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Accelerating The Degradation Kinetics of Azo Dyes Using Iron Oxide Nanoparticles

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Abstract: *Azo dyes have a wide spread industrial applications. When released in water bodies, these dyes hinder the penetration of light which results in adverse effects on aquatic life. Hence it is pertinent to treat the dyes before their discharge in environment. Present work focuses on degradation of azo dyes (via chemical route) using* $NaBH_4$ *as a reducing agent. For this purpose, Fast Sulphone Black F (FSB-F) dye was used as a model system. FSB-F has an absorption maxima* (λ_{max}) *at 464 nm in aqueous medium. On reduction, FSB-F is converted into its corresponding leuco-form which has poor absorption in visible region. Time required for complete degradation of FSB-F was observed to be ~ 7 hrs. With a view to enhance reaction kinetics, system was loaded with iron oxide nanoparticles, keeping all other experimental conditions identical. In presence of iron oxide nanoparticles, complete degradation of dye was accomplished within 1 hr. Thus, our study suggests that nanoparticles plays a potent role as catalyst for reaction involving dye degradation.*

Keywords: *Azo dyes, Fast Sulphone Black-F, Iron oxide nanoparticles,* $NaBH_4$*, Reduction Kinetics.*

I. Introduction

Dyes are major class of organic compounds that are abundantly used in various industries such as cosmetics, textiles, food, leather, dyeing, printing, etc[1, 2]. Out of several dyes, 'Azo dyes' finds the largest utility for commercial processes. Azo dyes are characterized by one or more azo groups (N=N). However, azo dye compounds are recognized as a potential carcinogens [3, 4]. Studies have revealed that during the dyeing operation ~20% of the dyes ended up in waste waters [5]. The waste water engendered from dyeing industries are found to contain high degree of pollutants not only in the dissolved state but also in the suspended forms [6, 7]. Further, coloured waste water in the environment is a source of water pollution. It reduces the penetration of sunlight thereby decreasing the photosynthetic effects [8-10]. This in turn has an adverse effect on aquatic life. Hence, there is an urgent need to convert the dyes in a form which is more environmental friendly.

Several steps are been undertaken for the treatment of the dyes and their safe disposal into environment. This includes converting the dye into biodegradable one, which is latter fed by micro-organisms. Problem associated with this method is that it is not a universal in nature [11-13]. Also, azo dyes are highly resistant to microorganisms which makes this biological treatment ineffective. Another strategy includes chemical treatment, wherein dye is made to react with suitable oxidizing/reducing agent before their discharge in water bodies. Dyes on interacting with oxidizing/reducing agent undergoes chemical change resulting in generation of product that is colourless [14, 15]. The resultant effluent has poor absorption cross-section forvisible radiation. This in turn facilitates penetration of light in water bodies and hence it is less harmful to aquatic life.

Though, treating dyes with suitable oxidizing/reducing agent generates a product that is less harmful to aquatic life. However, it has been observed that rate of degradation of dyes is quite slow. Hence, with an intention to increase the reaction rate, present work employs iron oxide nanoparticles (iron oxide np's) as catalyst. With reference to nanoparticles, it is pertinent to note that they play a constructive role in catalytic activity [16-18]. This can be attributed to high surface to volume ratio owing to small particle size. Further, high surface to volume ratio provides larger number of atoms on surface, which is essential for catalytic activity [19]. In present work we have employed iron oxide nanoparticles as a catalyst for degradation of Fast Sulphone Black F (FSB-F) azo dye. Iron oxide offers an additional advantage over pure metallic system by providing a bipolar core i.e. positively charge iron ion and negatively charge oxide ion. Such bipolar characteristic of iron oxide ensures efficient binding with FSB-F which is essential for catalytic activity. Also, as compared to other metal oxides, iron oxide is economical and non-toxic in nature. In present work, FSB-F dye was treated with $NaBH_4$ (reducing agent) in absence and presence of iron oxide nanoparticles. Our experimental results depicts a significant enhancement in degradation reaction rate of FSB-F in presence of iron oxide nanoparticles.

