# CHAP VI

# COMPARISON OF TS-1 ZEOLITE TO BISMUTH TITANATE PHOTOCATALYST FOR WASTE WATER TREATMENT USING REACTIVE BLACK 5 DYE AS MODEL

## 6.1 Abstract

The photocatalytic degradation of Reactive Black 5, a non-biodegradable dye, in the presence of hydrogen peroxide, was investigated by comparing two custom-made catalysts, viz. TS-1 zeolite and $Bi_{12}TiO_{20}$. The effect of pH, $H_2O_2$ concentration and Si/Ti ratio of the zeolite was explored, as assessed by degree of decoloration and mineralization (loss of total organic content). Experiments were conducted under low power of 6 W UV-A irradiation. We found that, whereas the decoloration rate of each catalyst was comparable and insensitive to pH, the degree of mineralization achieved by TS-1 diminished strongly with pH while that achieved by $B_{12}TiO_{20}$ was insensitive to pH change. This reflects that oxidative attack first occurs at the azo bond of the dye molecule, which is the source of color. Lower Si/Ti ratio (higher Ti loading) of TS-1 exhibits good catalytic efficiency up to 65% mineralization of RB5. The activation energies of TS-1 and bismuth titanate catalyst are 18.71 and 25.35 kJ/mol, respectively. The mineralization percentage achieved by TS-1 (Si/Ti = 12) was twice as high as that of $B_{12}TiO_{20}$ although the decoloration rate was not significantly different. The high catalytic efficiency indicates that the TS-1 zeolites tested have exceptionally high levels of catalytically active framework Ti which is uniformly distributed throughout the zeolite pore volume.

## 6.2 Introduction

Azo dyes constitute the largest and most important class of commercial dyes in wastewater. They are mostly non-biodegradable and resistant to destruction by conventional wastewater treatments.[1] The discharge of highly colored wastewater into the ecosystem generates environmental problems such as aesthetic pollution (even a small amount of dye is highly visible), and perturbation of aquatic life.[2]

Recent studies indicate that toxic and refractory organic compounds including dyes in wastewater can be destroyed by advanced oxidation processes (AOPs).[3-5] Photocatalytic degradation (UV/$TiO_2$) is one AOP which is receiving increased attention, because of the low cost and relatively high chemical stability of the catalyst, and the possibility to use sunlight as the source of irradiation.[6] Moreover, photocatalysis does not require expensive oxidants and can be carried out under mild temperature and pressure.[7] $TiO_2$ is known to be the most active photocatalyst for organic oxidation.[8] However, there are certain limitations in using bare $TiO_2$ in photocatalytic reactors. For example, due to their small size (about 4-30 nm), $TiO_2$ particles aggregate rapidly in a suspension, losing effective surface area, as well as catalytic efficiency. Being non-porous, $TiO_2$ exhibits a low ability to absorb pollutants.[9] Therefore, inserting titanium within the cavities which exist in the framework of zeolites, as, for example, in titanium silicalite (TS-1), may be advantageous, because zeolites have nanoscale pores, and high adsorption capacities and ion-exchange capacities.[10-12]

Another interesting catalyst is bismuth titanate ($Bi_{12}TiO_{20}$), which is reported to have high photocatalytic activity for decoloration of methyl orange.[13] Some part of this material has the absorption onset wavelength of visible region (around 500 nm), meaning that it has a possibility to use under weak UV light or may be sunlight. The $Bi_{12}TiO_{20}$ crystal belongs to a family of compounds known as sillenites, which have the general formula $Bi_{12}MO_{20}$, where M represents a tetravalent cation, or a combination of ions with an average charge of 4+. The framework of the $Bi_{12}TiO_{20}$ crystal structure is formed by Bi–O polyhedra, in which Bi ions are coordinated to five oxygen ions in an octahedral arrangement together with the stereochemically active $6s^2$ electron lone pair of $Bi^{3+}$. The Bi-O polyhedron network connects to geometrically regular $TiO_4$ tetrahedra. Each tetrahedron is formed by four oxygen anions with the Ti cation occupying the tetrahedral interstice.[14]

In this study, we compare the photocatalytic activities of these two catalysts, TS-1 and $Bi_{12}TiO_{20}$, in the dye-degradation process, as assessed by both decoloration and mineralization (loss of total organic content). The influence of the solution acidity and the concentration of $H_2O_2$ were studied. To observe the effect of Ti content in the TS-1 zeolite structure, different Si/Ti ratios was also investigated.

## 6.2 Experimental

Both TS-1[15] and bismuth titanate[16] catalysts were synthesized following previous reports, and using our custom-made moisture-stable silatrane[17] and titanium glycolate precursors[18]. It is important to note that use of the silatrane precursor enables us to prepare TS-1 with essentially complete incorporation of Ti into the zeolite framework at Si/Ti ratios as low as 5.[15]

### 6.2.1 Catalyst Preparation and Characterization

FTIR spectra were measured on a Thermo Nicolet, Nexus 670, by mixing sample powder with KBr to make a pellet. The crystallographic phases of the catalysts, TS-1 and $Bi_{12}TiO_{20}$, were characterized using a Rigaku X-ray diffractometer at a scanning speed of 5.0°/s and CuKα radiation. UV–visible measurements were performed on a Shimadzu UV-2550 with the ISR-2200 integrating sphere attachment, using $BaSO_4$ as a reference. Diffuse reflectance ultraviolet spectroscopy was obtained on a Shimatzu UV-2550 spectrometer. The reflectance output was converted using the Kubelka–Munk algorithm. The Si/Ti ratio was investigated using Perkin Elmer Optima 4300 DV, inductively coupled plasma (ICP) spectrometer.

