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# Heterogeneous photocatalytic reduction of Fe(VI) in UV-irradiated titania suspensions: effect of ammonia

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## Abstract

Results of the heterogeneous photocatalytic reduction of Fe(VI) in UV-irradiated $TiO_2$ suspensions in the presence of ammonia are presented. The initial rate of Fe(VI) reduction, $R$, may be expressed as $R = k_{Fe(VI)}[Fe(VI)]^{1.25}$ where $k_{Fe(VI)} = [Ammonia]/(a[Ammonia]+b)$, $a = 6.0 \times 10^3\ \mu M^{0.25}$ s and $b = 4.1 \times 10^6\ \mu M^{-1.25} s^{-1}$. The rate constant, $k_{Fe(VI)}$, increases with the ammonia concentration. The photocatalytic oxidation of ammonia is enhanced in the presence of Fe(VI). A mechanism involving Fe(V) as a reactive intermediate is presented which explains the faster photocatalytic oxidation of ammonia in the presence of Fe(VI).

## 1. Introduction

Heterogeneous photocatalysis using UV-irradiated aqueous titanium dioxide ($TiO_2$) suspensions has been investigated extensively [1–3]. $TiO_2$ photocatalysts have been shown to decompose and to mineralize pollutants in water [4–6]. In photocatalytic processes, electron-hole pairs are initially formed (Equation 1), of which some escape recombination and diffuse to the oxide/water interface where they either react with electron acceptors (e.g. $H^+$, $O_2$) or electron donors ($OH^-$,$H_2O$). The transfer of an electron to the $O_2$ molecule produces a superoxide radical anion ($O_2^{-\bullet}$) (Equation 2), an oxidizing agent that can react with pollutants. On the other hand, the hole can generate a hydroxyl radical in water (Equation 3) that can oxidize pollutants [7, 8].

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \tag{1}$$

$$e_{cb}{}^- + O_2 \rightarrow O_2^{-\bullet} \tag{2}$$

$$h_{vb}{}^+ + H_2O \rightarrow OH^\bullet + H^+ \tag{3}$$

The efficiency of oxidizing pollutants using $TiO_2$ is low due to the fast recombination of electrons and holes. However, doping $TiO_2$ with metal particles increases the photocatalytic activity of $TiO_2$ due to decrease in the efficiency of the recombination process [4, 9]. The use of metal ions such as silver (I), mercury(II), copper(II), and chromium(VI) has shown to increase the photocatalytic efficiency of $TiO_2$ to degrade pollutants in water [10–13]. We report here the use of ferrate(VI), also known as Fe(VI) or $Fe^{VI}O_4^{2-}$, to increase the efficiency of $TiO_2$ photocatalysis.

Fe(VI) has been of great interest because of its role as an environmentally friendly oxidant and disinfectant in remediation processes [14–16]. Fe(VI) has also shown promise as a green chemical for organic synthesis [14, 17]. A rechargeable super-iron battery using Fe(VI) as a cathode has also been reported [18]. Fe(VI) species are strong oxidizing agents which can be seen from the reduction potential of reactions 4 and 5 in acidic and alkaline solutions, respectively [19].

$$Fe^{VI}O_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \quad E^0 = 2.2V \tag{4}$$

$$Fe^{VI}O_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \quad E^0 = 0.7V \tag{5}$$

It is likely that the heterogeneous photocatalytic reduction of Fe(VI) takes place through three one-electron steps that would result in the sequential formation of Fe(V) and Fe(IV) (Equations 6–8) [20, 21].

$$Fe^{VI}O_4^{2-} + e_{cb}^- \rightarrow Fe^{V}O_4^{3-} \tag{6}$$

$$\mathrm{Fe^{V}O_4^{3-}} + \mathrm{e^-_{cb}} \rightarrow \mathrm{Fe^{IV}O_4^{4-}} \qquad (7)$$

$$\mathrm{Fe^{IV}O_4^{4-}} + 4\mathrm{H_2O} + \mathrm{e^-_{cb}} \rightarrow \mathrm{Fe(OH)_3} + 5\mathrm{OH^-} \qquad (8)$$

