

## A NOVEL APPROACH FOR OXIDATIVE DEGRADATION OF SOME ANIONIC AZO DYES BY ALKALINE HEXACYANOFERRATE (III) ION

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### ABSTRACT

The degradation of anionic azo dye via Hexacyanoferrate (III) ions (oxidant) in the aqueous alkaline medium has been investigated through kinetic-spectrophotometric technique. The efficiency of this treatment strongly depends on the chemical structure of dyes. The effect on the reaction of various parameters (concentration of dyes, oxidant, and pH solution) has been examined. The degradation of acid red 27, acid yellow 23, and azo violet dyes follow the first-order kinetic model concerning [HCF (III)] and [Dye]. The degradation rates of dyes follow the order: acid red 27 > acid yellow 23 > azo violet. The successive products of the dyes reveal that the dyes are effectively oxidized via HCF (III) in aqueous alkaline medium. Thermodynamic parameters of acid red 27 dyes at four different temperatures ranging between 40 to 55 °C reveal that the degradation rate of acid red 27 dye is much better from azo violet, acid yellow 23.

**KEY WORDS :** Kinetic-spectrophotometric method, Degradation, Hexacyanoferrate (III) ions, Anionic azo dyes, Chemical structure.

### INTRODUCTION

Industrialization is considered the key to development in economic terms. However, it is also recognized to be the root problem from an environmental perspective. It is recognition that environmental pollution is a worldwide threat to public health, and has given rise to new initiatives for ecological restoration for both economic and ecological reasons (Konstantinou and Albanis 2004). The industrial effluents contain a lot of toxic and hazardous pollutants in which one particular class of chemicals such as synthetic dyes and dye intermediates have existed, that is a matter of significant concern. Nowadays, in industries, the anionic azo dyes are widely used in textile, paper, plastic, leather, food, cosmetics, and pharmaceutical, etc. Most of the untreated or unused dyes are released into the environment without any treatment (Glenn *et al.* 1991). These untreated dyes mix into water bodies, and pollutes to the water bodies and give very harmful effects because it is used into the drinking and irrigation purpose. Nowadays, a lot of commercial dyes are available in

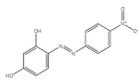
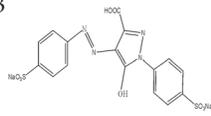
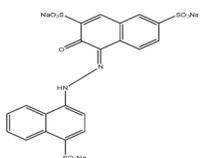
the market, but more than 50% of commercial dyes have belonged to the class of azo dyes. A lot of azo dyes are identified as persistent organic dyes in the environment in which many of them can develop very harmful diseases like cancer or tumor. One of the possible ways to decrease the environmental hazard caused by these dyes is to reduce its toxicity before discharging it into the environment (Saratale *et al.* 2011).

The azo dyes contain one or more azo group (-N=N-) as a chromophore, that are bonded with auxochromes, i.e., an aromatic moiety containing functional group like -OH, -Cl, -NO<sub>2</sub>, -COOH and -SO<sub>3</sub>H<sub>3</sub>. The color of azo dyes is prescribed through the azo bonds and their associated chromophores and auxochromes. The chromophore is a radical configuration that consists of the conjugated double bonds with delocalized electrons. The auxochrome is a functional group of atoms with non-bonded electrons attached to a chromophore alters, which have both the wavelength and intensity of absorption, and it can increase the color of any organic compound. (Konstantinou and Albanis 2004). In industries, the anionic azo dyes are widely

used. Still, conventional Industrial wastewater seasoning technologies have demonstrated to be uniquely insufficient for dealing with wastewater of mock textile dyes due to the chemical stagnation of these pollutants. Hence, it has been confirmed that of the 18 azo dyes measured 11 compounds elapsed via the activated slush procedure practically untreated, 4 (Acid Blue 113, Direct Violet 9, Acid Red 151, and Direct Violet 28) were sucked on the waste activated slush. Only 3 (Acid Orange 7, Acid Red 88, and Acid Orange 8) were biodegraded. (Glenn M. Shaul *et al.* 1991). The removal methods of dyes include physical adsorption (Jain *et al.*, 2007), coagulation (Mukhlis *et al.*, 2020), microbiological (Saratale *et al.*, 2011) or enzymatic decomposition (Singh *et al.*, 2015), biodegradation (Ishchi and Sibi 2020), ozonation (Tehrani-Bagha *et al.*, 2010), or the integrative treatments of different other techniques. Among them, the oxidative degradation of anionic azo dyes by hexacyanoferrate(III) ion has been paid much attention in recent years (Goel *et al.*, 2012; Goel and Lasyal, 2016). The conjugation of the azo group with some electron-donating or withdrawing groups plays an essential role in the oxidative mechanism (Suzuki *et al.*, 2001). It is also reported that different azo dyes with the same substituent show variable rate of degradation (Özen *et al.* 2004; Daneshvar *et al.* 2006; Zhang *et al.* 2007)

The present study on the anionic azo dyes reveals that chemical structure and substituent group shows a significant influence on the degradation pathway and the degradation kinetics of the azo dyes. So the main objective of this study is to investigate the effects of chemical structure on the oxidative degradation of azo dyes by hexacyanoferrate (III) ions in an aqueous alkaline medium. Acid red 27, acid yellow 23 and azo violet are selected as the model azo dyes with the substituent's groups such as nitrite, carboxylic, sulfonic, hydroxyl, and chemical structure of dyes are shown in Table 1. Anionic azo dyes such as acid red 27, acid yellow 23, and azo violet are widely used as commercial products in the textile and food industries. The present study sheds light on the degradation of organic dyes and reports the effect of the dyes chemical structure on the process efficiency. The work may provide new insight into the oxidative degradation of anionic azo dyes by hexacyanoferrate (III) ion. The recent technique seems to be superior to other traditional techniques because of its low expense, facile availability, and impact.

