Inquest of efficient photo-assist advanced oxidation processes (AOPs) for removal of azo dye (acid yellow 17) in aqueous medium: a comprehensive study on oxidative decomposition of AY 17

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Abstract

In this study, the photo-assist degradation of acid yellow (AY 17) dye is reported in detail by applying various UV radiation supported advanced oxidation processes (AOPs). The AY 17 dye in water solution (model and natural) is decomposed by direct photolysis, UV/oxidant, photo-Fenton, photo-Fenton-like, $\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$, and $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ system. All applied processes are found to be the comparably effective at pH 3.0. It is observed that the efficiency of AY 17 degradation increased with the initial concentration of the oxidants (H_2O_2 , HSO_5^- and $\text{S}_2\text{O}_8^{2-}$) and catalyst (Fe^{2+} and Fe^{3+}). Moreover, the initial concentration of the dye solution has inverse effect on the efficiency of applied AOPs. It is also reported that decomposition of dye through photo-assist AOPs followed *pseudo-first-order* kinetic while the efficiency of all processes increased with temperature. The activation energy (E_a) has been determined in the range of between 10 to 20 kJ/mol. The entropy of degradation is also calculated and has found to be positive. Finally, it is concluded that photo-Fenton process ($\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is comparably more efficient method for the removal of AY 17 dye from natural water sample.

Keywords Azo dye · Waste water treatment · UV light assist AOP · Hydroxyl radical ($\cdot\text{OH}$) · Sulphate radical ($\text{SO}_4^{\cdot-}$)

1 Introduction

Advanced oxidation processes (AOPs) may be defined as “the processes in which highly reactive species like hydroxyl radical ($\cdot\text{OH}$), hydrated electron (e_{aq}^-), or sulphate radical ($\text{SO}_4^{\cdot-}$) are produced in sufficient amount at near ambient temperature and pressure” [1]. These processes show efficient results in the purification of surface and ground water and in the degradation of biodegradable and non-biodegradable organic toxic wastes. To produce reactive radicals, various oxidants such as hydrogen peroxide, persulfate, peroxydisulphate ($\text{S}_2\text{O}_8^{2-}$) or simply called PS, and PMS (permonoxysulphate, HSO_5^-) are used. The hydroxyl radical is simpler and more reactive which is used in different advance oxidation technologies, like Fenton, Fenton like, photo Fenton etc., reactions. Under

appropriate conditions, it leads to mineralization, i.e., its end products are water and carbon dioxide. Therefore $\cdot\text{OH}$ radical is an environment friendly oxidizing agent. Because of its properties, H_2O_2 plays significant role in the fields of green engineering and chemistry [2, 3]

A novel oxidant, persulfate ($\text{S}_2\text{O}_8^{2-}$) showed a versatile efficiency in the field of AOPs. It has certain advantages, like low cost, high water solubility, moderate stability, easy to store, and high redox potential [4]. Another advantage of $\text{S}_2\text{O}_8^{2-}$ (PS) is that it is less reactive towards natural organic matters but appears to be more reactive towards aqueous solution which contains high value of natural organic matter (NOMs) [5]. Due to these properties, $\text{S}_2\text{O}_8^{2-}$ (PS) is a more effective oxidant for the treatment of wastewater. The third oxidant, HSO_5^- , is an active ingredient of oxone in aqueous solution and its trade name is triple

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salt of potassium ($2\text{KHSO}_4 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$). In recent years (HSO_5^-) has shown a tremendous role in the treatment of wastewater [2, 6, 7].

Since the redox potentials of HSO_5^- (PMS), $\text{S}_2\text{O}_8^{2-}$ (PS) and hydrogen peroxide (H_2O_2) are low so these cannot oxidize organic pollutants efficiently. The transition metal ion (Mn^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , etc.) can activate the oxidant through electron transfer mechanism to produce highly reactive radicals which can successfully degrade the toxic pollutants. When H_2O_2 is activated by ferrous ions, Fe^{2+} , this process is known as Fenton process. It is an important oxidizing process which is applied for the oxidation of organic pollutant since long time in the history of wastewater treatment. In Fenton process, hydroxyl radical ($\cdot\text{OH}$) is produced which attacks the pollutant and oxidizes them to less toxic compounds, such as inorganic salts, H_2O and CO_2 . It is a simple, easily handled and relatively cheaper process but it works under acidic conditions, i.e., optimum pH between 3.0 and 4.0, which is the main drawback of this process [8].

