

Enhanced sequestration of commercial Auramine O dye in a Fenton oxidative decolourization process

Khyati K Modi¹ & Kaushik Nath^{2*}

¹ Department of Environmental Engineering, Government Engineering College, Valsad 396 001, Gujarat, India

² Department of Chemical Engineering, G H Patel College of Engineering and Technology, Vallabh Vidyanagar 388 120, Gujarat, India

*E-mail: kaushiknath@gcet.ac.in

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The present work investigates the Fenton degradation of commercial Auramine O dye from a model solution through advanced oxidation process (AOP). The effects of initial pH, ferrous ion and H₂O₂ concentration have been evaluated with respect to the extent of decolourization of the feed solution. A maximum decolourization to the tune of 91.8% is accomplished at a pH of 3.0. The effect of various doses of Fe²⁺ and H₂O₂ on the percentage reduction in chemical oxygen demand (COD) is investigated at a constant pH. 84.9% reduction of COD is obtained using a combination of 48 mL/L H₂O₂ and 6 g/L Fe²⁺. The gas chromatography-mass spectrometry analysis reveals the presence of toxic non-biodegradable Auramine O dye in the model solution before the Fenton AOP, which is degraded into several compounds including CO₂ after 30 min of Fenton AOP. The spectral output from FTIR analysis corroborates the molecular rearrangement during Fenton process with consequent degradation.

Keywords: Auramine O dye sequestration, Fenton Advanced Oxidation Process, Chemical Oxygen Demand, Gas Chromatography-Mass Spectrography

Dyes are extensively used in a variety of industries including textiles, tannery, paint, pharmaceutical, cosmetics, pulp, and paper, as well as in chemical and radiochemical laboratories for analysis¹. Untreated (and sometimes even poorly-treated) effluent from these units generates a copious quantity of coloured wastewater with invariably high recalcitrant Chemical Oxygen Demand (COD) together with a high level of non-biodegradable toxic chemical compounds^{2,3} posing a major threat to groundwater and adjoining waterbodies. Auramine O (4,4'-carbonimidoyl-bis (N,N-dimethylaniline) hydrochloride) is classified as a cationic/basic dye, widely utilized to colour acrylic fibre, leather, silk, and wool. It is hazardous in nature with a potency to cause symptoms like short breathing, weakness, DNA damage, skin burns, cytotoxicity, oral toxicity, and genotoxicity⁴. Therefore, effective and affordable remediation of dye wastewater assumes paramount importance.

To mitigate the adverse effect of dye contamination in waterbodies a number of physico-chemical and biological treatment strategies are reported in literature. A majority of these reports focus on adsorption using different types of adsorbents, both natural or synthetic, electrochemical, photochemical,

and biological treatment⁵ used ZnS:Cu nanoparticle embedded activated carbon to remove Auramine O and Methylene blue from the aqueous solution. Close to 99.5% removal of both the dyes could be accomplished within a very short interval of time. Oxidized sugarcane bagasse and cellulose as absorbent was used for the removal of cationic dyes (Auramine O and crystal violet)^{6,7}. It is reported that metal-organic frameworks (MOFs) with the Ag₂O nanoparticles could remove about 89.45% Auramine O from the aqueous solution in an ultrasonic assisted adsorption process. Numerous other materials such as carboxylated cellulose⁸, oxidized sugarcane bagasse⁹, poly(acrylic acid)-halloysite nanoclay hydrogel¹⁰, have been reported for the treatment of Auramine O dye contaminated wastewater. A few attempts have been made with electrochemical methods using photocatalysts such as Zn:ZnO/Ni₂P¹¹, graphene oxide¹², and electrodes like carbon felt air-diffusion and Ti/PbO₂ electrodes¹³, lead oxide and boron-doped diamond anodes¹⁴. However, most of these methods have met with limited success with low benefit cost ratio. Even though classical technology of adsorption ensures considerable removal of dyes, it fails to warrant its degradation or sequestration. It is limited

to a mere transference of compounds from the solution to another phase. Furthermore, regeneration and reuse of adsorbents followed by desorption process could be susceptible to secondary pollution. Even the common biological techniques are not full-proof methods to treat wastewater as toxic organic substances seldom experience complete degradation.

