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Impact of Ferric Chloride and Fenton Reagent on Photocatalytic Decoloration of Azure B dye.

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Abstract : The present paper deals with the Study of Photocatalytic degradation of Azure B dye in aqueous suspension of TiO_2 Particles. Photocatalytic degradation of Azure B dye have been studied with the help of variety of parameters which are Effect of $Fecl_3$ and Fenton Reagent. The effect of $Fecl_3$ and Fenton Reagent on the rate of degradation was investigated. Result demonstrated that TiO_2 in the presence of visible irradiation can effectively degrade Azure B dye. The addition of $Fecl_3$ and Fenton regents had an important influence on the processes of the photocatalytic degradation of the dye.

Keywords : Degradation, Azure B, $Fecl_3$, Fenton Reagents, Visible, TiO_2.

Introduction - Interest in the application of titanium oxide in different fields has increased rapidly in recent years. Photocatalytic processes, Which had been reported as the pioneering work for the first time in 1972. [1] Purification of wastewater contaminated with these pollutants is very difficult since they are resistant to conventional treatment techniques. Advances oxidation processes are based on the production of highly reactive hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non selectively.[2] The mechanism of the photo assisted degradation of dyes under visible radiation follows different pathway compared to UV radiation. Electrons of dyes are exited by visible light to singlet and triplet states followed by electron injection from the exited dye to the conduction band of the catalyst TiO_2, Which plays as an electron transfer mediator. The cation radicals of the dye are formed and the transferred electron to TiO_2 band reacts with the Pre adsorbed O_2 from with the air to from oxidizing radical species like O_2 and OH radicals which start photoxidation of the dye. [3] Advanced oxidation method allows the complete degradation of organic pollutants to CO_2 and inorganic acids.

Experimental: Azure B was obtained from Loba Chemie. Photo catalyst TiO_2 was obtained from the S.D. Fine Company. All Solutions were prepared in doubly distilled water. Photo catalytic experiments were carried out with 50 ml of dye solution (3.8x10-5 mol dm-3) using 300mg of TiO_2 photo catalytic under exposure to visible irradiation in specially designed double-walled slurry type batch reactor vessel made up of Pyrex glass (7.5 cm height, 6 cm diameter) surrounded by thermostatic water circulation arrangement to keep the temperature in the range of 30±0.3.c. Irradiation was carried out using 500 w halogen lamp surrounded by aluminum reflector to avoid irradiation loss. During photo catalytic experiments after stirring for 10 min slurry composed of dye solution and catalyst was placed in dark for ½h in order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on photo catalyst surface. Then slurry containing aqueous dye solution and TiO_2 was stirred magnetically to ensure complete suspension of catalyst particle while exposing to visible light. At specific time intervals aliquot (3ml) was withdrawn and centrifuges for 2 min at 3500 rpm to remove TiO_2 particle from aliquot to assess extent of decolourisation photo metrically. Changes in absorption spectra were recorded at 480 nm on double beam UV-Vis, spectrophotometer (Systronic Model No. 166) Intensity of visible radiation was measured by a digital luxmeter (Lutron LX 101). pH of solution was measured using a digital pH meter.

Results and Discussion:

Effect of $FeCl_3$: The addition of $FeCl_3$ had an important influence on the processes of the photocatalytic decoloration of the dye. Catalytic influence of Fe^{3+} ions on the decoloration of dye depend on the concentration of $FeCl_3$, the applied amount of TiO_2 and on the initial concentration of the dye in the solutions. We have studied the effect of $FeCl_3$ on the photodegradation of Azure B by varying the concentration from 2.0×10^{-6} mol dm^{-3} to 14.0×10^{-6} mol dm^{-3}. In TiO_2 / $FeCl_3$ / Vis addition of $FeCl_3$ caused an increase in rate constant (5.64×10^{-4} s^{-1}), up to concentration 8×10^{-5} mol dm^{-3}. Fe^{3+} behaves as an electron scavenger thus preventing the recombination of electron-hole pairs. The above two reactions led to increase the

amount of OH and H_2O_2 thus improving the efficiency of the photocatalytic process. When Fe^{3+} concentration is in excess of 10×10^{-5} mol dm^{-3}, the photodegradation efficiency decreased gradually due to the deposition of Fe^{3+} ions on the semiconductor particles. Active sites of the catalyst are covered with Fe^{3+} ion and hence the photon absorption by the catalyst decreased (4).

