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# Removal of Acid Blue 29 in aqueous solution by Fenton and Fenton-like processes

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ABSTRACT

The decoloration and mineralization of the azo dye, Acid Blue 29 (AB 29) in aqueous solution was investigated in the presence and absence of air by Fenton and Fenton-like processes using hydrogen peroxide (HP) and sodium persulfate (SPS), respectively, as oxidants. The effect of various operational parameters and presence of $Cl^-$, $CO_3^{2-}$, $HCO_3^-$, and $SO_4^{2-}$ ions on the decoloration was examined. Higher decoloration was observed at pH 3 and 5 in both the cases. On the basis of mineralization efficiency (34.1 and 28.5%, respectively, with HP and SPS in 180 min), it was concluded that HP is a better oxidant than that of SPS. The decoloration in the absence of air is decreased until a certain time period, beyond which it increases and becomes same as that in the presence of air. This is explained on the basis of *in situ* generation of HP and peroxyl radicals. Although all ions under study inhibit decoloration significantly, the inhibition efficiency of $SO_4^{2-}$ is less than that of others.

*Keywords:* Acid Blue 29; Decoloration; Mineralization; Hydroxyl radical; Inorganic ions; Peroxyl radical

## 1. Introduction

Growth of population and modern lifestyle has resulted in the rapid growth of various industries including textile, pharmaceutical, and agrochemical industries. Wastewaters generated in those industries are released into water bodies without proper treatment. Textile industries produce large quantities of highly colored effluents, which are generally toxic and resistant to destruction by the biological treatment methods. Being designed to resist chemical and photochemical degradation, conventional physiochemical methods are not efficient for the degradation of dyes. So unless treated properly, the wastewaters released from textile industries would pose health hazard and threat the existence of aquatic life. Now-a-days advanced oxidation processes (AOPs) are being widely used for the treatment of wastewaters. AOPs are the technologies that employ the highly reactive hydroxyl radical as the main oxidative species for the breakdown of organic contaminants. Hydroxyl radicals having a high oxidation potential of 2.8 V, can completely mineralize the organic contaminants into $CO_2$ and $H_2O$. One of the most popular, convenient, and environmentally friendly AOPs, which involves *in situ* generation of hydroxyl radical is the Fenton's reaction. Fenton's reaction (Eq. (1)) involves rapid electron transfer between HP and $Fe^{2+}$, which acts as homogeneous catalyst [1,2]. The $Fe^{3+}$ ion produced in

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the process undergoes further reaction to regenerate $Fe^{2+}$, thereby initiating a cycle of reaction (Eqs. (2)–(4)) and providing a constant source of hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (1)$$

$$Fe^{3+} + H_2O_2 \leftrightharpoons Fe-OOH^{2+} + H^+ \quad (2)$$

$$Fe-OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

Compared to other AOPs, Fenton's reaction presents several advantages: (i) it is easier to operate and the reactions can be performed at ambient temperature and does not require illumination; (ii) the reagents are cheaper and readily available, easy to store and relatively safe to handle; and (iii) $H_2O_2$ is environmental friendly, since it slowly decomposes into oxygen and water. Besides the abundance, lack of toxicity and ease of removal from water makes $Fe^{2+}$ the most commonly used transition metal for applications associated with Fenton's reaction. In addition, the generation of harmful byproducts associated with Fenton's reaction is noticeably lower compared to some other AOPs [3].

Hydrogen peroxide (HP) is commonly used as the oxidant in the Fenton's process. However in recent years, the oxidizing capability of sulfate radical anion ($SO_4^{\cdot-}$) has received much attention. Having a higher oxidation potential ($E^0 = 2.5–3.1$ V *vs.* NHE) than that of $HO^{\cdot}$, $SO_4^{\cdot-}$ is expected to degrade and mineralize organic contaminants more efficiently according to the following three mechanisms: (i) hydrogen abstraction; (ii) addition and substitution reactions with alkenes and aromatic compounds; and (iii) electron transfer from carboxylate groups [4,5]. It has been reported that $SO_4^{\cdot-}$ is more efficient than $HO^{\cdot}$ as $SO_4^{\cdot-}$ is more selective to oxidation while $HO^{\cdot}$ reacts through hydrogen abstraction or addition [6,7]. Persulfate has been used alone or in combination with other AOPs to enhance their performance for the removal of organic contaminants [8–10]. Several studies on the degradation of organic contaminants like azo dyes, 4-chlorophenol, diphenylamine, etc. using $SO_4^{\cdot-}$ have been reported [8,11–14]. The increased use of persulfate in the AOPs is due to their high aqueous solubility, relatively low cost and benign end product, the sulfate ions. The generation of $SO_4^{2-}$ ions causes an increase in the concentration of salt content in the effluent. The $SO_4^{2-}$ ions are inert and are considered not to be pollutant. The USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/L, based on esthetic reasons.