$Fe^{V}O_4^{3-}$(Fe(V)) formed in reaction 6 is $10^3$ to $10^5$ times more reactive than $Fe^{VI}O_4^{2-}$ [22, 23]. Fe(V) has also shown selectivity and specificity in oxidizing compounds [24, 25]. Iron, unlike chromium and manganese, is considered nontoxic. Therefore, Fe(V) has a great potential for remediation of pollutants. Photocatalytic oxidation of pollutants can be enhanced in the presence of Fe(VI) [21].

In this work, we have studied photocatalytic reduction of Fe(VI) in UV-irradiated $TiO_2$ suspensions in the presence of ammonia.Ammonia is a pollutant that creates eutrophication of rivers and lakes and its removal is thus becoming important issue. Fe(VI) reduction was conducted at various concentrations of Fe(VI) and ammonia. The objectives of the present work were two fold: (1) to understand photocatalytic reduction of Fe(VI) in presence of ammonia, and (2) to study how Fe(VI) enhances the photocatalytic oxidation of ammonia.

## 2. Materials and methods

### 2.1. *Chemicals*

All chemicals were reagent or analytical grade and were used as received. Degussa P-25 $TiO_2$ (ca. 80% anatase and 20% rutile) was used for this study. Potassium ferrate ($K_2FeO_4$), of high purity (>98%) was prepared by a wet chemical method [26]. Doubly distilled ammonium hydroxide (28% ammonia) was used as a source of ammonia.

### 2.2. *Experimental procedure*

The reaction vessel was a borosilicate glass 500 ml, three-neck round-bottom flask. The solution was stirred with a magnetic stirrer and a sintered-glass sparging tube attached through one of the necks of the flask. Helium gas was sparged before and during the reactions to create anaerobic conditions in the solution. Oxygen may otherwise have an influence by reacting with photogenerated electrons from $TiO_2$ to form the superoxide radical ($O_2 + e^-_{aq} \rightarrow O_2^-$, $k = 1.9 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$) [27]. A glass tube was inserted into one of the necks of the flask to allow excess helium to escape from the reaction solution. A 10–ml syringe was attached to the flask for the removal of samples. The reactor vessel was illuminated with a 15-watt ultraviolet lamp (GE, T-15). For each experiment, the light intensity was determined using a radiometer (Cole-Palmer 9811) which measured a band of wavelengths ranging from 330 to 375 nm with a calibration center of 365 nm. Light intensity in the reaction vessel was calibrated with potassium ferrioxalate actinometry [28].

A 300 ml Fe(VI) solution of desired concentration containing 0.033 g $l^{-1}$ suspended $TiO_2$ was illuminated with ultraviolet light for a given period of time. The Fe(VI) solution was prepared by the addition. of solid samples of potassium ferrate ($K_2FeO_4$) to 0.001 M sodium borate ($Na_2B_4O_7.10\ H_2O$)/0.005 M sodium phosphate dibasic ($Na_2HPO_4$) solution at pH 9.0. The phosphate serves as a complexing agent for Fe(III), which otherwise precipitates rapidly as a hydroxide that interferes with the optical monitoring of the reaction and accelerates the spontaneous decomposition of Fe(VI). All experiments were conducted at pH 9, a condition under which Fe(VI) is most stable. The rate of spontaneous decomposition of Fe(VI) in water at pH 9 does not contribute significantly in studying the photocatalytic reduction of Fe(VI) [29, 30].

Samples were periodically withdrawn from the reaction vessel and were filtered through a Millipore (0.22 $\mu$m) membrane. Fe(VI) concentrations in the samples were determined spectrophotometrically (HP 8453 Diode Array Spectrophotometer). A molar extinction coefficient $\varepsilon_{510} = 1150\ \mathrm{M^{-1}\ cm^{-1}}$ was used for calculating the concentration of Fe(VI) at pH 9.0 [31]. The concentrations of ammonia in the reaction mixture were measured potentiometrically using an $NH_3$-selective electrode (ISE) (Orion model 93–18).