$Fe^{3+} + hv \rightarrow Fe^{2+} + {}^{\bullet}OH$ (1)

$Fe(OH)_2 + hv \rightarrow Fe^{2+} + {}^{\bullet}OH$ (2)

$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O$ (3)

$Fe^{2+} + HO^{\bullet}_2 + H^+ \rightarrow Fe^{3+} + H_2O_2$ (4)

Photoactivation of surface adsorbed complex ion (Fe^{3+} OH^-) resulted into Fe^{2+} OH species, which consequently injected electrons to conduction band of TiO_2. Increased rate of degradation in case of $FeCl_3$ is due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydro peroxide radicals. Higher concentration of $FeCl_3$ eliminated adsorption of cationic dye on TiO_2 surface and also inhibited reaction rate by reducing production of hydroxyl radicals (5).

$AB + hv\ visible \rightarrow {}^1AB^*$ or $^3AB^*$ (5)

$$1AB^* \text{ or } 3AB^* + TiO_2(Fe^{3+}\ OH^-) \xrightarrow{h\nu} TiO_2(Fe^{2+}\bullet OH) + AB^+. \quad (6)$$

$$TiO_2(Fe^{2+}\bullet OH) + H_2O_2 \rightarrow TiO_2(e^-\ CB) + TiO_2(Fe^{3+}\bullet OH) \quad (7)$$

$$TiO_2(e^-\ CB) + O_2 \xrightarrow{H^+} O^-_2 \rightarrow HO_2 \quad (8)$$

$AB/AB^+. + \bullet OH / O^-_2 / HO_2 \rightarrow$ Degradation products (9)

Table 1 Effect of $FeCl_3$: [AB] = 3.0×10^{-5} mol dm^{-3}, TiO_2 = 200 mg/100 mL
pH = 9.0, Light intensity = 25×10^3 lux, Temperature = 30 ± 0.3°C.

$FeCl_3 \times 10^5$ mol dm^3	$k \times 10^{-4}$ s^{-1}	$t_{1/2} \times 10^3$ s
0.0	4.10	1.69
2.0	4.30	1.61
4.0	4.60	*1.50*
6.0	4.99	1.38
8.0	5.64	1.22
10.0	4.50	1.54
12.0	2.95	2.34
14.0	2.30	3.01

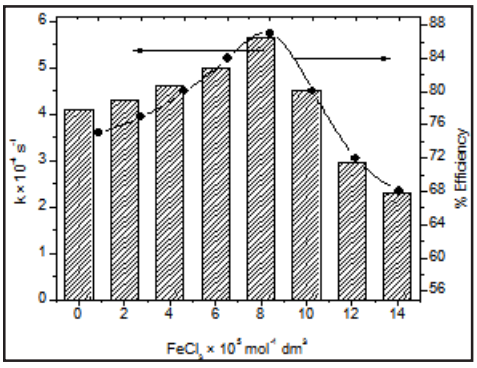

Fig.1 : Effect of $FeCl_3$

Effect of Fenton reagent: The mixture of ferrous ion and hydrogen peroxide is called Fenton reagent. It is known for oxidizing many organic compounds. Fenton system provides an economical approach in treatment of dye pollutants and played important roles in the degradation of dyes. Fenton's reagent is an attractive treatment for the effective decolorization and degradation of dyes because of its low cost, the lack of toxicity of the reagents (i.e. Fe^{2+} and H_2O_2) the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology (6). The Fenton system uses ferrous ion to react with hydrogen peroxide, producing hydroxyll radicals with powerful oxidizing ability to degrade organic pollutants. During reaction, ferric ions are formed which can be reacted to produce ferrous ions. The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction. Efficiency of Fe^{3+} / H_2O_2 system has been studied for decolorization of Azure B in the presence of TiO_2 and visible light irradiation. The results are shown in Table 2 and plotted in Fig.2. Rate constant has a value of 4.83 × 10-4 s-1 on the addition of (Fe^{3+} : H_2O_2) in molar ratio (3:1). In the presence of (Fe^{3+} : H_2O_2) in molar ratio (1.4:1), rate constant has been found 4.0×10-4 s-1. Upon irradiation of Fe^{3+}/ H_2O_2/TiO_2/AB system with visible light, production of •OH radicals involving a very complex mechanism.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$ (1)

${}^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+}$ (2)

$Fe^{3+} + H_2O + hv \rightarrow {}^{\bullet}OH + Fe^{2+} + H^+$ (3)

A dye molecule absorbs visible irradiation and is excited into high energy state. These excited dye molecules reduce the ferric ion complex to ferrous ion complex followed by the transfer to ferric ion. The reduced ferrous ions react with H_2O_2 to decompose and generate •OH hydroxyl radical as a strong oxidizing agent, which attack the dye molecules leading to the decolorization of the solution.