II. Materials & Methods

2.1 Materials

Ferric chloride (98.5%), sodium borohydride (99.6%) and ammonia solution (30%) were purchased from SD Fine Chemicals while Fast Sulphone Black F (FSB-F) (98.0%) was purchased from BDH chemicals Ltd. Each of these chemicals were used directly without any additional purification process.

2.2 Preparation of Iron oxide nanoparticles by using $FeCl_3$

0.2 M $FeCl_3$ solution was prepared using distilled water. 20 cm^3 of precursor solution was withdrawn in round bottom flask which was placed on rota mental. Solution was stirred vigorously for 15 minutes. Ammonia solution (3 M) was added dropwise(~2 drops/min) till precipitation completes. Precipitate was separated by centrifugation at ~8000 rpm. The particles thus obtained were washed ~3 to 4 times with water and later with acetone. Particle obtained were subjected to calcinations at 400°c. In the above reaction, the NH_4OH (ammonium hydroxide) performs major role like control the pH value of the solution as well as it supply hydroxyl ions to the solution. The $FeCl_3$ reacts with NH_4OH and forms FeOOH, which on heating, helps in the development of Fe_2O_3according to the chemical reactions [20] (i) -(iii).

$$NH_4OH_{(aq)} \leftrightharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad \text{(i)}$$

$$FeCl_{3(s)} \rightarrow Fe^{3+}{}_{(aq)} + 3Cl^-{}_{(aq)} \qquad \text{(ii)}$$

$$Fe^{3+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow FeOOH_{(aq)} + H^+ \qquad \text{(iii)}$$

$$FeCl_{3\,(aq)} + 2NH_4OH_{(aq)} \rightarrow FeOOH(aq) + 2NH_4^+{}_{(aq)} + H^+{}_{(aq)} + 3Cl^-{}_{(aq)} \qquad \text{(iv)}$$

On calcination FeOOH decomposes to form Fe_2O_3 as shown in reaction (v)

$$FeOOH_{(aq)} \rightarrow Fe_2O_{3(s)} + H_2O_{(l)} \qquad \text{(v)}$$

2.3 Characterization

Iron oxide nanoparticles were characterized using FT infrared spectrometer. On other hand crystal structure and crystalline size were estimated with the help of powdered X-ray diffraction technique. Philips PAN analytical instrument was employed for recording XRD spectra.

2.4 Catalytic activity of Iron oxide nano particles

In the present work, FSB-F was converted to *leuco*-form using $NaBH_4$. Dye solution (150 ppm) was loaded with sodium borohydride solution (0.2 g/100 ml). Change in concentration of FSB-F was monitored with the help of UV-Visible spectrophotometer. Spectra were recorded at time interval of 2 min. In order to explore catalytic activity, experiments were performed in absence and presence of iron oxide nanoparticles.

III. Results And Discussions

3.1 Characterization

Iron oxide nanoparticles exist in different forms such as α-Fe_2O_3 (hematite), γ-Fe_2O_3,iron (II) oxide, iron (II, III) oxide, magnetite (Fe_3O_4) iron (III) oxide, (β-Fe_2O_3) beta phase, etc. In order to identify form of iron oxide particle that is generated in present synthesis, XRD spectrum was recorded. Fig. 1 depicts XRD spectrum of iron oxide particles. Sharp peak in spectrum indicated crystalline character of iron oxide particles. Further, the spectrum matched with JCPDS file number 00-033-0664 which corresponds to Fe_2O_3 possessing face centered cubic (FCC) structure. This indicates that, under present experimental condition, iron oxide existed as Fe_2O_3 possessed FCC structure. Crystalline size of Fe_2O_3 particles can be estimated using Scherrer's formula which is given below

$$D=\frac{K\lambda}{\beta cos\theta} \qquad (1)$$

where, D = crystalline size, K = dimensionless factor which is close to unity, λ = wavelength of X-ray, □□ = FWHM of peak and θ Bragg's angle in degrees. Crystalline size of particles estimated by Scherrer's equation is shown in Table 1. From the above table it can be seen that estimated crystalline size of nanoparticles was ~18 nm. Hence, present system qualifies to be called as nanoparticles