Compared to several aforementioned traditional methods, advanced oxidation processes (AOPs) are distinctly unique in terms of delivering high efficiency and less secondary pollution¹⁵. In AOPs, the non-biodegradable toxic chemical compounds are degraded with the in situ generation of hydroxyl radicals (OH•), which have non-selectivity and high reactivity^{16,17}. Fenton AOP is one of the most promising treatment processes for the management of wastewater due to its high oxidation potential and operational ease¹⁸⁻²⁰. In Fenton AOP, the decomposition of the hydrogen peroxide (H₂O₂) into the highly reactive hydroxyl radical (OH•) is caused by ferrous ion (Fe²⁺) under the acidic environment²¹. The complete degradation of the toxic non-biodegradable chemical compounds present in wastewater using Fenton AOP requires a longer reaction time and is quite expensive because of the consumption of H₂O₂ and Fe²⁺ (Ref. 22). Hence, the Fenton AOP has been suggested as the pre-treatment of wastewater by various researchers²³⁻²⁵ to convert

complex non-biodegradables into biodegradable intermediates. Thereafter, further treatment of wastewater could be accomplished by using biological oxidation methods, which are less expensive. Several researchers have reported the use of AOPs to treat the non-biodegradable toxic chemical compounds present in wastewater^{15,26,27}.

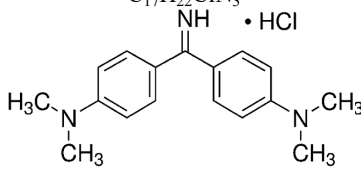
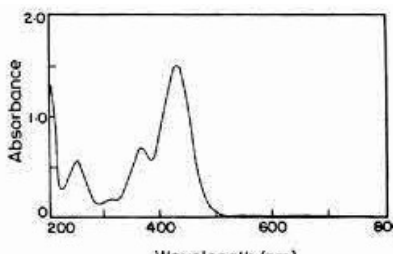
Despite the prolific bibliography reporting the Fenton AOP techniques in literature, remediation and sequestration of Auramine O dye in particular remains to be a less focussed area of research. Hence, the present study underscores the removal of Auramine O dye from a model wastewater using the Fenton AOP as a pre-treatment process. Thus, the rationale for taking up the present work is to broaden the present state of knowledge of Fenton as an AOP in wastewater remediation. It also attempts to shed some light on the theoretical and experimental insights pertaining to the plausible sequestration route of the Auramine O dye.

Experimental Section

Chemicals and reagents

Commercial grade Auramine O dye, used in the present study, was supplied by the M/s Ravi Raj Chemicals limited, Ankleshwar, Gujarat, India. The characteristics and chemical structure of the dye are presented in Table 1. The solutions of different

Table 1 — Characteristic of the dye used in the study

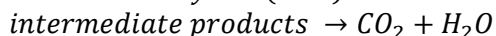
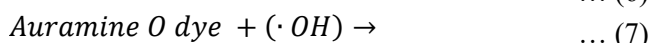
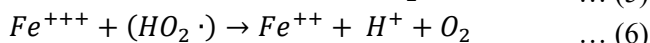
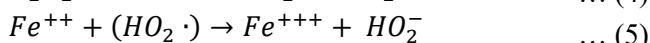
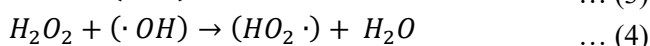
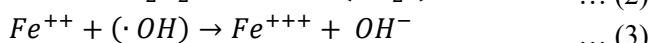
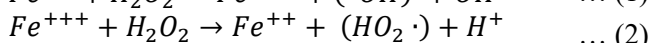
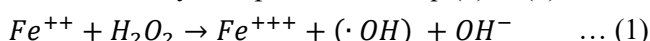
Characteristics	Details
IUPAC name	4 - [4 - (dimethylamino)benzenecarboximidoyl] - N, N - dimethylaniline; hydrochloride
Chemical Abstracts Service (CAS) number	2465-27-2
Molecular Formula	C ₁₇ H ₂₂ N ₃ • HCl
Molecular structure	
Molecular weight	303.37 g/mol
Type of dye	Azo dye, basic yellow (cationic)
Maximum absorption wavelength	485 nm in water
UV Absorption spectra	
Colour index number	41000
Physical description	Yellow flakes or powder
Chemical nature	Highly persistent

concentration of Auramine O dye were prepared by dissolving accurately weighed dye in de-ionized water. All other chemicals used in this experiment were of analytical reagent grade, supplied by Merck, India, and were used without further purification.