$AB + hv_{visible} \rightarrow {}_1AB^*$ or $_3AB^*$ (4)

$$_1AB^*\text{ or }{}_3AB^* + TiO_2(Fe^{3+}OH^-) \xrightarrow{h\nu} TiO_2(Fe^{2+}\bullet OH) + AB^{+\cdot} \quad (5)$$

$TiO_2(Fe^{2+}\bullet OH) + H_2O_2 \rightarrow TiO_2(Fe^{3+}\bullet OH) + OH^- + {}^{\bullet}OH$ (6)

$TiO_2(Fe^{3+}\bullet OH) + H_2O_2 \rightarrow TiO_2(Fe^{2+}\bullet OH) + HO^{\bullet}_2 + H^+$ (7)

$TiO_2(Fe^{2+}\bullet OH) \rightarrow TiO_2(Fe^{3+}\bullet OH) + TiO_2(e^-_{CB})$ (8)

$$TiO_2(e^-_{CB}) + O_2 \xrightarrow{H^+} O^{\bullet-}_2 \rightarrow HO^{\bullet}_2 \quad (9)$$

$H_2O_2 + O^{\bullet-}_2 \rightarrow {}^{\bullet}OH + OH^- + O_2$ (10)

$H_2O_2 + TiO_2(e^-_{CB}) \rightarrow {}^{\bullet}OH + OH^-$ (11)

${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO^{\bullet}_2$ (12)

$AB/AB^{+\bullet} + {}^{\bullet}OH/O^{\bullet-}_2/HO^{\bullet}_2 \rightarrow$ Degradation products (13)

Table 2 Effect of Fe^{3+} / H_2O_2: [AB] = 3.0×10^{-5} mol dm^{-3}, pH = 9.0
TiO_2 = 200 mg/100 mL, Light intensity = 25×10^3 lux, Temperature = 30 ± 0.3 °C.

$Fe^{3+}:H_2O_2$	With TiO_2		Without TiO_2	
	$k\times10^{-4}\ s^{-1}$	$t_{1/2}\times10^{3}s^{-1}$	$k\times10^{-4}\ s^{-1}$	$t_{1/2}\times10^{3}\ s^{-1}$
3:1	4.83	1.43	1.74	3.98
1.4:1	4.00	1.73	2.15	3.22
1:1.4	8.86	0.78	2.32	2.98
1:3	6.14	1.12	2.49	2.78
11:1	3.41	2.03	2.68	2.58

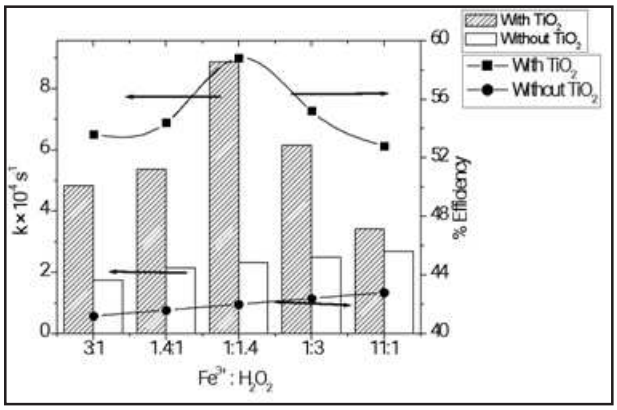

Fig.2 : Effect of Fenton reagent

Conclusion: The addition of $FeCl_3$ had an important influence on the processes of the photocatalytic decoloration of the dye. Catalytic influence of Fe^{3+} ions on the decoloration of dye depend on the concentration of $FeCl_3$, the applied amount of TiO_2 and on the initial concentration of the dye in the solutions. TiO_2 mediated degradation of dyes in combination with Fenton reagent has been found to be an effective treatment technology.

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