When the oxidants like H_2O_2 , HSO_5^- and $\text{S}_2\text{O}_8^{2-}$ are activated by ferric ion (Fe^{3+}) then this process is called Fenton-like process [9, 10]. Fenton-like process is based on the production of hydroxyl or sulfate or both radicals. The oxidant can also be activated by other metal ions like V^{3+} , Ce^{3+} , Ru^{3+} , Mn^{2+} , Ni^{2+} , Ag^+ and Co^{2+} [11]. All the above types of metals ions generate the same $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals. However, the efficiency of metal ions to produce reactive radical may be different.

The combination of UV radiation with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ are known photo Fenton and photo Fenton-like processes, respectively. The presence of UV radiation with Fenton and Fenton-like processes increases the degradation efficiency of these processes [5]. The difference between photo Fenton and photo Fenton-like processes is only the use of iron (Fe) as catalyst in different oxidation state. The production rate of reactive radicals and regeneration of Fe^{2+} and Fe^{3+} from its complex can also be enhanced by using UV radiation [11]. All the processes such as, photo-Fenton, photo-Fenton-like, $\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$ and $\text{UV}/\text{H}_2\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ are economic, environmentally friendly and very effective. Several photo-assist AOPs are shown in diagram (Fig. 1).

Azo dye—acid Yellow 17 have complicated and stable structure (see Table 1). It has a strong electron withdrawing character which stabilizes azo dyes against conversion by oxygenase in aerobic environment [12]. Under anaerobic conditions azo dyes are converted to toxic end products i.e. aromatic amines [13]. These aromatic amines are also mutagenic and carcinogenic [14]. It can cause various problems and diseases in humans and in aquatic life. It can affect respiratory system e.g., dyspnea, skin disease dermatitis, cardiovascular disease, eye irritation, nervous

Fig. 1 Scheme of the present study

Table 1 Physical and chemical properties of acid yellow 17

Azo dye	Acid yellow 17
MW	551.277 g/mol
Solubility in H_2O	Soluble
C.I	18,965
λ_{max}	400 nm
PK_a	5.3
Molecular structure	

system of human being and other animals [15]. The present work therefore demonstrates the decomposition of AY 17 by UV light assist AOPs which include a comprehensive comparative study—utilizing several effective, easy and environmental friendly AOPs such as direct photolysis, UV/ Oxidant, Fenton, Fenton-like, photo-Fenton, Photo-Fenton-like, $\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ for removal of acid yellow 17 dye in aqueous medium. A comparison in the efficiency, reaction kinetic, and mechanism for degradation of AY 17 dye in aqueous medium by AOPs of different AOPs is also investigated. Finally, the degradation of on AY 17 dye solution in pure water and natural water was carried out to assess the efficacy of UV light assist AOPs. To the best of our knowledge, the Photo-Fenton-like, UV/

$\text{HSO}_5^-/\text{Fe}^{2+}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ is applied for the first time for the degradation of acid yellow 17 dye. The effect of several parameters (as sketched in Fig. 1) on the decomposition of AY 17 are investigated.