The sulfate radical anions are generated *in situ* by the activation of persulfate (also known as peroxydisulfate or peroxodisulfate) by thermal (30–99˚C), photochemical (<270 nm), radiolytic, (Eqs. (5) and (6)) processes. The persulfate, being the sulfate peroxide, $[SO_3–O–O–SO_3]^{2-}$, can also be achieved by transition metal ions such as $Co^{2+}$, $Ag^+$ and $Fe^{2+}$ ions [15–17] by redox decomposition process (Eq. (7)). But owing to the adverse environmental impact of the former and iron being relatively inexpensive and nontoxic, $Fe^{2+}$ is generally used as the catalyst for activation. However, the only disadvantage of using $Fe^{2+}$ as catalyst is that it acts as a sulfate radical scavenger (Eq. (8)) at high concentration [12,18–21]. Thus maintaining the right concentration of $Fe^{2+}$ is critical to the decoloration and mineralization process.

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{\cdot-} \quad (5)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (6)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-} \quad (7)$$

$$Fe^{2+} + SO_4^{\cdot-} \rightarrow Fe^{3+} + SO_4^{2-} \quad (8)$$

The present study has been undertaken with an aim to fix the most suited operational variables for maximum mineralization of the diazo dye AB 29 by Fenton and Fenton-like processes using HP and SPS, respectively, as oxidants and to evaluate their efficiency. For the purpose, the effect of various operational parameters like pH, concentration of oxidant and $Fe^{2+}$, and presence of air on both the processes has been studied in detail. It may be mentioned that the operational parameters are fixed by analyzing each parameter at a time, keeping others constant and hence, refer to a set of best suited parameters valid for a particular set of conditions for maximum mineralization.

## 2. Materials and methods

### 2.1. Reagents

The diazo dye AB 29 (Synonyms: Amacid Navy Blue B; Cetil Black M; Fabracid Navy S-BL; Mordant

Blue 82; IUPAC name: 2, 7-Naphthalenedisulfonicacid, 4-amino-5-hydroxy-3-[2-(3-nitrophenyl)diazenyl]-6-(2-phenyldiazenyl)-, sodium salt, C. I. number: 20,460, molecular formula: $C_{22}H_{14}N_6Na_2O_9S_2$; molecular weight: 616.49 g $mol^{-1}$; $\lambda_{max} = 602$ nm), sodium persulfate (SPS) ($Na_2S_2O_8$, reagent grade), which are used in this work was purchased from Sigma Aldrich (Germany). Its molecular structure is shown in Fig. 1 (inset). Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), HP ($H_2O_2$, purified, 30% w/w), sulfuric acid ($H_2SO_4$), and sodium hydroxide (NaOH) used in this work were of GR grade unless otherwise stated and acquired from Merck. All the reagents were used without further purification.

### 2.2. Procedure

Aqueous solution of AB 29 of desired concentration was prepared by dissolving required amount in Millipore water (Make of the water system: Millipore India, Bangalore; Model: Elix3 Century). All the reactions were carried out in the presence of air and at room temperature (varying between 21–23℃) by placing required volume of the dye solution of required concentration in amber borosilicate reagent bottles. It may be mentioned that the temperature was not controlled during course of the experiments. Each bottle was designated to be sacrificed for analysis after a predetermined time interval. The bottles were covered with aluminum foil and two holes were pierced through it, to allow free passage of air. The initial pH of the solution was adjusted to the desired value with $H_2SO_4$ (the strength varying between $1 \times 10^{-4}$ and $1 \times 10^{-3}$ N depending on the pH required) or NaOH (the strength varying between $5 \times 10^{-5}$ and $2.25 \times 10^{-3}$N depending on the pH required) using a digital pH meter (Make: Chemiline; Model: CL 110). The reaction was initiated by adding $Fe^{2+}$ solution followed by addition of HP or SPS as an oxidant with constant stirring by a magnetic stirrer. Equal volumes of 3 and 215 mM each of different oxidant solutions (0.5 ml each) were added to the dye solution, and in all the cases the total volume of the solution were kept constant at 100 ml. Therefore, the actual strength of $Fe^{2+}$ and oxidants in the solution was maintained at 0.015 and 1.08 mM, respectively. All the solutions used in this work were freshly prepared except the dye solution, which was stored at 4℃ and used within three days. The same procedure was adopted in our recent publication [14].

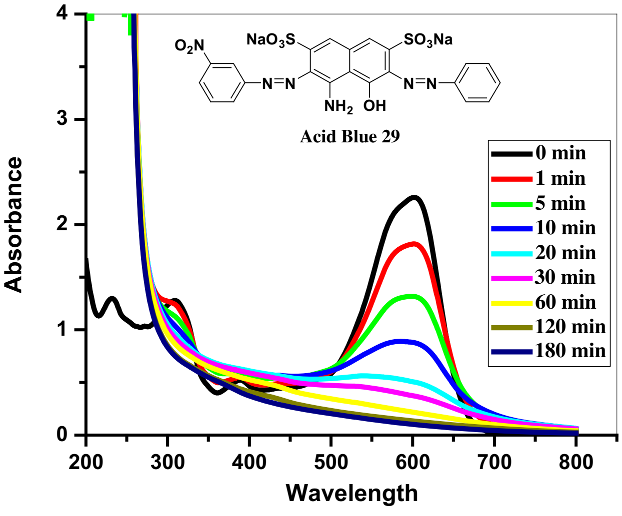

Fig. 1. UV–vis spectral changes of AB 29 in $Fe^{2+}$/HP system: [HP] = 1.08 mM, [$Fe^{2+}$] = 0.015 mM, [AB 29] = 0.07 mM, and pH = 3. Inset: Structure of AB 29.

