 to 9.0 g L^{-1} and halide ions such as F^- and Br^- from 0.01 to 0.07 g L^{-1} in all systems at 120 min of treatment period.

3. 4. 1. Effect of Anions in Fe^{2+}/Oxidant System

In the presence of Cl^-, the COD_{eff} decreased gradually as the concentration was increased from 1.0 to 7.0 g L^{-1}, beyond which a complete inhibitory effect was observed (Fig. 6a). The decrease in COD_{eff} in the presence of Cl^- is due to the scavenging of $HO^\bullet$ leading to the formation of less reactive $ClOH^{\bullet-}$ and $Cl_2^{\bullet-}$ radicals (Eqs. (21) – (23)).[40,41]

$$HO^\bullet + Cl^- \rightarrow HO^- + ClOH^{\bullet-} \tag{21}$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^\bullet + H_2O \tag{22}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \tag{23}$$

The inhibitory effect of Cl^- on the COD removal efficiency may also be due to the conversion of non-selective $HO^\bullet$ to selective RHS such as $ClOH^{\bullet-}$, $Cl^\bullet$, Cl^- and $Cl_2^{\bullet-}$ (Eqs. (24) and (26)). These species attack the electron-rich compounds in the effluent, rather than electron-deficient compounds.[42] Further, these species having low oxidation potential which does not contribute in the COD removal.[43] The formation of RHS may be shown as below:

$$HO^\bullet + X^- \rightarrow XOH^{\bullet-} \tag{24}$$

$$XOH^{\bullet-} + H^+ \rightarrow X^\bullet + H_2O \tag{25}$$

$$X^\bullet + X^- \rightarrow X_2^{\bullet-} \tag{26}$$

Decolorization was not affected in the presence of SO_4^{2-} and NO_3^-. There is a marginal decrease of 10 and 5% in COD_{eff} in the presence of 1.0 g L^{-1} of SO_4^{2-} and NO_3^-, respectively. No further change in COD_{eff} was observed on increasing the concentration of these anions (Fig. 6a). Based on the observations, we may conclude that the inhibiting effect of anions on COD_{eff} is in the order: $Cl^- > SO_4^{2-} > NO_3^-$. The decrease in the COD_{eff} in the presence of SO_4^{2-} is due to the reaction between SO_4^{2-} and $HO^\bullet$ (Eq. (27)) leading to the formation of $SO_4^{\bullet-}$ radicals, which dimerises to form less reactive peroxydisulphate ions (Eq. (28)).[44] The inhibitory effect of NO_3^- is due to the scavenging of $HO^\bullet$ (Eq. (29)).[45]

$$SO_4^{2-} + HO^\bullet \rightarrow SO_4^{\bullet-} + HO^- \tag{27}$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{28}$$

$$NO_2^- + HO^\bullet \rightarrow NO_2^\bullet + HO^- \tag{29}$$

In order to know the effect of other halogens on COD_{eff}, reactions were carried out in the presence of F^-, Br^- and I^-. In general, a decreasing trend in decolorization was observed with the increase in the concentration of the halogens. The decolorization was completely inhibited in the presence of I^- with a concentration of 0.3 g L^{-1}. However, an inhibition of 50% was recorded in the presence of 9.0 g L^{-1} of Cl^- and Br^- and 70% in the presence of 9.0 g L^{-1} of F^-. Thus, the inhibitory effect of halogens on decolorization is in the order: $I^- > F^- > Cl^- \approx Br^-$. As far as I^- is concerned, it inhibits COD_{eff} at all concentrations. While Cl^- shows inhibitory effect at higher concentrations, F^- and Br^- show at lower concentrations (Fig. 6b). As seen in the figure, the rate of inhibition is higher with Br^- than F^-. Near or complete inhibition is shown at 9.0 g L^{-1} of Cl^-, 0.05 g L^{-1} of Br^- and 0.07 g L^{-1} of F^-. Thus, the inhibitory effect of the halogens on COD_{eff} is in the order: $I^- > Br^- > F^- > Cl^-$. Although similar trends are observed with TBHP and SPB systems, the inhibitory effect is more pronounced at higher than in lower concentrations of anions.