Experimental procedure

The synthetic wastewater (500 ppm) was prepared by dissolving 0.5 g of Auramine O dye into one litre of deionized water. This particular choice was made because it was the optimum concentration at which the reactor could maximally degrade the dye with regard to the operating conditions applied. The speed of the mixing was selected at 200 rpm. Every sample was allowed to settle for about 5 min before filtration. The samples were filtered using a Whatman filter paper to remove coagulated substances. The range of wavelength of the synthetic solution of Auramine O dye was measured using a single beam UV-visible spectrophotometer. The wavelength of maximum absorption (λ_{max}) of Auramine O dye was 485 nm. The Fenton AOP, as a pre-treatment, was selected for the experimental analysis of the model solution of Auramine O dye. The Fenton reaction was carried out in a 1 L beaker by mixing different doses of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 30% w/v H_2O_2 , as reagents, with the model solution.

Chemical reactions that might have occurred in the Fenton AOP to degrade the synthetic solution of Auramine O dye are presented in Eq. (1) to (6)^{28,29},



Methods of analysis

The observations for the experimental analysis were noted at an interval of 30 min for the selected duration of time. Chemical oxygen demand (COD), a measure of oxygen consumed during the oxidation of the organic matter by a strong oxidizing agent was measured by open reflux method before and after treatment according to the standard methodologies (APHA. American Public Health Association 2005). The pH of the synthetic solution was measured using a pH meter (Systronics, India). pH sensors used for

the analyses allowed automatic and continuous correction of the values by taking into account the sample temperature. Freshly prepared 0.5 M NaOH and H_2SO_4 solutions were used for pH adjustment during pH study.

GC-MS analysis

The gas chromatography-mass spectrometry (GC-MS) analysis of the synthetic solution of Auramine O dye before Fenton AOP and post treatment products was carried out in a GC-MS, Model : 7890B (Agilent, USA). The oven, injector and detector temperatures were 260, 260 and 300°C, respectively. Helium was used as the carrier gas with a flow rate of 1.0 mL/min. Run time was 62.5 min.

FTIR analysis

Fourier transform infrared spectroscopy (FTIR, Make: Shimadzu) was conducted to ascertain the presence of various functional groups in Auramine O dye before and after treatment. The spectral outputs were recorded in the transmittance mode at the mid-infrared region of 4000–400 cm^{-1} as a function of wavenumber at a resolution of 4.0 cm^{-1} with an acquisition time of 1 min. The samples were kept under constant nitrogen flow at a rate of 10 mL min^{-1} to eliminate undesired absorbance by surrounding moisture and carbon dioxide. At least 2 replicates were obtained for every sample type without applying any baseline corrections.

Result and Discussion

Effects of several parameters such as solution pH, concentration of Fe^{2+} ions, concentration of hydrogen peroxide on the colour removal efficiency of dye solution are discussed in the following sections.

Effect of pH

pH plays a pivotal role in the Fenton oxidation of Auramine O dye, as it has a direct bearing on the concentrations of Fe^{2+} and H_2O_2 which in turn affect the yield of the active OH radical for the oxidation. The batch oxidation process was continued for 2 h and the decolourization efficiency of the dye was examined using five different pH values ranging from 2.0 to 4.0. pH was maintained constant during the process. The decolourization efficiency was observed to be maximum at 30 min for all the pH, and no significant increment in decolourization efficiency was observed thereafter up to 120 min. The maximum decolourization efficiency of 91.80% was obtained at a pH of 3.0 after 30 min compared to other values of

pH of the synthetic solution. For the chemical reaction mentioned in Eq. (1), to generate the maximum amount of hydroxyl radicals for the oxidization of the organic compound, the pH of the solution should be adjusted in the acidic range. The pH of the model dye solution should not be lower than 2.0, otherwise it could slow down the Fenton reaction due to the formation of oxonium ion and complex iron species³⁰. On the other hand, the pH of the solution should not exceed 4.0, because the formation of ferric-hydroxo complexes retards the generation of hydroxyl radicals³¹. In addition, excess H^+ ions may lead to scavenging of OH radicals as evidenced by the lower decolorization efficiency of model dye solution at pH of 2.5. Thus, the influence of various concentrations of Fe^{2+} and H_2O_2 on the percentage reduction in COD was analyzed at pH of 3.0 of synthetic solution of Auramine O dye.

