

Degradation mechanism of diazo dyes by photo-Fenton-like process: Influence of various reaction parameters on the degradation kinetics

L. G. Devi*, K. S. A. Raju, K. E. Rajashekhar, S. G. Kumar

Department of Post Graduate Studies in Chemistry, Central College Campus, Dr. B. R. Ambedkar Veedi, Bangalore University, Bangalore-560 001, India

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The degradation of diazo dyes Brilliant Yellow (BY) and Bismark Brown (BB) was investigated by the photo-Fenton-like process Fe^{2+} /ammonium persulphate (APS)/UV in acidic pH medium. The influence of various reaction parameters like pH, concentration of Fe^{2+} ions/APS, structure of the dye and effect of radical scavenger on the degradation kinetics is reported. The rate constant (k), catalytic efficiency (k_c) and process efficiency (Φ) are evaluated at different concentrations of Fe^{2+} ions. It was found out that the BB degrades at a faster rate than BY. The degradation process was followed by GC-MS technique. The results show that the initial step in the degradation of BB involves direct oxidation of azo chromophore, while in the case of BY the initial step is oxidation of azo group followed by the oxidation of ethylenic chromophore. Based on the obtained intermediates, probable degradation mechanism has been proposed. The results show that photo-Fenton-like process could be a useful and efficient technology for the mineralization of diazo dyes at lower concentrations of iron in acidic medium.

Key words: photo-Fenton-like process, ammonium persulphate, diazo dyes, GC-MS analysis.

INTRODUCTION

The textile industry produces large quantities of effluents that contain significant concentrations of organic matter. The coloured waste water is directly discharged into the rivers and other water ways. Traditional methods like adsorption on activated carbon, liquid-liquid extraction, ion-exchange, air or stream stripping, *etc.*, are ineffective on refractory and non-volatile pollutants and have another disadvantage as they simply transfer the pollutants from one phase to another. Hypochlorite oxidations and UV/ H_2O_2 or UV/ O_3 processes are found to be efficient methods for decolourisation, but they are not desirable due to the high cost of equipment and the secondary pollution arising from the residual chlorine, which further complicates the process. Photo-Fenton process is considered as a promising method for the treatment of wastewater containing dyes [1–5]. It is based on the reaction of Fe^{2+} ions and H_2O_2 under UV illumination for the generation of hydroxyl radicals *in situ*. Hydroxyl radicals are strongly potent oxidizing agent that can mineralize all organic contaminants to CO_2 and H_2O . However, the removal of sludge, containing iron ions, at the end of wastewater treatment is costly and requires large amount of chemicals and manpower [6]. Although H_2O_2 is extensively used as an oxidant in

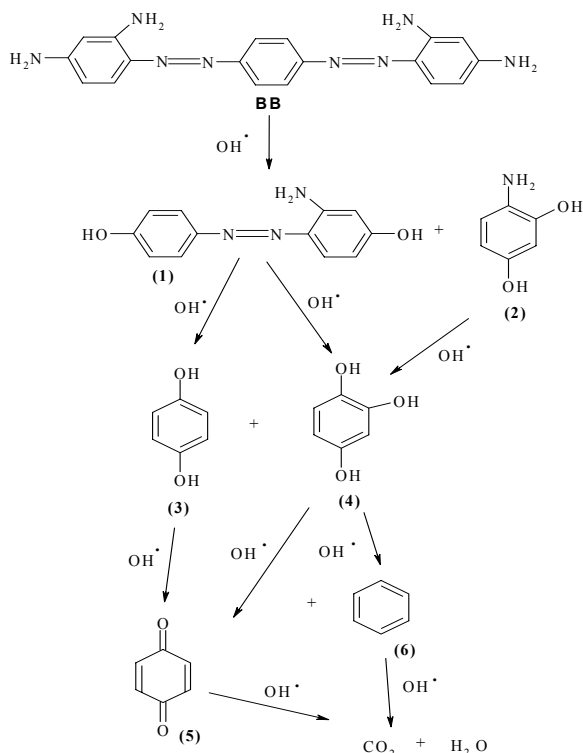
the classical photo-Fenton process, little attempt is made for the use of peroxy disulphate as oxidant. In view of this, the present research work highlights the utility of peroxy disulphate, which is termed as photo-Fenton-like process for the degradation of diazo dyes Brilliant Yellow (BY) and Bismark Brown (BB) at low iron concentration. Azo dyes are not biodegradable by aerobic treatment process [7]. Under anaerobic conditions, they can be decolorized by the reduction of azo bond [8] and the resulting fragment is aromatic amines, which are potentially carcinogenic [9]. Therefore, its mineralization by photo-Fenton-like process is simple, cost effective and important.