Decoloration studies were carried out by measuring the absorbance at 602 nm with the help of a UV–vis spectrophotometer (Make: Perkin–Elmer; Model: Lambda 25). Mineralization study was carried out by measuring the total organic carbon (TOC) of the samples using a TOC analyzer (Make: Elementar Analysensysteme GmbH, Model: Liqui TOC II). All the analyses were done immediately after the reaction and the reproducibility in TOC measurement was checked by frequent measurement of the standard (1:1 solution of potassium phthalate and sodium carbonate as TOC and total inorganic carbon standard respectively) as suggested by the manufacturer, and the error were always found to be within ±5%. The data presented in the text and figures were analyzed by standard deviation using "Origin 7" (Microcal Inc.) and has been rounded up to significant values.

## 3. Results and discussion

### 3.1. Spectrophotometric study

Fenton and Fenton-like processes involving iron catalyzed generation of hydroxyl ($Fe^{2+}$/HP) and sulfate radicals ($Fe^{2+}$/SPS) have been used in the decoloration studies of several organic contaminants. To evaluate the efficiency of these oxidants in the decoloration/mineralization of AB 29, a diazo dye, experiments were carried out in the presence of similar concentrations of HP and SPS, respectively. The typical UV–vis absorption spectra of AB 29 in both the oxidant systems follow the similar pattern. Hence, the changes in the absorption spectra of AB 29 solution during the oxidative decoloration process in $Fe^{2+}$/HP system at different time are described here (Fig. 1).

The spectrum of AB 29 before the reaction exhibits four clearly distinguishable absorption peaks: three in the UV region (232, 309 and 389 nm), and one in the visible region (602 nm). While the peaks at 309 and 389 nm ascribed to the $\pi \rightarrow \pi^*$ transitions representing of two adjacent rings (naphthalene ring), the peak at 232 nm is attributed to the $\pi \rightarrow \pi^*$ transition within the benzene ring. The disappearance of these peaks with time indicates the degradation of aromatic rings in AB 29. The peak in the visible region ($\lambda_{max} = 602$ nm), is responsible for the color of the dye, and it is attributed to the absorption of the $n \rightarrow \pi^*$ transitions of N=N, C=N, and C=O chromophore groups. The concentration or color of the dye solution is proportional to the absorbance at 602 nm and thus the decoloration of the dye is monitored quantitatively by measuring the decrease in absorbance at $\lambda_{max} = 602$ nm for the dye chromophore. It is observed that the peak at 602 nm declined rapidly until it disappeared completely at 180 min. This is due to the attack of the $HO^{\bullet}$ radical at the azo group leading to the opening of the –N=N– double bond followed by cleavage of the long chain of conjugated $\pi$ systems. Analysis of spectral data indicates that the peak in the visible region diminishes completely in 180 min, whereas during the corresponding period the peaks at 232, 309, and 389 nm diminish to the extent of 100% (in 1 min), 42 and 23%, respectively. Thus, we can conclude that the benzene rings undergo degradation at a very fast rate, followed by the chromophore group and other aromatic rings. Similar results were recently reported in the degradation of Ponceau S and Reactive black five [22,23].

### 3.2. Effect of oxidant dosage

It has been well established that the concentration of oxidants like HP and SPS plays an important role in the decoloration and degradation process. The addition of HP has been reported to increase decoloration/degradation by allowing an increase in the yield of hydroxyl radicals. Consequently, the decoloration is expected to be enhanced. Fig. 2 displays the decoloration of AB 29 at different HP concentrations at pH 3 when the concentration of $Fe^{2+}$ is fixed at 0.015 mM. There is a slow increase in decoloration when the concentration of HP is increased up to 1.08 mM, beyond which it remains practically unchanged. This is probably due to the scavenging of hydroxyl radicals [24] as soon as they are formed beyond a certain limit (Eqs. (9)–(11)). The hydroperoxyl radicals ($HO_2^{\bullet}$) generated in the presence of excess of HP are much less reactive and do not contribute to the oxidative decoloration of organic substrates, which occur only by the reaction with $HO^{\bullet}$. It is for this reason that we have considered 1.08 mM as the suitable concentration of HP under the given set of experimental conditions.