2 Experimental

2.1 Chemical and reagents

Acid yellow 17 dye (Cat. No. 191921000, dye content 60%) was purchased from Acros Organics (Belgium). hydrogen peroxide (H_2O_2 , 30% w/w, analytical grade), ferrous sulfate hepta hydrated (purity $\geq 99.5\%$, analytical grade), ferric sulfate (FeSO_4 , purity $\geq 98\%$, reagent grade), sodium nitrate (NaNO_3 , purity 98%, analytical grade), sodium nitrite (NaNO_2 , purity 98%, analytical grade) and buffer solutions (pH 4.0, 7.0 and pH 11.0) were purchased from Scharlau, Germany. Sulfuric acid (H_2SO_4 , purity $\geq 99.99\%$, analytical grade), sodium bicarbonate (NaHCO_3 , purity $\geq 99.5\%$, analytical grade), potassium iodate (purity 98%, analytical grade), potassium iodide (purity $\geq 99\%$, analytical grade), potassium dichromate (purity $\geq 99\%$, analytical grade), and sodium carbonate (NaCO_3 , purity $\geq 98\%$, analytical grade) were purchased from Sigma Aldrich, Germany. Potassium chloride (KCl) and Sodium chloride (NaCl) of analytical grade from Merck, (U.S.A) were used. All required standard solutions were prepared in Milli-Q ultra-pure water (Resistivity $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$). For adjustment of pH of solutions, dilute solutions of H_2SO_4 and NaOH were used.

2.2 Instrumentations

Millipore Milli-Q system (Bedford, U.S.A) was used to obtain ultra-pure water. For drying purposes, electronic oven (WTC Binder E 28, Germany) was used. The pH of solution was measured by pH meter (NeoMet ISTEK, Korea). For weighing purposes, digital microbalance AY220 (Shimadzu, Germany) was used. UV-visible spectrophotometer (Perkin Elmer, Model: Lambda-650, UK) was used for the quantitative analysis. For the absorbance calibration of UV-visible spectrophotometer, standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ was used. Percent degradation was calculated using Eq. (1).

$$\text{Percent degradation} = \left(\frac{C_t}{C_0} \right) \times 100\% \quad (1)$$

where, C_0 is the initial concentration of AY 17 at $t=0.0 \text{ min}$, while C_t is the concentration of AY 17 at time $t \text{ min}$ which was calculated from the absorbance measurement through Beer's Lambert law.

For the photolysis of aqueous solution of AY 17 dye, a photochemical apparatus fitted with a 4 W low pressure Hg-UV lamp (PENRAY, USA) was used. The wavelength of the light emitted by Hg-UV lamp was 254 nm. The lamp was enclosed in wooden box. A magnetic stirrer was used for stirring the sample to achieve homogenous flow of UV radiation through solution. The area of Pyrex glass beaker was 50 cm^2 which was used for sample solution for UV radiation treatment.

For the quantitative and qualitative analysis of anions and cations present in natural waters, Metrohm Ion chromatograph 800 series equipped with electrical conductivity was used. The columns used for analysis of anions and cations were Metrosep A supp 5 (250/4.0 mm) and Metrosep C₁ (125/4.6 mm) respectively. For anions analysis the ion-chromatographic determination were carried out with 50 mM H_2SO_4 /1 mM NaHCO_3 /3.2 mM Na_2CO_3 /milli-Q water as mobile phase. In case of cations analysis, the mobile phase was tartaric acid / 24 mM boric acid / 1 mM dipiclonic acid.

For identification of intermediates of AY 17 dye produced during the oxidation GC-MS analysis was performed by using a HP-6890 gas chromatograph coupled with a HP-5973 mass spectrometry instrument. With the help of HP-5 MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) separation of the sample components was achieved. Mass spectra were obtained by the electron-impact mode (EI) at 70 eV, using scan mode (50–500 m/z) under these conditions: purge time = 1 min, purge flow = $26.5 \text{ ml} \cdot \text{min}^{-1}$ and pressure = 7.63 psi. GC-MS information was compared with NIST mass spectra library for identification of unknown compounds.

3 Result and discussion

3.1 Photo-Fenton process ($\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$)

Prior to photo-Fenton process ($\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$), the degradation of AY 17 dye was first checked with UV, UV/Fe^{2+} , $\text{UV}/\text{H}_2\text{O}_2$ system. It was observed that only 2%, 3%, and 5% dye was degraded with UV light, UV/Fe^{2+} , $\text{UV}/\text{H}_2\text{O}_2$ system in 25 min at optimized experimental conditions, respectively (Fig. 2, Table. 2). In contrast, about 88.00% degradation in 25 min was achieved with $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system. The reason for high percent degradation with $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system is the frequent availability of both oxidant (H_2O_2) and catalyst (Fe^{2+}) in the system which facilitate the degradation process by producing large number of hydroxyl radical ($\cdot\text{OH}$) as shown by Eqs. (2–4) [16].