XRD study was complimented by FTIR. IR spectrum of iron oxide nanoparticles synthesized using $FeCl_3$ as a precursor is shown in Fig. 2. Fig. 2 depicts two peaks for Fe-O-Fe stretching vibration at a wavelength range of 420 cm^{-1} to 560 cm^{-1}, it is the signature of formation of Fe-O bond. Presence of Fe-O bond clearly indicates formation of iron oxide particles. Further, peak corresponding to Fe-Cl stretching vibration at 409 cm^{-1} is absent [21], signifying complete formation of product. It is pertinent to note here that present techniques could not differentiate between α &β formsof Fe_2O_3. For this purpose additional characterization tools are required [22].

3.2. Degradation of FSB-F in absence and presence of Fe_2O_3 nanoparticles

In order to degrade FSB-F, 150 ppm dye solution was loaded with 0.2 g/100 ml aqs. $NaBH_4$ solution. Change in concentration of FSB-F was monitored with the help of UV-Visible spectrophotometer. Spectra were recorded at time interval of 2 min (see Fig. 3). The spectra reveals gradual decrease in concentration of FSB-F as function of time. Decrease in concentration of FSB-F is evitable from decrease in area under the peak of UV-Vis spectra with increase in time. Kinetics of degradation was evaluated assuming that system obeys first order rate law, which is mathematically expressed as follows.

$$k = \left(\frac{2.303}{t} \right) . \log \frac{Co}{Ct} \qquad (2)$$

where t = time, C_0 = Area at time zero and C_t = Area at time 't' secs
Graph of $\ln(C_0/C_t)$ *Vs* t is shown in Fig. 4. The regression value (R^2) of this graph is 0.9896, which confirms that degradation of dye obeys first order kinetics. Further slope =(rate constant) ofabove graph is 0.0157 min^{-1}. Half-life and time required for complete degradation of FSB-F was estimated to be ~44.08 min and 7.334 hours respectively. Fig. 5 shows absolute conc. of FSB-F dye at varying time intervals obtaining from UV-Vis measurements. Above experiments shows that degradation time of FSB-F using $NaBH_4$ is significantly higher.

In order to accelerate the rate of reaction, another set of experiment were performed wherein dye solution was loaded with catalyst (iron nanoparticles) along with sodium borohydride. Fig. 6 shows that presence of catalyst facilitates rapid conversion of oxidative form of FSB-F to reductive form. Graph of $\ln(C_0/C_t)$ *Vs* t (see Fig. 7) displayed the regression value (R^2) of graph as 0.9907 thereby confirming that degradation of dye obeys first order kinetics. Further, slope = (rate constant) of graph is 0.1250 min^{-1}. Half-life and time required for complete degradation of FSB-F was estimated to be ~5.54 min and ~55.27 min respectively. Fig. 8 displays absolute conc. of FSB-F dye at varying time intervals obtaining from UV-Vis measurements. From above experiments it is clear that rate of degradation of dye increases ~7 to 8 times upon addition of iron oxide nanoparticles. Thus, Fe_2O_3 nanoparticles acts an efficient catalyst for degradation of FSB-F. Above phenomena can be qualitatively understood on the basis of electron relay mechanism according to which if the iron oxide nanoparticles possesses redox potential value intermediate to that of a dye and reducing agent then it can facilitate electron transfer process thereby enhancing the rate of degradation of dye. However, estimating the exact values of redox potentials is beyond the scope of present work.