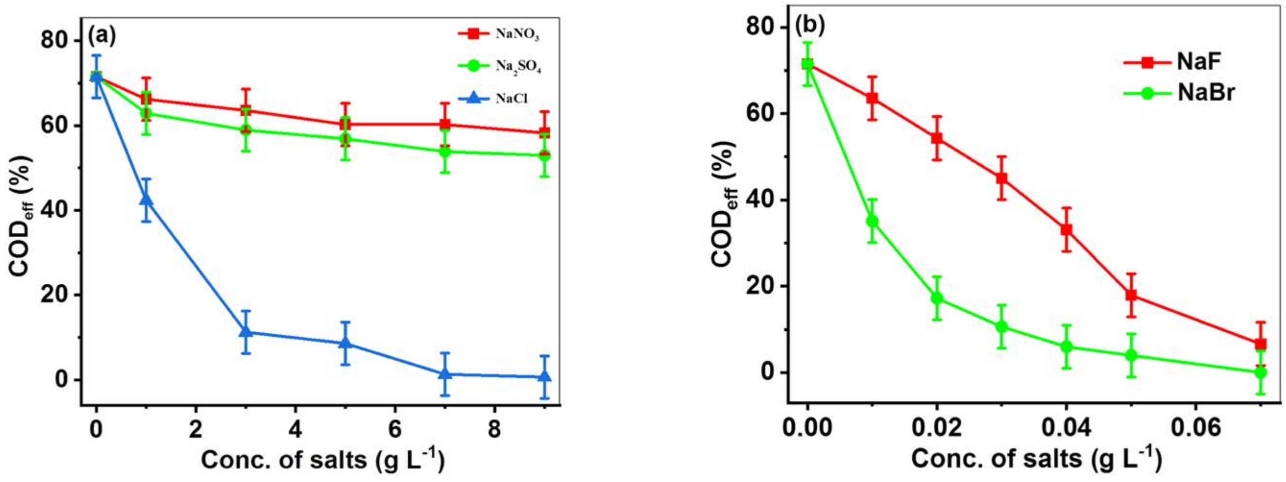

Figure 6. The inhibitory effect of various anions on COD_{eff} in the Fenton process: [AO 8] = 0.3 mM; $[Fe^{2+}]$ = 0.3 mM; [HP] = 7.0 mM; pH = 3.0; Treatment period = 120 min

3. 5. Ion Chromatographic Analysis of Intermediate Products and Ions

Ion chromatography technique was used to identify various ions and intermediate compounds generated in the degradative process. As the products identified in all the systems were same, the product identified in Fe^{2+}/HP system only are listed in Table S3. The ions, Na^+ and SO_4^{2-} are identified in all the systems. Na^+ has been identified as the dissociation product of AO 8. The attack of SO_3^- group by $HO^\bullet$ leads to the formation of SO_4^{2-}. As shown in Fig. 2 the dye has one source of nitrogen i.e., –N=N– bond and successive addition of $HO^\bullet$ radicals to the –N=N– bond results in the formation of aryl products, nitroso and nitro aromatic compounds.[46] Nitro aromatic compounds further undergoes oxidation by $HO^\bullet$ to give substituted phenols, which ultimately form aliphatic acids through ring opening.[47,48] Aliphatic acids are further degraded into CO_2 and H_2O. The probable mechanism of degradation of AO 8 based on the intermediate products and ions and literature review has been proposed and is presented in (Fig. S6).

4. Conclusion

Fenton oxidation, by far, is considered as the most studied and cost effective treatment process for the removal of various pollutants. However, there is a lack of elaborate study to find a suitable substitute for HP as an oxidant in the Fenton process. The substitutes were explored by inserting different substituents on the peroxo bond (–O–O–) in HP. The substituted peroxides used in the present study on colour and COD removal in AO 8 were SPS, TBHP, and SPB. Further, a literature survey indicates that the concentration of organic pollutants used in degradation studies varies in the range 10 to 30 ppm. For industrial applications, a higher concentration of target pollutant is essential and therefore, a higher concentration of AO 8 (0.3 mM) was used in this study. The optimal parameters for 0.3 mM of AO 8 in different systems were established as: Fe^{2+}/HP system – $[Fe^{2+}] = 0.3$ mM; [HP] = 7.0 mM; pH = 3.0; Fe^{2+}/TBHP system – $[Fe^{2+}] = 0.2$ mM; [TBHP] = 7.0 mM; pH = 3.0; Fe^{2+}/SPB system – $[Fe^{2+}] = 0.3$ mM; [SPB] = 2.0 mM; pH = 3.0. The decolorization and COD removal efficiency of the systems under optimal parameters follow the order: $Fe^{2+}/HP \approx Fe^{2+}/SPB > Fe^{2+}/SPS > Fe^{2+}/TBHP$ and $Fe^{2+}/SPB > Fe^{2+}/HP > Fe^{2+}/TBHP > Fe^{2+}/SPS$, respectively. However, SPS completely inhibit COD removal at any pH. This is a significant finding considering the fact that SPS was described as the most powerful oxidant at all pH in the degradation process. Thus, SPB may be considered as a substitute for HP and SPS in Fenton and Fenton-type processes respectively. In the HP system, complete decolorization was achieved in 30 min at pH 3.0, while at natural pH of the dye, i.e. pH 6.5 it is 85% in 30 min and ≈ 100% in 90 min of treatment. Under optimized parameters, COD removal was found to be 66.2 and 58.8% at pH 3.0 and 6.5, respectively, in Fenton process. The reactivity of different systems towards COD removal efficiency may be ascribed to their ability to generate $HO^\bullet$ radicals – two equivalents in HP system, one in TBHP and four in SPB system. Another factor responsible for the lower reactivity of TBHP is the generation of unreactive non-radical species through the formation of t-$BuOO^\bullet$. It is an established fact that presence of residual HP leads to over estimation of COD. To determine the effect of residual HP on COD in our study, the concentration of HP at different stages of the treatment was estimated using ion chromatography. It was found that 97.3% HP is consumed in 5 min and 100% in 10 min. This leads to the conclusion that the presence of HP has no visible effect in the COD values.