Fig. 2 Degradation of AY 17 dye at experimental optimized condition: pH=3.0, [H₂O₂]₀=1.0 mM, [AY 17]₀=0.14 mM, [Fe²⁺]₀=0.09 mM, T=298 K

It was observed that photo-Fenton process is highly effective at pH 3.0 due to formation of [FeOH]²⁺. The UV radiation accelerates the conversion of [FeOH]²⁺ into Fe²⁺ ion and ·OH and thus the degradation process improved (Eq. 5) [17, 18].

The degradation of photo-Fenton process also effected with concentration of oxidant (H₂O₂). The increased in degradation in with concentration of H₂O₂ is due to production of ·OH radical (Eq. 4) [19]. Since, Fe²⁺ concentration directly affects the yield of ·OH radical as

shown in (Eq. 2), a concentration of 0.09 mM Fe²⁺ was found as optimum Fe²⁺ concentration.

Initial concentration of AY 17 is another important parameter for degradation by photo-Fenton process. In present study the concentration of AY 17 dye varied from 0.1 to 0.22 mM was investigated. The optimum concentration of Ay 17 was attained. The effect of stirring velocity on degradation of AY 17 by photo-Fenton process, with stirring speed of 0, 100, 200 and, 400 rpm was also studied. Maximum degradation is achieved at 100 rpm. The reason for these fluctuations may be due to the aspiration of gases such as O₂ and CO₂ into solutions [20]. Under the influence high velocity of stirring CO₂ in the solution which produce HCO₃[−] and CO₃^{2−} ions (Eq. 6–7). The degradation was decreased due to the reaction of these ion complex (Eq. 8–11). The CO₃^{2−} and HCO₃[−] ions produced can scavenge hydroxyl radical. The degradation decreased due to the consumption of ·OH radical (Eq. 12,13) [21]. Similarly, the effect of CO₃^{2−} and HCO₃[−] was separately investigated. It was observed that degradation of AY 17 dye decreased due to the presence of CO₃^{2−} and HCO₃[−]. These produced ions scavenge the production of hydroxyl radical ·OH which is important for dye degradation.

Table 2 Optimized parameter for degradation AY 17 dye

Parameter	UV/H ₂ O ₂ /Fe ²⁺	UV/H ₂ O ₂ /Fe ³⁺	UV/HSO ₅ [−] /Fe ²⁺	UV/S ₂ O ₈ ^{2−} /Fe ²⁺
Optimized conditions				
H ₂ O ₂ (mM)	1.0	10	–	–
HSO ₅ [−] (mM)	–	–	2	–
S ₂ O ₈ ^{2−} (mM)	–	–	–	1
Fe ²⁺ (mM)	0.09	–	1	0.5
Fe ³⁺ (mM)	–	0.09	–	–
AY 17 (mM)	0.14	0.14	0.14	0.14
Time of Reaction (min)	25	60	60	60
% Degradation ^a	88	93	86	84
AY 17: Oxidant: Catalyst (ratio)	1.5: 11: 1	1.5: 111: 1	1: 14: 7	1: 7: 3.7

^aIn triply distilled water sample

The presence of chloride (Cl^-) also decreases the degradation. The decreased in degradation was due to the scavenging of hydroxyl radical by chloride ion. By addition of chloride ion, various inorganic radical like $\text{ClOH}^{\cdot-}$, $\text{HClOH}^{\cdot}$, $\text{Cl}^{\cdot}$ and $\text{Cl}_2^{\cdot-}$ were produced. Among all these the $\text{Cl}_2^{\cdot-}$ is the pre-dominant species due to which the degradation rate drastically decreased by inhibition of $\cdot\text{OH}$ radical production [22].