#### *6.2.1.1 TS-1 Zeolite Synthesis*[15]

Hydrothermal syntheses were carried out using microwave irradiation and a sample mixture containing an initial molar composition of $x\mathrm{SiO_2}{:}y\mathrm{TiO_2}{:}0.31\mathrm{TPA^+}{:}\ 0.4\mathrm{NaOH}{:}114\mathrm{H_2O}$ (where x:y = 100, 50, 33, 25, 20 and 12). The mixture was aged at room temperature for 110 h and heated in a microwave at 150°C for various ranges of reaction time, depending on the Ti loading; the higher the Ti-loading, the longer the reaction time, as discussed in Phonthammachai's work.[15] Hydrothermal treatment by microwave heating technique was conducted on ETOH SEL, Milestone Microwave Laboratory System (Spec 2500 W and 2450

MHz). Samples were heated in a Teflon tube. The TS-1 zeolite product was washed several times with distilled water, dried at 60 °C overnight and calcined at 550°C for 2 h at a heating rate of 0.5°C/min.

FTIR: 960 $cm^{-1}$ ν(Si-O-Ti), 550 $cm^{-1}$ δ(Si-O-Si) and 800 $cm^{-1}$ ν(Si-O-Si). DR-UV: 210 nm (tetracoordinated titanium). XRD: $2\theta = 24.4^\circ$ (Orthorhombic symmetry of TS-1).

#### *6.2.2.2 Bismuth Titanate Synthesis*[16]

Bismuth (III) nitrate pentahydrate was 98% purity (A.R. grade) from Fluka Chemical, and dissolved in nitric acid. The stoichiometric amount of titanium glycolate was added to the bismuth (III) nitrate solution with vigorously stirring until the mixture turned clear. The pH of the mixture was adjusted to 5.0 using 0.1 M nitric acid (Labscan Asia Co.) and 0.1 M ammonium hydroxide (Carlo Earba). After stirring for 1 h, the mixture was centrifuged to separate the precipitate out, followed by washing with water until the filtrate became neutral. The white solid obtained was dried at 60°C and then calcined at 600°C for 3 h using a heating rate of 1°C/min.

FT-IR: 457 $cm^{-1}$ (weak Bi–O rocking), 525 $cm^{-1}$ ν(O-Bi-O), 586 $cm^{-1}$ ν(O-Bi-O), 663 $cm^{-1}$ ν(O-Ti-O). DR-UV: 500 nm (visible absorption of intrinsic band transition of indirect gap bismuth titanate semiconductor). XRD: $2\theta =$ 24.7°: [220], 27.7°: [310], 30.4°: [222], 32.9°: [321].

### 6.2.3 Photocatalytic Decomposition of Reactive Black 5 (RB5) Dye

The photocatalytic reactions were carried out in a 500 ml batch reactor (Vt =600 ml, Ø=14 cm) equipped with a cooling water jacket to control the temperature at 25°C. The lamp was vertically immersed in the suspension and illuminated using a commercial 6 W UV lamp (Hg Philip; emission 320-400 nm). Reactive black 5 (RB5) purchased from Sigma-Aldrich was added into the continuously, magnetically stirred mixture solution at a concentration of 40 ppm, followed by bismuth titanate or TS-1 zeolite at Si/Ti molar ratios of 100, 50, 33, 25, 20 and 12. The activation energy of the reaction was studied at temperature ranging from 15-35°C (288-508 K). Hachem et al.[19] have pointed out that the adsorption equilibrium of the bismuth titanate system is quite fast, and the equilibrium concentration should be reached within about 45 minutes. Lee et al.[20] found that for the TS-1 system, adsorption equilibrium is attained around 60 minutes. Thus, in this study, the adsorption/degradation equilibrium of the suspensions was established by magnetically stirring in the dark for 60 minutes. The concentration of catalyst was fixed at 0.5 g/l using various amounts of $H_2O_2$ (10, 20, 30 mM/l). The samples were taken out, filtered and then analyzed to determine the concentration of RB5 using Shimadzu UV-240 spectrophotometer and the total organic content (TOC) using Shimadzu TOC-VCSH Analyzer. Kinetic analysis of this process was also done.

### 6.3 Results and Discussion

Photocatalytic activity of both TS-1 and bismuth titanate was evaluated not only with respect to the effects of pH and $H_2O_2$ concentration, but also with regard to the Ti level in TS-1, to assess whether these parameters had any influence on both coloration, represented as the ratio of the dye concentration at time t to the initial dye concentration, $C/C_0$, and mineralization, calculated as percent reduction in $\mathrm{TOC} = 100 \times \left( \frac{\mathrm{TOC}_0 - \mathrm{TOC}}{\mathrm{TOC}_0} \right)$ where $\mathrm{TOC}_0$ and TOC are total organic contents at time 0 and t, respectively.

#### 6.3.1 Effect of pH

The experiments were carried out with a dye concentration of 40 ppm, at pH 3, 5, 7 and 9, for 6 h illumination time, using a 6 W UV-A lamp. The effect of pH on decoloration and mineralization efficiency of RB5, using TS-1 with an Si/Ti ratio of 12, is illustrated in Figure 6.1.