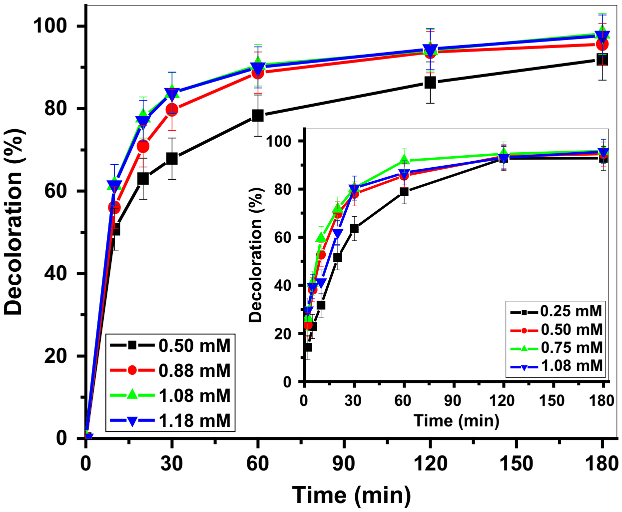

Fig. 2. Effect of HP and SPS (inset) dosage on the decoloration of AB 29: $[Fe^{2+}] = 0.015$ mM, [AB 29] = 0.07 mM, and pH = 3.

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{9}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{10}$$

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

However, a different trend is observed with persulfate as oxidant, which plays an important role as a source of $SO_4^{\bullet -}$ generation in the $Fe^{2+}$/SPS system. The effect of persulfate on the decoloration of AB 29 was examined by taking various concentrations of SPS and keeping the other parameters constant. It is observed that there is an increase in decoloration up to 0.75 mM, beyond which a slight decrease in decoloration is observed (inset of Fig. 2). Even though this result is in good agreement with that of our recent study [14], it contradicts other results reported earlier that there is an increase in decoloration with increase in persulfate concentration until a certain limit, beyond which the decoloration remains constant [8,11]. The concentration of persulfate in $Fe^{2+}$/SPS system is important as $SO_4^{\bullet -}$ radicals generated in the process are responsible to act on AB 29 molecules causing their decoloration and subsequent mineralization. The decoloration by $Fe^{2+}$/SPS process is due to the synergetic effect of both hydroxyl and sulfate radicals, which are generated (Eqs. (5) and (12)) as a result of interaction of $SO_4^{\cdot-}$ with water and hydroxyl ions in accordance with Eqs. (12) and (13) [25].

$$SO_4^{\cdot-} + H_2O \rightarrow HO^{\cdot} + SO_4^{2-} + H^{+} \quad \text{(all pHs)} \tag{12}$$

$$SO_4^{\cdot-} + HO^{-} \rightarrow SO_4^{2-} + HO^{\cdot} \quad \text{(alkaline pH)} \tag{13}$$

At higher persulfate concentration excess hydroxyl radicals generated are combined to give less reactive HP (Eqs. (9) and (11)), which is a known scavenger of $HO^{\cdot}$ radicals [26]. Presence of excess persulfate might lead to scavenging of sulfate and hydroxyl radicals (Eqs. (14)–(17)), thereby reducing decoloration [10,27,28].

$$SO_4^{\cdot-} + HO^{\cdot} \rightarrow HSO_4^{-} + \frac{1}{2}O_2 \tag{14}$$

$$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow 2SO_4^{2-} \tag{15}$$

$$SO_4^{\cdot-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot-} \tag{16}$$

$$HO^{\cdot} + S_2O_8^{2-} \rightarrow HO^{-} + S_2O_8^{\cdot-} \tag{17}$$

### 3.3. Effect of pH of the medium

Effluents released from dye industries usually have a wide range of initial pH values. Thus the solution pH may be an important operating parameter that might affect the removal efficiency of AB 29 and hence must be fixed. Previous studies on dye decoloration and degradation, indicate that pH of the medium can influence the Fenton process to a great extent by influencing the generation of hydroxyl radicals. It is wellknown that the pH range which has proved to work best for Fenton process is 2.5–3.0. The decoloration of AB 29 with HP is studied in a wide pH range and the results are depicted in Fig. 3. It is observed that pH of the medium has remarkable effect on the decoloration process and substantial decoloration occurs during the initial period of treatment leading to intermediate products. Highest decoloration is observed at pH 3 followed by pH 5 (98.1 and 89.6%, respectively, in 180 min) and lowest in neutral and basic media. Thus, pH 3 is considered as the preferable pH for effective decoloration of AB 29. The result is in good agreement with the fact, that hydroxyl radicals exhibit highest oxidative power at pH 3 [3].

At pH < 3, HP is stabilized by protonation to form oxonium ion, $H_3O_2^{+}$ (Eq. (18)). This increases the electrophilicity of HP and reduces its reactivity with ferrous ion. Further, the regeneration of $Fe^{2+}$ through the formation of peroxo complexes of $Fe^{3+}$ (Eqs. (2)–(4)) is also decreased [29,30] at this pH. Therefore, the generation of hydroxyl radicals is decreased and a corresponding decrease in the removal efficiency is observed.