Similarly, the degradation also decreased with SO_4^{2-} concentration. The reason for the decreased in degradation due to sulphate ion (SO_4^{2-}) was the reaction of sulphate anion with both Ferric and ferrous ions, which form complexes such as $\text{FeSO}_4^{\cdot}$, FeSO_4^+ and $\text{Fe}(\text{OH})_2^{\cdot}$ [23]. The adjustment of initial temperature plays a very important role in the degradation of dyes by AOPs. High temperature (in the range of 298 K–318 K) also improved generation of $\cdot\text{OH}$ radical hence favors high decomposition of dye. At high temperature the concentration of $[\text{FeOH}]^{2+}$ increased which result an increased in photo-production of Fe^{2+} from $[\text{FeOH}]^{2+}$ (Eq. 5) [24, 25].

3.2 Photo-Fenton-like process ($\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{3+}$)

The percent degradation by $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{3+}$ systems was found to be 93% in 60 min at optimized condition (shown in Table. 2, Fig. 3). Various types of reaction which are occurred during photo-Fenton-like process were given below (Eqns. 14–17) [26].

The experimental observation shows that photo-Fenton-like process is strongly depends upon initial pH of solution. The maximum degradation was achieved at pH 3.0. Here also the initial concentration of H_2O_2 also plays a very important role in the degradation of AY 17 dye. When concentration of H_2O_2 was increased from 1 to 10 mM, the degradation of AY 17 increased due to high generation of $\cdot\text{OH}$ radical. But when the initial concentration of H_2O_2 increased to 20 mM there was no significant increase in degradation was observed. This was due to the scavenging

Fig. 3 Degradation of AY 17 dye at experimental optimized condition: $[\text{H}_2\text{O}_2]_0 = 10$ mM, $[\text{AY 17}]_0 = 0.14$ mM and $[\text{Fe}^{3+}]_0 = 0.09$ mM pH = 3.0, $T = 298$ K

of $\cdot\text{OH}$ radical [27]. The effect of Fe^{3+} and concentration of dye is also a very important parameter which require to be optimized. The optimum concentration of Fe^{3+} and dye was found to be 0.09 mM and 0.14 mM, respectively. Similar to photo-Fenton, the degradation of dye through photo-Fenton like process also increased with temperature.

The effect of various salts of Fe^{3+} such as FeCl_3 , $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ were also studied. It was observed that maximum degradation was achieved by $\text{Fe}_2(\text{SO}_4)_3$ with the following order of reactivity of Fe^{3+} salts; $\text{Fe}_2(\text{SO}_4)_3 > \text{FeCl}_3 > \text{Fe}(\text{NO}_3)_3$. In case of $\text{Fe}_2(\text{SO}_4)_3$, highly reactive sulphato-iron(II) ($\text{H}_2\text{O}_2\text{-Fe(II)}$) complex was formed which enhance degradation. The reason for low degradation in case of by FeCl_3 and $\text{Fe}_2(\text{NO}_3)_3$ was due to the scavenging effect of $\cdot\text{OH}$ radical by counter ions (Cl^- and NO_3^-) [28, 29]. The experimental results show good correlation with literature [30]. A strong retardation effect was also observed by CO_3^{2-} and HCO_3^- . This is due to scavenging effect of $\cdot\text{OH}$ radical by CO_3^{2-} and HCO_3^- [31]. Since the waste water of textile industry contain a number of inorganic salts, among these, Cl^- and sulphate ion salt are very common [32]. These ions show negative effect on degradation due to scavenging of $\cdot\text{OH}$ radical by Cl^- and SO_4^{2-} [33].

3.3 UV/PMS(HSO_5^-)/ Fe^{2+} process

The degradation of AY 17 under various experimental conditions such as UV, Fe^{2+} , HSO_5^- , $\text{HSO}_5^-/\text{Fe}^{2+}$ and UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ were performed (Fig. 4). In the absence of both oxidant (HSO_5^-) and catalyst (Fe^{2+}), low percent degradation was observed with UV light. This was due

to generation of small amount of hydroxyl radical ($\cdot\text{OH}$) in water. In UV/ Fe^{2+} or UV/ HSO_5^- systems, the degradation was also low due to lack of catalyst (Fe^{2+}) or oxidizing agent (HSO_5^-), *vice-versa*. In system containing both HSO_5^- and Fe^{2+} , as the quantity of intermediates are increased, the degradation was reached up to 57% in 60 min of reaction time, this high degradation was due to the catalytic production of sulphate radical, which attacks the AY 17. The highest degradation (85%) was achieved by UV assists $\text{HSO}_5^-/\text{Fe}^{2+}$ system. In this system highly oxidizing species $\text{SO}_4^{\cdot-}$ radical produced in high amount which attack the dye molecule and degraded it (see Eqns. 18–20) [34].