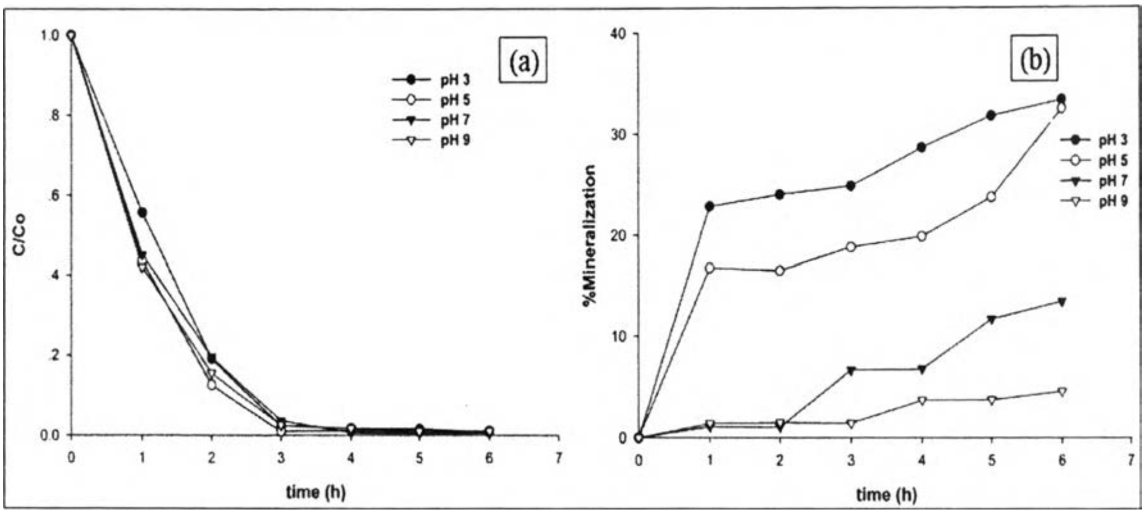

**Figure 6.1** Effect of pH on a) decoloration and b) mineralization of RB5 using TS-1 catalyst with Si/Ti = 12 in the presence of 10 mM $H_2O_2$ at 25°C.

The results indicate that, increase of pH does not significantly reduce the efficiency of decoloration of RB5, but the degree of mineralization is substantially altered. The mineralization dramatically decreases when the pH increases to 7 and 9. Adsorption and agglomerization of dye molecules are two key factors which influence the photocatalytic degradation of RB5. [20] These factors strongly depend on the pH of the solution. Zhan et al.[21] have previously studied the effect of pH on photocatalytic degradation of acid azo dyes in aqueous $TiO_2$ suspensions, and found that the pH value changes the structure of the azo dye, as well as the surface charge density of the catalyst, and therefore affects the catalytic efficiency. The structure of RB5 dye has a sulfonate group, which when negatively charged, favors adsorption of the dye molecules on the positively charged surface of the catalyst. The isoelectric pH ($pH_{iso}$) is 3.5 and the zero point charge pH ($pH_{zc}$) for anatase $TiO_2$ is approximately 6.4. Since $SiO_2$ is more acidic than $TiO_2$, it is expected that the $pH_{zc}$ of TS-1 may occur below pH 6.4. For pH values lower than the $pH_{iso}$ of $TiO_2$, the surface area of the catalyst becomes positively charged, and is negatively-charged at pH values higher than $pH_{zc}$. This observation suggests that electrostatic attraction will lead to dye adsorption at pH < 3.5 (Kusvuran, 2004), resulting in increased catalytic efficiency. On the other hand, electrostatic repulsions between charges on the catalyst surface and the dye molecules leads to dye agglomeration at $pH > 6.4$, resulting in a decrease of the efficiency. Thus, in highly acid media, RB5 dye molecules readily adsorb on the surface of the TS-1 zeolite catalyst, and, as a result, are effectively degraded with time.

An additional factor is that, in the presence of $H_2O_2$, TS-1 forms superoxo-Ti ($Ti(O_2^{\bullet -})$) and hydroperoxo-Ti ($Ti(OOH)$), reactive species that can generate hydroxyl radicals to react with dye molecules. It is reported that the peroxo complex formed in basic media has a higher stability than that formed in a neutral/acidic conditions.[22-23] Therefore, under basic conditions, hydroxyl radicals are generated less frequently than in acid conditions.

Interestingly, variation in pH had no effect on both the decoloration and the mineralization of RB5 when using bismuth titanate catalyst, as seen in Figure 6.2. However, it is clear that bismuth titanate does indeed show high photocatalytic activity for the decoloration of RB5, consistent with previous studies by Matjaz and Danilo[13] of the decoloration of methyl orange. These results are presumably due to the presence of Bi-O polyhedra in the bismuth titanate crystal structure. The photocatalytic mechanism of a semiconductor, such as $TiO_2$ or bismuth titanate, involves absorption of a photon in the band gap of the material, which generates electron hole-pairs in the semiconductor particles. Migration of the electron-hole pairs occurs to the surface of the catalyst, where trapping of electrons by adsorbed oxygen, or of holes by adsorbed hydroxyl ions, $OH^-$, results in the production of hydroxyl radicals, $^{\bullet}OH$, and oxidation of the adsorbed dye molecules.[24-26] Direct oxidation by reaction with holes ($h^+$) has also been reported.[24] The electron hole-pairs can recombine rapidly, so the interfacial electron transfer is kinetically competitive only when the relevant donor or acceptor is preadsorbed before photolysis[27]. In both acid and basic media, there is thus a small variation of degree of mineralization.

