

# KINETICS OF REDUCTION OF ANILINE BLUE DYE USING ZERO-VALENT IRON ( $\text{Fe}^0$ )

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## ABSTRACT

*Reductive degradation of dyes by zero-valent metal is a process in which zero valent metals such as Fe, Zn, and Cu are used to treat dye contaminants. These metals are moderate reducing agents and have been found capable of reductive degradation of many organic pollutants. The reduction of aniline blue by  $\text{Fe}^0$  has been studied in aqueous batch systems. Zero valent iron is current metal of choice because it is readily available, inexpensive, non toxic and a good reducing agent. The aqueous suspension was continuously stirred. The rate of discoloration of the dye was measured by following the change in the absorbance of the dye. Reaction rate has been found to be increased with increase in the mass of  $\text{Fe}^0$ , dye, acid and sodium chloride concentrations and decreased with increase in the concentration of EDTA, sodium acetate. On the basis of experimental, FTIR and mass spectra data, a probable mechanism of reduction of aniline blue by  $\text{Fe}^0$  has been proposed.*

**Keywords:** Reduction, Aniline blue, Zero-valent iron

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## INTRODUCTION

Dyes play a vital role in human civilization. Dyes have wide range of applications in textile dyeing, paper printing, photography, pharmaceutical, leather, food products etc. Dyes after use by various industries, are discharged to the water bodies like river, ponds etc. Thus, they become potential pollutants and need effective treatment. It has long been known that the oxidation of metals such as iron, tin and zinc can bring about the reduction of halogenated organics<sup>1</sup>. These reducing metals could be used for remediating water by constructing permeable reactive barriers (PRBs) composed of one of the reducing metals<sup>2,3</sup>. A PRB is a zone of granular metal that extends below the water table and intercepts the flow of contaminated water. As the contaminants pass through the PRB, they are reduced to non-toxic compounds and, thus, the water emerges free from hazardous substances<sup>4</sup>.

In the past, most investigations of the environmental application of reduction by  $\text{Fe}^0$  have focused on remediation of water contaminated with chlorinated solvents<sup>5</sup>. Now, there is a substantial body of literature on the potential for using  $\text{Fe}^0$  to treat materials contaminated with chlorinated aromatic compounds<sup>6</sup>, nitro aromatic compounds<sup>7,8</sup>, nitrate<sup>9</sup>, pesticides<sup>10,11</sup>. Dyes are another category of complex chemicals that may be labile to reduction by  $\text{Fe}^0$ . The literature available on reduction of dyes by  $\text{Fe}^0$  is scanty. However, the reduction of only few azo dyes using  $\text{Fe}^0$  has been reported<sup>12</sup>. Therefore, we have under taken the study of kinetics of reduction of aniline blue ( $\text{AB}^+$ ) by zero-valent iron. Zero-valent iron is current metal of choice because it is readily available, non-toxic, inexpensive and good reducing agent<sup>3</sup>. Aniline blue belongs to triphenylmethane class of dye and is water soluble dye. It is used for dyeing wool and cotton directly<sup>10</sup>. Due to its stability, it has long residence time in water. Thus, the studies of color removal of the dyes are still desirable to keep the environment clean. Therefore in the present work the detailed kinetics of reduction of aniline blue by zero-valent iron has been studied and a probable mechanism is proposed.

## EXPERIMENTAL

Reductive depletion kinetics of aniline blue by zero-valent iron has been studied spectrophotometrically. All chemicals used were of AR grade. All solutions were prepared by dissolving calculated amount of compound in double distilled water. Fine granules (100 mesh) of iron were used. Prior to use iron granules were immersed in 0.1 M HCl for 10 min to remove surface oxides or other contaminants, then washed with double distilled water. Rapid drying to avoid re-oxidation was achieved by rinsing with methanol during suction filtration. Acid washing of the iron results in faster and more reproducible kinetics of dye reduction.

### Kinetic Procedure:

Beer's law was valid for the measurements under experimental conditions. Total initial volume of reaction mixture was always kept 50 mL. Weighed quantities of iron granules were added in reaction system. The aqueous solution of the dye containing granular iron (100 mesh) was constantly stirred. The solution was centrifuged before taking into the cuvette for measuring the absorbance. For the kinetic study Systronics VIS spectrophotometer 106 was used. The course of reaction was monitored by observing the change in absorbance of dye at 600 nm at an intervals of 15 min.