IV. Conclusion

In present work, we have reported a chemical route for degradation of azo dye (Fast Sulphone Black-F) *i.e.* treatment via sodium borohydride. Rate constant for degradation reaction was estimated as 0.0157 min^{-1}. In presence of iron oxide nanoparticles, rate of above reaction was observed to increase significantly. Almost complete degradation of dye required the time of ~ 1 hr, against 7 hrs in absence of iron oxide nanoparticles. Thus, iron oxides serves as a catalyst for above reaction. A probabilistic electron relay mechanism is proposed to account for role of iron oxide nanoparticles for altering the reaction kinetics, according to which if the nanoparticles possesses redox potential value intermediate to that of a dye and reducing agent then it can facilitate electron transfer process thereby enhancing the rate of degradation of dye.

Table 1 : Estimation of crystalline size of iron oxide particles using Scherre's formula

2 □ (in degrees)	**FWHM**	**Crystalline size**
33.1754	0.3508	24.693 nm
35.6508	0.3624	24.0607 nm
24.1035	1.5596	5.44 nm
Average crystalline size		18 nm

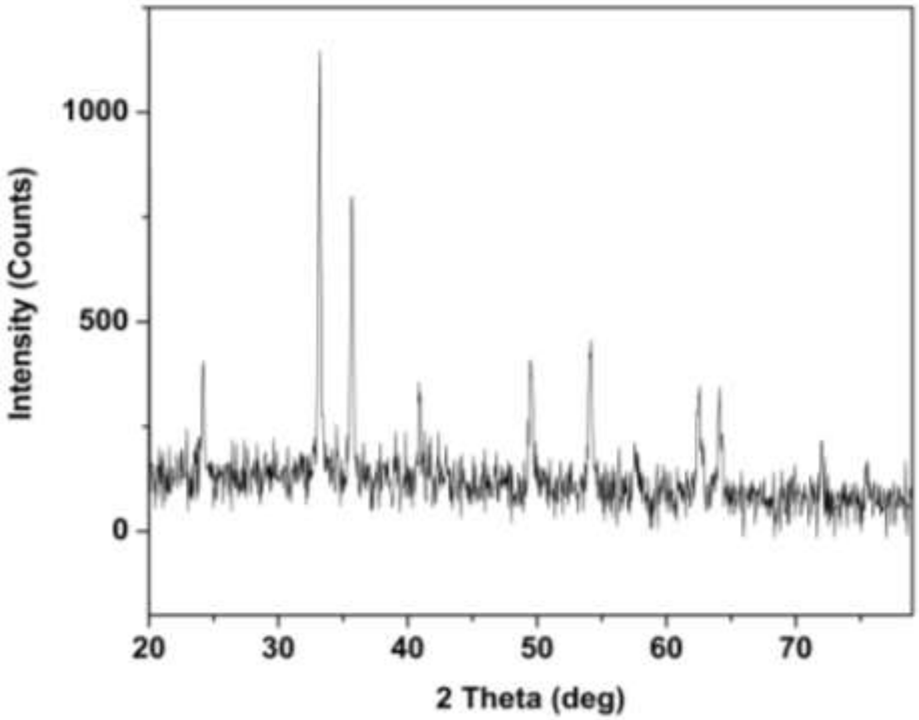

Fig. 1: Powdered X-ray diffraction ofiron oxide particles

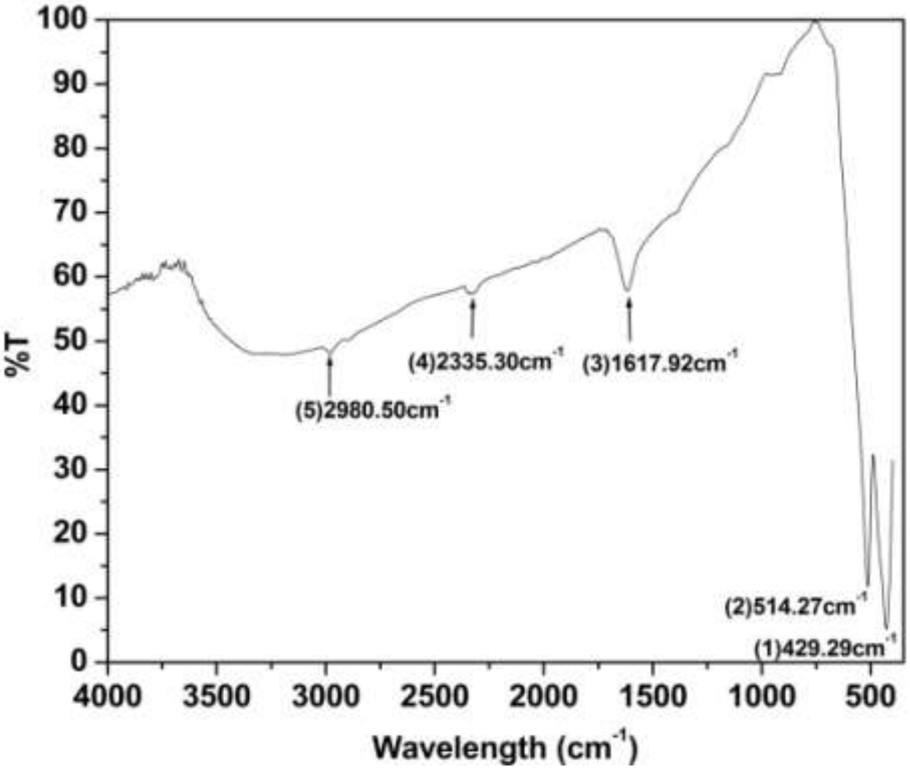

Fig. 2 : FT-infrared spectrum of iron oxideparticles

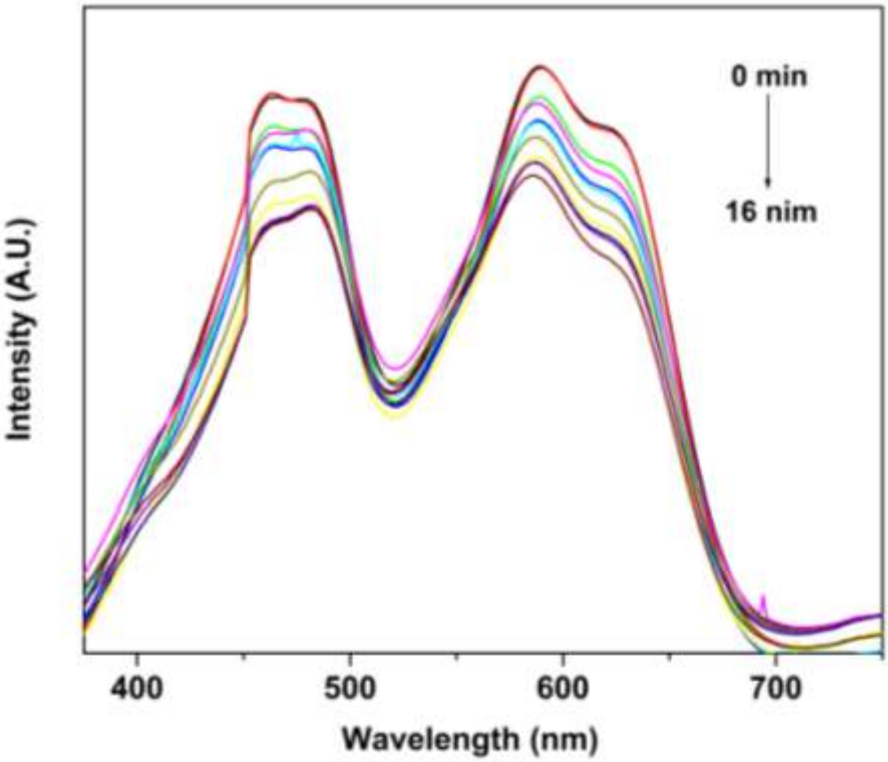

Fig. 3 : UV-Vis spectrum of FSB-F + $NaBH_4$, recorded as a function of time.