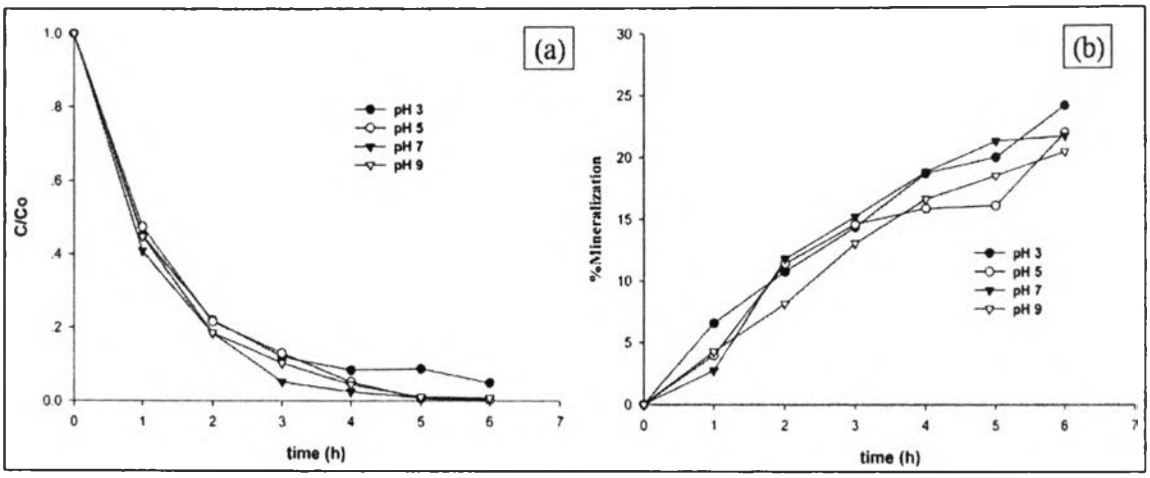

**Figure 6.2** Effect of pH on a) decoloration and b) mineralization of RB5 using bismuth titanate catalyst in the presence of 10 mM $H_2O_2$ at 25°C.

### 6.3.2 Effect of Amount of Peroxide

It has been reported that RB5 can be degraded by hydroxyl radicals, $^{\bullet}OH$, as reactive species[20]. Under UV-irradiation, $H_2O_2$ can be split photolytically to produce $^{\bullet}OH$ radical directly, which may enhance the reaction to some extent. In the presence of $H_2O_2$, titanium atoms in the TS-1 framework can form a reactive species, titanium-hydroperoxide complex, to react with the dye molecule. The O-O bond length in the titanium-hydroperoxide species, formed by the interaction of TS-1 with $H_2O_2$, is 1.52 Å [28] which represents a substantial activation of the O-O bond compared to that in $H_2O_2$ (1.49 Å )[10]. Decoloration efficiency and degree of mineralization therefore increases with a higher amount of $H_2O_2$. In this work, the highest dosage of $H_2O_2$ that generates the highest photocatalytic efficiency was determined to be 30 mM/l (Figures 6.3 and 6.4).

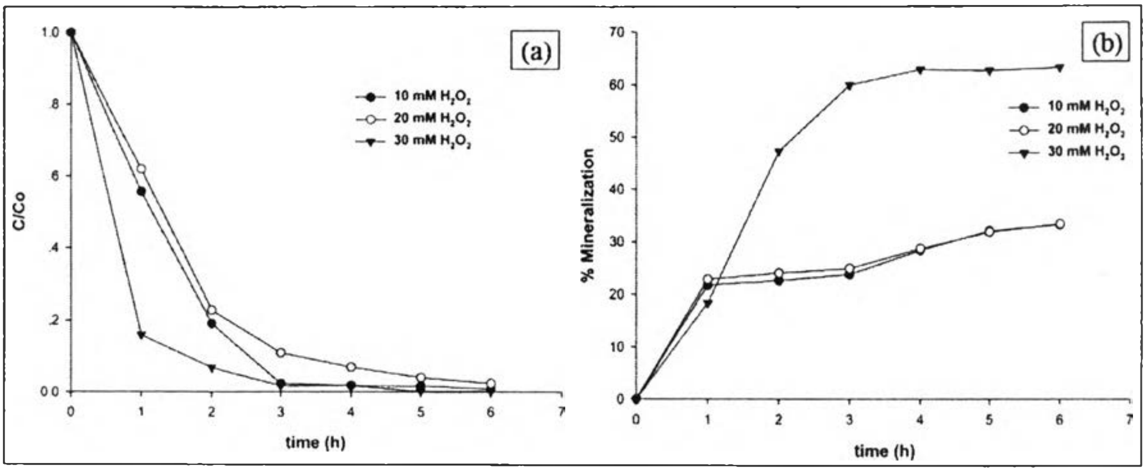

**Figure 6.3** Effect of $H_2O_2$ concentration on a) decoloration and b) mineralization of RB5 using TS-1 zeolite catalyst with Si/Ti = 12 at pH 3 and 25°C.