**Table 1.** Structure of dyes-

Dyes	Structure	Wavelength (nm)	Molecular weight
Azo violet		449	316.2
Acid yellow 23		425	543.3
Acid red 27		521	604.47

## Experimental section

**Materials:** Azo dyes such as azo violet, acid yellow 23, acid red 27 (Loba Chemie) were taken in the desired stoichiometric proportions and made the aqueous solution using the distilled water at room temperature. All used, chemicals and reagents were analytical grade. The calibration of the pH of the reaction mixture was satiate with a digital pH meter (Systronics pH system 361), that was adjusted through the potassium dihydrogen orthophosphate ( $\text{KH}_2\text{PO}_4$ ) and sodium hydroxide (NaOH) solutions as a buffer. The progress of the reaction was measured kinetic- spectrophotometric (Systronics - 117) with a spectrometric quartz cell (1cm in path length) at the  $\lambda_{\text{max}}$  of the reaction mixture. Deionized water was employed throughout the study. FTIR spectra were measured via Perkin Elmer-spectrum RX-IFTIR, LC-MS spectra were taken by LC-MS spectrometer model Waters Micromass Q-ToF Micro.

## Experimental procedure

The kinetic experiments were conducted at optimum pH and constant temperature ( $40 \pm 0.1$  °C) by the method, as reported previously (Goel and Chaudhary 2019). The requisite amount of each reactant was thermostated at 40 °C to attain thermal equilibrium. The appropriate quantities of reactants were mixed in a 250 ml stoppered iodine flask. The reaction was initiated by injecting the solution of dye into the aforementioned reaction mixture. Samples were withdrawn from the reaction mixture at preset time intervals using a pipette and were analyzed by noting absorbance of reaction mixture at  $\lambda_{\text{max}}$  of reaction mixture spectrophotometrically. It was confirmed experimentally that  $\lambda_{\text{max}}$  for the reaction

mixture in case of azo violet, acid yellow 23, acid red 27 was 449,425, and 521 nm respectively, and there was no shift in  $\epsilon_{\max}$  during the entire period of kinetic study. It was verified that there is a negligible interference from other species present in the reaction mixture at these wavelengths. Further the kinetic study was kept limited only to the period in which  $\epsilon_{\max}$  of the reaction mixture did not change and no precipitation took place during the study of any kinetic run. As the reaction proceeds, the absorbance of the reaction amalgam reduces with time revealing a linear relationship amid dye concentration and absorbance. The preparative rate recipe was employed to decide the kinetic behavior of the reaction. Preparative rates  $(da/dt)_i$  were estimated after 5 minutes from the beginning of the reaction through employing the plane mirror prescript from the plot of absorbance (a) vs. time (t) (Goel *et al.* 2012). The optimal fitting curve was acquired through the prescript of least square. The first-order rate constant was estimated through the plot of  $\log(a-x)$  vs. time with slope identical to  $-k_1/2.303$ . The degradation products were extracting through ethyl acetate using the solvent education method and identified via the LCMS technique. Mobile phase for the extracted products of azo violet consisted of n-Butylalcohol: acetonitrile: water (3:2:1), acid yellow 23 (ethyl acetate: acetic acid: water (3:1:2)), acid red 27 (acetonitrile: water (1:1)) respectively.

## RESULTS AND DISCUSSION

### Effect of pH

Variation of pH is one of the crucial parameters that affect the degradation of azo dyes such as azo violet, acid yellow 23, acid red 27. It was foreseen that the change in the pH of the solution influences the catalytic degradation processes. (Goel *et al.* 2012) In the present work to study the effect of pH, the pH of the reaction mixture was varied by using potassium di hydrogen orthophosphate and sodium hydroxide (0.1M) as a buffer by maintaining the concentration of dye and HCF (III) ions at a constant temperature for the oxidation of these dyes. The influence of pH was examined by varying it from 7 – 12. The results shown in fig.1 indicate that the degradation efficiency affected considerably over a wide range of pH (7 – 12). Fig- 1 shows that the optimum pH for the degradation of azo violet, acid yellow 23, and acid red 27 are 9.5, 8.0, and 10.5, respectively. It was observed that the degradation of azo violet, acid