End product was isolated chromatographically. For the identification of end product FTIR and mass spectra (obtained from Regional Research laboratory, Jammu, India) were used.

For product analysis 300 mg of dye and 25 g of 100 mesh Fe<sup>0</sup> granules were mixed and made up to 1000mL using deionised distilled water. After the reaction time of 5 days the organic components were extracted with ether. Preliminary studies were carried by TLC using benzene: ethyl acetate (8:2) mixture as an eluent. A distinct single spot was obtained. The IR spectra of the sample (Fig.1) showed medium band at 3416.96 cm<sup>-1</sup>, may be due to N-H stretching of NH<sub>2</sub>. Absorption band at 1348.92 cm<sup>-1</sup> shows C-H bending vibration of CH<sub>3</sub> groups. The band at 1748.56 cm<sup>-1</sup> is due to aryl overtone. The absorption band at 650.12 cm<sup>-1</sup> and 610.17 cm<sup>-1</sup> shows the presence of aromatic ring. The mass spectra of the sample (Fig.2) show molecular ion peak at m/z 456 and base peak at m/z 59. Other peaks appear at m/z 364, m/z 272, m/z 336, m/z 181, m/z 165, m/z 154, m/z 85 and m/z 60. On the basis of IR and mass spectra the product is diphenyl rosaniline (leuco) base or Aniline white.

## RESULTS AND DISCUSSION

### Effect of Iron oxide layer:

All of the granular iron is coated with a layer of iron oxide, but the thickness will depend on the source and prior handling of the iron. To examine the effect of the iron oxide layer on the kinetics of dye reduction, iron granules were washed with 0.1 M HCl for 10 min. The washed particles were dried to minimize re-oxidation by rinsing with alcohol during suction filtration<sup>5</sup>. Acid washing of iron results in removing surface oxide layer, and provides more reproducible kinetics of dye reduction. The  $k_{obs}$  values were  $1.09 \times 10^{-4} \text{ s}^{-1}$  and  $2.35 \times 10^{-4} \text{ s}^{-1}$  for untreated and HCl washed Fe<sup>0</sup> respectively. The results indicated that HCl washing approximately doubled the  $k_{obs}$  values because of the increase in the surface area of the iron.

### Effect of iron surface area :

To study the effect of change in surface area of iron surface area on the reaction rate, experiments were carried out with different mesh sizes and rate constants were measured for each fraction. The increase in rate constant values with the increase in the mesh size reveals the impact of surface area on the reduction kinetics. The iron particle surface area has been taken from literature<sup>5</sup>. After acid pretreatment, the 100 mesh iron had a specific surface area of

$\sim 0.7\text{m}^2\text{g}^{-1}$  and 300 mesh iron had a specific surface of  $\sim 0.21\text{m}^2\text{g}^{-1}$ . Reduction rate of aniline blue by 100 mesh iron is found to be  $2.35 \times 10^{-4} \text{ s}^{-1}$  and with 300 mesh iron is  $6.95 \times 10^{-4} \text{ s}^{-1}$ .

#### Effect of change in $\text{Fe}^0$ mass:

Reaction rate increases upto a certain  $\text{Fe}^0$  mass (750 mg) then became constant.  $k$  value increases from  $0.75 \times 10^{-4} \text{ s}^{-1}$  (for 100 mg  $\text{Fe}^0$ ) to  $6.66 \times 10^{-4} \text{ s}^{-1}$  (for 750 mg  $\text{Fe}^0$ ) as shown in Table 1. Reaction follows first order behavior up to certain limit and approaches to a zero order behavior. This shows surface site saturation typical for heterogeneous reaction. Initially the reaction rate has been found to be doubled on doubling the mass of iron. This experimental observation that the reduction of dye by  $\text{Fe}^0$  typically obeys the rate law as shown in Eq. (1)

$$\text{Rate} = -d[\text{dye}]/dt = -k[\text{Fe active sites}][\text{dye}] \quad (1)$$

Equation (1) can be simplified into a first order kinetic equation, since the concentration of iron active sites does not vary significantly during the course of the reduction.

$$-d[\text{dye}]/dt = -k_{\text{obs}}[\text{dye}] \quad (2)$$

It should be emphasized that  $k_{\text{obs}}$  is not a true first order rate constant and will depend on the concentration of active sites on the iron metal. Therefore  $k_{\text{obs}}$  should be proportional to the surface area of the iron particles as well as the mass of the iron present. The following relationship exists between  $k_{\text{obs}}$ , the specific surface area of the iron  $a_s$ , the mass concentration of iron  $p_m$  and the specific reaction rate constant  $k_{\text{sa}}$ <sup>14</sup>.

$$k_{\text{obs}} = k_{\text{sa}} a_s p_m \quad (3)$$

Equation (3) shows that  $k_{\text{obs}}$  should be proportional to the mass of iron used. The data reported here are consistent with Eq. (3). With increase in mass of iron from 250 to 500 mg, rate of reaction increased by a factor of 1.8.