Effect of concentration of Fe^{2+}

Another parameter we considered important to explore was the effect of the Fe^{2+} concentration. The influence of various Fe^{2+} doses (6, 12, 18, 24, 30 g/L) at a fixed concentration of H_2O_2 (36 mL/L) were studied on the percentage reduction in COD. The observations were noted at the time interval of 30 min (up to 120 min), and results are presented in Fig. 1. The percentage reduction in COD was observed to be maximum at 30 min at various doses of Fe^{2+} , and no significant percentage reduction in COD was observed up to 120 min. The results showed that with the increase in doses of Fe^{2+} with a constant concentration of H_2O_2 (36 mL/L), the percentage reduction in COD was minimized. Plausibly increased concentration in Fe^{2+} leads to the increase in the

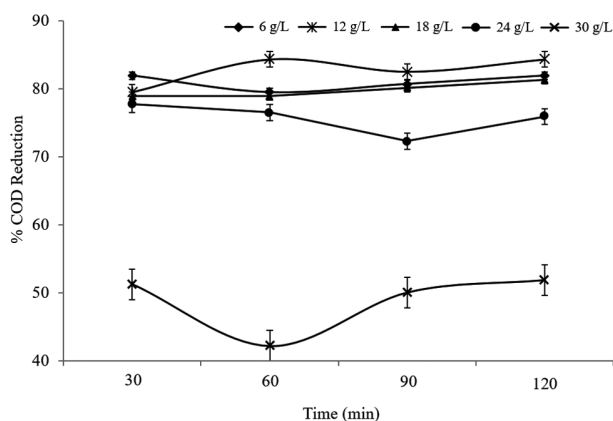


Fig. 1 — Effect of various dosages of Fe^{2+} on the percent reduction of COD of the model Auramine O dye wastewater in the present experiment (concentration of H_2O_2 : 36 mL/L)

generation of Fe^{3+} , which reacts with the H_2O_2 and forms $H_2O\bullet$. The reaction capacity of $H_2O\bullet$ is lower than the $OH\bullet$. The results obtained in the present work are consistent with several other findings reported in the literature^{32,33}. The literature indicates that a reduction in the ratio of (H_2O_2/Fe^{2+}) decreases the percentage reduction in COD³³. As the percent reduction in COD was maximum at Fe^{2+} dose of 6 g/L, the influence of variation in concentration of H_2O_2 was studied at Fe^{2+} dose of 6 g/L. It is intriguing to note that ferrous ion initiates and catalyses the decomposition of H_2O_2 resulting in the generation of hydroxyl radicals. These radicals attack organic compounds, producing organic radicals that can be further transformed through different pathways, among which ferric to ferrous ion reduction is an example. Furthermore, hydroxyl radicals may be partially scavenged by the oxidation of ferrous to ferric ion.

Effect of concentration of H_2O_2

The influence of various concentrations (dosage) of H_2O_2 (24, 30, 36, 42, 48, 54, 60 mL/L) was studied on the percentage reduction in COD by keeping the concentration of Fe^{2+} constant (6 g/L). The observations were noted at the time interval of 30 min (up to 120 min), and results are presented in Fig. 2. The results for the dosage of H_2O_2 of 24 and 30 mL/L have not been presented as the percentage reduction in COD was less than 60%. The percentage reduction in COD was observed to be maximum at 30 min at various doses of H_2O_2 , and no significant percentage reduction in COD was observed up to 120 min. The results showed that with the increase in doses of H_2O_2 (from 36 mL/L) at a constant concentration of Fe^{2+} (6 g/L), the percentage reduction in COD increased, and achieved a maximum at H_2O_2 doses of

