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# Degradation of tartrazine dye from aqueous solution by heterogeneous fenton-like reaction on $Fe_2O_3/SiO_2$ composite

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## Abstract

In this study, $Fe_2O_3/SiO_2$ composite was prepared by incipient impregnation method for degradation of tartrazine dye from aqueous solution by heterogeneous Fenton-like process. As-synthesized sample was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and $N_2$ adsorption–desorption isotherm. The results indicated that iron impregnation (7 wt.%) did not significantly change specific area but it leads to a clear change in the porous structure of silica. The effects of different reaction parameters such as initial solution pH, initial $H_2O_2$ concentration, and additive on the degradation of tartrazine were investigated. The optimal reacting conditions were found to be initial solution pH 3.0, the $H_2O_2$ concentration of 12 mM, at a temperature of 30 $^oC$ with a dosage of catalyst 50 mg and an initial dye concentration 50 mg/L. Under optimal condition, 98.5% degradation efficiency of tartrazine was obtained within 80 min of reaction. The as-synthesized $Fe_2O_3/SiO_2$ composite exhibited much better catalytic ability than commercial $Fe_2O_3$, as-synthesized $Fe_2O_3$, physical mixture $Fe_2O_3/SiO_2$ under the same experimental condition. In addition, the effects of NaCl and EDTA in the degradation of dye and reaction mechanism were investigated.

**Keywords.** Heterogeneous fenton, composite, $Fe_2O_3/SiO_2$, tartrazine, degradation.

## 1. INTRODUCTION

The discharge of several hazardous dyes from many textiles industries in waste water is the main cause of serious environmental problems that concerned with human health and the aquatic medium due to the toxicity and the carcinogenic effect of these materials [1]. Therefore, the removal of dyes from wastewater is a challenge to the related industries because of their high solubility in water, complex structure, and synthetic origin. Recently, advanced oxidation processes (AOPs) are promising substitute technologies for efficient elimination of organic pollutants from wastewater with high chemical stability and low biodegradability [2].

AOPs are based on the generation of non-selective $OH^\bullet$ radicals, which one of the most powerful oxidation species to degrade organic compounds into nontoxic products (ideally $CO_2$, $H_2O$) [3]. Homogenceous photo-Fenton is a common AOP, in which soluble iron II is the catalyst but the difficulty of catalyst recovery is a process drawback and tight pH range in which the reaction proceeds [4]. To overcome the disadvantages of the homogeneous Fenton process, some attempts have been made to develop heterogeneous catalysts, prepared by loading iron (III) oxide onto a porous support such as zeolites, clays, silica, activated carbon.

Recently, Fe-containing silica mesoporous has attracted much attention because of their high surface area and uniform pore size distribution. The catalytic activity strongly depends on the iron precursor and its preparation method. In the most previous investigation, iron (III) oxide supported on silica could be obtained via impregnation and sol-gel co-condensation. In general, impregnation could achieve higher loading of Fe on mesoporous support. In addition, the catalysts prepared by impregnation exhibited high efficient of organic dyes treatment and the negligible iron leaching from the catalyst.

The colour additive tartrazine, whose IUPAC name is trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate; CI number 19140; molecular formula $C_{16}H_9N_4Na_3O_9S_2$, molecular weight (534.4 mol/g) was selected as a model of azo dye because it widespread use in food products, drugs, cosmetics, pharmaceuticals and for dying some textile fiber. Also, it causes asthma, eczema, thyroid cancer, and some other behavioral problems [5].

The main objective of the present work is synthesis of $Fe_2O_3/SiO_2$ composite via the simply incipient impregnation method. The catalytic ability of composite was evaluated by the degradation of tartrazine in the presence of $H_2O_2$. The effect of different reaction parameters such as initial solution pH, initial $H_2O_2$ concentration and additive on the degradation of tartrazine were investigated to figure out the optimal reacting conditions. The catalytic ability of as-synthesized $Fe_2O_3/SiO_2$ composite was compared to the commercial material ($Fe_2O_3$ and $SiO_2$), as-synthesized $Fe_2O_3$, and a physic mixture of as-synthesized $Fe_2O_3$ and $SiO_2$. In addition, effects of NaCl and EDTA in the degradation of dye and reaction mechanism were studied.