#### Effect of change in dye concentration:

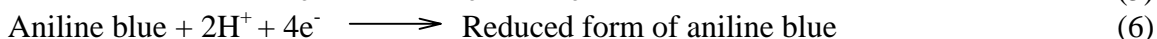
The effect of initial dye concentration on the kinetics of dye reduction was investigated with aniline blue. Reaction rate increases up to a certain concentration and then became constant. Reaction follows first order behavior up to a certain limit ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ) and approaches to a zero order behavior.  $k$  value increases from  $0.58 \times 10^{-4} \text{ s}^{-1}$  ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) to  $2.75 \times 10^{-4} \text{ s}^{-1}$  (for  $5 \times 10^{-5} \text{ mol dm}^{-3}$ ) as shown in Table 2. This shows surface site saturation, typical for heterogeneous reaction. Similar trends have been observed for the reduction of  $\text{CCl}_4$ <sup>14,15</sup> in batch system containing granular  $\text{Fe}^0$ . This system appear to give a transition from pseudo-first order to zero order kinetics with increasing dye concentration, which presumably is due to saturation of reactive surface sites. This site saturation behavior was modeled using formulation analogues to the Michaelis-Menton equation<sup>14</sup>. The model is

$$-\frac{dC}{dt} = \frac{V_m C}{K_{1/2} + C} \quad (4)$$

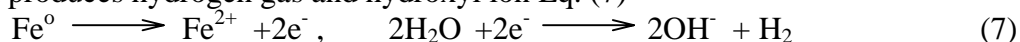
Where  $V_m$  is the maximum reaction rate for a particular experiment and  $K_{1/2}$  ( $C$  at  $V_m/2$ ) reflects the affinity of the metal surface for the organic reactant. It has been shown that  $K_{1/2}$  is roughly constant for a particular substrate because all iron tends to be coated with similar oxides<sup>15</sup> but  $V_m$  varies due to different concentrations of reactive sites<sup>14</sup>.

#### Effect of change in acid concentration:

Reaction rate increases with increase in acid concentration. It is due to the removal of iron-oxide layer.  $k$  value increases from  $9.11 \times 10^{-4} \text{ s}^{-1}$  (for  $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) to  $27.89 \times 10^{-4} \text{ s}^{-1}$  (for  $7 \times 10^{-4} \text{ mol dm}^{-3}$ ) as shown in Fig.3. Accelerated iron corrosion under acidic conditions may be responsible for the enhanced reduction rate<sup>16</sup>. Reduction of aniline blue is a consequence of direct oxidative corrosion of the iron by aniline blue. The reactions can be written as Eq. (5) and (6)



The other reaction that concurrently occurs with Eq. (5) and (6) is the corrosion of zero-valent iron (ZVI), which produces hydrogen gas and hydroxyl ion Eq. (7)



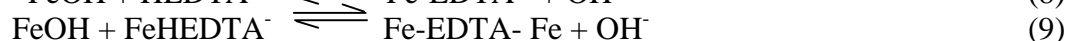
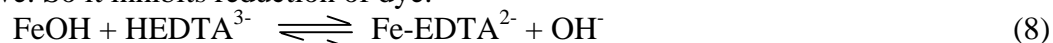
Equation (7) suggests that iron corrosion could have detrimental effect on the reduction of aniline blue as water competes with dye for the electrons from ZVI. At elevated pH, the ferrous and hydroxyl ions form ferrous hydroxide and precipitate. The precipitation of ferrous hydroxide on the surface of ZVI could hinder the transport of the  $\text{AB}^+$  and block the reactive site on ZVI, and decrease the overall reaction rate<sup>17</sup>.