It was observed that UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ shows the highest degradation at pH 3. The effect of concentration of HSO_5^- was also checked by keeping other parameters such as pH, temperature, initial concentration of Fe^{2+} (1 mM) and AY 17 (0.14 mM) dye constant. It was observed that degradation of AY 17 dye increased with increased of HSO_5^- concentration due to production of sulphate radical ($\text{SO}_4^{\cdot-}$). The optimum concentration of HSO_5^- was found as 2.0 mM. The effect of initial concentration of Fe^{2+} at constant concentration of AY 17 and oxidant (HSO_5^-) on the

degradation of AY 17 by UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ was also investigated. The degradation of AY 17 dye increased with Fe^{2+} concentration. The Fe^{2+} ion catalyzed the HSO_5^- to produced reactive sulphate radical ($\text{SO}_4^{\cdot-}$) through electron transfer mechanism [34].

Decomposition of dye in water by UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ also depends on initial concentration of dye AY 17. It was seen that upon increasing the initial concentration of AY 17, percent degradation decreased. The reason for decrease in degradation with increasing AY 17 concentration was the competing reactions of intermediates with $\text{SO}_4^{\cdot-}$ radical which formed during degradation of dye. As the quantity of intermediates are increase during AY 17 degradation, the $\text{SO}_4^{\cdot-}$ radical have greater chance to react with intermediates rather than AY 17 hence the percent degradation of AY 17 decreases [35]. The effect of initial temperature on the degradation of AY 17 by UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ process was also studied. At three temperatures (298, 308 and 318 K), the percent degradation was found to be 85, 92, and 94, respectively. The effect of various inorganic ions such as HCO_3^- and CO_3^{2-} , SO_4^{2-} and Cl^- were investigated. It was observed that the presences of these ions have negative effect on the degradation of AY 17 dye by UV/ $\text{HSO}_5^-/\text{Fe}^{2+}$ process. High concentration of these ions, decrease the degradation of AY 17 dye due to scavenging of $\text{SO}_4^{\cdot-}$ radical [36]. These results obtained in our study was in agreement with literature [37].

3.4 UV/ $\text{PS}(\text{S}_2\text{O}_8^{2-})/\text{Fe}^{2+}$ process

To study the degradation of AY 17 by UV/ $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ system, first AY 17 were decomposed by only UV, UV/ Fe^{2+} , UV/ $\text{S}_2\text{O}_8^{2-}$, $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$, and UV/ $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ (Fig. 5). The order of decreasing degradation is given as: UV/ $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+} < \text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+} < \text{UV}/\text{S}_2\text{O}_8^{2-} < \text{UV}/\text{Fe}^{2+} < \text{UV}$. The $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ system assist by UV radiation significantly increased the degradation of AY 17 because reactive species such as $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ are formed in excess amount. The reactions which favored the increase in the degradation of AY 17 by UV/ $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ are mentioned in literature by Eqs. (21–33) [38].

Fig. 4 Effect of various parameters on degradation. Experimental conditions: pH=3, T=298 K, $[\text{HSO}_5^-]_0=2$ mM, $[\text{Fe}^{2+}]_0=1$ mM, $[\text{AY 17}]_0=0.14$ mM

Fig. 5 Effect various parameters on degradation of AY 17 as a function of reaction time. Experimental conditions: [AY 17]₀ = 0.14 mM, [S₂O₈²⁻]₀ = 1.0 mM, [Fe²⁺]₀ = 0.5 mM, pH = 3.0