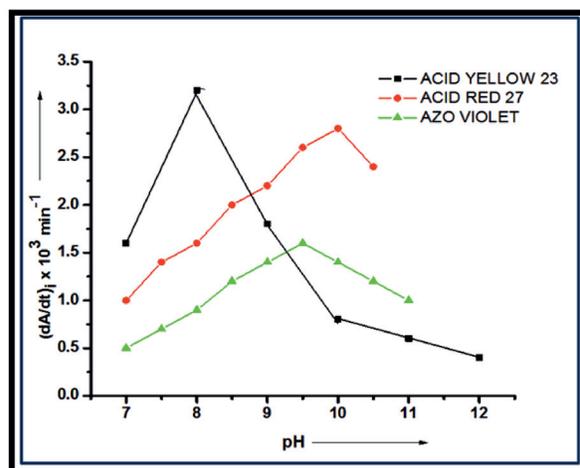


Fig. 1. Effect of pH on initial degradation rate of azo violet, acid yellow 23, acid red 27, by HCF (III) ions in aqueous alkaline medium. Experimental conditions [Dyes] =  $3 \times 10^{-5} \text{ mol dm}^{-3}$ ; [HCF (III)] =  $3 \times 10^{-6} \text{ mol dm}^{-3}$ ; temperature =  $40 \pm 0.1 \text{ }^\circ\text{C}$ .

yellow 23, acid red 27 does not occur in acidic pH range, i.e., below pH 7. It may be due to the electrostatic interaction between hydrogen ion and dye molecule (Goel *et al.*, 2014; Goel and Chaudhary, 2019).

### Effect of [HCF (III)]

To study the effect of HCF (III) ion concentrations on the rate of reaction, various kinetic runs were made for each substrate (azo violet, acid yellow 23, acid red 27) with different initial HCF(III) ion concentration covering a range of many folds, keeping the concentration of other reactants constant at constant temperature and optimum pH.

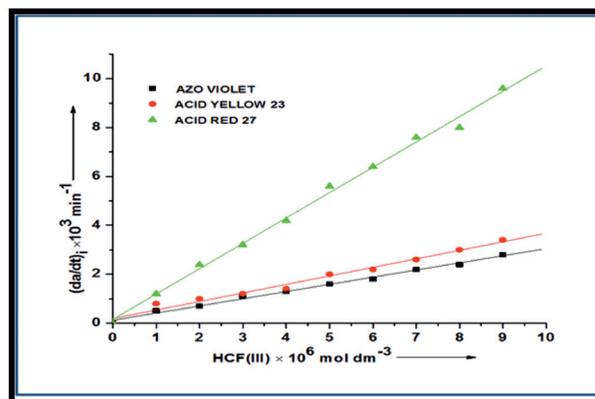


Fig. 2. Effect of [HCF(III)] on the initial degradation rate of azo violet, acid yellow 23, acid red 27 by HCF (III) ion in an aqueous alkaline medium. Experimental conditions [Dyes] =  $3 \times 10^{-5} \text{ mol dm}^{-3}$ ; pH = 9.5(azo violet), 8.0 (acid yellow 23) and 10.5 (acid red 27); temperature =  $40 \pm 0.1 \text{ }^\circ\text{C}$ .

The kinetic degradation results shown in fig. 2 represent that degradation of the above said three dyes follow first-order kinetics with respect to [HCF (III)]. The concentration of HCF (III) was varied from  $1 \times 10^{-6}$  to  $9 \times 10^{-6}$  mol dm<sup>-3</sup>.

### Effect of [Dyes]

To study the influence of dye concentration on the degradation rate of azo violet, acid yellow 23, acid red 27, the concentration of substrate was varied from  $1 \times 10^{-5}$  to  $9 \times 10^{-5}$  mol/dm<sup>-3</sup>, keeping the concentration of HCF (III), pH and temperature constant. The result presented in Fig.3 reveals that with the increase in dye concentration, the rate of the degradation of corresponding dye increases linearly, which follows the first-order kinetics model with respect to [Dyes]

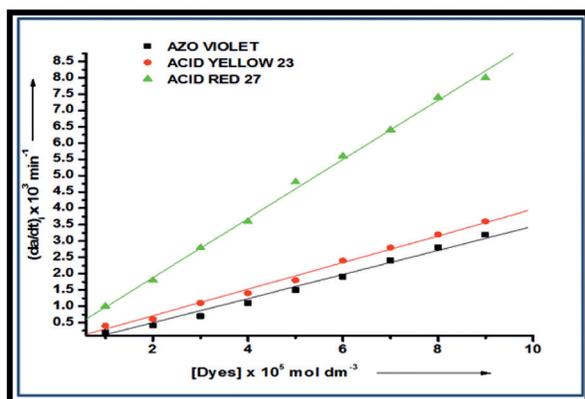


Fig. 3. Effect of [Dyes] on the initial degradation rate of azo violet, acid yellow 23, acid red 27 by HCF (III) ion in aqueous alkaline medium. Experimental conditions pH = 9.5(azo violet), 8.0 (acid yellow 23) and 10.5 (acid red 27); [HCF(III)] =  $3 \times 10^{-6}$  moldm<sup>-3</sup>; temperature =  $40 \pm 0.1$  °C.

### Thermodynamic parameters

An increase in temperature affects the rate of the chemical reaction. Generally, the specific rate of homogenous processes becomes double or triple for every 10 °C increase in temperature. So, the thermodynamic parameter for the oxidation of azo violet, acid yellow 23, and acid red 27 have been evaluated by studying the reaction at four different temperatures in the range of 40 to 55 °C. The degradation rate of these dyes follows the Arrhenius equation-

$$k = A \cdot e^{-E_a/RT} \quad \dots (1)$$

Where k is the rate constant, T is the absolute

temperature, A is Arrhenius factor,  $E_a$  is the activation energy, and R is the universal gas constant. Activation parameter,  $E_a$  and A were evaluated from straight-line Arrhenius plot between  $\log(da/dt)$  vs.  $1/T$ .