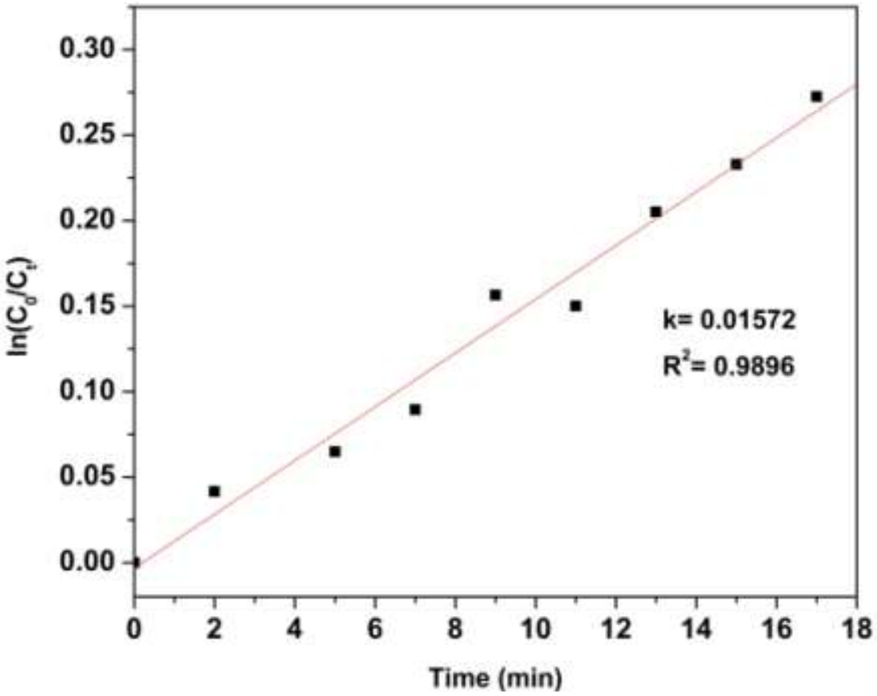

Fig. 4: Plot of $ln(C_0/C_t)$Vs time for the FSB-F +$NaBH_4$ system.