MATERIALS AND METHODS

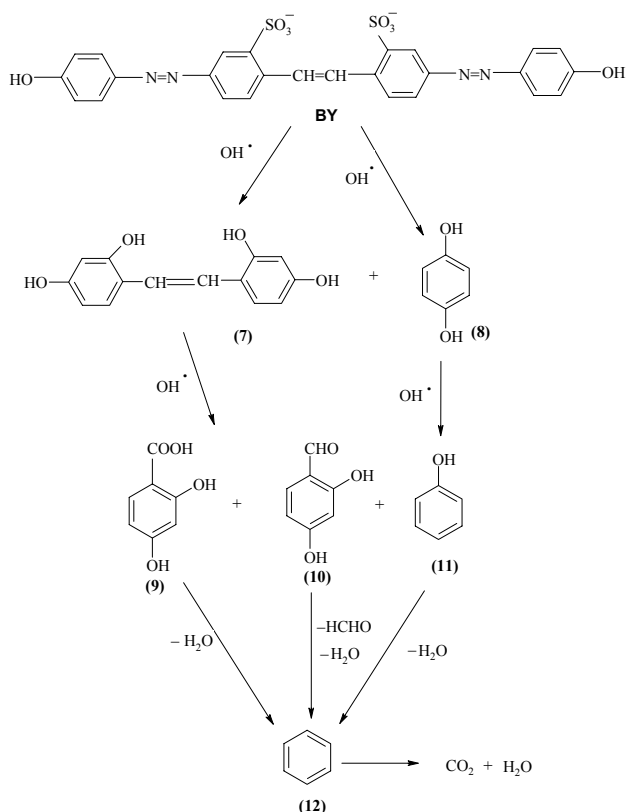
Materials

BY, BB, ammonium persulphate (APS), methyl alcohol, ferrous oxalate, sodium hydroxide and sulphuric acid were supplied from S D Fine Chemicals, Bombay, India and were used as received. The molecular formulae of BB and BY are $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{N}_8$ {4,4-(1,3-phenylene-bis(azo))bis-1,3-benzenediazamine dihydrochloride} and $\text{C}_{26}\text{H}_{18}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ {2,2¹-(1,2-ethenediyl)-bis[5-[(4-hydroxyphenyl)azo]-benzene sulphonic acid disodium salt} respectively. The structures of the dyes are given in the Schemes 1 and 2.

* To whom all correspondence should be sent:
E-mail: gomatidevi_naik@yahoo.co.in



Scheme 1. Probable degradation pathway for BB.



Scheme 2. Probable degradation pathway for BY.

Experimental setup

Artificial light source of 125 W medium pressure mercury vapour lamp with a photon flux of 7.75

mW/cm² (as determined by ferrioxalate actinometry) is used whose wavelength of emission is around 350–400 nm. In a typical experiment, 10 ppm dye solution is placed in a glass reactor whose surface area is 176 cm² and the required concentration of Fe²⁺ ions and APS are added. The light is directly focused on the solution at a distance of 29 cm in the presence of atmospheric oxygen as it is shown in Fig. 1.