#### Effect of change in NaCl concentration:

Reaction rate increased with increase in concentration of NaCl from  $1 \times 10^{-4}$  to  $8 \times 10^{-5}$  mol dm<sup>-3</sup>. The anions of hard bases such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{2-}$  are especially aggressive towards de-passivating oxides, because they diffuse readily into the film and form strong complexes with iron center. Chloride is of particular interest because it is the most abundant halide in groundwater. As chloride concentration increases from  $1 \times 10^{-4}$  to  $8 \times 10^{-4}$  mol dm<sup>-3</sup>, the k values increases from  $2.14 \times 10^{-4}$  s<sup>-1</sup> to  $9.07 \times 10^{-4}$  s<sup>-1</sup> respectively. Addition of chloride increases reaction rate by breaking down the oxide film. Chloride ions enhance dissolution of the oxide and often induce pitting<sup>18</sup>.

#### Effect of EDTA Concentration:

Reaction rate has been found to be decreased with the increase in EDTA concentration as shown in Fig.4. EDTA is a redox inactive ligand. The distinctive effect of EDTA can be explained in terms of its ability to form two types of surface complexes. The mononuclear species (Eq. 8) is not redox active. So it inhibits reduction of dye.



However the solution phase complex of Fe(II) - EDTA also adsorbs strongly to the oxide surface and the surface species is likely to retain some to serve as a reduction site for dye. The effect of competition between these two processes on magnetite dissolution was found to vary with the relative abundance of dissolved  $\text{Fe}^{2+}$  versus EDTA. When EDTA is in excess most dissolved  $\text{Fe}^{2+}$  is complexed and some fraction of this competes with uncomplexed EDTA for sites on the metal surface<sup>18</sup>. Increasing EDTA concentration from  $1 \times 10^{-4}$  to  $8 \times 10^{-4}$  mol dm<sup>-3</sup> favors Eq. (8) over Eq.(9) and proportionally decreases the population of surface sites available to react with aniline blue. Hence rate of reaction has been found to be decreased.

#### Effect of change in sodium acetate concentration:

Reaction rate decreased with the increase in the concentration of acetate from  $1 \times 10^{-4}$  to  $8 \times 10^{-4}$  mol dm<sup>-3</sup>. This is due to the passivation of oxide layer which inhibit dissolution of metal oxide. A simple kinetic model for ligand inhibited reduction of dye can be derived, which is analogous to equations that describe inhibition in enzyme kinetics. Assuming that reduction of the substrate, P, involves reversible formation of a precursor complex at the metal surface, P-Fe, followed by rate limiting charge transfer to form products of the reaction (Eq. 4). If the interfering ligand, L, also adsorbs reversibly, forming the surface complex, L<sub>n</sub>-Fe, then there are competing processes.



$k_5$ 

Where  $n$  represents the stoichiometry of  $L$  per blocked reaction site for  $P$  (Eq.11) Adjusting Eq. (1) to reflect competition for the same surface sites by Eq. (11) yields;

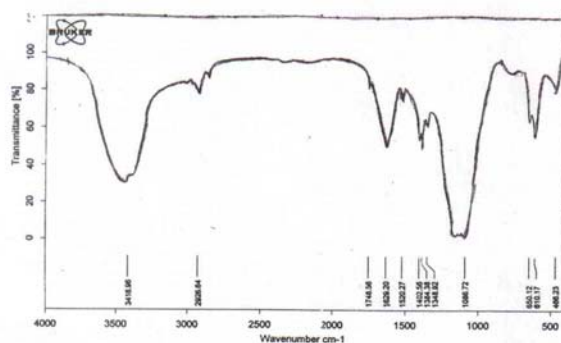
$$-d[P]/dt = V_m[P] / K_{1/2}(1+[L]^n/K_L)+[P] \quad (12)$$

where  $K_L = k_4/k_5$ . If  $L$  interferes by adsorbing to sites other than the surface sites responsible for reduction, then a slightly different model results, where the correction

$1 + [L]^n / K_L$  applies in Eq. (12) rather than just  $K_{1/2}$ . However, at low initial concentrations of  $P$ , pseudo first order conditions apply, and both cases simplify to the same expression<sup>18</sup>.

$$k_{AB^+} = V_m / K_{1/2} / 1 + [L]^n / K_L \quad (13)$$

The steep decline and eventual stabilization of  $k_{dye}$  with increasing acetate concentration was fitted to Eq. (13) by nonlinear regression. Equation 13 suggests that dye forms a weak precursor complex at the oxide-water interface prior to reduction and that this initial step is easily blocked acetate that complex more strongly to the surface.