The effect of various anions including halogens, generally present in the effluents of textile and dye stuff industries, are also established in this study. All the target anions show inhibitory effect on colour and COD removal and their inhibition effect follow the order: $Cl^- > SO_4^{2-} > NO_3^-$. Among halogens, Br^- and F^- show inhibition at lower concentration and Cl^- at higher concentration. Near or complete inhibition is shown at 9.0 g L^{-1} of Cl^-, 0.05 g L^{-1} of Br^- and 0.07 g L^{-1} of F^-. It is important to note here that I^- display inhibitory effect on colour and COD removal at all concentrations. Thus, the inhibitory effect of halogens follow the order: $I^- > Br^- > F^- > Cl^-$. Although similar trends are observed with TBHP and SPB systems, the inhibitory effect is more pronounced at higher than in lower concentrations of anions.

The kinetics of COD removal was determined in different systems. COD removal in all the systems proceeds through two steps except in Fe^{2+}/SPB where a single step removal process (5 to 240 min) was observed. The rate constant in Fe^{2+}/HP system was found to be 11.67 and 00.39 ($10^{-3}min^{-1}$) for first and second step, respectively. The initial rate in Fe^{2+}/HP system is higher than that in Fe^{2+}/TBHP and Fe^{2+}/SPB systems.

The various intermediate ions such as Na^+, NH_4^+, SO_4^{2-}, NO_2^-, NO_3^- and different aliphatic acids such as formic acid, malonic acid, maleic acid, and fumaric acid were identified using ion chromatography. Based on these data, a degradation mechanism of AO 8 has been proposed.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Povzetek

Vodikov peroksid (HP) se pogosto uporablja v naprednih oksidacijskih procesih (AOP). Ta študija ocenjuje kemijsko potrebo po kisiku (KPK) učinkovitosti odstranjevanja barvila Acid Orange 8 (AO 8) pri višji koncentraciji z modificiranim Fentonovem postopku ter uporabo substituiranega HP, kot sta tert-butil hidroperoksid (TBHP) in natrijev perborat (SPB) ter natrijev persulfat (SPS) kot oksidant. Pri optimalnih pogojih je bilo ugotovljeno, da je bila KPK odstranitve 72,8 in 58,9 % pri pH 3,0 in 6,5 v Fentonovem procesu v 300 minutah. KPK učinkovitosti odstranjevanja različnih sistemov je v vrstnem redu: Fe^{2+}/SPB > Fe^{2+}/HP > Fe^{2+}/TBHP > Fe^{2+}/SPS, kar kaže na možnost uporabe SPB kot nadomestka za HP in SPS. Vrstni red učinkovitosti je med drugim pripisan njihovi sposobnosti proizvajanja $HO^{•}$ radikalov. Pokazalo se je, da različni anioni izkazujejo zaviralni učinek v vrs⁻ tnem redu: I^- > Br^- > F^- > Cl^-> SO_4^{2-} > NO_3^-. Zaviralni učinek Cl^- opazimo pri višjih koncentracijah kot F^- in Br^-, vendar I^- zavira pri vseh koncentracijah. Na koncu sta bila v tej študiji določena kinetika KPK odstranjevanja in mehanizem razgradnje na podlagi identificiranih vmesnih produktov.