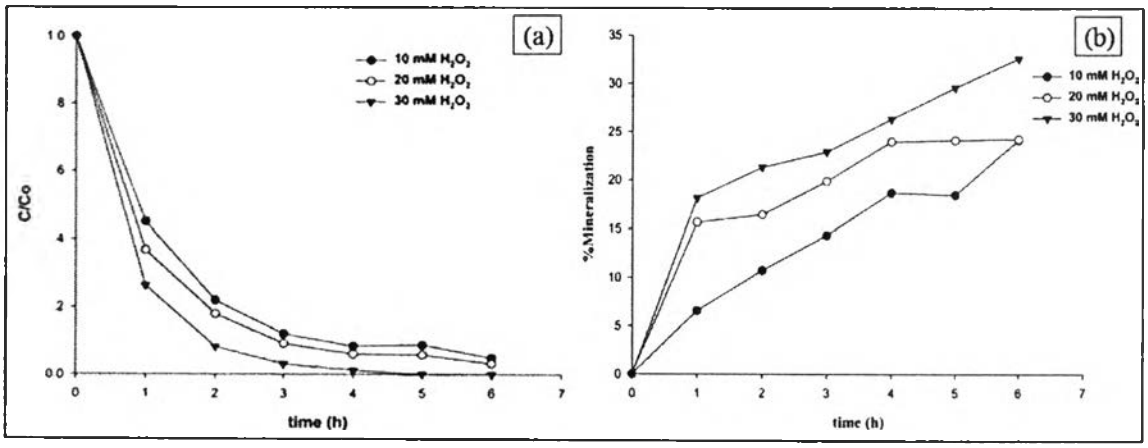

**Figure 6.4** Influence of $H_2O_2$ concentration on a) decoloration and b) mineralization of RB5 using bismuth titanate as catalyst at pH 3 and 25°C.

Due to the greater numbers of hydroxyl radicals generated from $H_2O_2$, the mineralization efficiency of the photocatalytic process is substantially enhanced as seen in Figures 3b and 4b. In the case of bismuth titanate, the effect of $H_2O_2$ level appears to be substantially smaller than for TS-1, particularly with respect to the degree of mineralization. The enhanced reactivity in the presence of $H_2O_2$ is attributed in part to the fact that the resulting reactive radical intermediates exert a dual function: as strong oxidants themselves and as electron scavengers, thus inhibiting the electron-hole recombination at the semiconductor surface.[29]

### 6.3.3 Effect of Si/Ti Ratio

Lower Si/Ti ratio means higher titanium content in the zeolite framework. The Si/Ti ratios in a mixture solution containing silatrane and titanium glycolate precursors and in TS-1 final product investigated using inductively coupled plasma (ICP) spectrometer are shown in Table 6.1. It is shown that most of titanium species added into the reaction of TS-1 formation were reacted.

**Table 6.1** Si/Ti ratios in the starting precursor mixture and TS-1 final product using ICP spectroscopy.

| Si:Ti ratio (starting materials) | Si:Ti ratio (final product) |
|---|---|
| 100 | 98.6 |
| 50 | 50.1 |
| 33 | 33.4 |
| 25 | 26.9 |
| 20 | 20.3 |
| 12 | 10.4 |

Figure 6.5a shows the decoloration of RB5 using TS-1 with various Si/Ti ratios. The decoloration performance does not vary significantly with Si/Ti ratio. In contrast, the degree of mineralization increases significantly as the Si/Ti ratio decreases, and exhibits a remarkable enhancement for an Si/Ti ratio of 12.

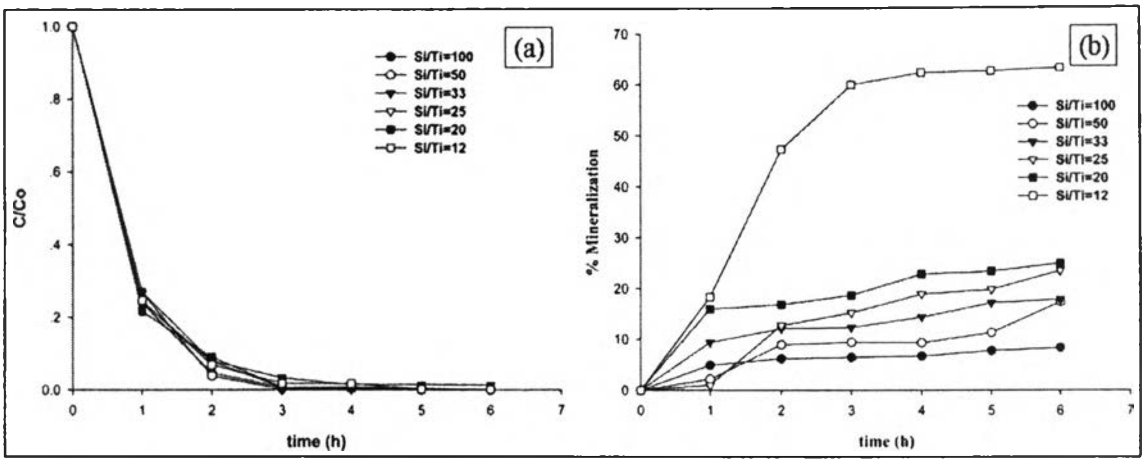

**Figure 6.5** a) Decoloration and b) mineralization of RB5 in the presence of 30 mM $H_2O_2$ at pH 3 and 25°C using various Si/Ti ratios of TS-1 zeolite catalysts.

In the TS-1 structure, Brønsted acid sites, which react with peroxide to form catalytically-active titanium peroxide, arise from formation of tetrahedral Si-O-Ti species.[30] As decreasing the Si/Ti ratio from 100 to 12, the number of Brønsted acid sites increase. The fact that decoloration occurs faster than mineralization suggests that the $^{\bullet}OH$ radicals react first at the azo bond, which is the chromophore of the RB5 dye.