Further, the entropy of activation ( $\Delta S^\ddagger$ ) can be calculated by employing the equation-

$$k_r = (kT/h) e^{\Delta S^\ddagger/R} \cdot e^{-\Delta E_a/RT} \quad (2)$$

The free energy of activation ( $\Delta F^\ddagger$ ) might also be calculated by applying the thermodynamic relation-

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S \quad \dots (3)$$

The data of  $E_a$ ,  $\Delta H^\ddagger$  and A, presented in the table. 2 confirm the highest rate of oxidation of acid red 27 and a low rate of azo violet. The almost same value of  $\Delta F^\ddagger$  suggests the involvement of some type of mechanism of oxidation as reported earlier (Goel *et al.*, 2012; Goel and Lasyal, 2016).

### Comparison of degradation ability between azo violet, acid yellow 23 and acid red 27; Influence of the chemical structure of dyes

The data presented in the foregoing sections reveal that the oxidative process efficiency depends on different system parameters and chemical structure of azo dyes and the nature of the functional group attached to the dyes molecules. To find out the effect of the different substituent (i.e., nitrate, hydroxyl, carboxylic and sulphonic groups) on the degradation rate of anionic mono azo dyes as azo violet, acid yellow 23 and acid red 27 are some typical examples. These three dyes have different structures and substituent's (table. 1). The following discussion sheds light on the substituent's and structure degradability relation of the oxidative degradation of organic dyes and reports the effect of the dyes chemical structure on the rate of degradation.

**Influence of the number of sulfonic groups**  
Surprisingly, the presence of more powerful electron-withdrawing sulphonic groups on molecules makes it more sensitive to oxidative degradation. It decreases electron density in the aromatic rings and the beta nitrogen atom of the azo bonds by -I (inductive) and -R (resonance) effect. Indeed, molecules with or without one or two sulphonic functional groups have almost the same reactivity with respect to HCF (III). That's why acid yellow 23 and azo violet are less reactive in an oxidative degradation process in comparison with acid red 27 containing three sulfonic groups

(Guillard *et al.*, 2003; Anjaneyulu *et al.*, 2005; Lair *et al.*, 2008; Khataee and Kasiri, 2010).

**Influence of hydroxyl groups :** The presence of the more powerful electron-donating hydroxyl group on a molecule makes it only very slightly less sensitive to oxidative degradation. The electronic properties of hydroxyl groups are  $-I$ (inductive effect) and  $+R$ (resonance effects). Azo violet containing two hydroxyl groups is less reactive in an oxidative degradation process in comparison with acid yellow 23 and acid red 27 that contain one or no hydroxyl substituent (Galindo and Kalt, 1999; Chakrabarti and Dutta, 2004).

**Influence of carboxylic groups:** In order to evaluate the influence of carboxylic groups, the degradation of an analogous pair of dyes, i.e., Acid yellow 23 and azo violet, has been chosen here. Acid yellow 23 contains a carboxylic group in the beta position with respect to the azo bond, which destabilizes the structure of dyes. So that rate of acid yellow 23 slightly higher than that of azo violet (Lachheb *et al.* 2002; Pandey *et al.*, 2007; Khataee *et al.*, 2009; Khataee and Kasiri, 2010).

**Influence of nitrite groups:** To explore the effect of the presence of nitrite groups on oxidative degradation of anionic mono azo dyes, the pair of dyes, i.e., azo violet, acid yellow 23 and acid red 27 has been mentioned here (Table 1). Azo violet contains a nitrite group in the para position with respect to the azo bonds. This substituent interacts with the phenyl ring and there is a consequent delocalization of the pi-electron of the rings and of the unpaired electron of the heteroatom. As a result, the phenyl ring is electron enriched, and the nitrite group disfavors the breaking of the azo bond. This is because the degradation rate of azo violet is slightly lower than that of acid yellow 23 and acid red 27 (Bredereck and Schumacher, 1993; Sharma *et al.*, 2003; Qamar *et al.*, 2005; Khataee *et al.*, 2009; Raliya *et al.*, 2017).

**Influence of naphthalene rings:** It was suggested that the larger conjugation system of naphthalene rings of acid red 27 is favorable for the degradation,

compared with the structure of acid yellow 23, azo violet. The higher degradation rate of acid red 27 might be ascribed to its effective electron delocalization and presence of strong electron-withdrawing group (sulphonic groups)(Hou *et al.* 2007).

### Identification of degradation products

The degradation products of all dyes were separated through solvent extraction and chromatographic methods, and the analysis part of all dyes has been monitored via three techniques such as UV-vis spectroscopy, FT-IR, and LCMS.