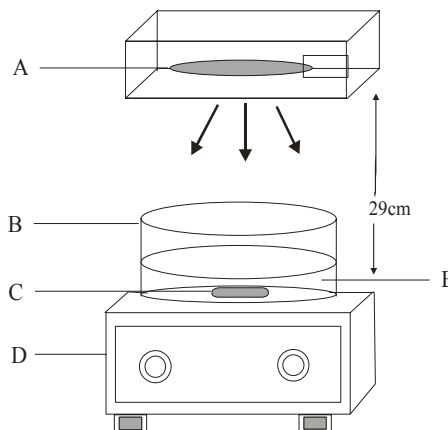


Fig. 1. Schematic illustration of experimental setup used for UV irradiation.

A - Medium pressure mercury vapour lamp; B - glass reactor; C - magnetic bit; D - magnetic stirrer; E - dye solution.

The pH value of the solution is adjusted either by adding dilute NaOH or H₂SO₄.

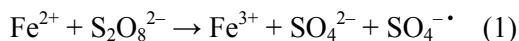
Analytical methods

Sample solutions (5 ml) were taken out of the reactor at definite time intervals and centrifuged. The centrifugates were analyzed by UV-visible spectroscopic technique using Shimadzu UV-1700 Pharmaspec UV-visible spectrophotometer. The centrifugates were extracted into non-aqueous medium and 1 μL was subjected to GC-MS analysis (using GC-MS-QP-5000 Shimadzu) and Thermo Electron Trace GC Ultra, coupled to a DSQ mass spectrometer, equipped with an Alltech ECONO-CAP-EC-5 capillary column (30 m, 0.25 mm i.d., 0.25 mm film thickness) was used. Pure helium was used as the carrier gas at a flow rate of 1.2 ml/min. The injector/transfer line/trap temperatures were kept at 220/250/200°C respectively. Electron impact ionization was carried out at 70 eV.

RESULTS AND DISCUSSION

Photo-Fenton reaction of Fe²⁺ with S₂O₈²⁻

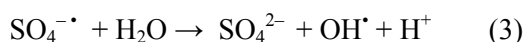
Ferrous ions react with persulphate anion resulting in the formation of sulphate anion and sulphate radical are oxidized to ferric ions [10].



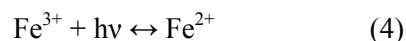
Ferric ion can also react with persulphate ion generating two sulphate radicals, being reduced to ferrous ion:



The sulphate radicals, produced in the above reactions, can react with water molecules to generate the highly oxidative hydroxyl radicals:



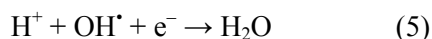
This cyclic process leads to a continuous generation of free radicals, which activates the degradation mechanism. To compare the efficiency of photo-Fenton-like process with the real Fenton process, the experiments were conducted in the dark. Only 12 and 4% of BB and BY respectively were degraded in the dark with Fe^{2+} ions as the catalyst and APS as an oxidant. The complete mineralization could be achieved in 60 and 90 minutes by photo-Fenton-like process under UV illumination for BB and BY respectively. This is due to the fact that Fe^{2+} ions can be oxidized to Fe^{3+} in the presence of APS even in the dark. But the reverse reduction process of Fe^{3+} ion is slow and rate determining step in the dark, which limits the efficiency of the process. Under UV light, the reverse photoreduction of Fe^{3+} ions takes place at a faster rate as it is shown in Equation (4) [5]. The photoreduced Fe^{2+} ions can participate actively in the cyclic Fenton reactions generating excess oxidative free radicals enhancing the degradation rate.



Direct photolysis of the oxidants additionally contributes to the overall enhancement of the process.

Effect of pH

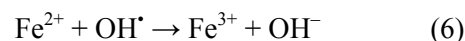
The pH of the solution plays a significant role for the effective mineralization of pollutants by the Fenton's reagent. Kang *et al.* reported that photo-Fenton process is efficient and can degrade pollutants effectively only under acidic conditions [11], since higher pH values are reported to be unsatisfactory [12]. The degradation of the dye was carried out in the pH range 1.0–9.0 by maintaining constant concentration of Fe^{2+} ions and APS. At lower pH 1.0, the degradation rate is reduced due to the presence of excess H^+ ions in the solution, which can act as hydroxyl radicals scavenger according to Eqn. (5) [13].



