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DECOLOURISATION OF REACTIVE BLUE 28 FROM DYE WASTE WATER BY PHOTO FENTON PROCESS AND SONO FENTON PROCESSES

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ABSTRACT

In recent years, textile waste water has become a serious environmental problem due to vast and increasing uses of variety of dyes such as vat dyes, sulfur dyes, napthol dyes, azo dyes and reactive dyes. Among these varieties reactive dyes are extensively used in textile industry in the last years due to their superior performance, but they are environmentally hazardous and difficult to treat effectively. In this study, treatment of Reactive blue 28 (RB 28) was studied using photo Fenton ($UV/H_2O_2/Fe^{2+}$) and sono Fenton ($US/H_2O_2/Fe^{2+}$) processes. The effects of operating parameters such as initial dye concentration, pH, H_2O_2 dosage, Fe^{2+} dosage were studied. So this present study focuses treatment by using the above processes. It is cleared from the studies the expected degradation of photo Fenton is higher than sono Fenton process.

Key words: Reactive blue 28 dye, Photo Fenton ($UV/H_2O_2/Fe^{2+}$), Sono Fenton ($US/ H_2O_2/Fe^{2+}$) process, Initial dye concentration, pH, H_2O_2 dosage, Fe^{2+} dosage.

INTRODUCTION

Dyeing wastewater contain large amounts of dye stuff together with significant amounts of suspended solids, dispersing agents, salts and trace elements. This dyeing waste water can cause serious environmental problems due to their high colour, large amount of suspended solids (SS) and high chemical oxygen demand (COD). Moreover, the composition of waste water from the dyeing and textile processes varies greatly from day to day and hour to hour, depending on the dyestuff type, the fabric type and the concentration of the fixing components, which are added[1].

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In recent years, pollution from dye waste water has become a serious environmental problem due to vast and increasing use of variety of dyes. The dyes usually have a synthetic origin & typically have complex aromatic structures that are more stable and difficult to degrade. The textile, paper and cosmetics industries releases a large amount of effluents includes dyes, which are toxic and can cause serious ecological problems. Therefore, dye in pollution water such as discharge effluent into streams and ground water becomes major environmental problem. Because of toxicity and persistency of dyes, their removal from textile waste water has become an issue of interest during last few years[1-3].

Textile industries consume two thirds of 10,000 different types of pigments produced annually. One of the major bottlenecks in the textile industry is dye fixation. Although dye fixation depends upon the class of dye, type of fabric and other dyeing parameters, nearly 10% of dye is usually discharged into effluent as a result of this process. The disposal of toxic contents such as dyes and phenol compounds which are harmful to environment and difficult to degrade by natural means.

The main mechanism is oxidation of the dye and subsequent degradation of its fragments from $^{\bullet}OH$, a process that occurs mainly on the surface of semiconductor particles. The second mechanism involves possible excitation of the dye, reaction with a surface hole. Most studies deal with the degradation of dyes under different working conditions and are focused. On the factors that influence there action rate, but little information is provided on kinetic modeling based on mechanistic steps and including radiation absorption effects. Also, information concerning the evolution of toxicity and biodegradability of the treated samples is scarce. The uses of AOPs as a pre-treatment step to enhance the biodegradability of waste water scan significantly reduces operation accost and increase the efficiency of the overall process.

Therefore, determining the biodegradability and toxicity of intermediate species is critical point in evaluating the possibility of photocatalysis is to been employed as a pre-treatment process. Such as dyes has been recently developed. But are often very costly methods, ineffective for complete degradation of some recalcitrant organic dyes or only transfer the contaminant from one phase to another in some cases. Photocatalytic oxidation process based on UV-radiated TiO_2 is a highly effective method for the degradation and mineralization of priority pollutants like pesticides, fungicides, herbicides, dyes, chloral phenol, organic acids but also microorganisms in water and wastewater. Several books and reviews have been devoted to this problem and many publications deals with photocatalytic degradation of dyes[4-7].