In order to investigate the effect of initial pH on degradation, A pH of the dye solution was also change from 3 to 9. It was observed that highest degradation was achieved at pH 3. In acidic pH, the dominant specie was $\text{SO}_4^{\cdot-}$ radical which significantly decomposed the AY 17 dye therefore, the increase of the pH of solution tend to decrease degradation. At high pH (range: 7–9), both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radical exist which recombine with each other much fast, hence the degradation decreased [39]. The initial concentration

of $\text{S}_2\text{O}_8^{2-}$ also affect decomposition of dye. The optimum concentration of $\text{S}_2\text{O}_8^{2-}$ was found to be 1 mM. The effect of initial concentration of Fe^{2+} on degradation of AY 17 by UV/ $\text{S}_2\text{O}_8^{2-}$ / Fe^{2+} process was also examined. The results show that when then the concentration of Fe^{2+} increased from 0.05 to 0.5 mM the percent degradation increased considerably. At optimum condition the ratio between of Fe^{2+} and $\text{S}_2\text{O}_8^{2-}$ were found to be 1: 2. The effect of AY 17 dye concentration has also been investigated. the results degradation decreased with dye concentration. The effect of temperature on dye degradation was also monitored. During temperature study, other parameters such as initial pH, concentration of AY 17, Fe^{2+} and $\text{S}_2\text{O}_8^{2-}$ were kept constant. From the results, it is proposed that high temperature has positive effect on the degradation of AY 17 due to the fact that per sulfate can also be thermally activated to produce sulfate radical [40]. It was also ascertained that the concentration of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions decreased degradation process. In absence of carbonate ion the percent degradation was 86%, while in the presence of 0.01, 0.1 and 0.5 mM carbonate concentration the % degradation decreased to 81, 74 and 69% respectively. Similarly, in the absence of bicarbonate ion degradation was 86%, but in presence of 0.01, 0.1 and 0.5 mM the percent degradation were slightly decreased to 81, 79 and 76% respectively. The decreased in percent degradation was due to the scavenging effect of sulphate and hydroxyl radical [41]. The effect of chloride and sulphate ion show slight negative effect on degradation.

3.5 Identification of degradation products and proposed degradation pathway

GC–MS analysis of AY 17 solutions which was treated with UV/ H_2O_2 / Fe^{2+} process has already been reported in our previous study [31]. It was also reported that during degradation, nine degradation intermediates product were formed through photo-Fenton process while after 25 min of reaction times the intermediates product was completely decomposed into inorganic ions.

Degradation mechanism of AY 17 by UV/ $\text{S}_2\text{O}_8^{2-}$ / Fe^{2+} process at pH 3 is showed in Fig. 6. During the degradation reaction, the spectrum was also recorded for monitoring intermediates products (Fig. 7). It was found that after 60 min, all the degradation products were converted into simple inorganic ions (Fig. 8). The structures of degradation intermediates were obtained from their degree of protonation, chemical formula and m/z value. From GC spectrum it was ascertained that the major degradation product, $\text{C}_6\text{H}_4\text{O}_2$ (DP2) with 100 percent relative abundance was obtained at retention time of 2.75 and 3.06 min (Fig. 8). The degradation product

Fig. 6 Proposed degradation pathway of AY 17 by UV/S₂O₈²⁻/Fe²⁺ process

(DP1) was monitored at retention time 1.65 with relative abundance 20%. Other degradation products (DP3, DP4, DP5, DP6, DP7 and DP8) were monitored at retention time (4.46/4.89) 4.56, 6.03, 7.46 8.82, 10.10/12.49 and 14.65 min have relative abundance round about in between 15 to 20%. The degradation products (DP8) have relative abundance less than 10%. The proposed degradation mechanism of AY 17 dye by (UV/S₂O₈²⁻/Fe²⁺) process is given in Fig. 6.

3.6 Degradation of dye by UV light-assist AOPs in model and natural water sample: comparison

The efficiency of AOPs for degradation were checked in tape and model (prepared in triply distilled) water sample. It was observed that the degradation is maximum in model water sample as compared to natural water sample (Table.3). The reason for such a low degradation was the presence of certain anions are present in aqueous medium such as CO₃²⁻ (0.252 mM), HCO₃⁻ (0.298 mM),

Fig. 7 GC spectra of AY 17 dye during $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ process for identification of intermediates

Cl^- (0.335 mM), and SO_4^{2-} (0.5 mM) as confirmed by Ion Chromatography (IC). These anions act as scavengers for hydroxyl radical [42]. The trend of degradation of natural water sample of AY 17 shows that the photo-Fenton like process is excellent method for the degradation of both model and natural water sample.