When the pH of the medium is increased from 1.0 to 3.0 complete mineralization of both dyes was achieved. This is due to the fact that at pH 3, half of the iron species exist as Fe^{3+} ions and the other half as complex ion $\text{Fe}[\text{OH}]^{2+}(\text{H}_2\text{O})_5$. Both are dominant photo active species that possess highest light absorption coefficient and give high yield of hydroxyl radicals along with Fe^{2+} ions in the wavelength range of 280–370 nm [14]. The change in this optimum pH leads to the decrease in the concentration of $\text{Fe}[\text{OH}]^{2+}$ complexes and it can also result in the precipitation of ferrous ion as oxy-hydroxides. The various photoactive species of iron, formed under different pH conditions, are $\text{Fe}[\text{H}_2\text{O}]_6^{3+}$ (pH 1–2), $\text{Fe}[\text{OH}][\text{H}_2\text{O}]_5^{2+}$ (pH 2–3) and $\text{Fe}[\text{OH}]_2[\text{H}_2\text{O}]_4^+$ (pH 3–4) [15]. Beyond this optimum pH (pH \approx 3), the degradation rate decreases. This inefficiency at higher pH values may be due to the instability of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, since they precipitate as iron oxy-hydroxide, which reduces the concentration of hydroxyl radicals in the solution thus affecting the degradation rate.

Effect of Fe^{2+} dosage

The influence of Fe^{2+} ion on the degradation kinetics is investigated by maintaining the other reaction parameters constant. When the concentration of Fe^{2+} ions is increased from 5 to 15 ppm, due to the excess generation of hydroxyl radicals the rate constant of the degradation increases for both dyes (Tables 1 and 2). With further increase in the concentration (30 ppm) the degradation rate decreases. This is because excess of Fe^{2+} ions, produced by the photo reduction of Fe^{3+} ions in the solution, compete for the hydroxyl radicals along with the dye molecules and act as hydroxyl radical scavenger [13].



The above process reduces the concentration of hydroxyl radicals in the solution and hence the degradation rate also decreases. Moreover, it is better to optimize the photo-Fenton's process at lower iron concentration in order to avoid the sludge production resulting from the iron complexes.

The efficiency of the catalyst is calculated by the term catalytic efficiency (k_c), which is a kinetic parameter, calculated using Eqn. (7):

$$k_c = \frac{k^1 - k_0}{[\text{Fe}^{2+}]^n} \quad (7)$$

Where k_c is the catalytic efficiency, k^1 is the rate constant of the reaction in the presence of catalyst, k_0 is the rate constant of the reaction in the absence

of catalyst, n is the order of the reaction ($n = 1$) and $[Fe^{2+}]$ is the concentration of the catalyst used.

Table 1. Rate constant, catalytic efficiency and process efficiency at different concentrations of Fe^{2+} ions for the degradation of BB.

$[Fe^{2+}]$, ppm	Rate constant (k) from $-\log(C/C_0)$ vs. time plot, $(\times 10^{-2}) \text{ min}^{-1}$	Catalytic efficiency (k_c), $\text{ppm}^{-1} \cdot \text{min}^{-1}$	Process efficiency (Φ), $(\times 10^{-12}) \text{ ppm Einstein}^{-1}$
5	1.1	1.05	16.5
10	1.7	1.67	24.3
15	0.96	0.94	17.4
20	0.7	0.68	13.3
30	0.52	0.51	9.8
0 (k_0)	0.26	-	

Table 2. Rate constant, catalytic efficiency and process efficiency at different concentrations of Fe^{2+} ions for the degradation of BY.