## 3. Results

Initially, experiments to study the photocatalytic reduction of Fe(VI) were conducted in a $TiO_2$ suspension containing 126 $\mu$M ammonia at various concentrations of Fe(VI) at pH 9.0. Similar experiments were repeated with various concentrations of $NH_3$. All the results are shown in Figure 1. The reduction rate of Fe(VI) increased with increasing Fe(VI) concentration at all ammonia concentrations. Interestingly, the initial rates of Fe(VI) reduction linearly increase with initial concentrations of Fe(VI) (Figure 2a). Also, the amount of increase was related to ammonia concentration in the solution.

The initial rate ($R$) may be expressed by the following equation:

$$R = k_{\mathrm{Fe(VI)}}[\mathrm{Fe(VI)}]^m \qquad (9)$$

where $k_{\mathrm{Fe(VI)}}$ and $m$ are the rate constant and the order, respectively, of the photocatalytic reduction of Fe(VI). The data in Figure 2a were analyzed by plotting log[initial rate] vs. log[Fe(VI)] (Figure 2b). The values of m and $k_{\mathrm{Fe(VI)}}$ obtained from the plot are given in Table 1. The order, 1.25 ± 0.03 of reduction reaction of Fe(VI) was found to be dependent of concentration of ammonia in the solution (Table 1). Non-integer-orders are not uncommon in heterogeneous reactions where

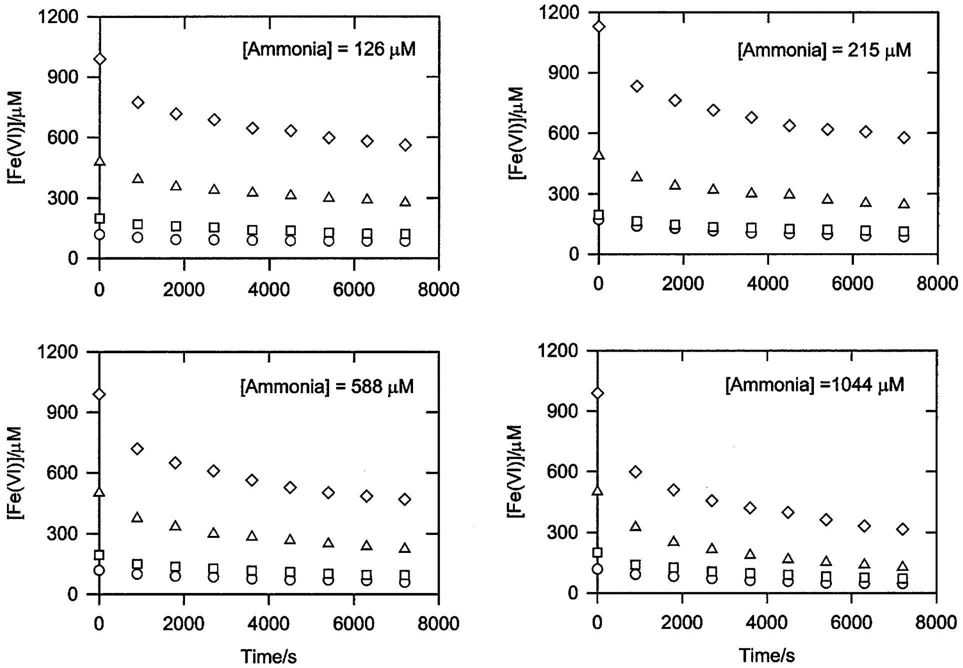

*Fig. 1.* Photocatalytic reduction of Fe(VI) in suspensions containing different ammonia concentrations at pH 9.0. $TiO_2$ = 0.033 g $l^{-1}$ and Intensity = $1.0 \times 10^{-7}$ einstein $s^{-1}$.

both mass transport and chemical reaction process can affect the reaction rate [32]. The rate in heterogeneous processes thus depends on the ions in the solution and often includes a specific expression for an adsorption isotherm [33]. A double layer (surface, Stern layer or diffuse layer) containing the Fe(VI) species surrounding the $TiO_2$ particle would determine the shapes of adsorption isotherm [34]. Adsorption processes in the double layer usually give non-integer order dependence on dissolved ion concentration. If the reaction takes place in the double layer, the rate would be proportional to the non-integer-order for Fe(VI).