## 2. EXPERIMENTAL

### 2.1. Chemicals and regents

Tartrazine was purchased from Sigma-Aldrich without any purification. $SiO_2$ powder (GF254 for thin layer chromatography), $Fe(NO_3)_3.9H_2O$ (99.5 %), $H_2O_2$ (30 % w/w), NaCl (99.7 %), EDTA (99.5 %) were obtained from Merck. Distilled water was used throughout the experiments. The initial pH of the solution was adjusted to the desired value using dilute solutions of $H_2SO_4$ and NaOH.

### 2.2. Preparation of catalyst

The $Fe_2O_3/SiO_2$ composite was prepared by incipient impregnation method. The iron content in composite was about 7 wt.% in theory. Typically, 1.44 g of silica powder immersed in 10 mL of $Fe(NO_3)_3$ 2.0 M solution under vigorous stirring for 24 h at room temperature. After impregnation, the sample was dried at 80 $^oC$ for 24 h and then followed by calcination at 500 $^oC$ for 5 h in a muffle furnace. Then, it was cooled to room temperature and stored in a stoppered bottle (denote as as-synthesized $Fe_2O_3/SiO_2$) for catalytic use.

Commercial $Fe_2O_3$, as-synthesized $Fe_2O_3$ prepared by vaporizing $Fe(NO_3)_3$ solution at 80 $^oC$ for 24 h and then calcined at 500 $^oC$ for 5 h, and physical mixture $Fe_2O_3/SiO_2$ prepared by mixed synthesized $Fe_2O_3$ with commercial $SiO_2$ were compared with the as-synthesized $Fe_2O_3/SiO_2$ composite for degradation of tartrazine from water solution.

### 2.3. Characterization

The crystalline phase of samples was investigated by X-ray powder diffraction. XRD patterns were obtained by using Bruker D8 Ax XRD-diffractometer (Germany) with CuKα irradiation (40kV, 40 mA). The 2θ ranging from 10 to 70° was selected to analyze the crystal structure.

The morphology and size of the samples were observed by transmission electron microscopy (TEM, JEM-2010) and field emission scanning electron microscopy (FE-SEM, JEOL-7600F). Energy Dispersive Spectrometry (EDS) was performed on JEOL-7600F to determine the chemical composition of the composite.

Textural properties were measured via $N_2$ adsorption/desorption isotherm using a Quantachrome instrument (Autosorb iQ, version 3.0 analyzer). The specific surface area was calculated by using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was obtained by using the Barrett-Joyner-Halenda (BJH) method.

### 2.4. Catalytic activity study

The experiment on the degradation of tartrazine was conducted in batch mode reactor. Typically, 50 mg of catalyst and premeasured amounts of $H_2O_2$ solution were added to beaker 250 ml containing 100 mL of 50 mg/L dye solution adjusted pH under magnetic stirring. At given time intervals, 2 mL of samples were withdrawn from the suspension and immediately filtered by using syringe filter (pore size 0.45 μm). The dye concentration of the filtrate was analyzed by a UV-Vis spectrophotometer (Agilent 8453) at the maximum absorbance wavelength 428 nm. The degradation efficiency (%) of tartrazine can be calculated by the following equation:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0}.100\% \qquad (1)$$

Where $C_0$ (mg/L) is the initial concentration of tartrazine and $C_t$ (mg/L) is the concentration of tartrazine at reaction time, t (min).

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of as-synthesized sample

#### *3.1.1. SEM, TEM and EDS analysis*

Figure 1 reveals the FE-SEM, TEM and EDS spectrum of as-synthesized $Fe_2O_3/SiO_2$ and commercial $SiO_2$. The morphology of $Fe_2O_3/SiO_2$ composite (Figure 1b) was different from commercial $SiO_2$ (Figure 1a). However, both of samples showed the assembling morphology, the bulk shape was 10-20 nm. The silica and iron could not be observed from SEM images however iron oxide nanoparticles of smaller size about 5 nm were well dispersed on silica particles, as seen in TEM image (figure 1 (c)). The Fe and Si contents were detected in EDS spectrum (figure 1d), 32.6 wt.% and 7.7 wt.%, respectively, this was close to the theory value of Fe (7 wt.%). These results showed that the Fe content could be transferred to iron (III) oxide and it was well dispersed on the $SiO_2$ particles after incipient impregnation and calcination at 500 °C for 5 h. The EDS spectra Ca and S could be attributed to the $CaSO_4$ content in the commercial $SiO_2$.

