

Heterogeneous photocatalytic reduction of ferrate(VI) in UV-irradiated titania suspensions: Role in enhancing destruction of nitrogen-containing pollutants

Virender K. Sharma,[†] Kurt Winkelmann, Yekaterina Krasnova, Changyoul Lee, and Mary Sohn

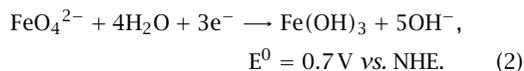
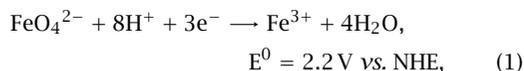
Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, Florida 32901, USA

ABSTRACT. The results of the heterogeneous photocatalytic reduction of Fe(VI) in UV-irradiated TiO₂ suspensions are presented and suggest indirect observation of the formation of Fe(V) by the photoreduction of Fe(VI) with e_{cb}⁻ at TiO₂ surfaces. Because Fe(V) selectively and rapidly oxidizes low reactivity pollutants with the production of the non-toxic by-product, Fe(III), the photocatalytic reduction of Fe(VI) has a role in pollution remediation processes. The experiments were conducted as a function of TiO₂ suspension concentrations, Fe(VI) concentrations, and pH in basic media. The initial rate of Fe(VI) reduction gave a fractional order with respect to initial Fe(VI) concentrations and adheres to simple Langmuir-Hinshelwood kinetics. Results suggest that the surface reaction (Fe(VI) + e_{cb}⁻ → Fe(V)) is the rate-controlling step. The photocatalytic reduction of Fe(VI) in the presence of less reactive nitrogen-containing species (ammonia, cyanate, and fulvic acid) were also investigated. Enhancement in the rate of Fe(VI) reduction was observed. A reaction scheme involving Fe(V) as an intermediate is presented which explains the faster photocatalytic oxidation of pollutants in the presence of Fe(VI).

1. INTRODUCTION

Semiconductor photocatalysis (TiO₂) has been studied extensively for treating water polluted with inorganic and organic compounds [1, 2]. The valence-band holes (h_{vb}⁺) and conduction-band electrons (e_{cb}⁻) are formed in the primary step of the photocatalytic process [3]. The valence-band hole can oxidize a variety of molecules as well as generate hydroxyl radicals in water, while the conduction-band electrons are good reductants. Transition metals ions (Hg(II), Ag(I), Ni(II), and Cr(VI)) can be reduced by the photogenerated electrons of TiO₂ photocatalysis [3, 4]. Recently, much interest has been shown in the reduction of Fe(VI) in UV-irradiated TiO₂ suspensions because of its potential in environmentally friendly synthesis and remediation processes [5, 6].

Fe(VI) species are strong oxidizing agents which can be seen from the reduction potential of reactions (1) and (2) in acidic and alkaline solutions, respectively [7]



The reduction potential of Fe(VI) is more positive than that of the conduction-band potential ($E_{\text{cb}} = -0.6$ to 0.8 V) in basic solution and the thermodynamic driving

force for the formation of OH⁻ ions is significantly higher than that of the photocorrosion of TiO₂ pathway in basic media. This indicates that the photocatalytic reduction of Fe(VI) in TiO₂ suspensions is feasible. The photoreduction of Fe(VI) likely takes place through one-electron transfer steps that would result in the sequential formation of Fe(V), Fe(IV), and Fe(III) [5]. The Fe(V) species, produced in this process, is 10³–10⁵ times more reactive than Fe(VI) [8, 9]. Fe(V) thus has the ability to oxidize compounds which cannot be rapidly oxidized by Fe(VI). This paper reports the photocatalytic reduction of Fe(VI) in the presence of nitrogen-containing pollutants (ammonia and cyanate), and fulvic acid, which react sluggishly with either aqueous Fe(VI) solutions or illuminated TiO₂ suspensions individually. Results suggest the production of Fe(V) and thus the enhancement of the photocatalytic oxidation of pollutants in the presence of Fe(VI).

2. EXPERIMENT

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 was 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 TiO₂ to form the superoxide radical ($\text{O}_2 + \text{e}_{\text{aq}}^- \rightarrow \text{O}_2^-$, $k = 1.9 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) [10]. A glass tube was inserted into

[†]E-mail: vsharma@fit.edu

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, light intensity was determined using a radiometer (Cole-Parmer 9811) which measured a band of wavelengths (8) that ranged from 330–375 nm with a calibration center of 365 nm. Light intensity in the reaction vessel was calibrated with potassium ferrioxalate actinometry [11].