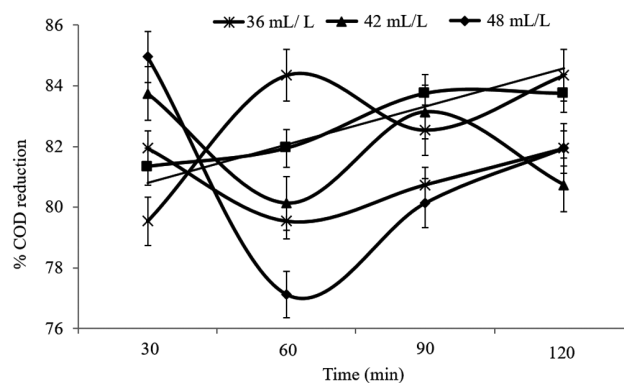


Fig. 2 — Effect of various dosages of H_2O_2 on the percent reduction of COD of the model Auramine O dye wastewater in the present experiment (concentration of Fe^{2+} : 6 g/L)

48 mL/L. The further increase in doses of H_2O_2 (54 & 60 mL/L) reduces the percentage reduction in COD. This was due to the fact that with the increase in the concentration of H_2O_2 the generation of $\text{OH}\cdot$, also increased thereby promoting the percentage reduction in COD²⁶. The further increase in the concentration of H_2O_2 may cause the reaction between $\text{OH}\cdot$ and H_2O_2 that inhibits the oxidation reaction between $\text{OH}\cdot$ and organic substances³⁴. Due to undesirable $\text{OH}\cdot$ scavenging reaction, reduction in COD was observed³⁵. These trends are in line with the earlier findings reported in the literature^{32,36}. The low doses of H_2O_2 (less than 36 mL/L) result in less generation of $\text{OH}\cdot$ in the reaction of H_2O_2 with Fe^{2+} , which is insufficient for the degradation of organic substances. The experimental analysis indicates that for the maximum percentage reduction in COD, the optimum dose of H_2O_2 and Fe^{2+} are 48 mL/L and 6 g/L, respectively.

Further, the authors conducted the experimental analysis of the synthetic solution of Auramine O dye with the various combination of doses of H_2O_2 and Fe^{2+} such as (36 mL/L and 2 g/L; 30 mL/L and 2 g/L; 36 mL/L and 4 g/L; 30 mL/L and 4 g/L; 30 mL/L and 12 g/L; 24 mL/L and 12 g/L), but none of the combinations could achieve a percentage reduction in COD as achieved in the optimum doses.

In order to identify the optimum time for percentage reduction in COD analysis was carried out using a fixed dose of Fe^{2+} and H_2O_2 of 6 g/L and 36 mL/L, respectively. The percent reduction in COD at 5 min interval for the fixed doses of Fe^{2+} and H_2O_2 of 6 g/L and 36 mL/L, respectively, is presented in Fig. 3. The results indicate that percentage reduction in COD increases with increase in time and achieved a maximum value at 30 min thereafter no significant increase is observed with time. Based on our

experimental studies, Fenton AOP could be aptly considered as an important pre-treatment strategy for the synthetic solution of Auramine O dye with doses of Fe^{2+} and H_2O_2 of 6 g/L and 36 mL/L, respectively, for a run time of 30 min.

GC-MS analysis

The process of dye degradation and sequestration gives rise to various degraded compounds which need systematic identification for better understanding. To that end, the GC-MS analysis was made use of in the present study. Since in the present experimental work, commercial Auramine O dye was used. Fig. 4 represents the GC-MS analysis graph of Auramine O dye (with the spectrographic fragmentation peaks at 267.2 m/z) present in synthetic solution before Fenton AOP. The peak eluting at a time other than 267.2 m/z plausibly indicates the presence of impurities in the commercial Auramine O dye. Fig. 5 represents the GC-MS analysis graph of treated synthetic solution after the Fenton AOP of 30 min. GC-MS

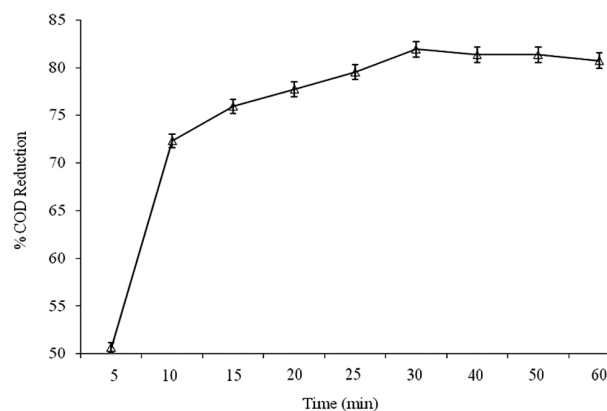


Fig. 3 — Percent reduction in COD as a function of time with fixed doses of Fe^{2+} (6 g/L) and H_2O_2 (36 mL/L)