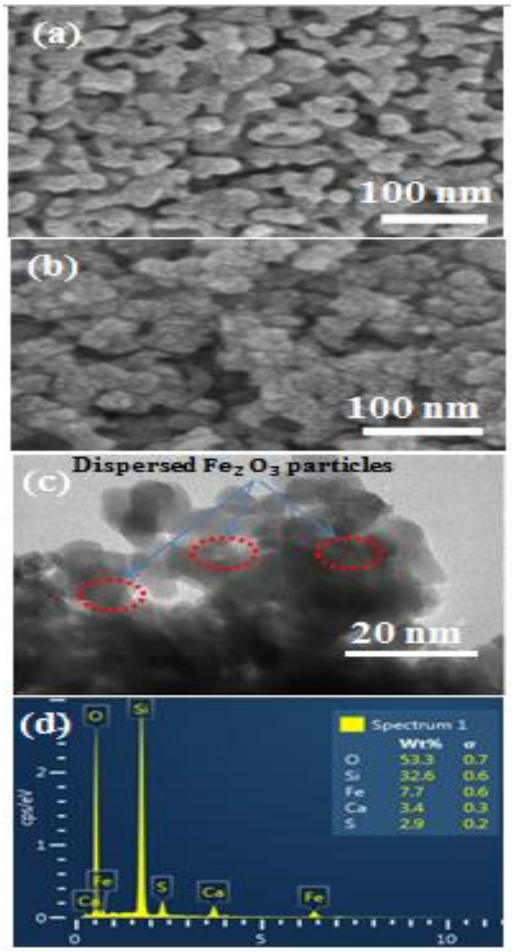

*Figure 1:* SEM images of $SiO_2$ (a), as-synthesized $Fe_2O_3/SiO_2$ (b), TEM image of as-synthesized $Fe_2O_3/SiO_2$ (c) and EDS spectrum of as-synthesized $Fe_2O_3/SiO_2$ (d)

### *3.1.2. XRD analysis*

The XRD patterns of the $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ composite are shown in Figure 2. The diffraction peak at $2\theta = 22^o$ was assigned to amorphous silica and the other peaks at $2\theta$ from 30 to $50^o$ could be assigned to $CaSO_4$ content in commercial $SiO_2$ [6]. For a composite, the XRD pattern peaks at $2\theta$ = 25, 32 ,41 and $49^o$ were broad and low intensity indicating the low content, low degree of crystallinity, and well dispersion of small particle of $Fe_2O_3$ in the composite. In addition, the disappearance of diffraction peaks of $CaSO_4$ indicated that $CaSO_4$ converted into amorphous form after heat treatment at 500 °C for 5 h.

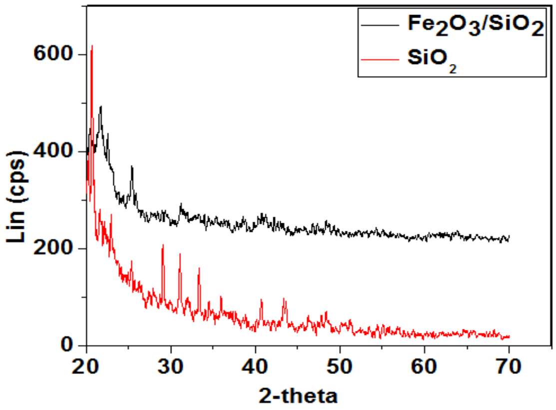

*Figure 2:* XRD pattern of $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ composite

### *3.1.3. $N_2$ adsorption–desorption isotherm*

Typical $N_2$ adsorption–desorption isotherms and pore size distributions of $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ samples are presented in figure 3. The isotherm curves were classified as type IV with type H1 hysteresis loops according to the UIPAC classification, indicating the mesoporous material consisting of well-defined cylindrical-like pore channels or agglomerates of compacts of approximately uniform spheres. The shape of the hysteresis loop of as-synthesized $Fe_2O_3/SiO_2$ was similar to that of $SiO_2$, but the hysteresis level of as-synthesized $Fe_2O_3/SiO_2$ was lower. The adsorption-desorption braches of the hysteresis loop at relative pressure $p/p_0$ of 0.78/0.96 and 0.87/0.98 for $Fe_2O_3/SiO_2$ and $SiO_2$, respectively.