A 300 mL Fe(VI) solution of desired concentration 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 borate/0.005 M phosphate, pH 9.0, conditions under which Fe(VI) is most stable. 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). The desired pH was achieved with either phosphoric acid or sodium hydroxide addition. Different amounts of TiO_2 were suspended in the solution. The experiments were conducted in the pH range 8.5–10.0. The rate of spontaneous decomposition of Fe(VI) in water at $pH \geq 8.5$ does not contribute significantly in studying the photocatalytic reduction of Fe(VI) in an alkaline medium [12, 13].

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 8452 Diode Array Spectrophotometer). A molar extinction coefficient, $\epsilon_{510} = 1150 M^{-1} cm^{-1}$ was used for calculating the concentration of Fe(VI) at pH 9.0 [14].

In order to determine the extent of the photocatalytic reduction of Fe(VI) due to UV-irradiated TiO_2 , three different experimental set-ups were conducted at each pH: (1) The solution was in contact with the catalyst but kept in the dark; (2) The solution was exposed to UV light in the absence of the catalyst; (3) The solution was exposed to UV light in the presence of the catalyst.

A similar experimental set-up as described above was used for a study of the photocatalytic reduction of Fe(VI) in the presence of ammonia, cyanate, and fulvic acid. Samples were periodically withdrawn from the reaction vessel and the concentrations of Fe(VI) in the filtered samples ($0.22 \mu m$) were determined. In experiments with ammonia in the reaction mixtures, the concentration of ammonia was measured using the phenate method [15].

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 the study. Potassium ferrate (K_2FeO_4) of high purity ($> 98\%$) was prepared by a wet chemical method [16]. Doubly

distilled ammonium hydroxide (28% ammonia) was used as a source of ammonia. Suwannee River Fulvic Acid (SRFA) was purchased from the International Humic Substances Society.

3. RESULTS AND DISCUSSION

Recently, we have initiated studies on the photocatalytic reduction of Fe(VI) in the presence and absence of nitrogen-containing pollutants in basic media. Fe(VI) reduction as a function of TiO_2 suspension concentration, Fe(VI) concentration, and pH was studied in detail [5]. Preliminary measurements of the photocatalytic reduction of Fe(VI) in the presence of pollutants showed indirectly the formation of Fe(V) at TiO_2 surfaces. The results suggest the enhancement of the removal of pollutants in the presence of Fe(VI).

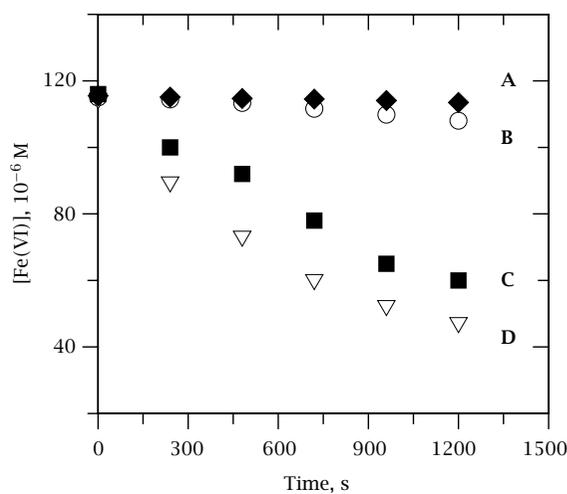
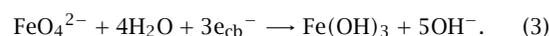


Figure 1. Photocatalytic reduction of Fe(VI) at pH 9.0. A = dark; B = UV only; C = UV + TiO_2 ($0.033 g L^{-1}$); D = UV + TiO_2 ($0.066 g L^{-1}$). Intensity = $1.62 \times 10^{-6} einstein s^{-1}$.

3.1. Photocatalytic reduction of Fe(VI). Initially, experiments monitoring the photocatalytic reduction of Fe(VI) were conducted at two different TiO_2 suspension doses as a function of Fe(VI) concentration at pH 9.0. As shown in Figure 1, the photoreduction of Fe(VI) in the TiO_2 suspensions occurred at a faster rate than in the absence of TiO_2 . Additionally, photoreduction was greater at higher TiO_2 suspension doses. The photoreduction of Fe(VI) to $Fe(OH)_3$ at TiO_2 surfaces can be expressed by the following equation:



It is unlikely that the photoreduction of Fe(VI) proceeds through a multi-electron process. Therefore, it is assumed that the photoreduction of Fe(VI) occurs in successive one-electron steps with the formation of Fe(V) in the first stage (eq. (4)). Fe(V) has been detected