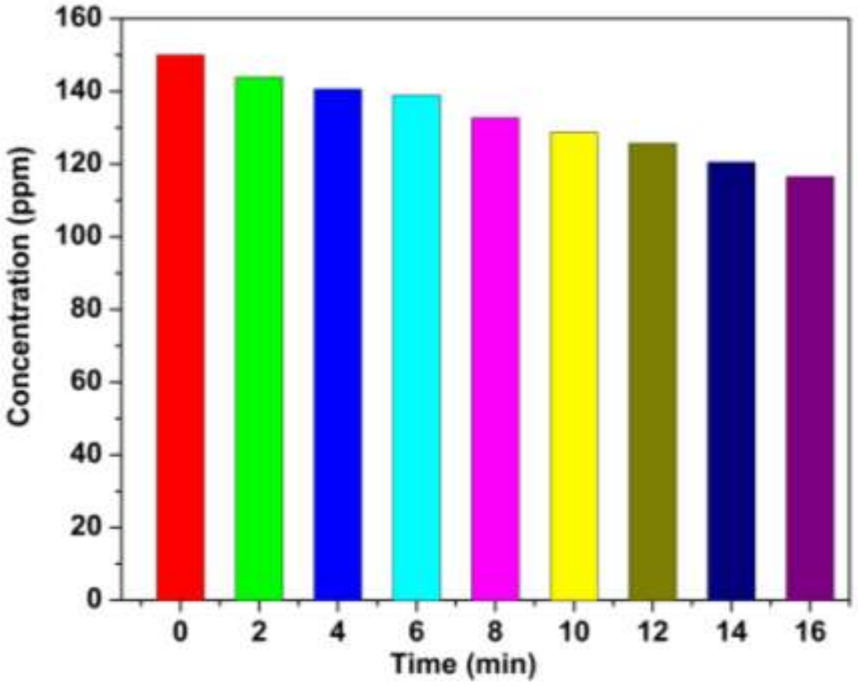

Fig. 5 : Absolute conc. of FSB-F dye, at varying time intervals, obtained from UV-Vis measurements for FSB-F $+NaBH_4$ system.

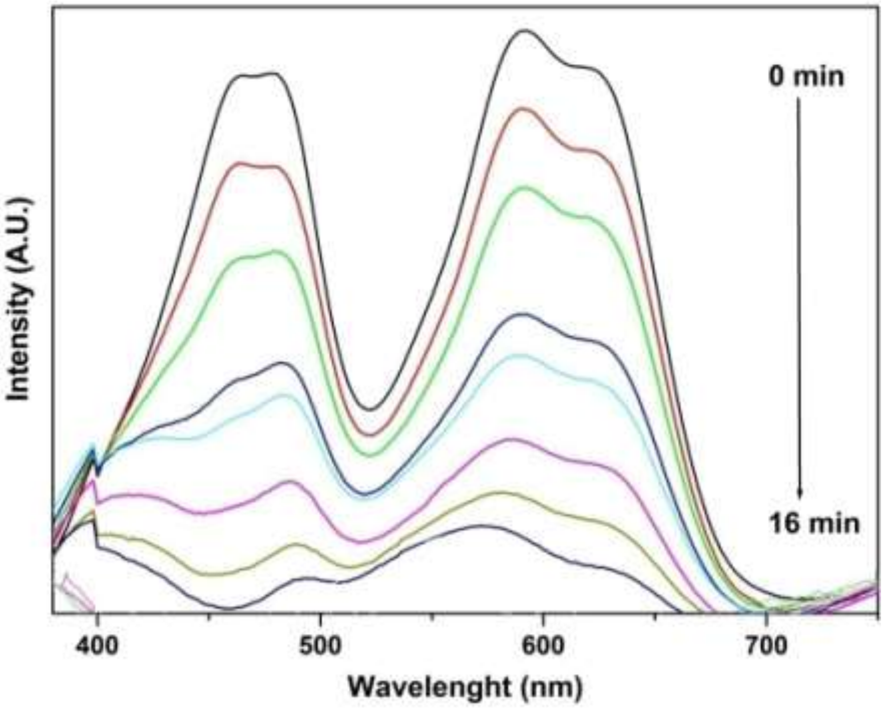

Fig. 6 : UV-Vis spectrum of FSB-F + $NaBH_4$ + Fe_2O_3np’s, recorded as a function of time.