EXPERIMENTAL

Materials and methods

Commercially available reactive dye i.e. Reactive blue 28 was selected for this study. Dye, ferrous sulphate heptahydrate and hydrogen peroxide (30% w/v, Indian Research Products) were purchased from local market. The pH of dye solution was adjusted by using 0.1 N H_2SO_4 and 0.1 N Na_2CO_3.

Preparation of solutions

Preparation of dye solution

1 g of dye powder (Reactive Blue 28) was taken and it can be dissolved in a 1 L of distilled water in a standard measuring flask (SMF). This solution is known as stock solution. Further the other concentrations are prepared from this stock solution.

Preparation of H_2O_2 solution

Different concentrations of H_2O_2 are freshly prepared (5, 10, 20, 30, 40 mM). The concentrations of H_2O_2 are large excess in comparison to dye solutions, so that H_2O_2 concentration can be considered constant during whole experiments.

Preparation of Fe^{2+} solution

Different concentrations of Fe^{2+} freshly prepared (0.05, 0.1, 0.15, 0.2, 0.25 mM) as using $FeSO_4.7H_2O$.

Photo reactor and light source

Photocatalytic process was performed in a 1.2 L cylindrical glass reactor. UV radiation was provided by UV-lamp of (11 watts, 254 nm, 1000 lux) placed in a quartz glass.

A Pyrex cylindrical jacket located around the plugging tube contained circulating water to oxidation reagent evolved during the reaction, as specifications as follows, volume of the reactor is 1.39 L, inner height is 245 mm, outer height is 265 mm, inner diameter is 85 mm, and outer diameter is 105 mm and jacket is15 mm.

Sono chemical reactor

Sono Fenton experiments are carried out in sono chemical reactor as in the specifications of, Type OU MINI 120, Power output of 120 W, Frequency is 34 KHZ, Water bath Size is 200X 150X 125 mm and Capacity is 3.5 L.

Determination of λ_{max}

The λ_{max} value is calculated by using UV-visible spectrometer. The raw dye solution is analysed by UV-visible spectrometer. It shows wavelength of 572 nm. So we selected the maximum wavelength of 572 nm, for our analysis because the intensity of colour is high at high wavelength.

Experimental procedure

Photo Fenton and Sono Fenton process

The experiments were carried out in a 1L batch type reactor. H_2O_2 and Fe^{2+} are acted as oxidizing agent and UV light as illuminating light source. These experiments were carried out at room temperature in a 1L reactor using varying pH values at constant H_2O_2 and Fe^{2+} dosages, Dye concentration in order to determine the optimum pH value for best % decolourisation. The reaction time was recorded when the H_2O_2 solution was added, for photo Fenton process. It is recorded when the UV lamp is turned on and the sono Fenton process will be carried out in a 1L sono reactor.

The concentrations of dye in the reactions mixture at different time intervals (2 min) were obtained by measuring the λ_{max} (572 nm) of dye and computing the concentration from a calibration curve and then find at the % decolourisation. The remaining experiments will be repeated by varying pH, H_2O_2 concentration, Fe^{2+} concentration and dye concentration to determine the % decolourisation then to find out the optimum values for these experiments using rate constant analysis method.

RESULTS AND DISCUSSION

The dye solution was prepared different dilution and their absorbance was found by using UV-Visible spectrometer. The experiment was conducted by changing different parameters. They are, initial dye concentration, pH of the solution, H_2O_2 dosage and Fe^{2+} dosage. Then the % decolourisation is as follows:

$$\% \text{ Color removal} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100$$

In this study**,** the effect of various parameters on colour removal was investigated as follows:

- Photo Fenton process
- Sono Fenton process

Photo Fenton process

Effect of pH

The effect of pH on the decolourisation of reactive blue 28 dye by photo Fenton process is shown in Fig. 1. This Fig. 1 shows that pH significantly influence the conversion of reactive blue 28 dye. The experiment was carried out at pH 2 to 6. At low pH 2, we have a very low decolourisation. By increasing the pH 2 to 3, we can obtain the highest decolourisation, 93.9% at 12 min. However at pH > 3, the decolourisation decreased with increasing pH from 4 to 6. The decrease is probably due to the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH ranges[8].