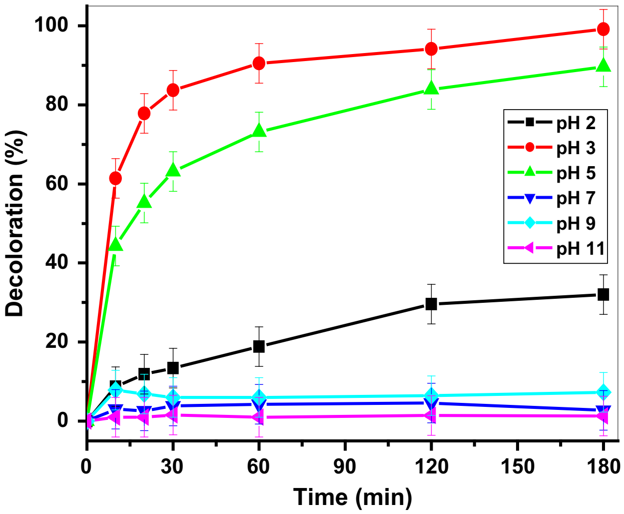

Fig. 3. Effect of pH on the decoloration of AB 29 in $Fe^{2+}$/HP system: [HP] = 1.08 mM, [$Fe^{2+}$] = 0.015 mM, [AB 29] = 0.07 mM.

$$H_2O_2 + H^{+} \rightarrow H_3O_2^{+} \tag{18}$$

At pH > 5, oxidation of $Fe^{2+}$ and subsequent formation of insoluble $Fe(OH)_3$ is significant, which reduces the availability of $Fe^{2+}$, as well as the dissolved fraction of $Fe^{3+}$, which is responsible for the regeneration of $Fe^{2+}$ [31,32]. But the contribution of this factor is minimal as precipitation may not be significant at this concentration of $Fe^{2+}$. The most probable reason for the reduced decoloration at higher pH seems to be the $Fe(OH)_3$ catalyzed decomposition of HP into $H_2$ and $H_2O$ [33]. Another factor which partially contribute to low decoloration at higher pH is due to the oxidation of sodium hydroxide present in the solution by HP (Eq. (19)), which limits its availability for decoloration [34,35].

$$2NaOH + H_2O_2 + 6H_2O \rightarrow Na_2O_2{\cdot}8H_2O \tag{19}$$

Several decoloration/degradation studies have been carried out with persulfate system activated either by iron, heat, UV light, or ionizing radiation. But in no case, specific pH range has been recommended for efficient decoloration. Salari et al. [36] have reported a high degree of decolorization of Basic Yellow 2 by the UV/$S_2O_8^{2-}$ system at all pH level, whereas in the same system maximum decoloration of acetic acid has been reported to occur at pH 5 [37]. On the other hand, pH 6 was found to be optimum for the highest decoloration efficiency of 4-chlorophenol by the $Fe^0$/SPS system [13]. Li et al. [11] have reported that the degradation of diphenylamine by persulfate activated by iron decreases with increase in pH, although substantial degree of degradation was observed in acidic and basic pHs [11]. In another study involving persulfate radical based degradation, no degradation was observed at high pH, whereas maximum degradation was achieved at pH 2 [38].

The pH dependency of AB 29 decoloration with SPS as oxidant is depicted in Fig. 4. It is apparent that pH of the solution has also great impact on the decoloration process in the presence of SPS, that is, highest decoloration is shown at pH 3 followed by pH 5 (95.8 and 92.4%, respectively, in 180 min) and almost negligible decoloration is observed at pH 2, and higher pHs. The decrease in decoloration at higher pHs could be due to the generation of relatively higher amounts of $HO^{\cdot}$ (Eq. (13)) resulting in the rapid decay of $SO_4^{\cdot-}$ and $HO^{\cdot}$ radicals through their recombination (Eqs. (11) and (14)). The increased decoloration efficiency at lower pH may be due to the acid catalyzed generation of additional $SO_4^{\cdot-}$ radicals [39]. This explains our finding that pH 3 is the most favorable for the decoloration of AB 29. It is interesting to note that with further decrease in pH to 2, the decoloration dropped to 19.4 from 95.8% at pH 3 in 180 min. This can be explained on the basis of scavenging effect in the presence of excess $SO_4^{\cdot-}$ radicals as described before.

