Degradation of Azo Dye, Acid Red-14 by Hexacyanoferrate(III) Using Iridium Nanoclusters: A Kinetic Study

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In the present work, a novel method for the treatment of wastewater containing an azo dye, acid red-14 by hexacyanoferrate [HCF(III)] in presence of iridium nanoclusters has been proposed. The effect of some important operational parameters such as pH, temperature and catalyst concentration (iridium nano) has been investigated by kinetic spectrophotometric method at λ_{max} 515 nm of the reaction mixture. The results reveal that degradation kinetics of acid red-14 follows first order kinetic model with respect to [HCF(III)], [acid red-14] and Ir nano concentration. Iridium nanoclusters were recovered with the help of centrifugation and reused for three consecutive cycles. Thermodynamic parameters E_a, $\Delta S^{\#}$, $\Delta F^{\#}$, $\Delta H^{\#}$ and 'A' have been calculated by studying the reaction rate in the range of temperatures 40 to 55 °C. The formation of degradation products was characterized by chromatographic and spectroscopic techniques after the extraction with ethyl acetate. 1-Hydroxy-2-amino naphthalene and naphthalene sodium sulphate were identified as major degradation products. The results can provide fundamental knowledge for the treatment of wastewater containing acid red-14/other azo dyes.

Keywords: Kinetics, Degradation, Acid Red-14, HCF(III), Iridium nanoclusters.

INTRODUCTION

Fiber dyeing produces a great deal of wastewater [1]. The effluent from the dyeing process is colourful and the release of the associated wastewater to natural stream and rivers poses severe problems to aquatic life and humans [2]. Considerable efforts have been made by many researchers to find appropriate treatment systems to remove pollutants and impurities of wastewaters from the textile industries. The conventional treatment techniques applied to textile wastewaters, such as chemical coagulation/flocculation, membrane separation or elimination by activated carbon adsorption, are costly and result in phase transfer of pollutants [3-5]. Recently nanotechnology has been extended to waste water treatments. Degradation of dye-stuffs using nanoparticles has gained prominence due to their low cost, easy availability and effectiveness [5-7]. Among the different transition metals as catalyst the interest in iridium based nanocatalyst is increasing due to their high activity, stability and selectivity under different reaction conditions [8]. The aim of the present study is to develop a new method for the treatment of wastewater containing, acid red-14 (AR-14) by hexacyanoferrate(III) ions in presence of iridium nanocluster by kinetic spectrophotometric method in alkaline medium and to investigate the effect of operational parameters such as pH, temperature and catalyst concentration (iridium

nanoclusters) on the degradation of acid red-14. These are the major variables governing the degradation process. Acid red-14 is the common dye for fiber dyeing, especially for woolen fibers [9]. Furthermore, the kinetics and mechanism of the degradation of acid red-14 has also been elucidated based on the experimental data.

EXPERIMENTAL

All the chemicals used in the study were of analytical grade. Acid red-14 dye (chemical structure shown in Fig. 1.) and $IrCl_3 \cdot 3H_2O$ were purchased from Loba Chemie Pvt. Ltd, Mumbai, India and Sisco Research Laborateries Pvt. Ltd., India respectively. pH of solution was kept constant by using KH_2PO_4 and NaOH solutions as buffer. Measurements of pH of solution were carried out with a digital pH meter (Systronics µ pH system 361). Iridium-nanoclusters (particle size 4.5 ± 0.5 nm) were synthesized by wet reduction method using polyvinyl-pyrrolidone (PVP) as protecting agent after the reduction of precursor salt, $(IrCl_3 \cdot 3H_2O)$, by methanol as reported earlier by Goel *et al.* [10].