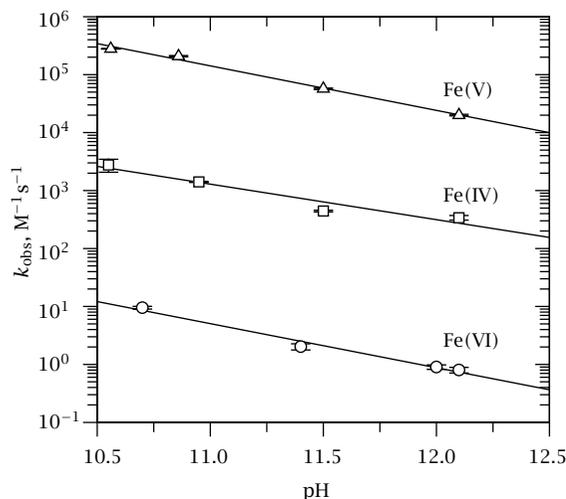
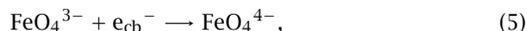
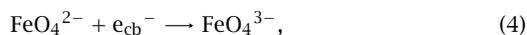


Figure 2. Rate constants for Fe(VI), Fe(V) and Fe(IV) oxidation of cyanide as a function of pH at 22°C [9].

in alkaline media so the assumption is made that Fe(V) was rapidly formed under existing experimental conditions (the observed rate constant for the homogeneous reaction of the hydrated electron with Fe(VI) is $k = 2.2 \pm 0.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [17]. Successive one-electron reduction steps will form Fe(IV) and Fe(III) (eqs. (5) and (6)). In this reaction scheme, the self-decompositions of Fe(V) and Fe(IV) species have been ruled out because these reaction rate constants are of the order of 10^6 – $10^8 \text{ M}^{-1} \text{ s}^{-1}$. In comparison, reactions (5) and (6) must be occurring at diffusion-controlled rates because Fe(V) and Fe(IV) species are much more reactive than Fe(VI) [8, 9, 18, 19]. For example, the greater reactivity of cyanide with both Fe(V) and Fe(IV) compared with Fe(VI) is shown in Figure 2. The reduction of Fe(VI) to Fe(V) (eq. (4)) is postulated to be the rate determining step



The Fe(III) formed from reaction (6) may be reduced further to Fe(II) at illuminated TiO₂ surfaces. The possibility of Fe(II) reacting with hydrogen peroxide, produced by the reaction of water with the valence-band hole ($2\text{H}_2\text{O} + 2h_{vb}^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+$), to initiate a Fenton-type reaction is not considered in the proposed scheme. Fe(II) would preferentially react with Fe(VI), which is a more powerful oxidant than H₂O₂ [20]. Moreover, higher solution concentrations of Fe(VI) than H₂O₂ ensure that Fe(II) is consumed by Fe(VI).

Photoreductions of Fe(VI) at TiO₂ surfaces at different Fe(VI) concentrations were analyzed using a plot of log [initial rate] versus log [Fe(VI)] (Figure 3(A)).

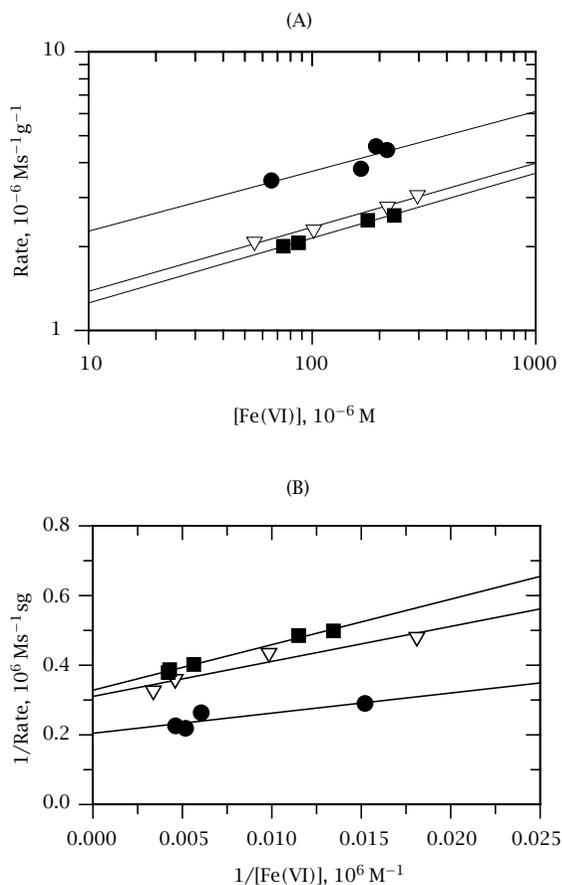


Figure 3. (A) A plot of initial rate vs. [Fe(VI)] (B) Langmuir plots. TiO₂ (0.033 gL⁻¹); Intensity = $1.62 \times 10^{-6} \text{ einstein s}^{-1}$ (•-pH = 8.5; ▽-pH = 9.0; ■-pH = 10.0).