### UV-vis spectroscopy

UV-vis spectroscopy has been used as a primary technique to determine the degradation of anionic azo dyes due to the oxidation process. The spectrums of all dyes were recorded in the range of 220 nm to 700 nm with the help of a UV-vis spectrophotometer. The spectro-photometrical analysis indicates the maximum absorbance wavelength ( $\lambda_{max}$ ) at 521 nm, 425 nm, and 449 nm, which are related to acid red 27, acid yellow 23, and azo violet dyes respectively. The dyes concentration in the reaction mixture at various time (0 to 60 minutes) were found through the measuring of the absorption intensity of reaction mixture which exists at 521 nm, 425 nm, and 450 nm. The absorbance vs. wavelength data demonstrated that the complete disappearance of peaks in the visible region indicates the successful degradation of anionic azo dyes, which are shown in fig. 4 (a,b,c). After the disappearance of peaks at 521 nm, 425 nm, and 450 nm, some new peaks appear, those shifted from 521 to 282 nm, 425 to 256 nm, and 449 to 352 nm. The Peak shifting from visible to ultra-violet region is the cause of the cleavage of the azo bond, due to which the degradation of the azo dyes into the new products, those are less harmful.

### Liquid chromatography-mass spectrometry

The end degraded oxidative products of anionic azo dyes were analyzed using the LCMS technique,

**Table 2.** The values of thermodynamic parameters

Thermodynamic parameters	Azo violet	Acid yellow 23	Acid red 27
Energy of activation ( $E_a$ ) (kJ mol <sup>-1</sup> )	66.79	59.04	39.2
Enthalpy of activation, ( $\Delta H^\ddagger$ ) (kJ mol <sup>-1</sup> )	64.13	56.40	36.6
Entropy of activation ( $-\Delta S^\ddagger$ ) (J K <sup>-1</sup> mol <sup>-1</sup> )	-7.04	-14.72	-29.22
Free energy of activation ( $\Delta F^\ddagger$ ) (kJ mol <sup>-1</sup> )	73.65	76.14	75.73
Frequency factor (A) (l mol <sup>-1</sup> sec <sup>-1</sup> )	6.215×10 <sup>10</sup>	9.1×10 <sup>10</sup>	11.4×10 <sup>10</sup>

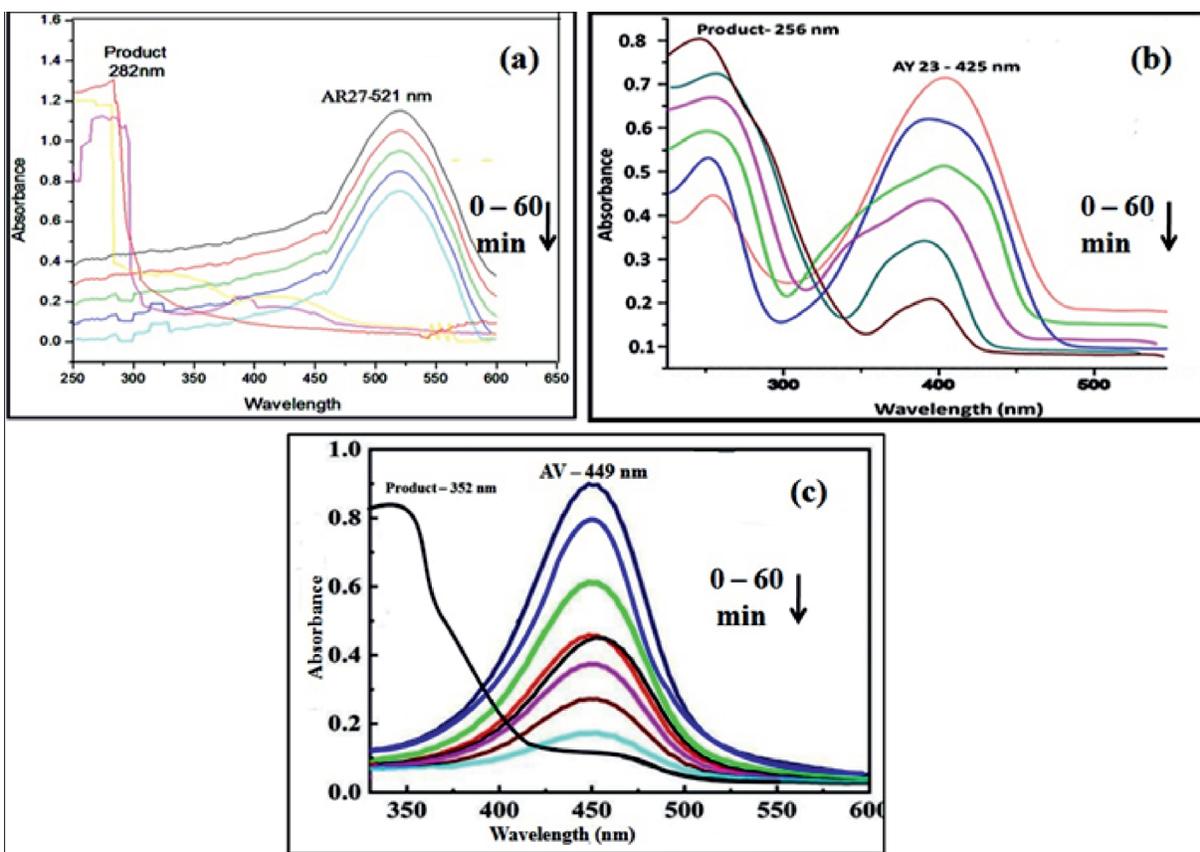


Fig. 4. UV-Vis spectra showing the degradation of anionic azo dyes (a) Acid red 27, (b) acid yellow 23, (c) Azo violet.