The results in Table 1 show an increase in $k_{\mathrm{Fe(VI)}}$ with an increase in the concentration of ammonia. A plot of $1/k_{\mathrm{Fe(VI)}}$ vs. 1/[Ammonia] was found reasonably linear ($r^2 = 0.87$). $k_{\mathrm{Fe(VI)}}$ can then be expressed as

$$k_{\mathrm{Fe(VI)}} = [\mathrm{Ammonia}]/(a[\mathrm{Ammonia}] + b) \quad (10)$$

where $a = 6.0 \times 10^3\ \mu\mathrm{M}^{0.25}$ s and $b = 4.1 \times 10^6\ \mu\mathrm{M}^{-1.25}\ \mathrm{s}^{-1}$

Next, the photocatalytic oxidation of ammonia at two concentrations, 126 and 215 μM, was studied with and without Fe(VI) in the solution. The concentrations of Fe(VI) in solution mixtures were varied from 110 to 1129 μM. The significant enhancement of oxidation of ammonia was observed at [Fe(VI)]/[Ammonia] > 2 (Figure 3). At the highest molar ratio of 9:1 (FeVI):Ammonia), the oxidation of ammonia was found to be approximately seven times faster in the presence of Fe(VI) than with no Fe(VI) in the solution mixture. Under the studied experimental conditions, the results show an increase in the rate of ammonia oxidation due to higher molar ratios of Fe(VI):Ammonia (Figure 4). The rate for ammonia oxidation was also independent of initial ammonia concentration (Figure 4).

## 4. Discussion

The enhancement in Fe(VI) reduction and ammonia oxidation can be explained by the suggested reactions in Scheme I. The following assumptions were Made in Scheme I: (1) equilibrium exists between species of ammonia and Fe(VI) in the bulk solution and at $TiO_2$ surfaces, and (2) rates of reduction or oxidation of species are not limited by their transport from the bulk solution to $TiO_2$ surfaces.

### Scheme I

*Reduction of Fe Species*

$$FeO_4^{2-} + e^-_{cb} \rightarrow FeO_4^{3-} \quad (11)$$

$$FeO_4^{2-} + NH_2^{\bullet} + OH^- \rightarrow FeO_4^{3-} + NH_2OH \quad (12)$$

$$FeO_4^{3-} + NH_3 + 3H_2O \rightarrow Fe(OH)_3 + NH_2OH + 3OH^- \quad (13)$$

$$2FeO_4^{3-} + NH_2OH + 4H_2O \rightarrow 2Fe(OH)_3 + NO_2^- + 5OH^- \quad (14)$$