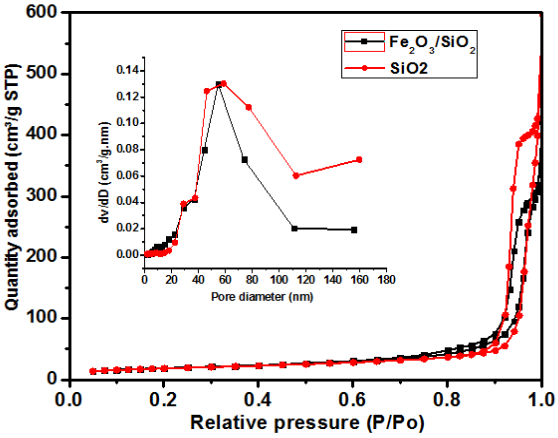

*Figure 3:* $N_2$ adsorption/desorption isotherm of (inset: pore size distributions) of $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ composite

The pore size distribution of $SiO_2$ was broader than that of as-synthesized $Fe_2O_3/SiO_2$, this can be ascribed to the re-structure of $SiO_2$ and well distribute of ion in the composite. The pore size distributions of both samples were comparatively concentrated at around 30-70 nm. The average pore diameters of $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ were 40.3 and 28.8 nm, respectively, as shown in table 1. The surface area of as-synthesized $Fe_2O_3/SiO_2$ slightly increased but pore volume was decreased compared to those of $SiO_2$. These results indicated that the good dispersion of $Fe_2O_3$ by using our simple incipient impregnation method could give a small effect to textural properties of samples.

*Table 1:* Textural properties of $SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$ composite

| Sample | $S_{BET}$ ($m^2/g$) | Vpore ($cm^3/g$) | Dpore[a] (nm) |
|---|---|---|---|
| $SiO_2$ | 64 | 0.61 | 40.27 |
| $Fe_2O_3/SiO_2$ | 66 | 0.49 | 28.80 |

[a] Average pore size.

### 3.2. Degradation of tartrazine

Figure 4 shows the degradation of tartrazine in different reaction systems. The degradation efficiency was about 2.9 % when only $H_2O_2$ was in dye solution within 80 min, in figure 4a. This indicated that tartrazine was stable and hardly degraded in the presence of $H_2O_2$ even thought $H_2O_2$ was a powerful oxidizing agent. For reaction system with only $SiO_2$ or $Fe_2O_3/SiO_2$, the degradation efficiency was also negligible, 0.7 and 1.6 % for $SiO_2$ and $Fe_2O_3/SiO_2$ as shown in figures 4b and c, respectively. The change of dye concentration was due to the adsorption on $SiO_2$ and $Fe_2O_3/SiO_2$. The higher adsorption of tartrazine on $Fe_2O_3/SiO_2$ than that of $SiO_2$ was due to tartrazine being negatively charged in aqueous solution, whereas positively charged iron (III) ions on the $Fe_2O_3/SiO_2$ could increase the electrostatic adsorption of tartrazine.

The reaction rate of tartrazine for commercial $Fe_2O_3/H_2O_2$/dye and as-synthesized $Fe_2O_3/H_2O_2$/dye systems (Figure 4d and e) were fast within an initial 10 min, it becomes more stable. The degradation efficiencies were 9.6 and 1.6 %, respectively for commercial $Fe_2O_3/H_2O_2$/dye and as-synthesized $Fe_2O_3/H_2O_2$/dye, respectively, in 80 min. The reaction rate of tartrazine for the physical mixture $Fe_2O_3/SiO_2/H_2O_2$/dye system (figure 4f) was slow, its removal efficiency was 13.5 % in 80 min. The catalytic activity of $Fe_2O_3$ with $SiO_2$ was higher than that of single metal systems $Fe_2O_3$. It reveals that $SiO_2$ can be used as a supporter to improve the removal efficiency of tartrazine in presence of $H_2O_2$.