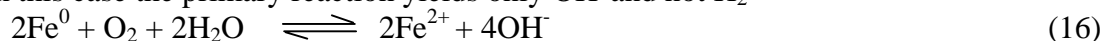
**Fig.1. IR spectra of product of aniline blue**

### Mechanism:

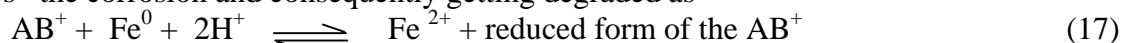
Zero-valent iron,  $Fe^0$  is readily oxidized to ferrous iron,  $Fe^{2+}$ , by many substances<sup>5</sup>. In aqueous systems, this phenomenon leads to dissolution of the solid, which is the primary cause of metal corrosion. It is an electrochemical process in which oxidation of  $Fe^0$  to  $Fe^{2+}$  is the anodic half reaction. The associated cathodic reaction may vary with the reactivity of available electron acceptors. In anoxic pure aqueous media, the acceptors include  $H^+$  and  $H_2O$ , the reduction of which yields  $OH^-$  and  $H_2$ . Thus the overall process of corrosion in anaerobic  $Fe^0 - H_2O$  systems is classically described as shown in Eq. (14) and (15):



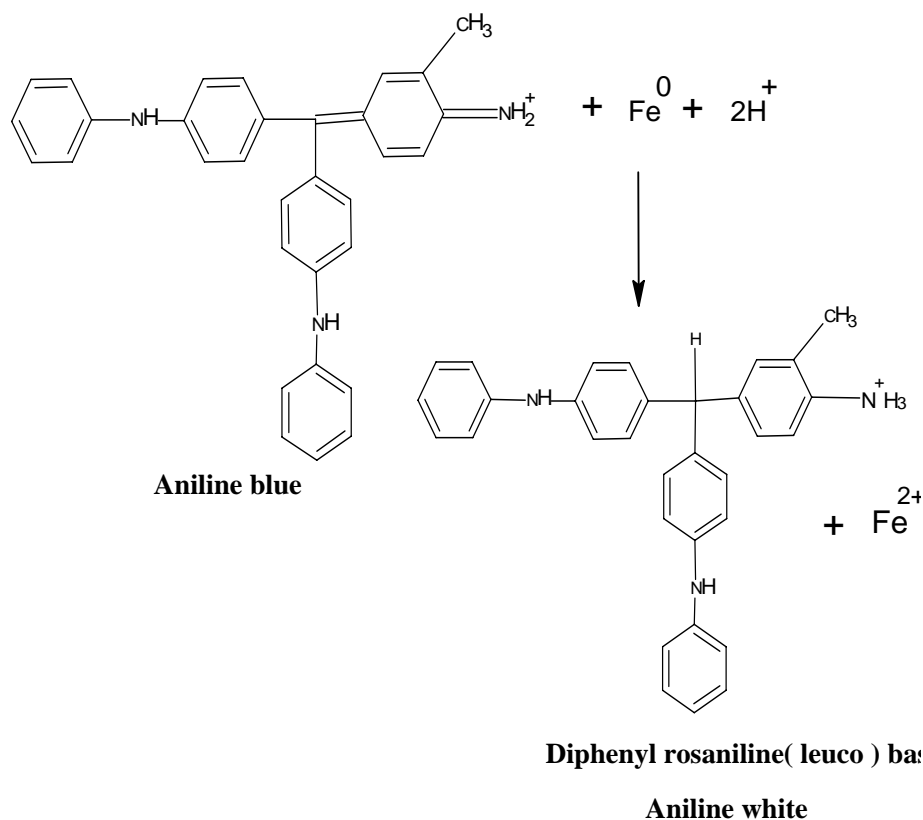
The preferred cathodic half reaction under aerobic conditions involves  $O_2$  as the electron acceptor. In this case the primary reaction yields only  $OH^-$  and not  $H_2$



In the presence of other electron acceptors additional cathodic reactions contribute to iron corrosion<sup>7</sup>. As in the present investigation the aniline blue acts as an electron acceptor, thereby accelerates the corrosion and consequently getting degraded as



Equation (17) contributes to the decolorisation of the Aniline blue by  $Fe^0$  and can be further represented as follows:



### CONCLUSIONS

The proposed method of discoloration of dyes by Fe<sup>0</sup> has been found to quite efficient, fast and cost effective. Since iron is inexpensive, readily available, non-toxic, establishing real projects would not be a costly affair. This method would require very little maintenance after installation. As is evident from the results, the advancements in zero-valent metal reduction have immense potential for treating dye contaminants. Zero-valent metal reduction seems to be a large step in the fight for helping out the water pollution problem.