The kinetic experiments were carried out at pH (7.5) and constant temperature (40 ± 0.1 °C). The appropriate quantities of all reactants except substrate were mixed in a 100 mL iodine flask and kept at 40 ± 1 °C. The reaction was initiated by
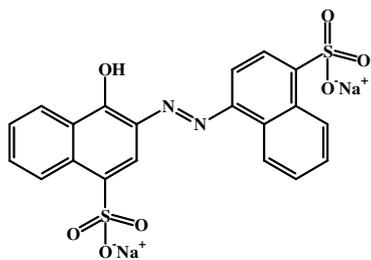
Fig. 1. Chemical structure of acid red-14

injecting the solution of acid red-14 into the aforementioned reaction mixture which was also kept in thermostat at 40 ± 1 °C. The progress of the reaction was measured spectrophotometrically (Systronics -117) with a spectrometric quartz cell (1 cm path length) at 515 nm corresponding to λ_{max} of the reaction mixture. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The reaction rate was calculated by the plot of absorbance *vs.* time using plane mirror method. For product analysis the reaction mixture was kept at atmospheric conditions for 24 h and the products were extracted with ethyl acetate. The degradation products were characterized by UV-visible spectroscopy and LC-MS (BRUKER, ELITE) methods of analysis. The mobile phase consisted of methanol:water: acetonitrile (25:50:25) at the flow rate of 300 μL/min.