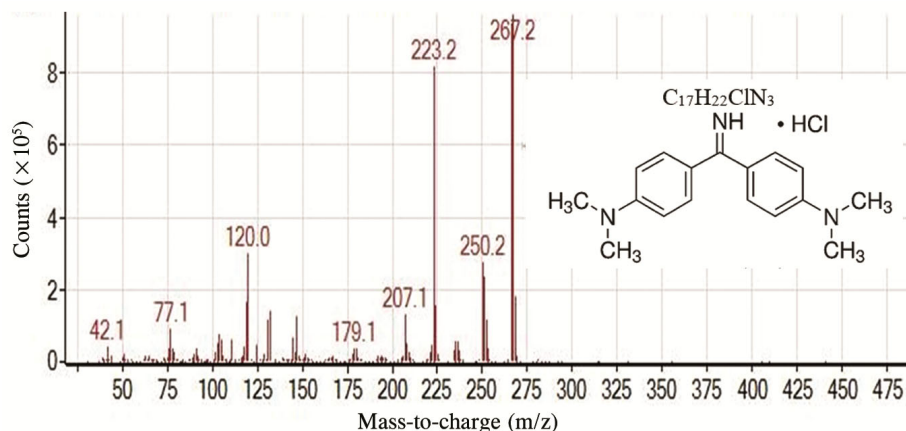


Fig. 4 — GC-MS analysis of synthetic solution before Fenton AOP treatment indicates the presence of Auramine O dye

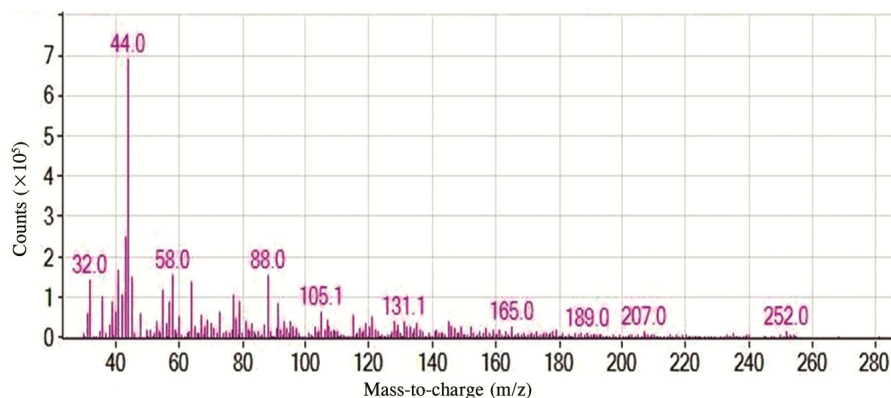


Fig. 5 — GC-MS analysis of treated synthetic solution after Fenton AOP treatment of 30 min

chromatogram of the treated dye solution indicates the decrement of parent peak with subsequent emergence of various new peaks thereby implying break-down products of the degradation process. The GC-MS analysis of the treated synthetic solution shows that the Auramine O dye is degraded into CO₂ (with spectrographic fragmentation peaks at 44.0 m/z). Since the commercial Auramine O dye was used in the present study, other degraded impurities were also observed in the GC-MS analysis apart from the CO₂. The proposed pathway for the degradation of Auramine O dye was also studied in this work. In the proposed degradation process, reaction begins among the Auramine O and the hydroxylation that produces the Michler's ketone. Further, (OH•) radical attacks on the bond C = O of the Michler's ketone to form 4-dimethylaminobenzoic acid, which is quickly oxidized to 4-hydroxybenzoic acid, that is changed to Hydroquinone. Hydroxyl radicals further attack on the Hydroquinone and form the Maleic acid. The oxidation of Maleic acid produces Oxalic acid, which is directly converted into CO₂. Although these degradation intermediates, observed at various m/z were not present in the starting mixture, these were produced during the Auramine O degradation. Besides this, some smaller species (e.g., m/z 165, 131 and 105) were also observed. These masses were attributed to other intermediates that might have co-eluted with the main intermediate. Nonetheless, due to low resolution of the chromatogram obtained in the present study, further investigation is needed on the exact structure of these moieties. Despite wide acceptability of GC-MS as a powerful analytical tool, it has limited success in recognizing isomers except for the cases where highly precision standards are available. For example, the accurate position of an