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**Table 1: Effect of change in mass of Fe<sup>0</sup>**

[AB<sup>+</sup>] = 4.0×10<sup>-5</sup> mol dm<sup>-3</sup>, Fe<sup>0</sup> (100 mesh), Temperature = (298 ± 0.1) K

Fe <sup>0</sup> mass (mg)	k × 10 <sup>4</sup> s
100	0.75
250	2.35
350	2.75
500	4.01
650	5.83
750	6.66
850	7.00
1000	7.08

**Table-2: Effect of change in dye concentration**

Amount of Fe<sup>0</sup> (100 mesh) = 250 mg, Temperature = (298 ± 0.1) K

[Dye] × 10 <sup>5</sup> mol <sup>-1</sup> dm <sup>3</sup>	k × 10 <sup>4</sup> s
1	0.58
2	1.08
3	1.83
4	2.35
5	2.75
6	2.76
7	2.78

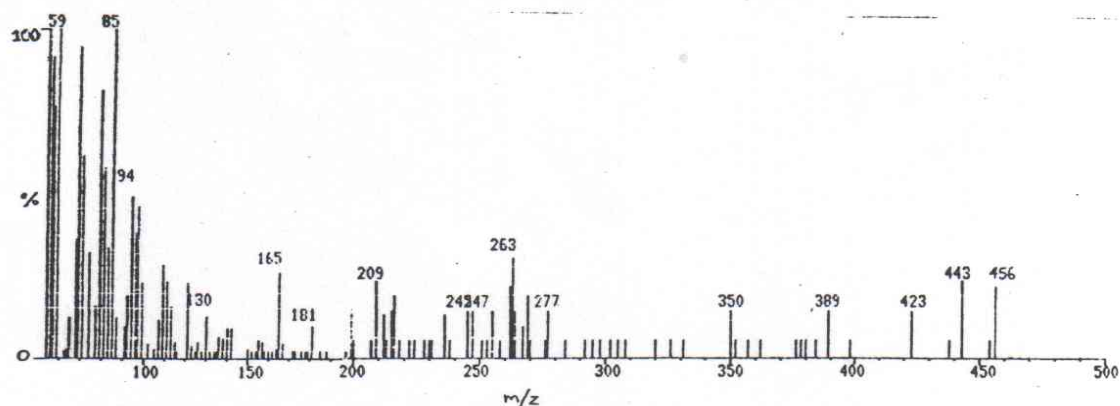


Fig.2. Mass spectra of product of aniline blue

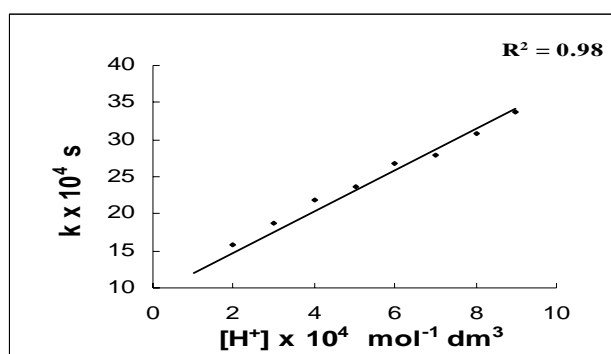


Fig.3. Effect of acid concentration on reduction rate of aniline blue by Fe<sup>0</sup>

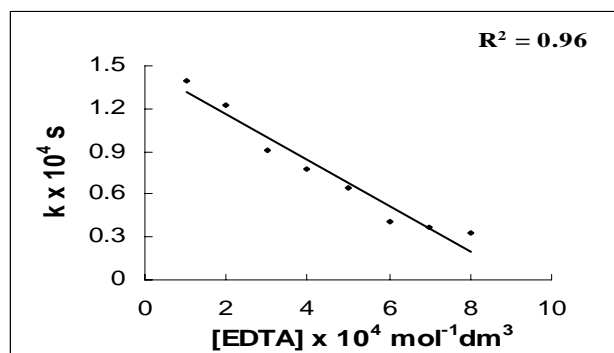


Fig.4. Effect of EDTA concentration on reduction rate of aniline blue by Fe<sup>0</sup>

Legends: Fig: 1. Dye concentration =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>, amount of Fe<sup>0</sup> = 250 mg ;Fig: 2. Dye concentration =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>, amount of Fe<sup>0</sup> = 250 mg

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