Table 1: Effect of pH on photo Fenton process

S. No.	Time (min)	% Decolourisation				
		pH 2	pH 3	pH 4	pH 5	pH 6
1	0	0	0	0	0	0
2	2	0.4	72.67	64.78	48.61	15.22
3	4	1.06	78.72	67.22	54.50	20.11
4	6	5.97	82.78	69.28	58.93	30.28
5	8	15.70	85.88	72.79	60.06	39.83
6	10	34.00	89.88	74.56	64.83	44.67
7	12	59.11	91.90	82.70	68.78	49.50

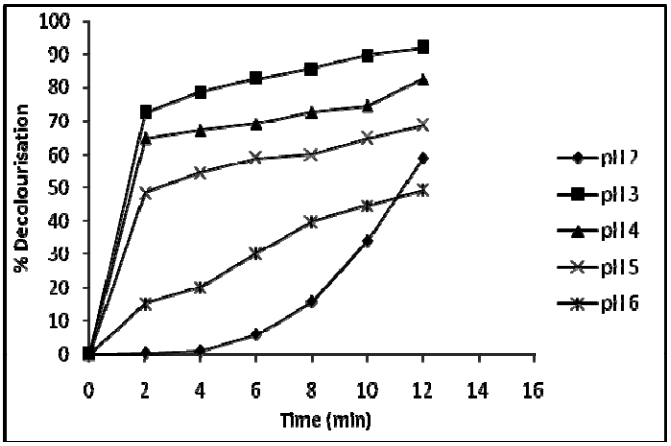

Fig. 1: Effect of pH on photo Fenton process (Conditions: Initial dye concentration: 200 mg/L, H_2O_2 dosage: 10 mM, Fe^{2+} dosage: 0.1 mM)

The effect of initial dye concentration, of aqueous solution of reactive blue 28 dye on the photo Fenton process was investigated, since pollutant concentration, is an important parameter in waste water treatment. The influence of the concentration is shown in Fig 2. It is possible to see that the extent of decolourisation decreases with the increase in the initial dye concentration. Increase of dye from 100-500 mg/L decreases the decolourisation from 97.89% to 87.62% for photo Fenton process. The increase in dye concentration increases the number of dye molecules and not the HO radicals' concentration and so the removal rate decreases[8,9].

Table 2: Effect of initial dye concentration on photo Fenton process

S. No.	Time (min)	% Decolourisation				
		Initial dye concentration				
		100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
1	0	0	0	0	0	0
2	2	84.33	86.90	84.22	75.56	69.53
3	4	87.88	89.83	86.93	81.36	73.07
4	6	89.90	94.39	84.05	83.94	79.04
5	8	93.96	96.17	89.07	87.56	83.09
6	10	95.78	97.56	90.63	89.28	85.36
7	12	97.89	99.08	92.96	90.67	87.62

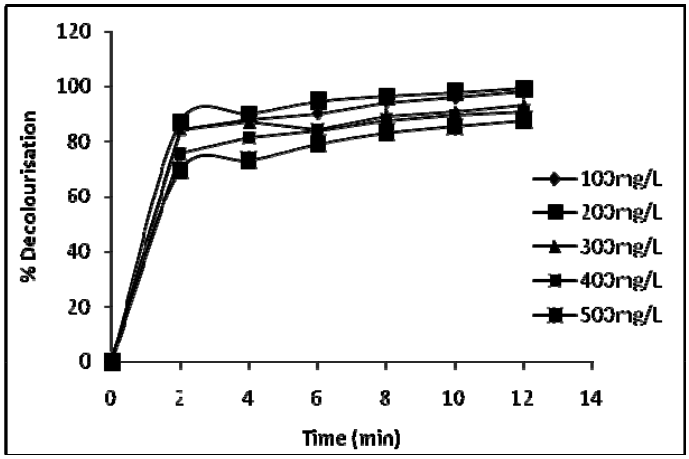

Fig. 2: Effect of initial dye concentration on photo Fenton process (Conditions: pH: 3, H_2O_2 dosage: 10 mM, Fe^{2+} dosage: 0.1 mM)

Effect of H_2O_2 dosage

Dosage of H_2O_2 plays an important role in photo Fenton process. The effect of addition of H_2O_2 (5, 10, 20, 30, 40 mM) on the decolourisation of Reactive Blue 28 dye is shown in Fig 3. In photo Fenton process, the addition of H_2O_2 from 5, 10, 20 mM is increases the decolourisation. Further increase from 30, 40 mM causes no significant change in decolourisation.