Initial rates were obtained from the slope of linear least squares regression lines of the concentrations of Fe(VI) versus the corresponding time intervals. Initial rates were corrected for the photoreduction of Fe(VI) in the absence of TiO₂. This correction also eliminated any effects related to buffers present in the reaction mixtures [21–24]. Slopes of the linear least squares fit curves in Figure 3(A) were 0.21 ± 0.02 , 0.23 ± 0.02 , and 0.24 ± 0.03 at pH 8.5, 9.0, and 10.0, respectively. This suggests a fractional order with respect to Fe(VI) concentration in the rate expressions. Similar results were also observed in the Cr(VI) reduction at TiO₂, WO₃, γ -Fe₂O₃ and SrTiO₃ surfaces [25]. Fractional reaction orders are not uncommon in heterogeneous processes [26].

A fractional order can be explained by considering that the rate depends on the ions in the solution and specific expression of an adsorption isotherm [27]. A double layer (surface, Stern layer or diffuse layer) containing the Fe(VI) species surrounding the TiO₂ particle would determine the shapes of the adsorption isotherms [28]. Adsorption isotherm processes in the

Table 1. Rate constants (k) and apparent binding constants (K) for photoreduction of Fe(VI) at TiO₂ surfaces at different pH.

pH	k ($\times 10^{-6} \text{ Ms}^{-1} \text{ g}^{-1}$)		K ($\times 10^4 \text{ M}^{-1}$)	
	TiO ₂ = 0.033 gL ⁻¹		TiO ₂ = 0.066 gL ⁻¹	
8.5	4.6 ± 0.5	4.7 ± 1.4	5.3 ± 0.8	1.3 ± 0.3
9.0	3.3 ± 0.1	3.1 ± 0.3	3.9 ± 0.3	2.0 ± 0.4
10.0	3.1 ± 0.1	2.5 ± 0.1	2.9 ± 0.2	1.7 ± 0.3

double layer usually give fractional order dependence on dissolved ion concentrations. If the reaction takes place in the double layer, rates would be proportional to the fractional order of Fe(VI) concentrations.

The initial rate of disappearance of a variety of organic substrates at illuminated TiO₂ surfaces has been described in a Langmuirian-Hinshelwood form (eq. (7)) by many workers [26–32]

$$\frac{1}{\text{rate}} = \frac{1}{k} + \frac{1}{kK[\text{Substrate}]} \quad (7)$$

In eq. (7), k is the reaction rate constant and K is the constant of adsorption. Some workers have also used Langmuirian analysis to describe chromium(VI) reduction reactions at TiO₂ surfaces which are driven by photogenerated holes and reduction reactions [29]. Similar analysis of Fe(VI) reduction data gave a reasonable fit between $1/\text{rate}$ vs. $1/[\text{Fe(VI)}]$ ($r^2 = 0.97$) (Figure 3(B)). A value for $k = 3.68 \times 10^{-6} \text{ Ms}^{-1}$, was obtained from the intercept of the data. In comparison, k for the photoreduction of Cr(VI), normalized to TiO₂ suspension dose, has been found to be $4.12 \times 10^{-8} \text{ Ms}^{-1}$ in alkaline media [29]. Generally Fe(VI) has shown higher reactivity than Cr(VI) which is probably related to a lower E^0 value for Cr(VI) [$E^0(\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3) = -0.12 \text{ V}$] than Fe(VI) [$E^0(\text{FeO}_4^{2-}/\text{Fe}(\text{OH})_3) = 0.72 \text{ V}$] in a basic medium.

Next, experiments were conducted in two TiO₂ suspension doses at pH 8.5 and 10.0. Reaction rate constants and adsorption constants were obtained from Langmuirian plots (Figure 3(B)) and are given in Table 1. Generally, the k values are pH dependent and decrease with an increase in pH. Literature results suggest the existence of four Fe(VI) species, H₃FeO₄⁺, H₂FeO₄, HFeO₄⁻ and FeO₄²⁻ over the entire pH range [33]. The dissociation constants for protonated Fe(VI) species are $pK_1 = 1.6 \pm 0.2$, $pK_2 = 3.5$, and $pK_3 = 7.3 \pm 0.1$ [34]. The Fe(VI) species in the studied pH range are HFeO₄⁻ and FeO₄²⁻ (Figure 4). An increase in pH has two combined effects on the photoreduction of Fe(VI) at TiO₂ surfaces. The reduction rates of Fe(VI) by substrates decreased with an increase in pH and were largely related to the decreased concentration of HFeO₄⁻, which is more reactive than FeO₄²⁻ [6, 8, 35]. An increase in electrostatic repulsion between the negatively charged TiO₂ surface and the two Fe(VI) species may result from an increase in the concentration of the more negative FeO₄²⁻ species relative to the concentration of HFeO₄⁻ at higher pH values. A combined effect of these