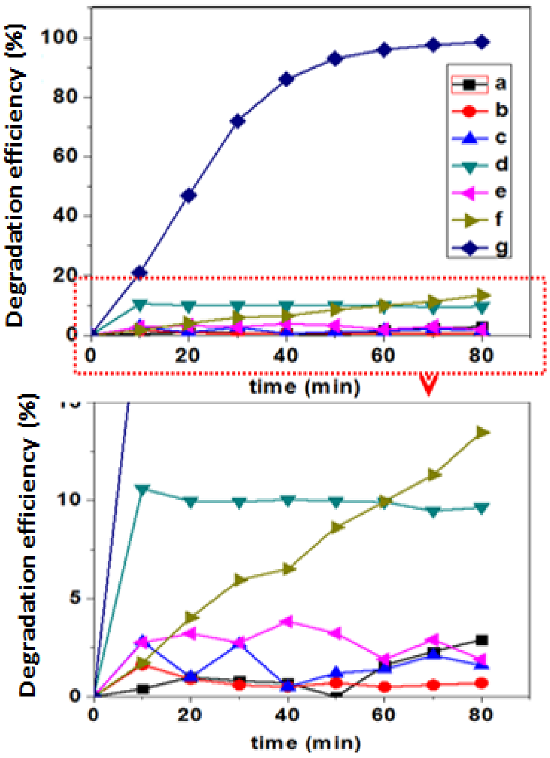

*Figure 4:* The degradation of tartrazine in different reaction systems. Reaction conditions: (a) $H_2O_2$/dye, (b) $SiO_2$/dye, (c) $Fe_2O_3/SiO_2$/dye, (d) Commercial $Fe_2O_3/H_2O_2$/dye, (e) as-synthesized $Fe_2O_3/H_2O_2$/dye, (f) physical mixture $Fe_2O_3/SiO_2/H_2O_2$/dye, (g) as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye. (50 mg of catalyst, 50 mg/L of tartrazine, 12 mM of $H_2O_2$, pH = 3.0, temperature of 30 $^{o}C$)

The degradation of tatrazine in the commercial $Fe_2O_3/H_2O_2$/dye, as-synthesized $Fe_2O_3/H_2O_2$/dye, and physical mixture $Fe_2O_3/SiO_2/H_2O_2$/dye systems could be attributed to Fenton-like system oxidation. In addition to the Fenton-like reaction that lead to the formation of $OH^{\bullet}$ and the decomposition of $H_2O_2$ by $Fe_2O_3$ via heterogeneous catalysis has also been reported to yield hydroxyl and superoxide radicals [7]. The reaction ability of tartrazine for as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye (Figure 4g) was much higher than other systems and the removal efficiency reached 98.5 % in 80 min. As presented in section 3.1.3, the surface area of as-synthesized $Fe_2O_3/SiO_2$ was not much different to $SiO_2$ but pore volume was decreased after impregnation. It was expected that the same results with the physical mixture $Fe_2O_3/SiO_2$ for the low content of ion. However, the existence of Si-O-Fe bond in as-synthesized $Fe_2O_3/SiO_2$ [8] indicating the interaction between silica and iron ions. Thus, iron disperses within the pores of silica and surface of the silica support. This may be unclear in the physical mixture $Fe_2O_3/SiO_2$. Therefore, with regard to surface area and pore volume of physical mixture $Fe_2O_3/SiO_2$ and as-synthesized $Fe_2O_3/SiO_2$, the dispersion of $Fe_2O_3$ on $SiO_2$ structure showed more important factor than textural properties of composite materials. This result indicated that $Fe_2O_3$ on the surface of the $SiO_2$ prepared by incipient impregnation method has a higher dispersion than that of physical mixture method.

### 3.3. Effect of initial solution pH

The effect of initial solution pH on degradation of tartrazine on as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye system was investigated. The pH values were varied from 2.0 to 6.0 while other conditions were fixed (inital tartrazine concentration of 50 mg/L, 50 mg of the catalyst, $H_2O_2$ concentration of 12 mM, and temperature of 30 $^oC$) and the results are shown in figure 5.