### 6.3.4 Kinetic Analysis

#### *6.3.4.1 Reaction Rate and Adsorption Coefficient*

The Langmuir-Hinshelwood (L-H) model was used to determine the photodegradation kinetics of the dye. The second order of dye decomposition can be expressed as

$$r = k'C_0C_{OH} \qquad (1)$$

where r is the initial degradation rate, k' is the surface second order rate constant, $C_0$ and $C_{OH}$ are the initial concentrations of the dye and the $^{\bullet}OH$ radical, respectively. If the concentration of very active $^{\bullet}OH$ radicals takes on a steady-state value of the process, the decoloration kinetics can be simplified to a pseudo-first-order rate expression.

The second-order rate equation can be rewritten as follows:

$$-\frac{d[C]}{dt} = k_{app}Co \qquad (2)$$

where Co represents initial concentration of the dye and C is the concentration of the dye at time t. The pseudo-first-order kinetic constant was calculated from the slope of plot of ln(Co/C) versus time at each condition.

The reaction rate and half life of each condition are shown in Table 6.2. From the results, pH, dosage of $H_2O_2$ and Si/Ti ratio effects do not rapidly change the reaction rate. When the amount of $H_2O_2$ increases from 10 mM/l to 30 mM/l, the reaction rate of TS-1 goes up from $11.52 \times 10^{-3}$ to $13.17 \times 10^{-3}$ $min^{-1}$ and bismuth titanate from $9.06 \times 10^{-3}$ to $13.24 \times 10^{-3}$ $min^{-1}$. The smaller increase of reaction rate can suggest that the dosage of $H_2O_2$ has reached a maximum efficiency to decolorize the RB5. This study conforms to Lucas et al.[31] who investigated the $H_2O_2$ effect for RB5 dye with Fenton's reagent-yeast. They found that if the dosage of $H_2O_2$ reached a certain value, the decoloration efficiency did not significantly improve. From table 2 the reaction rate was affected by the turbidity resulted from catalyst particles blocking UV-absorption of $H_2O_2$ molecule, causing $H_2O_2$ not to be able to become reactive radicals to react with dye or other organic molecule. Moreover highly turbidity solution reduced light penetrability to dye and then the direct oxidation of dye with electron transfer from $TiO_2$ particles was reduced. This result responded to Tang *et al.*[32] that studied the photocatalytic degradation of reactive black 5 using $TiO_2$/UV in an annular photoreactor. Highly turbidity solution from $TiO_2$ leaded to reduction of efficiencies of catalyst. In the absence of catalyst, the kinetic reaction rate was highest followed by $SiO_2$. The $TiO_2$ as catalyst had the lowest reaction rate because it has a large turbidity while the reaction rate of $Bi_2O_3$ was close to bismuth titanate and TS-1.

Although bismuth oxide does not have Bi-O polyhedra in crystal structure like bismuth titanate, the presence of this bond may help reduce the recombination of electron-hole in bismuth oxide semiconductor particle, as discussed previously, Bi-O polyhedra in crystal structure could help reduce the recombination of electron-hole recombination.[13]

**Table 6.2** Reaction rates of the photocatalytic process using TS-1, bismuth titanate (BTO), bismuth oxide, titanium dioxide, silicon dioxide and no catalyst.

| Catalyst | Condition | Reaction Rate ($\times 10^{-3}$ min$^{-1}$) | Half Life (min) |
|---|---|---|---|
| **TS-1 (Si:Ti=12)** | pH 3[a] | 11.52 | 60.17 |
| | pH 5 | 11.38 | 60.91 |
| | pH 7 | 10.50 | 65.99 |
| | pH 9 | 10.81 | 64.11 |
| | 10 mM[b] | 11.52 | 60.17 |
| | 20 mM | 12.13 | 57.60 |
| | 30 mM | 13.17 | 52.60 |
| **Si:Ti** | Si:Ti = 100[b] | 14.59 | 59.77 |
| | Si:Ti = 50 | 14.77 | 46.91 |
| | Si:Ti = 33 | 14.05 | 68.95 |
| | Si:Ti = 25 | 13.96 | 49.64 |
| | Si:Ti = 20 | 13.50 | 49.48 |
| **BTO** | pH 3[a] | 9.06 | 76.49 |
| | pH 5 | 11.18 | 61.99 |
| | pH 7 | 10.68 | 64.89 |
| | pH 9 | 10.40 | 66.63 |
| | 10 mM[b] | 9.06 | 76.49 |
| | 20 mM | 10.27 | 58.50 |
| | 30 mM | 13.24 | 52.35 |
| **Bismuth Oxide** | 30 mM[b] | 13.30 | 52.10 |
| **Titanium dioxide** | 30 mM[b] | 7.89 | 87.90 |
| **Silicon dioxide** | 30 mM[b] | 16.54 | 41.89 |
| **$H_2O_2$ without catalyst** | 30 mM[b] | 18.85 | 36.77 |

Note: [a] using 10 mM of $H_2O_2$ , [b] at pH 3

### *6.3.4.2 Activation Energy*

The activation energy of the reaction can be assumed to generally follow the Arrhenius law:

$$k_{app} = k_o \exp\left[-\frac{E_a}{RT}\right], \qquad (3)$$

where $E_a$ is apparent activation energy, R is the gas constant, $k_o$ is a constant pre-exponential factor, and $k_{app}$ is a pseudo-first-order rate constant of decoloration. The reaction rates were studied at various temperatures ranging from 15°-35°C, as shown in Table 3. The linear transformation of Eq. 3 is

$$\ln k_{app} = \ln k_o - \frac{E_a}{RT} \qquad (4)$$

The activation energy was obtained from the plot of $\ln k_{app}$ versus $\frac{1}{T}$. The slope is equal to $-\frac{E_a}{R}$. Figure 6.6 shows the correlations between $\ln k_{app}$ and $\frac{1}{T}$ of TS-1 and bismuth titanate, as followed Eq. 5 for TS-1 and Eq. 6 for bismuth titanate:

$$\ln k_{app} = 3.17 - \frac{2.25}{T} \qquad R^2 = 0.97 \qquad (5)$$

$$\ln k_{app} = 5.89 - \frac{3.07}{T} \qquad R^2 = 0.93. \qquad (6)$$

The activation energies of the reaction calculated from these equations are 18.7 kJ/mol for TS-1 and 25.4 kJ/mol for bismuth titanate.