Table 3: Effect of H_2O_2 dosage on photo Fenton process

S. No.	Time (min)	%Decolourisation				
		Dosage of H_2O_2				
		5 mM	10 mM	20 mM	30 mM	40 mM
1	0	0	0	0	0	0
2	2	65.83	88.67	89.17	90.44	80.78
3	4	73.94	90.70	91.61	92.56	85.33
4	6	78.33	93.72	92.72	93.00	88.44
5	8	89.06	97.78	93.11	93.28	90.17
6	10	93.33	98.89	94.67	94.33	93.78
7	12	95.80	99.94	96.83	95.50	94.89

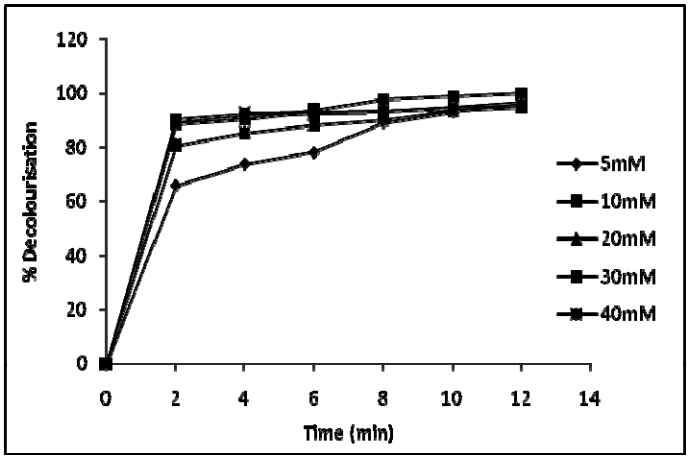

Fig. 3: Effect of H_2O_2 dosage on photo Fenton process (Conditions: pH: 3, Initial dye concentration: 200 mg/L, Fe^{2+} dosage: 0.1 mM)

This little increase is due to the fact that at a highest H_2O_2 dosage scavenging of OH radicals will occur, which can be expressed by the equation. This increase in the decolourisation is due to the increase in hydroxyl radical concentration by addition of H_2O_2. Hence 10 mM of H_2O_2 appears as an optimum H_2O_2 dosage for photo Fenton process[8-10].

$$HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$$

Effect of Fe^{2+} dosage

The effect of addition of Fe^{2+} ion on the decolourisation of reactive blue 28 dye has been studied. The results are shown in Fig 4. The amount of ferrous is one of the main parameter influencing the photo Fenton process. The results indicate that the extent of decolourisation increases with the increase in Fe^{2+} dosage. Photo Fenton process, addition of Fe^{2+} from 0.05 mM to 0.25 Mm increases colour removal from 96.11% to 99.89% at 12 min. From the result, it is possible to say that the efficiency of the reactive blue 28 dye destruction increases wide increasing initial Fe^{2+} dosage.

It may be explained by the redox reaction since HO radicals may be scavenged by the reaction with H_2O_2 or with another Fe^{2+} molecule as low. The lower decolourisation capacity of Fe^{2+} at small concentration is probably due to the lowest HO radicals' production available for oxidation. Fe^{2+} of 0.1 mM can be used as an optimum dosage for this process[8,9,11].