Overall results indicated that the degradation of tartrazine was significantly influenced by the solution pH. The reaction rate at pH 2.5 was slightly lower than that at pH 3.0 but the degradation efficiency at both pH values 2.5 and 3.0 reached 98.5 % in 80 min. The solution pH 3.0 was more suitable than 2.5 because it allows using less acid to acidify the medium and lower ion leaching is produced. This is in agreement with the classical Fenton. At pH lower than 2.5, the reaction rate was decreased and the degradation efficiency decreased to 39.7 % in 80 min at pH 2.0. The reaction rate was slowed down might be attributed to the stabilization of $H_2O_2$ through the formation of oxonium ion ($H_3O_2^+$) leading to substantially reduce the reactivity with the ferrous ion. In addition, the Fenton reaction was retarded due to the scaveging effect of hydroxyl radicals ($OH^\bullet$) by overbundance of $H^+$ ion at low pH [9] as the equation follows.

$$OH^\bullet + H^+ + e = H_2O \qquad (2)$$

Furthermore, formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also react more slowly with $H_2O_2$ [10].

At greater pH value than 3.0, the reaction rate was rapidly decreased with an increase of pH. The degradation efficiencies at pH = 3.5, 4.0 and 6.0 were 64.3, 7.9 and 1.1 %, respectively. In the previous report [8], at high pH value, $Fe_2O_3/SiO_2$ solid catalyst surface becomes negatively charged making interaction with tartrazine dye less frequent and a part of $H_2O_2$ undergoes self-decomposition into molecular oxygen without appreciable amounts of radicals in the less acidic medium leading to lose the oxidizing ability. In addition, the deactivation of catalyst with the formation of ferric hydroxide complexes leads to a reduction of $OH^\bullet$ radical. As a result, reaction rate and degradation efficiency of tartrazine in as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye at greater pH than 3.0 were dropped.

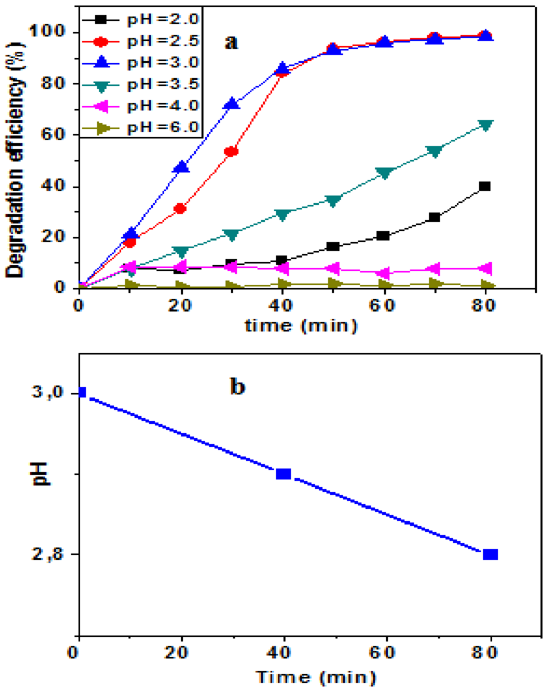

*Figure 5:* (a) Effect of initial solution pH and (b) pH drop versus time with initial solution pH 3.0. At condition: 50 mg/L of tartrazine, $H_2O_2$ concentration of 12 mM, 50 mg of catalyst and temperature of 30 $^oC$

We observed that the solution pH has a critical impact on the degradation of tartrazine because of its role in controlling the catalytic reaction, resulting in iron ions and the stability of $H_2O_2$. The optimum pH was found to be 3.0 in which the reaction a good catalytic and could respond to $H_2O_2$ to produce $^OH^\bullet$radicals to degrade the tartrazine dye molecules. At initial solution pH 3.0, the drop of pH during reaction was slight. The pH value decreased to 2.9 in first 40 min and final to 2.8 after 80 min of reaction when initial solution pH was 3.0, as shown in Figure 5b. The decrease of pH value could be attributed to the formation of $HNO_3$, $H_2SO_4$, and other organic acids such as oxalic acid, acetic acid, and succinic acid [11].