### 3.4. Effect of Fe(II) concentration

Fe(II) acts as a catalyst in the Fenton Process, and it has been well established that decoloration/degradation of an organic contaminant is dependent on concentrations of $Fe^{2+}$ ions. To show the dependence of decoloration of AB 29 on the $Fe^{2+}$ concentration in $Fe^{2+}$/HP system, experiments were carried out at various $Fe^{2+}$ concentrations. The results indicate that decoloration increases with increase in concentration of $Fe^{2+}$ from 0.005 to 0.015 mM. Since, iron acts as a catalyst and the reactions are nearly irreversible, its role in the reaction is to accelerate the radical generation. Thus, the higher efficiency of AB 29 decoloration at higher $Fe^{2+}$ concentration may be considered due to the faster generation of $HO^{\cdot}$ radicals in the redox cycle of iron ($Fe^{2+} \leftrightarrow Fe^{3+}$). However, beyond 0.015 mM of $Fe^{2+}$, the increase is slow and complete decoloration is achieved at 180 min with each of 0.015, 0.025, and 0.035 mM of $Fe^{2+}$ (Fig. 5). It is reported recently [22] that higher concentration of $Fe^{2+}$ leads to a decrease in the decoloration of Ponceau S due to the scavenging of $HO^{\cdot}$ radicals (Eq. (20)). Apprehending that such a decrease in decoloration would occur in the present case, we have not increased the concentration of $Fe^{2+}$ beyond 0.035 mM and therefore, 0.015 mM is considered as the suitable concentration of $Fe^{2+}$ for breaking down of AB 29 molecules in the $Fe^{2+}$/HP system.

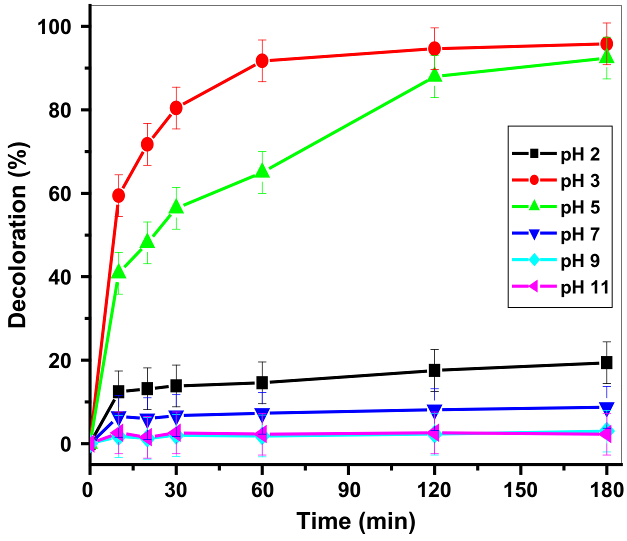

Fig. 4. Effect of pH on the decoloration of AB 29 in $Fe^{2+}$/SPS system: [SPS] = 0.75 mM, $[Fe^{2+}]$ = 0.015 mM, [AB 29] = 0.07 mM.

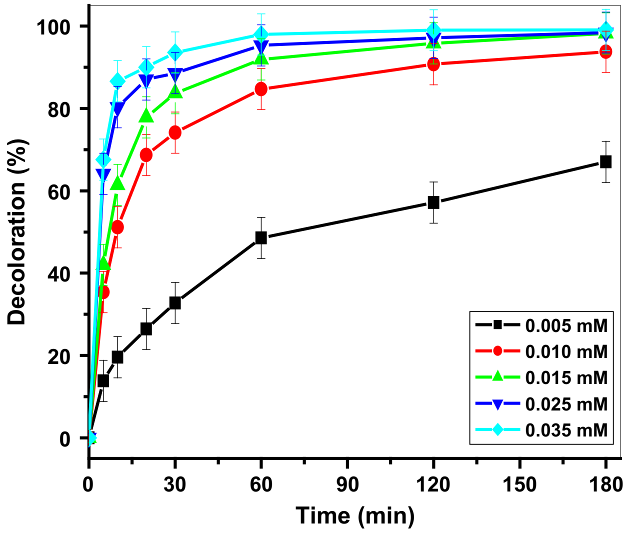

Fig. 5. Effect of $[Fe^{2+}]$ on the decoloration of AB 29 in $Fe^{2+}$/HP system: pH = 3, [HP] = 1.08 mM, and [AB 29] = 0.07 mM.

$$\mathrm{Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-}} \tag{20}$$

To show the dependence of AB 29 decoloration on $Fe^{2+}$ concentration in $Fe^{2+}$/SPS system, experiments were performed at various $Fe^{2+}$ concentrations and the data are presented in Fig. 6. It is seen that 34.4, 54.0, and 80.42% decoloration is achieved in 30 min in the presence of 0.005, 0.010, and 0.015 mM of $Fe^{2+}$, respectively. The higher efficiency of AB 29 decoloration at the higher $Fe^{2+}$ concentration might be due to generation of additional $SO_4^{\cdot-}$ radicals in the reaction. However, when the $Fe^{2+}$ concentration is increased to 0.020 mM the decoloration is reduced to 73.7%, indicating that an excess of $Fe^{2+}$ acts as an intrinsic scavenger of sulfate radicals as expressed by Eq. (8). Thus, 0.015 mM is also considered as the suitable concentration of $Fe^{2+}$ for the decoloration of AB 29 in $Fe^{2+}$/SPS system.

## 4. Mineralization study

The success of any AOP lies in its ability to remove organic carbons, which are the main sources of pollution. During the decoloration process, as described above the dye molecules are degraded to their intermediates, thus removing the parent compound and destroying the apparent color. But complete degradation may not lead to complete or at least substantial mineralization.