Table 4: Effect of Fe^{2+} dosage on photo Fenton process

S. No.	Time (min)	% Decolourisation				
		Dosage of Fe^{2+}				
		0.05 mM	0.1 mM	0.15 mM	0.20 mM	0.25 mM
1	0	0	0	0	0	0
2	2	75.67	78.68	79.80	80.09	78.70
3	4	80.22	87.51	87.83	89.33	80.61
4	6	84.78	89.72	90.39	91.17	85.33
5	8	90.60	94.78	95.17	94.56	89.97
6	10	93.39	97.89	97.56	96.78	91.90
7	12	96.11	98.86	99.08	99.89	99.89

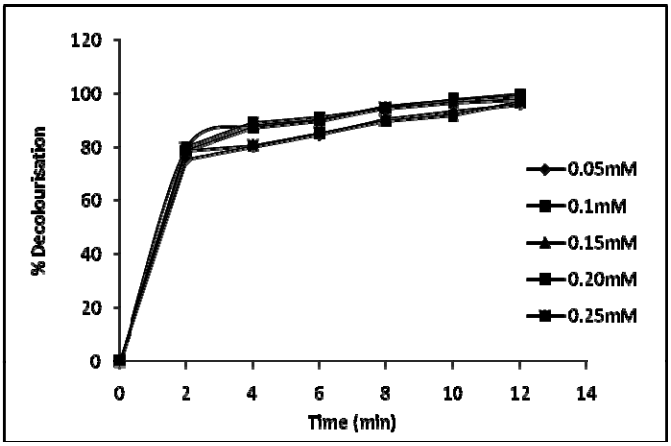

Fig. 4: Effect of Fe^{2+} dosage on photo Fenton process (Conditions: pH: 3, Initial dye concentration: 100 mg/L, H_2O_2 dosage: 10 mM)

Sono Fenton process

Effect of pH

The effect of pH on the decolourisation of reactive blue 28 dye by sono Fenton process is shown in Fig. 5. This Fig. 5 shows that pH significantly influence the conversion of reactive blue 28 dye. The experiment was carried out at pH 2 to 6. At low pH 2, we have a very low decolourisation. By increasing the pH 2 to 3, we can obtain the highest decolourisation, 90.92% at 12 min. However at pH > 3, the decolourisation decreased with increasing pH from 4 to 6. The decrease is probably due to the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH ranges[7,12,13].

Table 5: Effect of pH on sono Fenton process

S. No.	Time (min)	% Decolourisation				
		pH 2	pH 3	pH 4	pH 5	pH 6
1	0	0	0	0	0	0
2	2	0	67.67	64.22	38.61	11.22
3	4	0.008	70.72	67.22	47.80	17.11
4	6	0.90	74.78	70.28	53.83	25.28
5	8	3.34	80.82	75.39	59.06	32.83
6	10	9.68	84.88	79.56	65.83	45.67
7	12	17.11	90.92	83.72	68.78	53.50

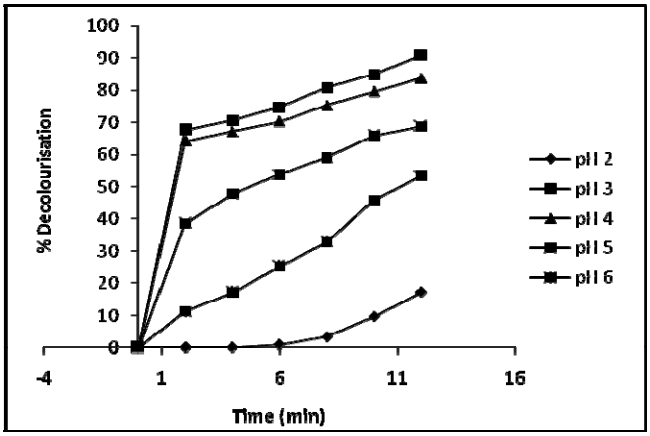

Fig. 5: Effect of pH on sono Fenton process (Conditions: Initial dye concentration: 200 mg/L, H_2O_2 dosage: 10 mM, Fe^{2+} dosage: 0.1 mM)

Effect of initial dye concentration

The effect of initial dye concentration, of aqueous solution of reactive blue 28 dye on the sono Fenton process was investigated, since pollutant concentration, is an important parameter in waste water treatment. The influence of the concentration is shown in Fig. 6. It is possible to see that the extent of decolourisation decreases with the increase in the initial dye concentration. Increase of dye from 100-500 mg/L decreases the decolourisation from 90.08% to 77.62% for sono Fenton process. The increase in dye concentration increases the number of dye molecules and not the HO radicals' concentration and so the removal rate decreases[7,12,13].