$$FeO_4^{3-} + NO_2^- + 3H_2O \rightarrow Fe(OH)_3 + NO_3^- + 3OH^- \quad (15)$$

*Oxidation of Nitrogen Species*

$$OH^-_{ad} + h^+_{vb} \rightarrow OH^{\bullet} \quad (16)$$

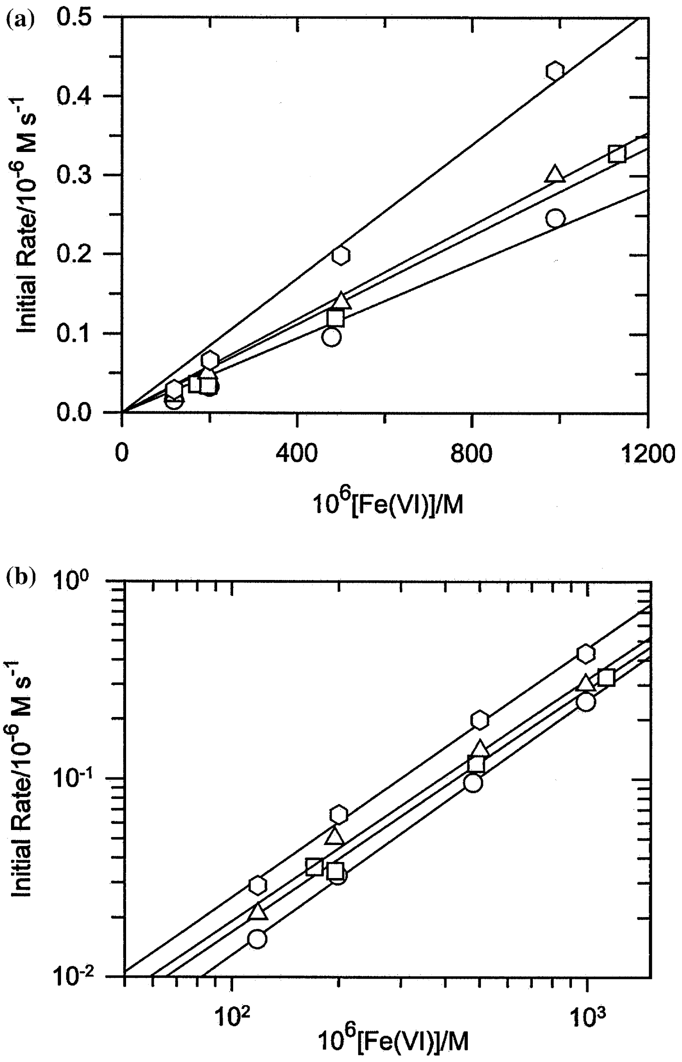

*Fig. 2.* (a) Initial rate vs. Fe(VI) concentrations. (b) log–log plot. Plots constructed from the data in Figure 1 and lines are least squares fits. O – 1.26 μm; □ – 215 μm ; △ – 588 μm; ◇ – 1044 μm.

$$NH_3 + OH^\bullet \rightarrow NH_2^\bullet + H_2O \quad (17)$$

In this scheme, $OH^\bullet$ radical preferentially reacts with ammonia (Equation 17) rather than dimerizing to form hydrogen peroxide. The rate constant for $OH^\bullet$ dimerization ($k = 5.5 \times 10^9$ M$^{-1}$ s$^{-1}$) is greater than $k_{17} = 1 \times 10^8$ M$^{-1}$ s$^{-1}$ [35, 36]. However, the ammonia concentrations, 126–1044 μM, are many orders of magnitude greater than the expected steady state concentration of $OH^\bullet$, which ensures that dimerization of $OH^\bullet$ does not contribute significantly to the reaction. In aqueous solution, Fe(VI) reacts with a hydrated electron at the diffusion-controlled rate constant (Fe (VI) + $e^-_{aq}$ → Fe(V), $k = 2 \times 10^{10}$ M$^{-1}$ s$^{-1}$ [35]). Fe(VI) and ammonia therefore inhibit the recombination of electrons and holes ($e^-_{cb} + h^+_{vb}$ → heat) and thus increase the photocatalytic reduction of Fe(VI) (Figure 1). An increase in Fe(VI) concentration will increase the possibility of electrons reacting with Fe(VI), which will further reduce the recombination of electrons and holes. The reduction rate of Fe(VI) therefore increases with the concentration of Fe(VI) in the reaction mixture, as has been found in our study (Figure 2). Other studies have also reported an acceleration in the photocatalytic reduction of metal ions with the addition of organic additives [12, 37–39].