Aromatic amines, which are generally formed as intermediates during the degradation process of azo dyes, are carcinogenic and thus more toxic than the original dye. Therefore, further degradation of the intermediate molecules is necessary if toxicity is to be eliminated or reduced. This can be done by achieving mineralization to the maximum extent and hence the operational parameters should not be fixed on the basis of degradation or decoloration. In order to evaluate the efficiency of both the processes, we have investigated the mineralization at pH 3, where the decoloration is highest. Although complete decoloration with $Fe^{2+}$/HP system is achieved from 180 min onwards, the degree of mineralization varies from 34.1% in 180 min to 52.9% in 1,440 min (inset of Fig. 6) at pH 3, respectively. It is evident that mineralization at pH 3 involving $Fe^{2+}$/SPS system practically remains constant throughout the course of reaction as there is only 6% rise in mineralization (27.6% in 5 min to 33.8% in 1,440 min) over a wide range of period. This makes $Fe^{2+}$/HP system more efficient than the $Fe^{2+}$/SPS system. On the contrary, it is expected that mineralization with SPS should have been higher than that of HP due to the factors already described before. It may be assumed that though $SO_4^{\cdot-}$ radicals are able to decompose AB 29 molecules efficiently, they are not able to interact with the intermediates causing further degradation and increasing mineralization. Further, the low mineralization in both the systems is in good agreement with the fact that the solution pH practically remains constant throughout the process.

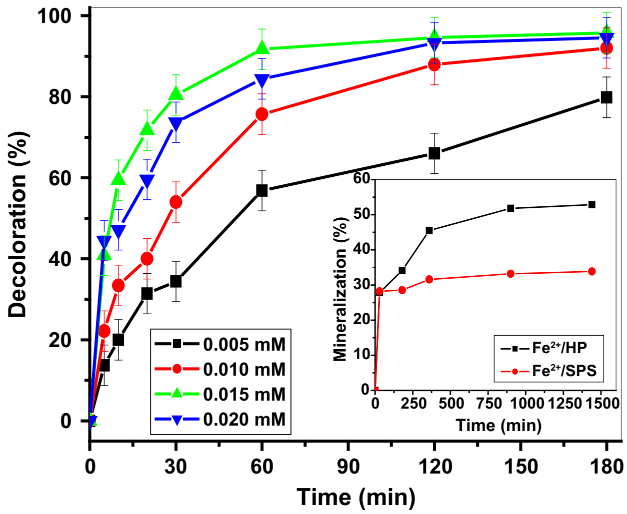

Fig. 6. Effect of $[Fe^{2+}]$ on the decoloration of AB 29 in $Fe^{2+}$/SPS system: pH = 3, [SPS] = 0.75 mM, [AB 29] = 0.07 mM. In set: Mineralization of AB 29 at pH 3: [AB 29] = 0.07 mM, $[Fe^{2+}]$ = 0.015 mM, [HP] = 1.08 mM, and [SPS] = 0.75 mM.

## 5. Effect of oxygen on decoloration

In order to determine the effect of oxygen on the decoloration process, the solutions were purged with nitrogen for 20 min before the addition of oxidants. The decoloration percentage of AB 29 in the presence and absence of air is presented in Table 1. An analysis of the data shows that the decoloration is retarded in the absence of air, especially until 30 min of the reaction in both the systems. Beyond 30 min, the decoloration becomes more or less similar to that in the presence of air. The enhancement of decoloration in the presence of oxygen is partly due to the generation of additional HP molecules (Eqs. (21) and (22)) and is partly due to the formation of peroxyl radicals. It has been shown that the benzene ring in an azo dye opens through the formation of peroxyl radical, which on oxidation by $HO^{\cdot}$ leads to mineralization [32].

$$\mathrm{Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\cdot-}} \tag{21}$$

$$\mathrm{2O_2^{\cdot-} + 2H^+ \rightarrow H_2O_2 + O_2} \tag{22}$$

Table 1
Decoloration of AB 29 in the presence and absence of air and mineralization in presence of air: [AB 29] = 0.07 mM; $[Fe^{2+}] = 0.015$ mM; Initial pH = 3; [HP] = 1.08 mM; and [SPS] = 0.75 mM

| Time (min) | $Fe^{2+}$/HP | | | $Fe^{2+}$/SPS | | |
|---|---|---|---|---|---|---|
| | Decoloration (%) | | Min (%) | Decoloration (%) | | Min (%) |
| | Presence of air | Absence of air | Presence of air | Presence of air | Absence of air | Presence of air |
| 5 | 42.0 | 28.5 | 13.7 | 52.6 | 30.2 | 27.6 |
| 10 | 61.3 | 45.7 | 15.4 | 60.2 | 40.6 | 27.9 |
| 30 | 83.7 | 72.8 | 27.8 | 79.1 | 62.2 | 28.2 |
| 60 | 90.5 | 91.9 | … | 91.7 | 87.7 | … |
| 120 | 94.1 | 95.8 | … | 94.6 | 93.0 | … |
| 180 | 98.1 | 98.2 | 34.1 | 95.8 | 95.8 | 28.5 |
| 360 | 99.5 | – | 45.5 | 97.2 | – | 31.6 |
| 480 | 99.6 | – | 46.4 | 97.9 | – | 31.9 |
| 600 | 99.7 | – | 51.2 | 98.3 | – | 32.8 |
| 900 | 99.8 | – | 51.8 | 98.7 | – | 33.2 |
| 1,440 | 100 | – | 52.9 | 99.2 | – | 33.8 |