$[Fe^{2+}]$, ppm	Rate constant (k) from $-\log(C/C_0)$ vs. time plot, min^{-1}	Catalytic efficiency (k_c), $\text{ppm}^{-1} \cdot \text{min}^{-1}$	Process efficiency (Φ), $(\times 10^{-12}) \text{ ppm Einstein}^{-1}$
5	0.64	0.58	8.4
10	1.12	1.09	16.2
15	0.78	0.76	8.8
20	0.48	0.46	5.2
30	0.36	0.35	3.6
0 (k_0)	0.26	-	

The effectiveness of the process is calculated by process efficiency (Φ). Φ is defined as the change in concentration divided by the amount of energy in terms of intensity and exposure of surface area per unit of time.

$$\Phi = \frac{C_0 - C}{t \cdot I \cdot S} \quad (8)$$

C_0 is the initial concentration of the dye and C is the concentration at moment t and $(C_0 - C)$ denotes the concentration of the dye degraded in ppm. I is the irradiation intensity [$I = \text{Einstein}/\text{m}^2 \cdot \text{s} = 8.36 \times \lambda \text{ (nm)} \times \text{Power (Watt)}$] (where λ is 370 nm and Power is 125 W). S denotes the solution irradiated plane surface area in cm^2 and t represents the irradiation time interval in minutes. The values obtained for k , k_c and Φ suggests that the present experimental conditions, used for the degradation, are efficient at lower concentration of iron. The rate constant calculated for the degradation of BB under optimized conditions is 1.5 times higher than that of BY degradation. This is due to the presence of four

bulky aromatic rings and the ethylenic chromophore, which takes longer time interval for complete mineralization.

Effect of oxidizing agent

The present study investigates the application of peroxy disulphate ($S_2O_8^{2-}$), which is a symmetrical peroxide and it can be a potential oxidant in the light induced reaction processes. Persulphate can also generate free radicals like sulphate and hydroxyl radicals, which enable free radical mechanism similar to hydroxyl radical pathways generated in the classical Fenton's chemistry. Sulphate radical is one of the strongest oxidizing species in aqueous media with an oxidation potential of 2.6 V. It is inferior only to the hydroxyl free radical, whose oxidation potential is 2.8 V. When the concentration of APS was increased from 10 to 20 ppm, the degradation rate increased (Fig. 2).

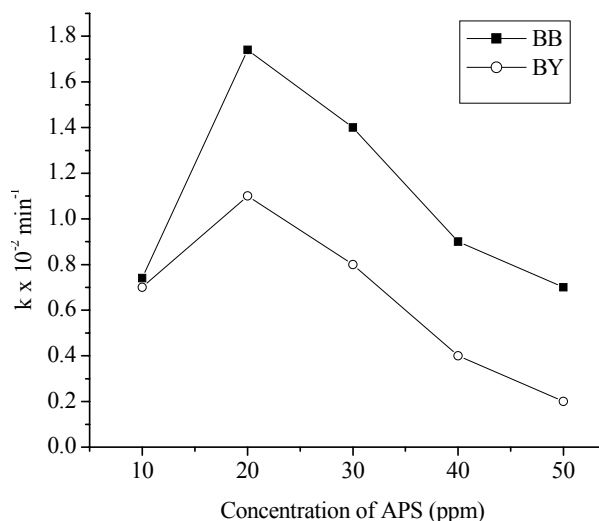
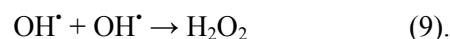


Fig. 2. Dependence of rate constant on concentration of APS (ppm) for both BB and BY.

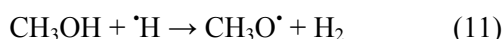
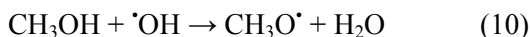
This is due to the generation of excess sulphate radicals, which in turn can produce higher number of hydroxyl radicals during reaction with water molecules (Eqn. (3)). Upon further increase in the concentration of APS the degradation rate decreases. The excess hydroxyl radicals generated might undergo recombination reaction or may take part in the unwanted reaction pathways:



Further APS generates protons, along with the hydroxyl radicals, as it is shown in the Eqn. (3). Since the reaction was carried out in acidic pH medium, the generated protons further lower the pH of the reaction medium, which exerts negative effect on the degradation rate (Eqn. 6). Hence, the rate constant decreases at higher concentration of APS.