RESULTS AND DISCUSSION

Kinetic study: The catalyzed oxidation of acid red-14 has been studied at constant pH and temperature at different concentrations of one reactant keeping the concentration of others constant. The pH value is an important operational parameter in actual wastewater treatment. To study the effect of pH on the reaction rate, it varied from the value 6 to 7.5 only as above 7.5 the colour of dye changes. Fig. 2 showed that the rate of degradation was maximum at pH 6. At high pH values, the rate of degradation decreases which may be due to columbic repulsion between anionic dye surface and hydroxyl anion, hence they do not have opportunity to react with dye molecules [11,12]. Fig. 3 suggested that the rate of degradation of acid red-14 with respect to [HCF(III)] follows first order kinetics at its lower concentrations tending towards zero order at its higher concentrations. The effect of [HCF(III)] on the rate of degradation has been studied by varying its concentration from 1×10^{-6} to 9×10^{-6} mol dm^{-3} as shown in Fig. 3. The effect of variation of dye concentrations has also been studied by varying its concentration from 1×10^{-5} to 8×10^{-5} mol dm^{-3}. Fig. 4 shows the first order dependence of rate on the concentration of substrate. The effect of concentration of Ir nano on the rate of degradation was also studied. A gradual increase in rate with iridium nanoclusters concentration reveals first order kinetics with respect to [Ir-nano]. The concentration of iridium nanoparticles was varied about many times from 0.2×10^{-7} to 1.204×10^{-7} mol dm^{-3} (Fig. 5). The variation in rate with the amount of catalyst shows that the rate of reaction may have been controlled by the mass of catalyst. The effect of precursor Ir was studied to compare its effect with Ir-nano on the rate of degradation of acid red-14 by hexacyanoferrate(III) in aqueous alkaline medium.
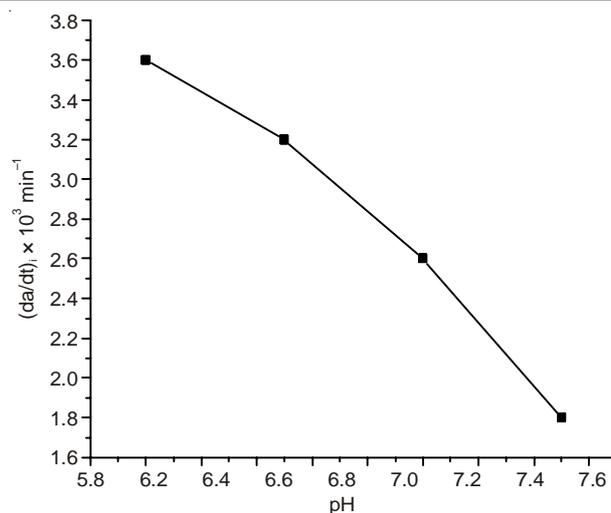
Fig. 2. Effect of pH on the degradation of acid red-14 by HCF(III). Experimental conditions: [acid red-14] = 3.0×10^{-5} mol dm^{-3}; [HCF(III)] = 3.0×10^{-6} mol dm^{-3}; [Ir nano] =1.004×10^{-7} mol dm^{-3}; Temperature = 40 ± 0.1 °C
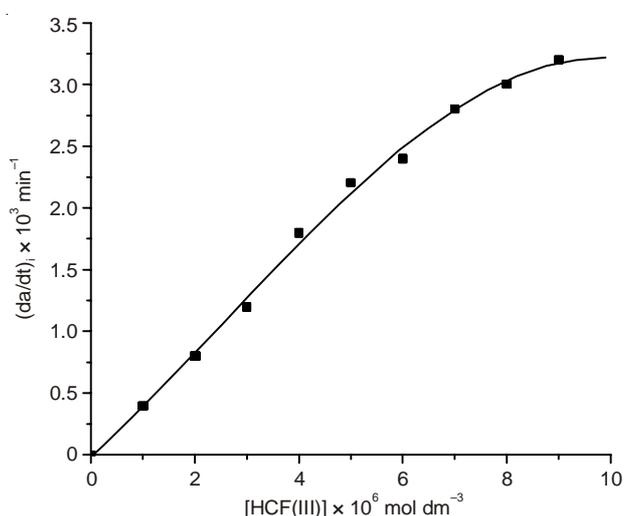
Fig. 3. Effect of [HCF(III)] on the degradation of acid red-14 by HCF(III). Experimental conditions: [acid red-14] = 3.0×10^{-5} mol dm^{-3}; [Ir nano] = 1.004×10^{-7} mol dm^{-3}; pH = 7.5; Temperature = 40 ± 0.1 °C
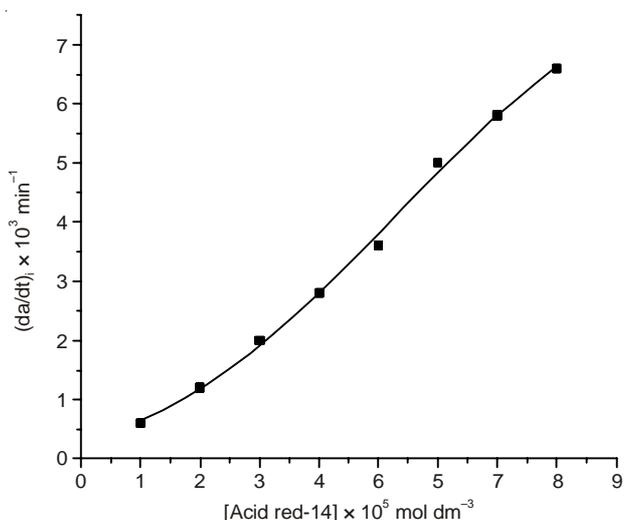
Fig. 4. Effect of [acid red-14] on the degradation of acid red-14 by HCF(III). Experimental conditions: [HCF(III)] = 3.0×10^{-6} mol dm^{-3}; [Ir nano] =1.004×10^{-7} mol dm^{-3}; pH = 7.5; Temperature = 40 ± 0.1 °C
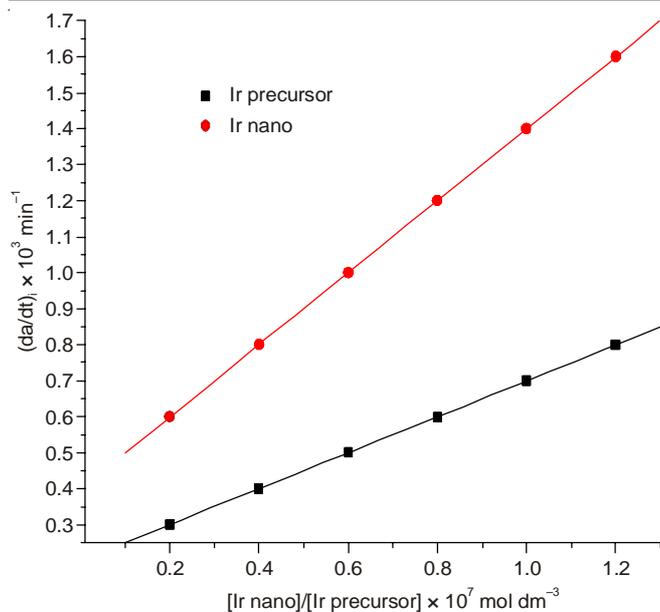
Fig. 5. Effect of [Ir nano/Ir precursor] on the degradation of acid red-14 by HCF(III). Experimental conditions: [acid red-14] = 3.0×10^{-5} mol dm^{-3}; [HCF(III)] = 3.0×10^{-6} mol dm^{-3}; pH = 7.5; Temperature = 40 ± 0.1 °C