Table 6: Effect of initial dye concentration on sono Fenton process

S. No.	Time (min)	% Decolourisation				
		Initial dye concentration				
		100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
1	0	0	0	0	0	0
2	2	62.09	76.17	68.22	65.56	60.53
3	4	70.00	80.83	73.98	67.36	63.07
4	6	79.09	86.39	77.85	69.84	65.04
5	8	86.00	88.17	85.07	77.56	70.09
6	10	89.98	90.56	87.63	78.28	73.36
7	12	90.08	93.78	88.96	80.67	77.62

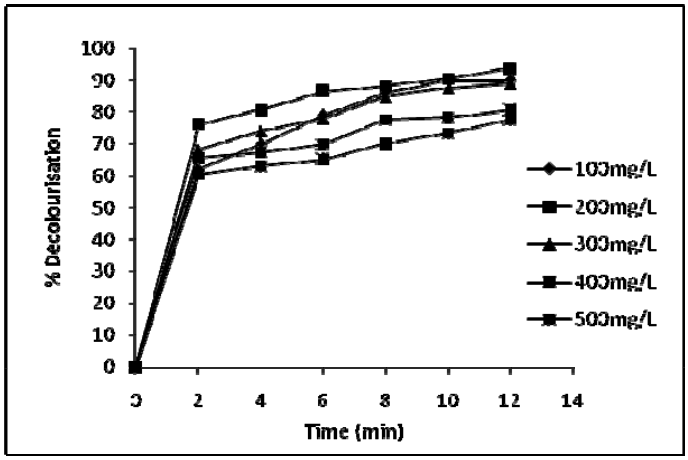

Fig. 6: Effect of initial dye concentration on sono Fenton process (Conditions: pH: 3, H_2O_2 dosage: 10 mM, Fe^{2+} dosage: 0.1 mM)

Effect of H_2O_2 dosage

Dosage of H_2O_2 plays an important role in Sono Fenton process. The effect of addition of H_2O_2 (5, 10, 20, 30, 40 mM) on the decolourisation of reactive blue 28 dye is shown in Fig 7. In sono Fenton process, the addition of H_2O_2 from 5, 10, 20 mM is increases the decolourisation. Further increase from 30, 40 mM causes no significant change in decolourisation.

Table 7: Effect of H_2O_2 dosage on sono Fenton process

S. No.	Time (min)	% Decolourisation				
		Dosage of H_2O_2				
		5 mM	10 mM	20 mM	30 mM	40 mM
1	0	0	0	0	0	0
2	2	45.83	57.67	59.17	67.44	77.78
3	4	53.94	65.70	70.61	73.56	80.39
4	6	68.33	72.72	75.72	76.00	85.40
5	8	74.06	78.78	79.11	78.28	87.17
6	10	79.33	82.89	80.67	81.33	88.78
7	12	84.78	90.94	87.83	86.50	89.89

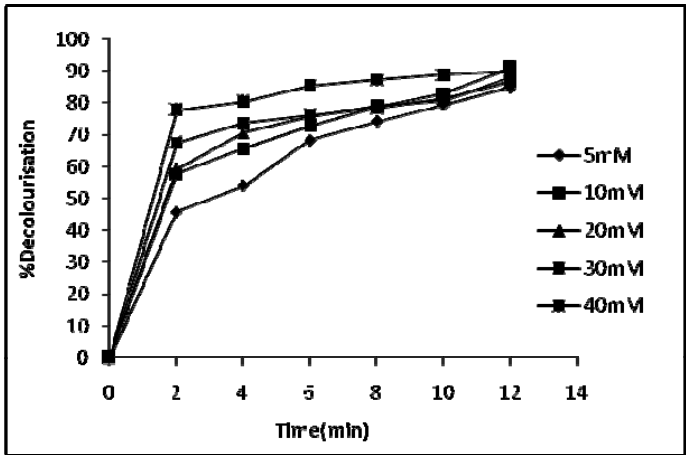

Fig.7: Effect of H_2O_2 dosage on sono Fenton process (Conditions: pH: 3, Initial dye concentration: 200 mg/L, Fe^{2+} dosage: 0.1 mM)