Effect of hydroxyl radical scavenger

The role of hydroxyl radicals in the degradation mechanism of the photo-Fenton process is confirmed by carrying out the experiment in the presence of hydroxyl radical scavenger like methyl alcohol. Methyl alcohol is known to deactivate hydroxyl radical and its derivatives [10]. Methanol reacts with hydroxyl radical and to a smaller extent with hydrogen radical, whose second order rate constants are $9.7 \times 10^8 \text{ mol}^{-1} \cdot \text{sec}^{-1}$ and $2.6 \times 10^6 \text{ mol}^{-1} \cdot \text{sec}^{-1}$, respectively (Eqns. (10), (11)).



When the concentration of methyl alcohol is increased from 0.05 to 0.125 M, the rate constant decreases gradually and then it remains constant (Fig. 3). This is due to the inability of methyl alcohol to deactivate sulphate radicals. The sulphate radical produced in the case of APS shows the following possible reaction mechanisms in the process of mineralization: (i) Abstraction of hydrogen atom from the saturated carbon. (ii) The former is capable of adding to the unsaturated compounds. (iii) It can remove an electron from anions and neutral molecules [10, 16]. This provides evidence for the role of hydroxyl radical in the photo-degradation process.

GC-MS analysis

Degradation of BB. The BB solution containing Fe^{2+} ions and APS on UV irradiation for 15 minutes showed two m/z peaks at 229 and 125 corresponding to the formation of 2-amino-4,4¹-dihydroxyazobenzene (**1**) and 4-aminocatechol (**2**). This suggests that the degradation of BB proceeds through the cleavage of one azo group and the hydroxylation of a terminal amine group ($-\text{NH}_2$). The solution after 30 minutes of irradiation shows two m/z peaks of 110 and 142 due to the formation of hydroquinone (**3**) and 1,2,4-benzenetriol (**4**). The attack of hydroxyl radical on the site of C–N bond and substitution of $-\text{NH}_2$ by $-\text{OH}$ group in the intermediate (**1**) leads to the formation of (**3**) and (**4**). The intermediate (**2**) can also result in (**4**) upon the replacement of $-\text{NH}_2$ group by $-\text{OH}$. After 45 minutes of illumination, the mass spectra showed m/z peaks at 108 and 78 of high intensity due to the formation of *p*-benzoquinone (**5**) and benzene (**6**). The subsequent dehydroxylation of intermediates (**3**) and (**4**) can result in the formation of benzene (**6**). The oxidation of intermediates (**3**) results in compound (**5**). The other peaks of lower intensity 101, 94, 74, 56 and 43 were not accounted. After 60

minutes, no characteristic m/z peak of any functional group appeared, which confirms the complete mineralization.

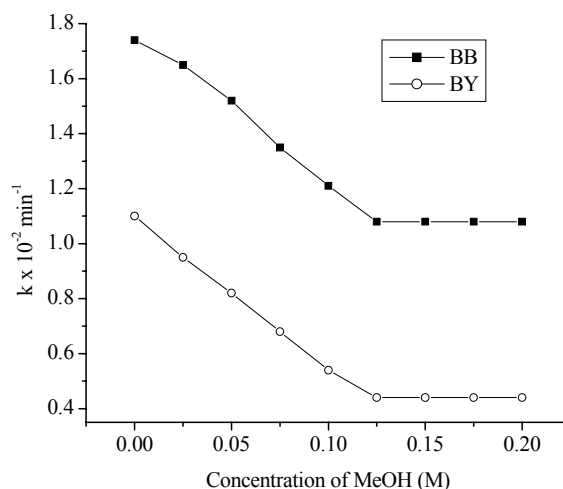


Fig. 3. Dependence of rate constant on concentration of MeOH (Molar) for both BB and BY.