OH on an aryl group may not be ascertained by GC-MS alone. So many such structures are based on predictive speculation. The use of 1D and 2D NMR techniques, which were outside the scope of the present investigation, could have provided more insights on the same.

FTIR analysis

A closer perusal of FTIR spectra provides better insight of the functional groups present the dye sample before and after treatment. These are presented in Fig. 6. FTIR spectra of the untreated Auramine O dye indicates a very broad and intense band at 3412.41 cm⁻¹ as a result of N-H stretching vibration of imines (=N-H), the intensity of which is reduced 3317.98 in the post treatment products. The peaks at 1631.87 and 1636.17 cm⁻¹ are due to N = N stretching vibration in azo compounds. The band at 991.08 cm⁻¹ is attributed to the C-H bending in the alkyl monosubstituted vinyl groups, while the one at 701.61 cm⁻¹ is due to C-H bending in aromatic substitution type due to five adjacent hydrogen atoms. Frequently the peak at shorter wavelength (higher wavenumber) is not readily observed, because it may be obscured by strong absorptions owing to C-H stretching vibrations in other parts of the molecule. A few minor absorptions detected near 2361.01 and 2342.92 cm⁻¹ were probably due to water molecules as a result of inadequate drying of the test sample. These absorptions might have obscured some of the expected bands leading to erroneous assignments of few bands. In summary, the partial weakening, disappearing, and shifting of the characteristic absorption bands may result from the interaction dye molecule and Fenton during the process of oxidation. These results spectral analysis suggest degradation of

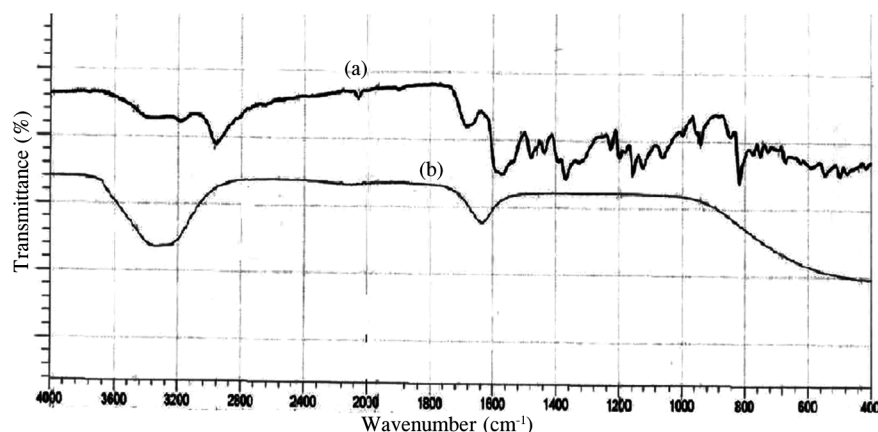


Fig. 6 — FTIR spectra of Auramine O dye (a) before and (b) after Fenton oxidation

Table 2 — Economic analysis for the treatment of 1 L synthetic solution of Auramine O dye using Fenton AOP with variable doses of Fe^{2+} (Fixed dose of $\text{H}_2\text{O}_2 = 36 \text{ mL/L}$)

Sr. No.	Doses of Fe^{2+} (g/L)	Cost of Fe^{2+} Dose (\$/L)	Cost of DM water (\$/L)	Cost of H_2O_2 dose (\$/L)	Cost of H_2SO_4 for pH adjustment (\$/L)	Total cost (\$/L)
1	6	0.047	0.257	0.395	0.013	0.712
2	12	0.094			0.020	0.766
3	18	0.141			0.020	0.814
4	24	0.189			0.020	0.866
5	30	0.236			0.020	0.914