### 3.4. Effect of initial $H_2O_2$ concentration

The concentration of $H_2O_2$ is critical for the degradation of the tartrazine dye during Fenton oxidation. The impact of $H_2O_2$ concentration on the degradation of tartrazine in as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye is shown in figure 6. The concentration of $H_2O_2$ was varied from 6 to 60 mM, while other conditions remained at the constant (initial tartrazine concentration of 50 mg/L, catalyst dosage of 50 mg, pH 3.0, and temperature of 30 $^oC$). The reaction rate at a $H_2O_2$ concentration of 12 mM was larger than that at 6 mM but the degradation efficiencies at these pH values were not much different to each other, 95.2 and 98.5 % at 6 and 12 mM, respectively. However, the reaction rate and degradation efficiency were gradually reduced as the $H_2O_2$ concentration increased to more than 12 mM, it was 97.0, 95.0, and 88.0 % at $H_2O_2$ concentration of 18, 30, 60 mM, respectively. The increase of the oxidant concentration from 6.0 to 12 mM led to increasing degradation efficiency of dye because more $OH^{\bullet}$radicals were formed. However, the high $H_2O_2$ concentration (>12 mM) results in a decrease in degradation process because surplus $H_2O_2$ molecules act as scavenger of hydroxyl radical to generate perhydroxy radical ($HO_2^{\bullet}$ ) which has lower oxidation potential than the former. The reaction equation can be expressed as follow [7]:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (3)$$

Therefore, the effect of $H_2O_2$ adding for the tartrazine degradation is two sided and the appropriate amount of $H_2O_2$ plays an important role in the degradation process. The $H_2O_2$ concentration of 12 mM was the optimal value for removal of tatrazine by $Fe_2O_3/SiO_2$ composite and it was used to further study.

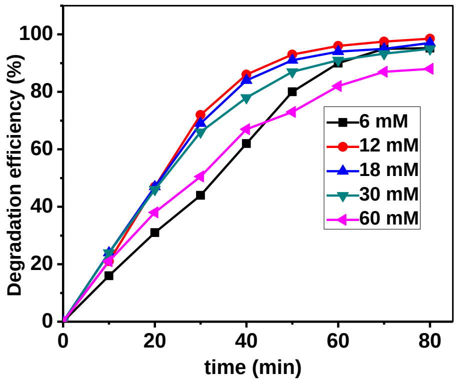

*Figure 6:* Effect of initial $H_2O_2$ concentration on degradation of tartrazine with reaction conditions: initial tartrazine concentration of 50 mg/L, dosage of catalyst of 50 mg, pH 3.0, and temperature of 30 $^oC$

### 3.5. Effect of additive (NaCl and EDTA)

Industrial wastewater might contain the inorganic salts (sodium chloride, potassium chloride, sodium sulphate, potassium sulphate, etc.) which were electrolytes and organic agent (EDTA, tartaric acid, formic acid, glycine, nitrilotriacetic acid, etc.) which were iron-ligands. Therefore, it was thought worthwhile to investigate the effects of dissolute salt and chelating agents (NaCl and EDTA were selected, respectively) on the degradation of dye by $Fe_2O_3/SiO_2$ catalyst. The effects of NaCl and EDTA additives were studied only at optimum concentration of dye, $H_2O_2$, and pH, the results are shown in figure 7. The reaction rate was slightly decreased with an addition of NaCl (20 mg), the degradation efficiency decreased to 95 % indicating that NaCl played a passive role in the degradation of tartrazine in $Fe_2O_3/SiO_2/H_2O_2$ system. The negative effect of NaCl in common advance oxidation process technologies has been studied in previous reports [12]. In the presence of sodium chloride, $Cl^-$ ions could react with the active radical during the reaction process, causing a decrease in the degradation rate, (equations (4) - (6)) [13].

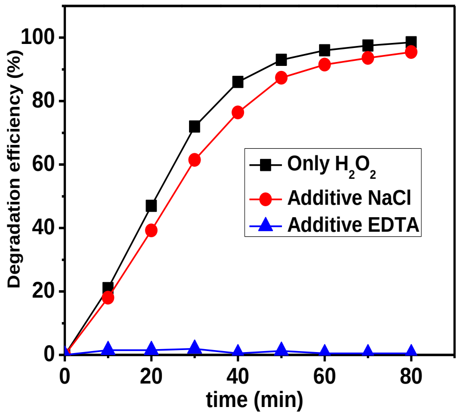

*Figure 7:* Effect of NaCl and EDTA on degradation of tartrazine with reaction conditions: 50 mg of catalyst, 50 mg/L of dye, 12 mM of $H_2O_2$, pH 3.0, 20 mg of NaCl/20 mg of EDTA, temperature of 30 $^oC$