3.7 Effect of temperature

The rate of chemical reaction, product yield, and distribution critically depend upon the temperature of system. In the present work the effect of temperature on rate of reaction were determined by changing temperature from 298 to 318 K. It was observed that the degradation increased with temperature due to the fact that at higher temperature, oxidizing species (like $\cdot\text{OH}$ radical $\text{SO}_4^{\cdot-}$ radical) are generated in high quantity from oxidants (i.e. H_2O_2 / HSO_5^- or $\text{S}_2\text{O}_8^{2-}$) [20, 43]. The activation energy, entropy and enthalpy of the degradation can be determined using straight line Eq. (35)

$$\ln k = \ln A - E_a^* / RT \quad (34)$$

$$\ln k = \Delta S^* - \Delta H^* / RT \quad (35)$$

where, k , is the rate constant (*pseudo-first-order* reaction rate constant), T is temperature of solution in Kelvin (K), A is the Arrhenius constant, R is ideal gas constant

(0.0082 kJ/mol. K) and E_a is the activation energy. The thermodynamic parameter values are given in Table 4. Low activation energy value (9.545–17.60 kJ/mol) may show that the photo-assist AOPs were proceeds with low energy barrier.

4 Conclusions

From present work, it was concluded that among several photo assist AOPs, photo-Fenton like process is an efficient process for degradation of AY17 dye in natural water samples. The optimum pH for all processes was determined as about ~ 3 . The optimum concentration ratio of oxidants (H_2O_2 , HSO_5^- or $\text{S}_2\text{O}_8^{2-}$) and catalyst (Fe^{2+} , Fe^{3+}) for photo-Fenton, photo-Fenton-like, $\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ process were evaluated to be 11: 1, 111: 1, 15: 1, 14: 7, and 7: 3.5 respectively. A 100-rpm stirring speed was found to optimum. It was seen that degradation increased with increased in temperature. It was also observed that various anions such as CO_3^{2-} , HCO_3^- , Cl^- and SO_4^{2-} decreased the degradation efficiency. The overall decreased in degradation by anions were in order were found to be $\text{CO}_3^{2-} < \text{HCO}_3^- < \text{Cl}^- < \text{SO}_4^{2-}$. The degradation of AY 17 dye by photo-assist AOPs in this study followed *pseudo-first-order* kinetics. The efficiency of AOPs was

Fig. 8 GC Spectra of AY 17 dye after 60 min of $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ process

observed to be high in model (triply distilled water) sample than natural water sample. The photo Fenton process decompose AY 17 dye in less time as compared to

Table 3 Efficiency of various UV light assist AOPs for model and natural water sample

Sample	$\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$	$\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{3+}$	$\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$	$\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$
Percent degradation				
Model	88	93	86	84
Natural	43	60	65	63

Table 4 Kinetic parameters for degradation of AY 17 for various AOPs

Kinetic parameter	$\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$	$\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{3+}$	$\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$	$\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$
E_a^* kJ/mol	9.545	12.88	16.74	17.60
ΔS^* kJ/mol.K	0.0124	0.0183	0.0284	0.0314

other processes. The activation energies (KJ/mol) were also different, the increasing order of activation energy is (Fenton-like = 9.487) < (photo Fenton = 9.545) < (photo-Fenton-like = 12.88) < ($\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$ = 16.74) < ($\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ = 17.60). The entropy (KJ/mol.K) of applied process were in order (photo Fenton = 0.0124) < (photo-Fenton-like = 0.0183) < ($\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$ = 0.0283) < ($\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ = 0.0314). The order of % degradation of natural water was in order (photo Fenton) < (photo-Fenton-like) < ($\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$) < ($\text{UV}/\text{HSO}_5^-/\text{Fe}^{2+}$).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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