Degradation of BY. The BY solution containing Fe^{2+} ions and APS on UV irradiation for 30 minutes showed m/z peaks at 244 and 110, corresponding to the formation of 2,4,2¹,4¹-tetrahydroxy stilbene (**7**) and hydroquinone (**8**). This indicates that the initial mechanism in the degradation of BY involves the cleavage of two azo groups since the C–N bond is more susceptible to free radicals attack, compared to the C–C bond. The sulphonate group moiety might be eliminated as sulphuric acid. After 60 minutes of irradiation, m/z peaks at 154, 138 and 94 appear which correspond to the formation of 2,4-dihydroxy benzoic acid (**9**), 2,4-dihydroxy bezaldehyde (**10**) and phenol (**11**). This suggests that the degradation at the later stages involves the oxidation of ethylenic chromophore to aldehyde and carboxylic acid respectively. The dehydroxylation of intermediate (**8**) results in compound (**11**). After 75 minutes of irradiation mass spectra showed intense m/z peak at 78 corresponding to the formation of benzene (**12**). The loss of substituent groups in the intermediates (**9**), (**10**) and (**11**) might result in the formation of benzene as it is shown in Scheme 2. At 90 minutes of UV irradiation, no characteristic peaks are observed in mass spectra confirming the complete mineralization of BY.

CONCLUSION

The degradation of two diazo dyes BB and BY was carried out using photo-Fenton-like process under acidic pH 3 and optimum conditions of the experiment. The rate constant, catalytic efficiency and process efficiency for both degradation processes have been calculated. The decrease in the

rate constant in the presence of methanol confirmed the role of hydroxyl radicals in the degradation mechanism. The degradation was followed by GC-MS technique. The results show that the initial step in the degradation of BB involves direct oxidation of azo chromophore, while in the case of BY, the oxidation of the azo group is followed by oxidation of ethylenic chromophore. A probable degradation mechanism has been proposed based on the obtained intermediates.

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МЕХАНИЗЪМ НА ФОТОХИМИЧНО РАЗЛАГАНЕ НА ДИАЗОБАГРИЛА ПО РЕАКЦИЯ НА ФЕНТЪН: ВЛИЯНИЕ НА РАЗЛИЧНИ РЕАКЦИОННИ ПАРАМЕТРИ ВЪРХУ КИНЕТИКАТА НА РАЗЛАГАНЕ

Л. Г. Деви, К. С. А. Раджу, К. Е. Раджашекар, С. Г. Кумар

Департамент по химия, Колеж Д-р Б. Р. Амбедкар Вееди, Университет на Бангалор, Бангалор 560001, Индия

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(Резюме)

Изследвано е фотохимично разлагане на диазобагрила Брилятно жълто (BY) и Бисмарково кафяво (BB) по реакцията на Фентън Fe^{2+} /амониев персулфат (APS) в кисела среда. Представено е влиянието на различни реакционни параметри като рН, концентрация на Fe^{2+} /APS, структура на багрилото и ефекта от улавяне на радикалите върху кинетиката на разлагане. Определени са скоростната константа (k), каталитичната ефективност (k_c) и ефективността на процеса (Φ) при различни концентрации на Fe^{2+} йони. Намерено е, че Бисмарково кафяво (BB) се разлага с по-голяма скорост от Брилятно жълто (BY). Процесът на разлагане е изследван с газова хроматография и маспектрален анализ. Резултатите показват, че началния стадий в разлагането на (BB) включва пряко окисление от азохромфора докато при BY началният стадий е окисление на азо-групата последвано от окисление на етиленовия хромофор. Предложен е вероятен механизъм на разлагане на основата на получените междинни прозукти. Резултатите показват, че фотохимичния процес по реакцията на Фентън може да бъде полезна и ефикасна технология за минерализация на диазобагрила при ниски концентрации на желязо в кисела среда.