Table 3 — Economic analysis for the treatment of 1 L synthetic solution of Auramine O dye using Fenton AOP for variable doses of H_2O_2 (Fixed Dose of $\text{Fe}^{2+} = 6 \text{ g/L}$)

Sr. No.	Doses of H_2O_2 ($\text{mL}^{-1} \text{ L}$)	Cost of H_2O_2 Dose (\$/L)	Cost of DM water (\$/L)	Cost of Fe^{2+} dose (\$/L)	Cost of H_2SO_4 for pH adjustment (\$/L)	Total cost (\$/L)
1	36	0.394	0.257	0.047	0.013	0.712
2	42	0.460			0.020	0.786
3	48	0.526			0.025	0.856
4	54	0.591			0.025	0.915
5	60	0.657			0.038	1.00

dye has taken place to a considerable extent. However, additional experiments in this direction need to be carried out to obtain further interpretation of infrared spectra.

Economic considerations

Table 2 presents the basic cost analysis for the treatment of 1 L synthetic solution of Auramine O dye using Fenton AOP for the various doses of Fe^{2+} and 36 mL/L fixed dose of H_2O_2 , whereas Table 3 presents that for the various doses of H_2O_2 and 6 g/L fixed dose of Fe^{2+} . The economic analysis shows that cost of \$0.86 was required for the treatment of 1 L synthetic solution of Auramine O dye to achieve the maximum of 84.95% reduction in COD using the Fenton AOP at the doses of 6 g/L of Fe^{2+} and 48 mL/L of H_2O_2 . From the economic analysis, it is evident that at a fixed dose of Fe^{2+} of 6 g/L, a 3.01% higher percentage reduction in COD was obtained for the dose

of H_2O_2 of 48 mL/L than the 36 mL/L. However, to achieve the 3.01% higher percentage reduction in COD, 12 mL/L additional amount of H_2O_2 is required, which leads to an additional economic burden on the industry. For example, if the industry produces 100,000 L/day of Auramine O dye wastewater, the additional cost of 1440/- \$/d is required compared to the dose of H_2O_2 of 36 mL/L. In one study³⁷ estimated the cost for the treatment of 1 m³ wastewater containing Sudan Black B was 1.86 \$/kg of dye removal. Identifying the optimum process conditions is of prime importance to treat dye wastewater whenever the cost criteria will be one of the major concerning factors. In the present study the process of Fenton AOP was found to be effective at doses of H_2O_2 and Fe^{2+} of 36 mL/L and 6 g/L, respectively. However, use of other methods either as stand alone or in combinations could further improve the process by reducing the COD to a considerable extent.

Conclusion

In the present work, Fenton oxidation process was attempted to convert the non-biodegradable compounds present in the synthetic solution of commercial Auramine O dye into biodegradable compounds. The maximum decolourization efficiency of 91.80% was obtained at a pH of 3.0. at a fixed dose of H₂O₂ of 36 mL/L, the optimum dose of Fe²⁺ of 6 g/L was observed. At a fixed dose of H₂O₂ of 36 mL/L, with the increase in doses of Fe²⁺ reduction in percentage reduction in COD was observed. At a fixed dose of Fe²⁺ of 6 g/L, with the increase in doses of H₂O₂ from 36 mL/L up to 48 mL/L, an increase in percentage reduction of COD was observed. The maximum percentage reduction in COD of 84.95% was obtained at the dose of Fe²⁺ of 6 g/L and H₂O₂ of 48 mL/L at 30 min. The GC-MS analysis shows the presence of Auramine O dye in synthetic solution before the Fenton AOP, which however got degraded into various break-down compounds along with carbon dioxide. A plausible pathway for the formation of the degradation products was also proposed. FTIR analysis of the post-treated dye sample resulted in partial weakening, disappearing, and shifting of a few salient absorption bands thereby corroborating molecular rearrangement during the process of oxidation. From an economical point of view, the authors have suggested the Fenton AOP as a pre-treatment process with the use of the doses of Fe²⁺ and H₂O₂ of 6 g/L and 36 mL/L, respectively, for 30 min, which resulted in a percentage reduction in COD of 81.94%. In essence, data obtained in the present study could be useful for possible scale-up of the Fenton-oxidation process for similar types of azo dyes.

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