Thermodynamic parameters: To evaluate the thermodynamic parameters for the oxidation of acid red-14, the reaction has been studied at four different temperatures *i.e.* 40, 45, 50 and 55 °C. The calculated values of energy of activation (E_a), entropy of activation ($\Delta S^{\#}$), energy of formation ($\Delta F^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and Arrhenius factor (A) are presented in Table-1. Low value of energy of activation reveals good catalytic activity of Ir nano while large entropy of activation shows the formation of polar species during the reaction.

TABLE-1
THERMODYNAMIC PARAMETERS

Parameters	Values
E_a (kcal mol^{-1})	8.08
$\Delta H^{\#}$ (kcal mol^{-1})	7.44
$\Delta S^{\#}$ (e.u.)	-34.38
$\Delta F^{\#}$ (kcal mol^{-1})	18.72
A (L mol^{-1} s^{-1})	5.55×10^5

Efficiency of recycled catalyst: In order to investigate the economy of the present method, iridium nanoparticles were recovered and reused for three consecutive cycles. After the first degradation cycle the treated reaction mixture was centrifuged. The obtained nanoparticles were washed thoroughly with double distilled water five to six times and were further reused as catalyst in the kinetic study. The same method was used further for two successive cycles at fixed experimental conditions. The results are presented in Table-2. It was found that the rate of reaction decreased with each successive cycle. This may be due to increase in size of nanoparticles because of agglomeration.

Identification of degradation products: Degradation of acid red-14 was monitored by UV-visible spectroscopy (Fig. 6). Acid red-14 is characterized by maximum absorption at 515 nm attributed to the chromophore containing azo linkage

TABLE-2
RATE OF DEGRADATION OF REACTION MIXTURE
FOR THREE CONSECUTIVE CYCLES

No. of cycles	-dA/dt × 10^3 (min^{-1})	Particle size (nm) by XRD
Before recovery	2.0	4.50
After I cycle	1.4	17.03
After II cycle	0.8	49.34
After III cycle	0.6	56.50
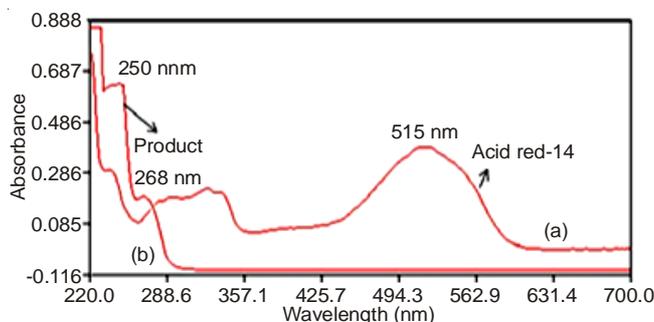
Fig. 6. UV-visible spectra of (a) acid red-14 and (b) extracted product