This little increase is due to the fact that at a highest H_2O_2 dosage scavenging of OH radicals will occur, which can be expressed by the equation, this increase in the decolourisation is due to the increase in hydroxyl radical concentration by addition of H_2O_2. Hence 10 mM of H_2O_2 appears as an optimum H_2O_2 dosage for sono Fenton process[14].

$$HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$$

Effect of Fe^{2+} dosage

The effect of addition of Fe^{2+} ion on the decolourisation of reactive blue 28 dye has been studied. The results are shown in Fig. 8. The amount of ferrous is one of the main parameter influencing the sono Fenton process. The results indicate that the extent of decolourisation increases with the increase in Fe^{2+}dosage. Sono Fenton process, addition of Fe^{2+} from 0.05 mM to 0.25 Mm increases colour removal from 83.11% to 95.00% at 12 min. From the result, it is possible to say that the efficiency of the reactive blue 28 dye destruction increases wide increasing initial Fe^{2+}dosage[7,13].

It may be explained by the redox reaction since HO radicals may be scavenged by the reaction with H_2O_2 or with another Fe^{2+} molecule as low. The lower decolourisation capacity of Fe^{2+} at small concentration is probably due to the lowest HO radicals' production available for oxidation. Fe^{2+} of 0.1 mM can be used as an optimum dosage for this process[13,14].

Table 8: Effect of Fe^{2+} dosage on sono Fenton process

S. No.	Time (min)	% Decolourisation				
		Dosage of Fe^{2+}				
		0.05 mM	0.1 mM	0.15 mM	0.20 mM	0.25 mM
1	0	0	0	0	0	0
2	2	46.00	57.89	62.19	66.73	67.50
3	4	56.20	69.51	76.83	78.90	75.61
4	6	67.88	79.72	81.39	83.17	80.33
5	8	74.22	89.88	86.17	85.56	84.67
6	10	78.33	92.89	90.56	88.78	87.54
7	12	83.11	94.94	93.78	94.89	95.00

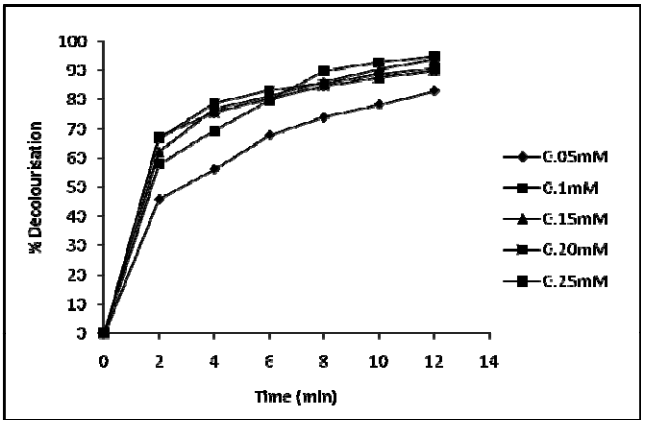

Fig. 8: Effect of Fe^{2+} dosage on sono Fenton process (Conditions: pH: 3, Initial dye concentration: 100 mg/L, H_2O_2 dosage: 10 mM)

CONCLUSION

After comparing photo Fenton and sono Fenton process, following results are obtained as –

- At pH 3, decolourisation is high in both process. But comparing these processes photo Fenton is best for decolourisation of dye.
- In photo Fenton process the addition of H_2O_2 from 5 mM to 40 mM increases the decolourisation from 65.83% to 94.89% at 12 min and for sono Fenton process as 45.83% to 89.89% at same time.

- In photo Fenton process the addition of Fe^{2+} from 0.05 to o.25 mM increases the decolourisation from 75.67% to 99.8% at 12 min and sono Fenton process as 46% to 95% at same time.

Thus, the results states that, the decolourisation of reactive blue 28 was affected by the pH of the solution, initial dye concentration, H_2O_2 dosage and Fe^{2+} dosage. Photo Fenton showed higher efficiency than sono Fenton process.

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