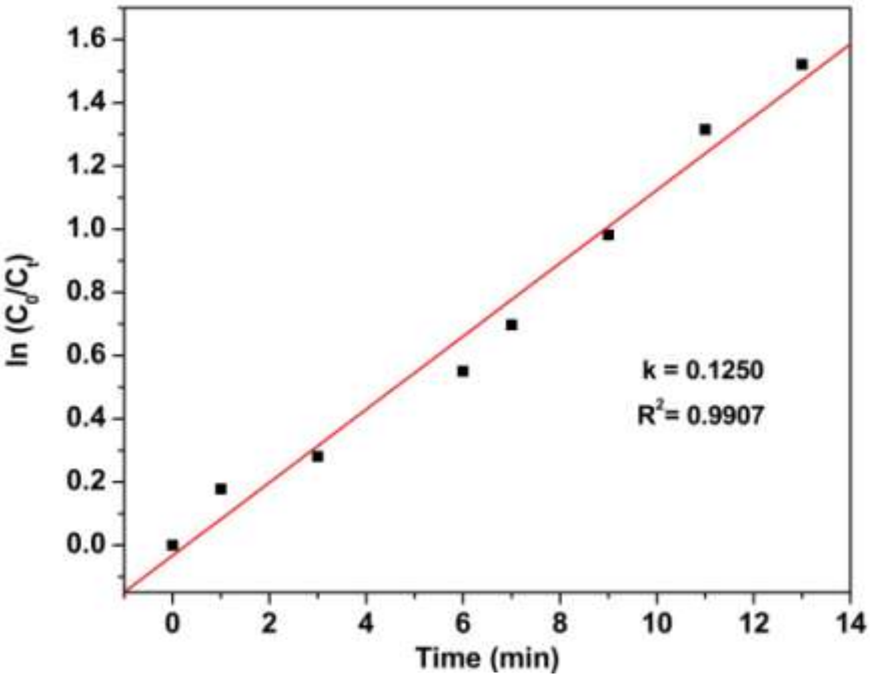

Fig. 7 : Plot of ln(C_0/C_t)Vs time for the FSB-F +$NaBH_4$ + Fe_2O_3np's system.

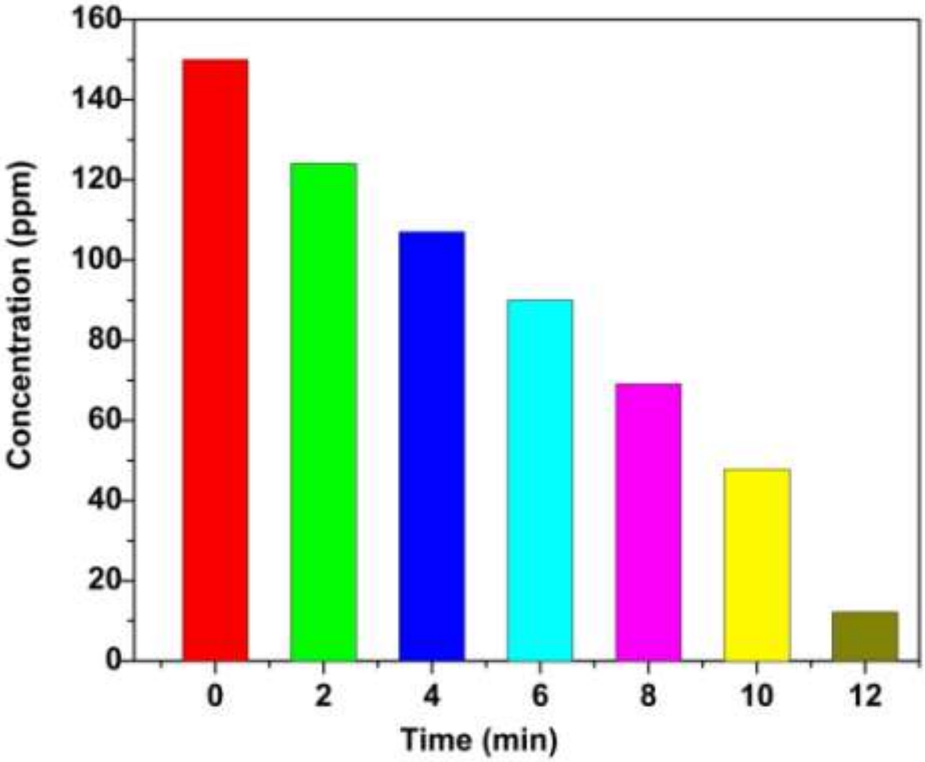

Fig. 8 :Absute conc. of FSB-F dye, at varying time intervals, obtained from UV-Vis measurements for FSB-F +$NaBH_4$ + Fe_2O_3np's system.

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