*Table 1.* Rate constant ($k_{Fe(VI)}$) and order ($m$) for photocatalytic reduction of Fe(VI), in $TiO_2$ suspensions at various concentrations of ammonia at pH 9.0

| Ammonia/μM | $10^5\ k_{Fe(VI)}/\mu M^{-0.25}\ s^{-1}$ | $m$ |
|---|---|---|
| 126 | 2.19 ± 0.03 | 1.29 ± 0.02 |
| 215 | 6.02 ± 0.03 | 1.23 ± 0.07 |
| 588 | 6.91 ± 0.03 | 1.22 ± 0.08 |
| 1044 | 7.76 ± 0.26 | 1.26 ± 0.05 |

The faster rate of photocatalytic oxidation of ammonia in the presence of Fe(VI) compared to no Fe(VI) in the solution mixture (Figure 3) may be explained by the involvement of Fe(V) ($Fe^VO_4^{3-}$) (Scheme I). Fe(V) is a

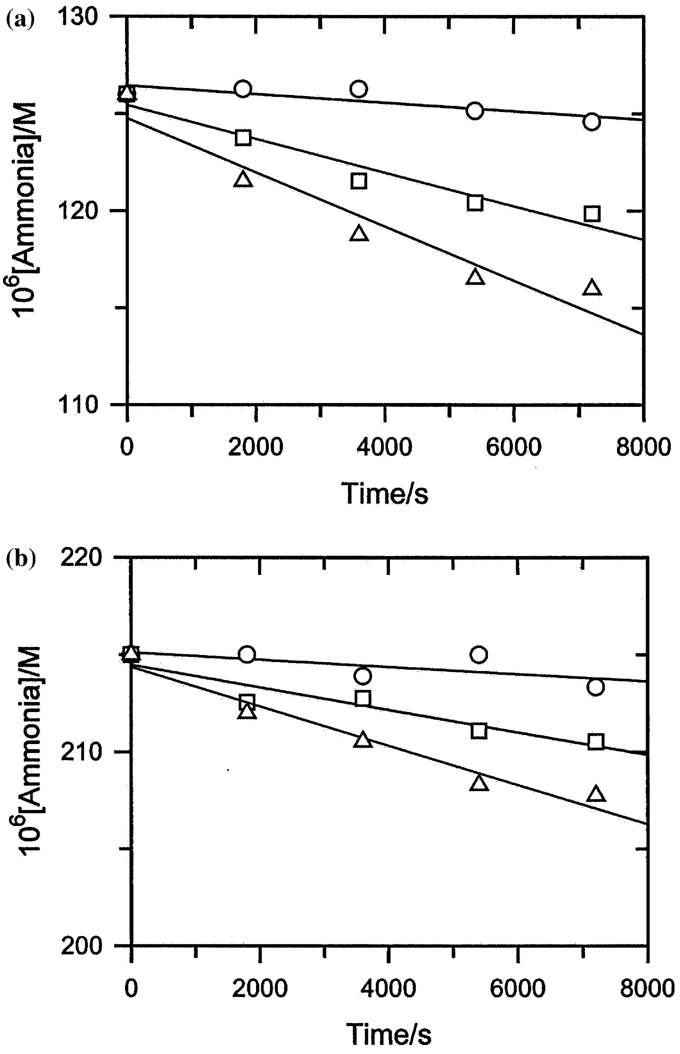

*Fig. 3.* Photocatalytic oxidation of ammonia in suspensions containing different concentrations of Fe(VI) at pH 9.0. Initial Ammonia Concentration = 126 $\mu$M (a) and 215 $\mu$M (b) TiO$_2$=0.033 g l$^{-1}$ and Intensity=1.0 × 10$^{-7}$ einstein s$^{-1}$. O – no Fe(VI); □ – 500 $\mu$M Fe(VI); △ – 1129 $\mu$M Fe(VI).

highly reactive species [40], which is produced by the reduction of Fe(VI) by electrons at the conduction band (reaction 11) and the amino radical reduction of Fe(VI) (reaction 12). Recently, the formation of an intermediate Cr(V) in the heterogeneous photocatalytic reduction of Cr(VI) using TiO$_2$ in the presence of oxalate and ethylenediaminetetracetic acid (EDTA) was directly obtained by EPR spectroscopy [41, 42]. These results support the occurrence of reaction 11 to give Fe(V) in Scheme I. In homogeneous solution, the rate constants for the Fe(VI) reduction by amino acid radicals [43] are of the order of $10^9$ M$^{-1}$ s$^{-1}$ and it is assumed that the rate constant for reaction 12 will be similarly fast. The amino radical in the proposed Scheme I results from the reaction of ammonia with a hydroxyl radical. The reported rate constant value of such a reaction is $1 \times 10^8$ M$^{-1}$ s$^{-1}$ measured at pH = 11.4 (reaction 17) [44].