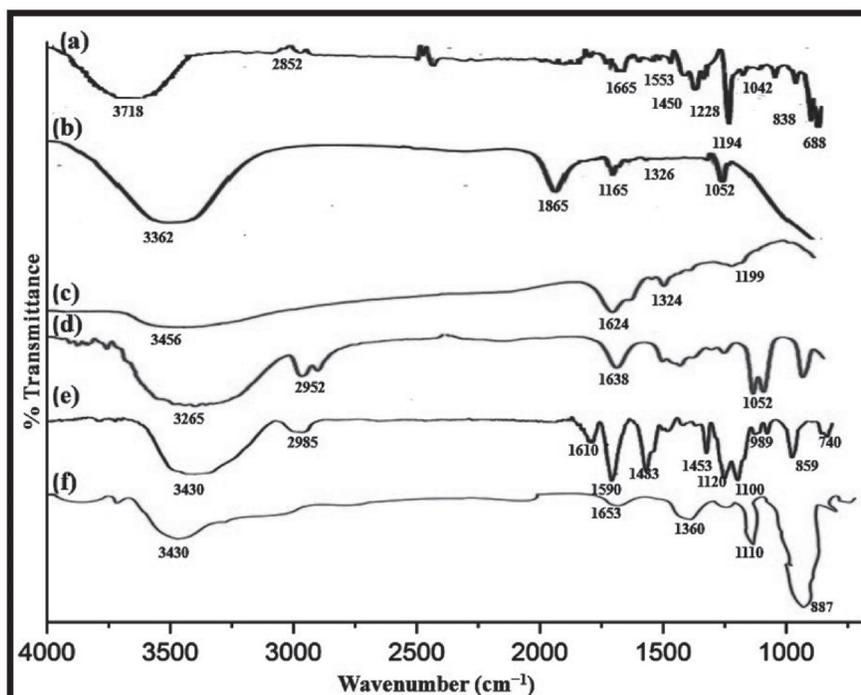


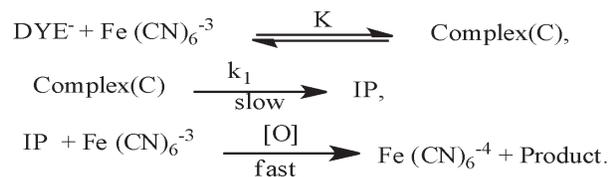
Fig. 5. FT-IR spectra of anionic azo dyes (a,b) Acid red 27 and degradation products, (c,d) Acid yellow 23 and degradation products, (e,f) Azo violet and degradation products.

which is exhibited in Fig. 6(a,b,c). The change of the intermediate product of the dyes into the successive product with various  $m/z$  values is presented in the possible oxidation degradation pathway, which is demonstrated in the Fig. 7(a,b,c). The successively formed products have a simple structure, and less harmful quality compare to the parent compound. The less hazardous products such as 1,4-dibutanoic acid ( $m/z=102$ ), 4-hydroxy naphthalene sulphonic acid ( $m/z=249$ ), hydroxy benzene ( $m/z=94$ ), pentanoic acid ( $m/z=102$ ), 4-hydroxyamino benzene sulphonic acid ( $m/z=188$ ), malonic acid ( $m/z - 104$ ), pentanoic acid ( $m/z- 102$ ), 4- aminobenzene 1,3-diol ( $m/z- 125$ ), and 4- nitroaniline ( $m/z = 138$ ) are found from the major degradation of the acid red 27, acid yellow 23, and azo violet dyes respectively. That shows the cleavage of the azo bond of dyes into the simple products.

### Mechanism

In view of the above kinetic investigation, thermodynamic information and LC-MS examination and recently revealed work (Goel and Chaudhary 2019). The accompanying reaction mechanism for the oxidation of dye can be proposed.

As indicated by the above mechanism, it is assumed that dye ( $DYE^-$ ) molecule exists as an anion



in the alkaline medium, which forms a complex with HCF(III) ions. This complex dissociates through a slow step into the product and short-lived  $Fe(CN)_6^{4-}$ . The intermediate product is further oxidized to minimal end product mainly.

**Derived rate law-** In light of the above mechanism and test realities, the accompanying rate law has been determined

$$r = k_1 K [DYE^-] [HCF(III)]$$

which is similar to the following experimental rate law -

$$R_{obs} = k [DYE^-] [HCF(III)], \text{ where } k = k_1 K$$

### CONCLUSION

The thermodynamic parameters and rate of degradation demonstrate that azo violet, acid red 27