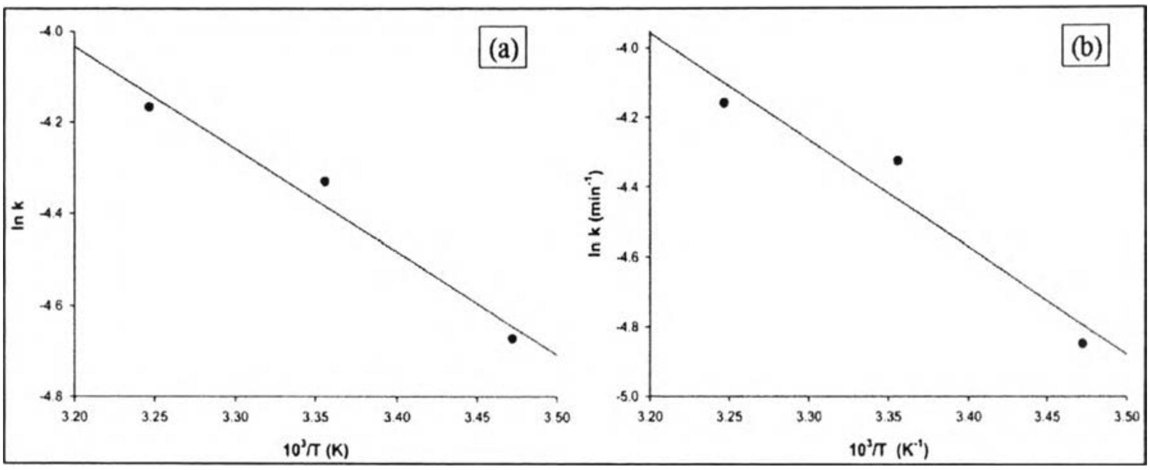

**Figure 6.6** Activation energies of a) TS-1 and b) bismuth titanate in the presence of 30 mM of $H_2O_2$ at pH 3.

**Table 6.3** Temperature dependence of pseudo-first-order decoloration rate.

| **Catalyst** | **Temperature (K)** | **Reaction Rate ($x10^{-3}$ $min^{-1}$)** | **$R^2$** |
|---|---|---|---|
| **TS-1** | 288 | 9.35 | 0.99 |
| | 298 | 13.17 | 0.94 |
| | 308 | 15.51 | 0.97 |
| **BTO** | 288 | 7.84 | 0.98 |
| | 298 | 13.24 | 0.98 |
| | 308 | 15.64 | 0.98 |

$R^2$ is a coefficient of determination in statistic method. $R^2$=1 indicated the linear relationship between the response variable and regressors, while $R^2$ = 0 indicates no 'linear' relationship.

### 6.3.5 Comparison of TS-1 to Bismuth Titanate Catalysts

The photocatalytic efficiency of TS-1 for decoloration and mineralization of RB5 in the presence of 30 mM $H_2O_2$, relative to that of bismuth titanate, is contrasted in Figure 6.7, which also shows data for $Bi_2O_3$, $TiO_2$, $SiO_2$, and in the absence of any catalyst (+30 mM $H_2O_2$ alone). The decoloration rate in the presence of $H_2O_2$ alone is the fastest in Figure 6.7a; it can be assumed that this reaction does not suffer from the increased turbidity associated with the presence of catalyst particles. Thus, the $^{\bullet}OH$ radicals can react with directly the dye molecules, which results in the highest rate of degradation.

However, $H_2O_2$ alone does not degrade the dye completely to mild environmental products such a $CO_2$ and water, as indicated by the fact that the % mineralization remains very small (Figure 6.7b). To accomplish a substantial reduction in TOC of the dye, the use of a catalyst is necessary, as demonstrated in Figure 7b. In terms of TOC removal, TS-1 with Si/Ti = 12 is the most effective catalyst, when compared to the other systems.

The mechanism of degradation of each catalyst is different. The effectiveness of TS-1 depends on the amount of the reactive species titanium-hydroperoxide, whereas the catalytic action of bismuth titanate depends on the relative ease of hydroxyl radical generation and electron-hole recombination. The fact that TS-1 with high Ti content (Si/Ti = 12) in the presence of 30 mM $H_2O_2$ has a superior performance (65% mineralization) over bismuth titanate (30% mineralization under identical conditions) suggests that this TS-1 has large numbers of reactive centers distributed throughout the material as Ti-atoms in the zeolite framework. Moreover, since they are completely oxidized into water and $CO_2$ at the end of the process, it is clear that the dye molecules, as well as intermediate products, are smaller than the pore sizes of TS-1 cavities, and so can penetrate into the channels in the zeolite structure, to react with the catalytic sites[33]. Kusvuran *et al.*[34] studied the mineralization of RB5 with wet-air oxidation and found that organic materials were not completely mineralized because of the formation of stable intermediates, such as acetic acid. However, in the presence of $H_2O_2$ and acetic acid, the framework titanium can form ‘framework peroxyl titanium complex’, as studied by Sooknoi et al.[35]. The framework peroxyl titanium complex is more hydrophobic than that formed by $H_2O_2$ alone; therefore, a stronger interaction of a non-polar substrate with the active site can be easier promoted.