The low decoloration in the absence of oxygen is, therefore, in good agreement with the above discussion. We can see that oxygen is evolved during the decoloration process (Eqs. (14) and (22)), and it is due the accumulation of this oxygen, the decoloration enhances and becomes the same as that in the presence of air. It is important to note that the pH in $Fe^{2+}$/HP and $Fe^{2+}$/SPS systems does not change during the course of the reaction and remains constant at ≈ 3. This result is in good agreement with our earlier conclusion that decoloration proceeds well in the presence of air.

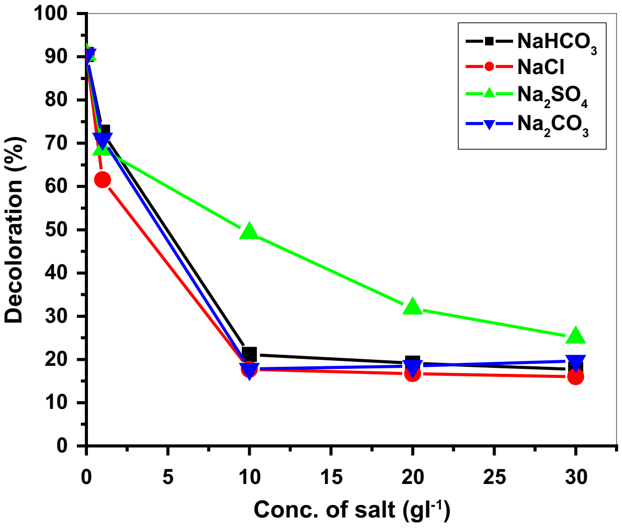

Fig. 7. Effect of inorganic ions on the decoloration of AB 29 by $Fe^{2+}$/HP system: [AB 29] = 0.07 mM, pH = 3, $[Fe^{2+}] = 0.015$ mM, [HP] = 1.08 mM, and Reaction time = 60 min.

## 6. Effect of inorganic anions

Wastewaters released from textile industries usually contain inorganic salts with varying concentrations, which are generally ionized in solution and the strength of dissolved inorganic ions may affect the efficiency of decoloration. The effect of various inorganic ions such as $Cl^-$, $CO_3^{2-}$, $HCO_3^-$, and $SO_4^{2-}$ on AB 29 decoloration by $Fe^{2+}$/HP system were examined in the concentration range from 0.1 $g\,l^{-1}$ to 30 $g\,l^{-1}$ and the results are depicted in Fig. 7. It is noted that the initial decoloration of 90.5% in 60 min, drops sharply to around 18% in the presence of 10 $g\,l^{-1}$ of all ions other than $SO_4^{2-}$, and further increase in the concentration of ions does not have any impact on the decoloration, indicating complete scavenging of hydroxyl radicals. Sulfate ions, on the other hand, show less inhibition effect in comparison to other ions and the decoloration declines to 25% under similar conditions. The scavenging of hydroxyl radicals by chloride and sulfate ions are described in our earlier publication [40] and it was shown that presence of sulfate ions leads to the generation of reactive sulfate radicals, a factor which balances the inhibition effect to some extent. The inhibition effect by $CO_3^{2-}$ and $HCO_3^-$ is due to the scavenging of hydroxyl radicals [27] to produce carbonate radicals according to Eqs. (23) and (24).

$$HO^{\cdot} + CO_3^{2-} \rightarrow CO_3^{\cdot-} + HO^- \quad (23)$$

$$HO^{\cdot} + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O \quad (24)$$

The carbonate radicals, having much lower oxidation potential (1.85 V) than hydroxyl radicals (2.80 V) are obviously less reactive and hence are responsible to bring down the decoloration to a great extent.

## 7. Conclusion

From the present study, it is concluded that decoloration and mineralization of AB 29 by the two processes is pH dependent and is efficient at pH 3. Other factors which affect these processes are the concentrations of iron and oxidant. Most importantly higher concentration of SPS shows detrimental effect on the decoloration process, while that of HP shows no such effect. Based on the results, it is concluded that $Fe^{2+}$/HP system is more efficient than $Fe^{2+}$/SPS system for the removal of AB 29 in the aqueous solution. Since the inorganic anions such as $Cl^-$, $CO_3^{2-}$, $HCO_3^-$, and $SO_4^{2-}$ inhibit decoloration significantly, it is recommended to remove the ions before the mineralization process. It is evident from the result that the decoloration is enhanced in the presence of oxygen and thus aeration during the decoloration process would reduce the treatment cost significantly.

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