The oxidation of ammonia is enhanced in the presence of Fe(VI) because ammonia reacts with Fe(V) produced by reactions 11 and 12. The significant increase in the rate of photocatalytic oxidation of ammonia at high levels of Fe(VI) in the solution mixture suggests Fe(VI) is reacting with the amino radical to produce Fe(V), which is then oxidizing ammonia (reaction 13). Hence, the rate of NH$_3$ oxidation increases at higher Fe(VI) concentrations (Figures 3 and 4).

The oxidation of ammonia by Fe(V) gives hydroxylamine (reaction 13). The possibility of forming hydroxylamine through a reaction, $NH_2^\bullet + OH^\bullet \rightarrow NH_2OH$, $k = 9.6 \times 10^9$ M$^{-1}$ s$^{-1}$ [45], as an alternative to equation 13 is ruled out because of the much higher concentrations of Fe(VI) (5.6 –10.4× 10$^{-4}$ M) than the steady state concentration of OH$^\bullet$ in the reaction mixture. Further reactions of Fe(V) with intermediates, hydroxylamine and nitrite, will result in nitrate (reactions 14 and 15). The formation of nitrate in the photocatalytic oxidation of ammonia has been observed by many workers [46–49].

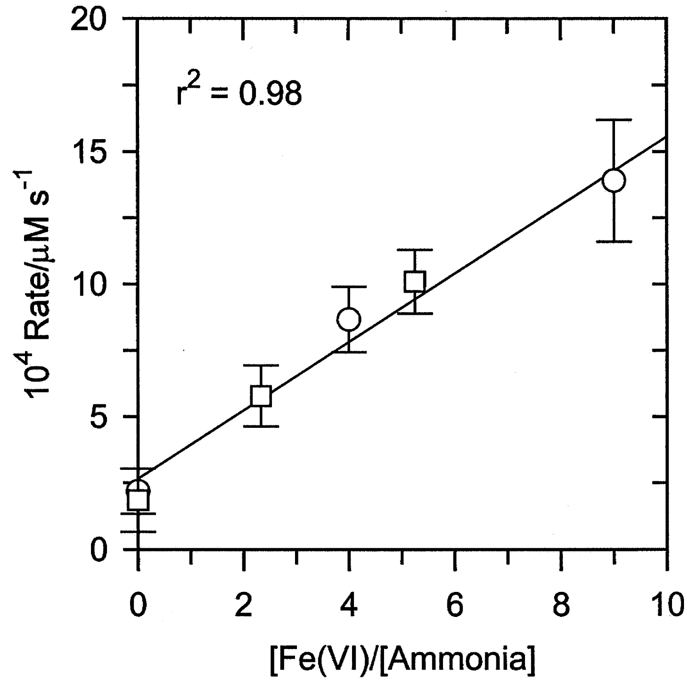

*Fig. 4.* Rate of ammonia oxidation versus molar ratios of Fe(VI) to ammonia at pH 9.0. Initial ammonia concentration: O – 126 μM; □ – 215 μM.

## 5. Conclusions

The rate of photocatalytic reduction of Fe(VI) in ammonia solution increases with the concentration of Fe(VI) and the rate constant depends on the concentration of ammonia. Results suggest the photocatalytic production of a highly reactive species, Fe(V), a powerful oxidant, to oxidize ammonia. A combination of Fe(VI) and $TiO_2$ photocatalyst has the potential to enhance the oxidation of ammonia.

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