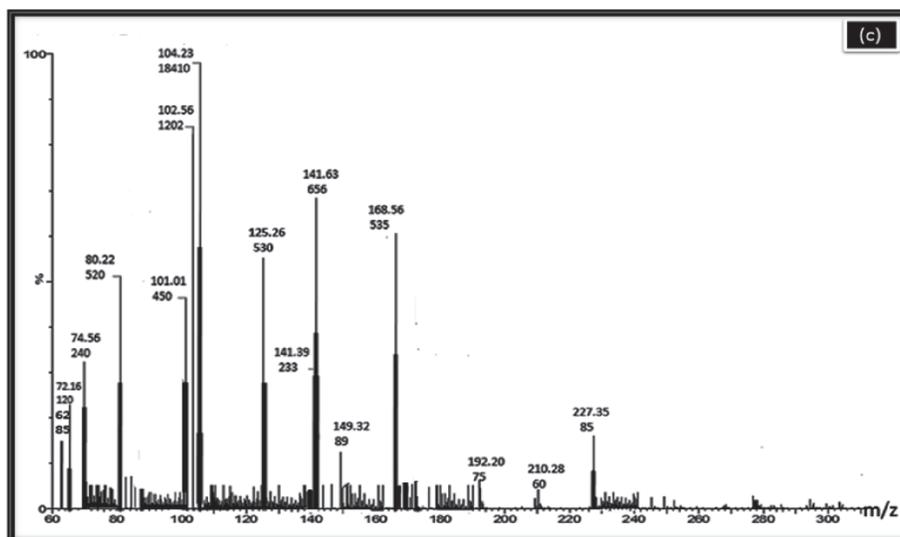
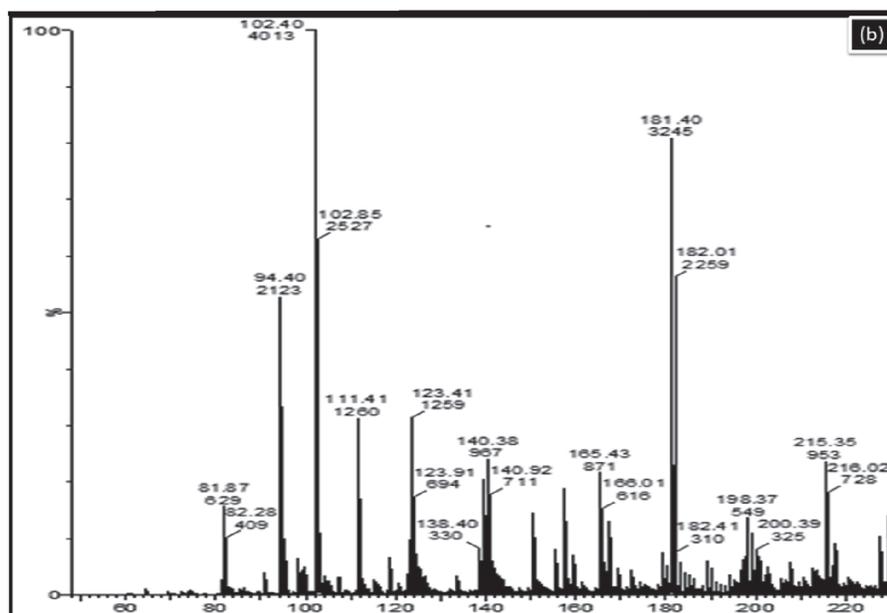
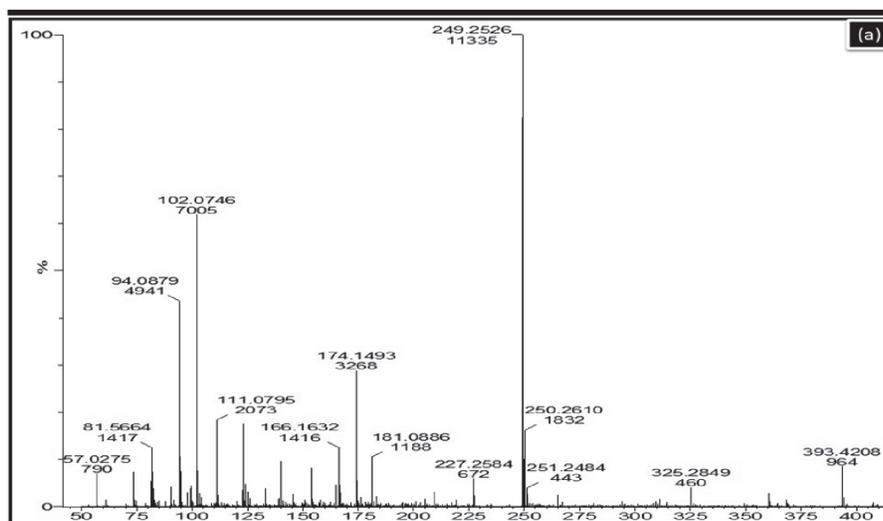
and acid yellow 23 dyes were effectively reduced by hexacyanoferrate(III) ions in aqueous alkaline medium and the degradation rate followed the order as acid red 27 > acid yellow 23 > azo violet under same reaction condition, The higher degradation rate of acid red 27 is due to the presence of naphthalene rings, and also might be ascribed to its effective electron delocalization and presence of strong electron-withdrawing sulphonic groups as compared to azo violet and acid red 23. Those dyes have more sulphonic substituent, show the more reactive in the oxidative degradation, while the hydroxyl group intensifies the electron resonance in the molecules, and decreases the degradation rate of the dyes. The degradation of these dyes, i.e., acid red 27, acid yellow 23, azo violet follows the first-order kinetic model with respect to  $[HCF(III)]$  and  $[Dye]$  at optimum pH 9.5 (azo violet), 8 (acid yellow 23) and 10.5 (acid red 27) and constant temperature  $40 \pm 1^\circ C$  respectively. The value of activation energy ( $E_a$ ) for all dyes confirms that the acid red 27 dye has the highest degradation rate compare to acid yellow 23 and azo violet dye. Product analysis also reveals that the degradation of dye forms less harmful and less hazardous products as 1,4- dibutanoic acid ( $m/z-102$ ), 4-hydroxy naphthalene sulphonic acid ( $m/z-249$ ), hydroxy benzene ( $m/z-94$ ), pentanoic acid ( $m/z-102$ ), 4-hydroxyamino benzene sulphonic acid ( $m/z-181$ ), malonic acid ( $m/z - 104$ ), pentanoic acid ( $m/z- 102$ ), 4- aminobenzene 1,3-diol ( $m/z- 125$ ), and 4- nitroaniline ( $m/z = 138$ ) major degradation product of acid red 27, acid yellow 23 and azo violet respectively showing the cleavage of azo bond into simple products. It may be concluded that the oxidative degradation of anionic azo dyes by hexacyanoferrate(III) ion strongly depends on the chemical structure of dyes. The novelty of the method is that the requirement of oxidant for degradation about 10 times less compared to the other reported methods.