of the dye molecule in the solution [13]. The disappearance of this band and formation of new bands at 250 and 268 nm supports the degradation by hexacyanoferrate(III) ions. In order to provide supported evidences for degradation, identification of degradation products was carried out by LC-MS (Fig. 7). 1-Hydroxy-2-amino naphthalene and naphthalene sodium sulphate have been confirmed as the major degradation products. Proposed chemical structures of the expected degradation products are given in Table-3.
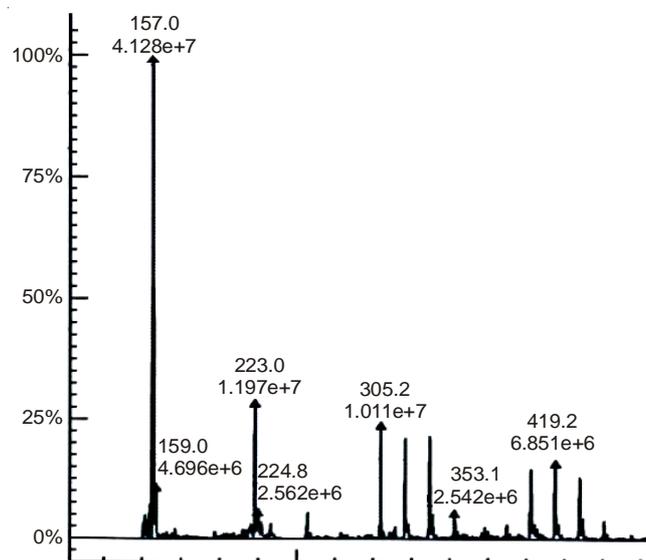
Fig. 7. LC-MS spectra of degraded products of acid red-14

Mechanism: Though it is difficult to propose a mechanism for such complex reaction, however, based on the above experimental results and previously reported work, the following tentative mechanism reaction for the oxidation of acid red-14 can be proposed:

$$D^- + Ir_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex (C)} \qquad (1)$$

TABLE-3
PROPOSED STRUCTURES OF ACID RED-14
DEGRADATION PRODUCTS

m.w.	Proposed structure
159	1-Hydroxy-2-amino naphthalene
353	Naphthalene sodium sulphate
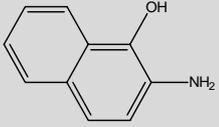
$$C + Fe(CN)_6^{3-} \xrightarrow[\text{slow}]{k_2} Ir_n + Fe(CN)_6^{4-} + \text{Products} \qquad (2)$$
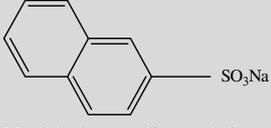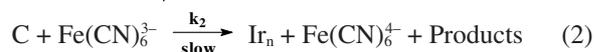
From the above reaction mechanism, it is assumed that in alkaline medium mono azo dye acid red-14 (D) exist as anion (D⁻) [14] which forms a loosely bonded complex with iridium nanoparticles (Ir_n). This complex (C) slowly reacts with HCF(III) ion resulting into products along with Ir_n and $Fe(CN)_6^{4-}$.

Conclusion

The present work shows that acid red-14 can be easily degraded by hexacyanoferrate(III) in presence of iridium nanoparticles. The reaction follows first order kinetics with respect to acid red-14 at pH of 7.5 and constant temperature of 40 ± 0.1 °C while the order of reaction with respect to [HCF(III)] has been found to be one at its lower concentration tending towards zero at its higher concentration. Degradation products are simple and less hazardous. Iridium nanoparticles proved as an efficient catalyst for the oxidation of acid red-14 as they demonstrated the enhanced degradation rate compared to iridium precursor which may be due to large surface area to volume ratio. Moreover, these nanoparticles can be recovered and reused making them potential candidates for dye degradation technologies. The work provides an economical solution to aquatic environment in terms of time saving, use of very small concentration of catalyst and is equally useful in the degradation of several other dyes.

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