The Bi-O polyhedra in bismuth titanate crystals are assumed to eliminate electron-hole recombination by oxide donors and enhance the electron transfer to $O_2$[13]. However, bismuth titanate may encounter problems due to agglomeration as exhibited by other semiconductor catalysts, such as $TiO_2$.[9] As the reaction proceeds, bismuth titanate particles may agglomerate and hence lose catalytically- effective surface area.

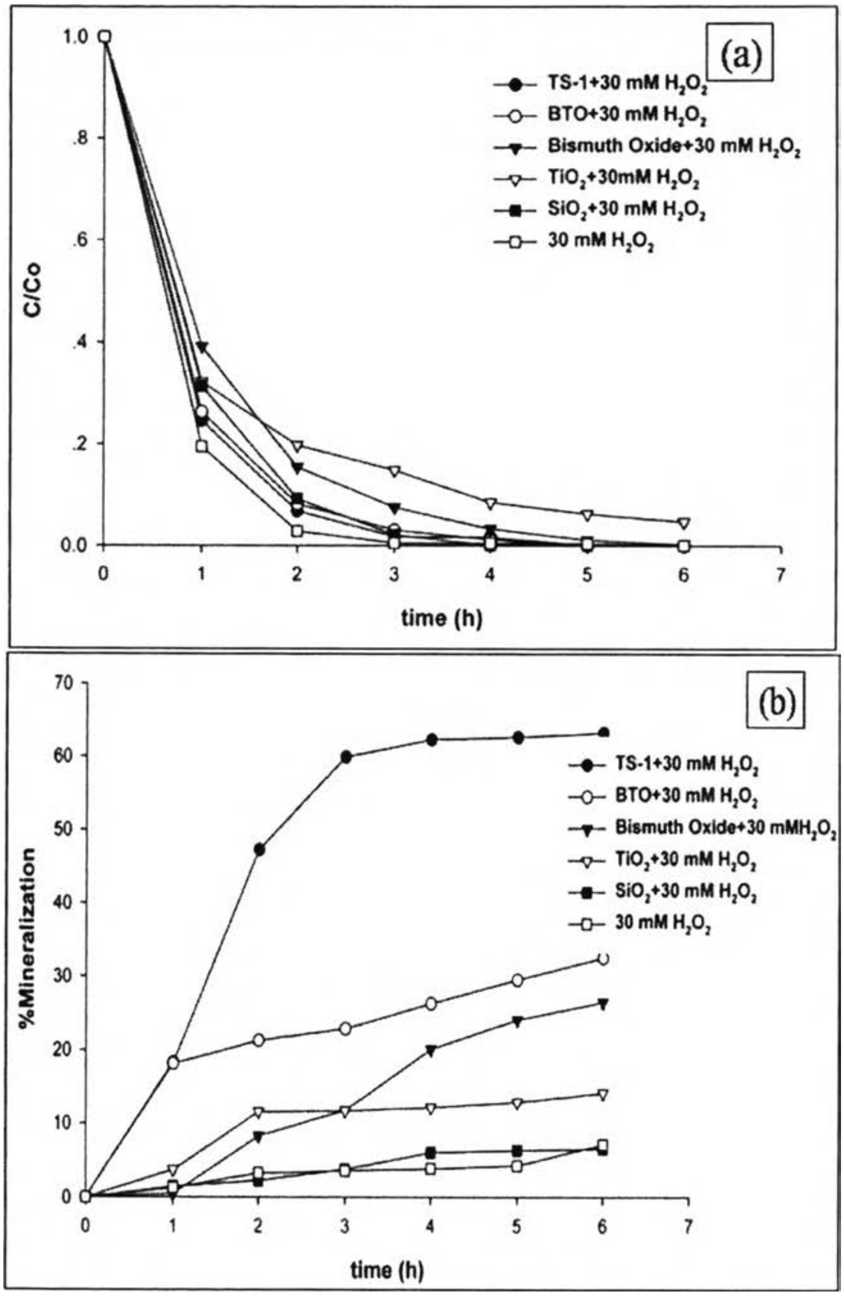

**Figure 6.7** a) Decoloration and b) mineralization of RB5 in the presence of 30 mM $H_2O_2$ at pH 3 and 25°C in various systems containing TS-1 with Si/Ti = 12, bismuth titanate, bismuth oxide, $TiO_2$, $SiO_2$ and no catalyst.

## 6.5 Conclusions

The photocatalytic performance of TS-1 and bismuth titanate for oxidation of RB5 was evaluated under a 6 W UV-A lamp. We observed that the catalytic efficiency of TS-1 deteriorates substantially as the pH is increased, whereas that of bismuth titanate is relatively pH insensitive. The reactivities of both TS-1 and bismuth titanate can be enhanced using high dosages of $H_2O_2$. The rate of decoloration was not significantly different when comparing TS-1 versus bismuth titanate, however, the degree of mineralization achieved by TS-1 with high Ti loading (Si/Ti = 12) was twice as high as bismuth titanate due to the uniform distribution of reactive Ti-centers in the zeolite framework, which enhance the reaction process. The activation energy was determined at temperatures ranging from 15-35°C using the Arrhenius law. The activation energy of the TS-1 catalyst is 18.7 kJ/mol and the bismuth titanate 25.4 kJ/mol.

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