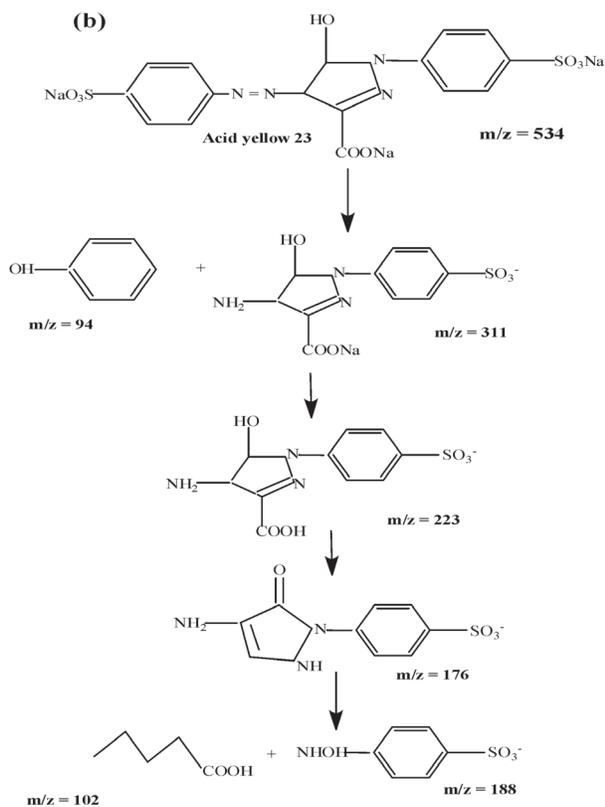
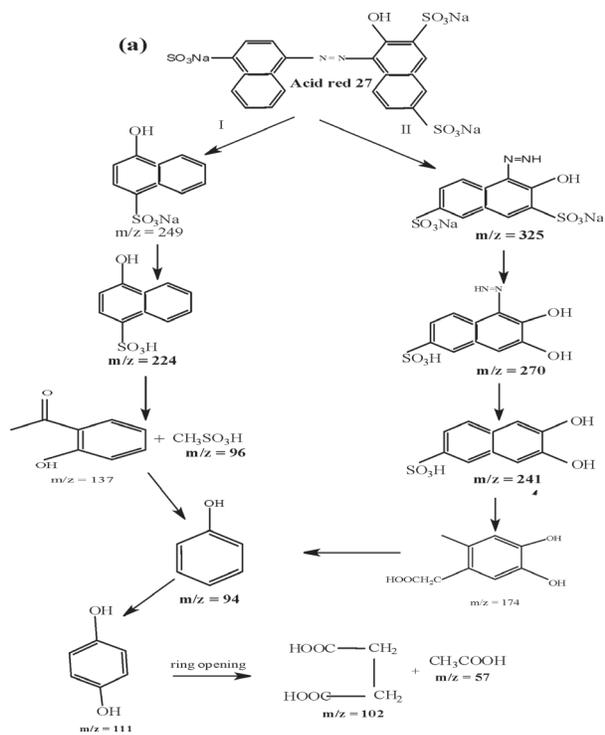
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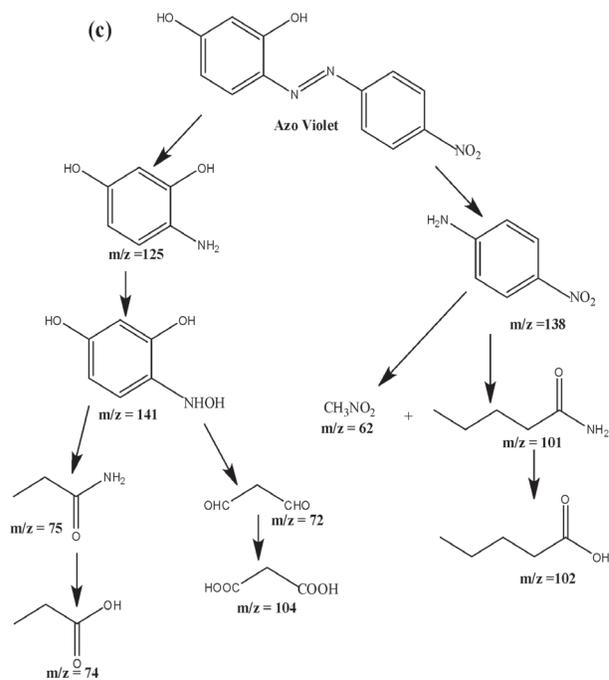
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