$$Cl^- + OH^{\bullet} = ClOH^{\bullet-} \qquad (4)$$

$$ClOH^{\bullet-} + H^+ = Cl^{\bullet} + H_2O \qquad (5)$$

$$ClOH^{\bullet-} + Fe^{2+} = Cl^- + OH^- + Fe^{3+} \qquad (6)$$

In the presence of the chelating agent, the reaction rate tartrazine was decreased significantly and the degradation efficiency was neglected with an addition EDTA of 20 mg. The mechanism of the heterogeneous Fenton reactions in the presence of chelating agents EDTA remains unclear, due to the possible concurrence of homogeneous and heterogeneous reactions. Chelating agents can induce an enhanced homogeneous Fenton mechanism by increasing the dissolution of solid catalysts. In contrast, the surface complexed ligands can compete for the surface active sites with organic compounds and $H_2O_2$ leading to a decreased $H_2O_2$ activation [14, 15] and the generation of high-valent iron species is also speculated according to some inhibitive effects of different scavengers [16]. In this study, the insignificant decrease in degradation of dye at pH 3.0 may be due to the decrease of $H_2O_2$ activation. This will hinder the heterogeneous and homogeneous reaction. However, it cannot be certainly declared that the negative effect of the presence of EDTA in the Fenton-like reaction systems for degradation of dye. The degradation of bisphenol A (BPA) was decreased from 87.0 to 20.4 in the EDTA-$H_2O_2$-$BiOFeO_3$ systems at pH = 3.0. The degradation efficiency increased when pH solution increased [17]. The similar phenomena occurred in other reports [16]. Thus, the effect of pH value is a crucial factor for degradation of dye and the result in removal of tartrazine in the EDTA-$H_2O_2$-$Fe_2O_3/SiO_2$ system is going to be presented in the next report.

### 3.6. Reaction mechanism discussion

Figure 8 shows the change with time in UV-Vis spectra of tartrazine degradation during 80 min of reaction period. As can be seen from dye spectrum, before oxidation (t = 0), the absorption spectrum of tartrazine dye was characterized by one band in the ultraviolet region located at 257 nm and by one band in visible region which its maximum absorption at 428 nm. The peak at 257 nm is due to benzene-like structure in the molecules while the band in the visible region was associated with the chromophore-containing azo linkage. The disappearance of the absorbance pic at 428 nm with the time was due to the fragmentation of the azo links by oxidation. In addition to this rapid degradation effect, the decay of the absorbance at 257 nm was considered as an evidence of aromatic fragment degradation in the dye molecule and its intermediates [18-20].

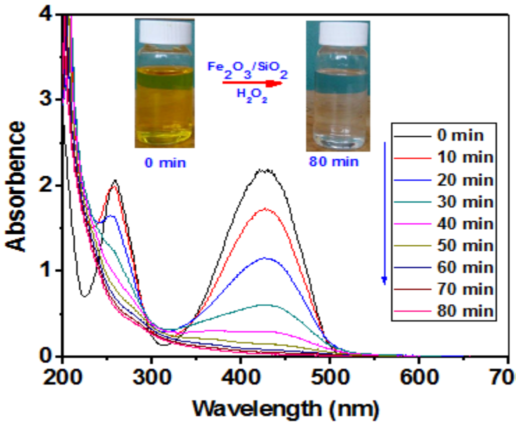

*Figure 8:* UV-Vis spectra during degradation process with as-synthesized $Fe_2O_3/SiO_2/H_2O_2$/dye systems. (50 mg/L of tartrazine, $H_2O_2$ concentration of 12 mM, dosage of catalyst 50 mg, pH 3.0, temperature 30 $^oC$)

## 4. CONCLUSION

In this study, the $Fe_2O_3/SiO_2$ composite has been successfully prepared via a simple impregnation method. The $Fe_2O_3$ with small particle size was highly dispersed on silica and exhibited excellent efficiency for the Fenton degradation of tartrazine, 98.5 % in 80 min. It was much higher than that of physic mixture $Fe_2O_3/SiO_2$, and other materials. The effects of $H_2O_2$ concentration, pH on reaction rate were investigated. The optimal parameters obtained for this investigation were found to be 2.0 mM of $H_2O_2$, pH 3.0, at 30 $^oC$ under maintaining condition 50 mg of catalyst, 50 mg/L of dye. The addition of NaCl and EDTA played a passive role in the degradation of dye. In which, EDTA showed much strong decrease in reaction rate and degradation efficiency of dye by as-synthesized $Fe_2O_3/SiO_2$ composite compared to that of NaCl.

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