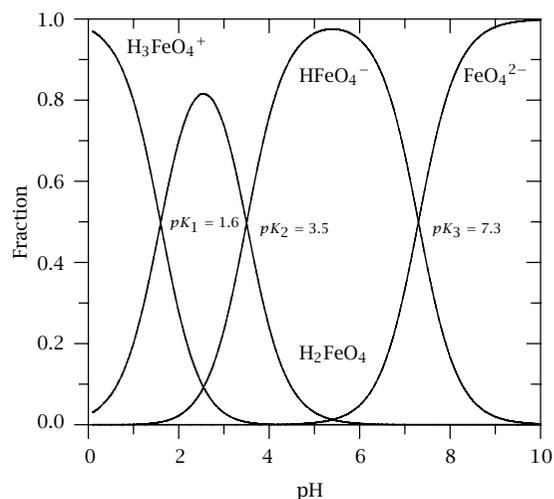


Figure 4. Speciation of Fe(VI) [34].

processes will result in slower photoreduction of Fe(VI) at TiO₂ surfaces with an increase in pH.

The differences in electrostatic repulsion between the negatively charged surfaces of TiO₂ and Fe(VI) species at different pH values may cause a slight pH dependence in adsorption constants at lower doses (Table 1). The decrease in values of K with an increase in TiO₂ doses (Table 1) is expected because of a decrease in the equilibrium adsorption capacity at higher doses of TiO₂ [36].

It should be pointed out that there is a possibility of a decrease in the available active sites of TiO₂ in studied reactions due to possible adsorption of Fe(OH)₃, a product of Fe(VI) photoreduction. However, the complexing phosphate buffer in the present study should minimize catalyst poisoning [37]. Also, effects related to chemisorption of phosphate and borate buffers to TiO₂ particle surfaces were minimal due to the alkaline pH of the solution [21–24].

3.2. Photocatalytic reduction of Fe(VI) in the presence of pollutants and fulvic acid

3.2.1 Ammonia

The pollution of surface and ground waters caused by waste waters with a high concentration of ammonia results in an increase in biochemical oxygen demand. In drinking water, ammonia decreases the available free chlorine (Cl₂ or OCl⁻) by the formation of chloramines. Studies on the photocatalytic oxidation

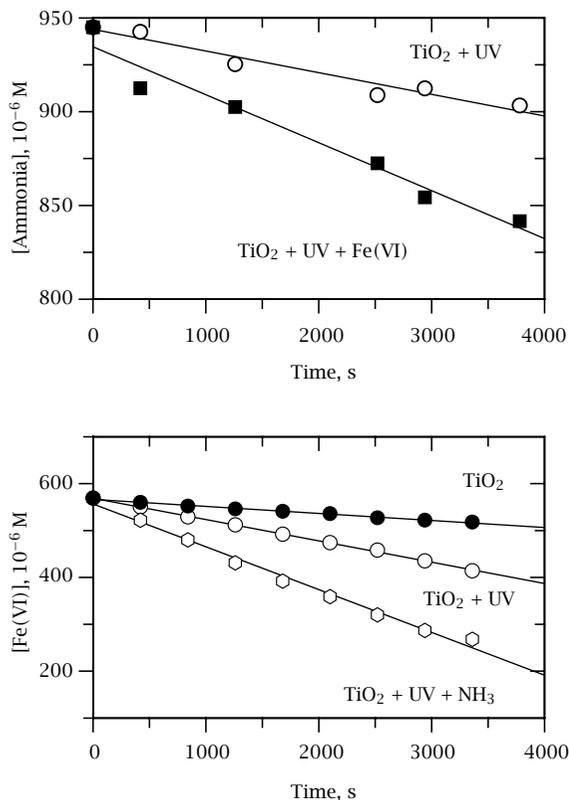


Figure 5. Photocatalytic oxidation of ammonia and reduction of Fe(VI) at pH 9.0. $[\text{Fe(VI)}] = 560 \mu\text{M}$; $[\text{Ammonia}] = 940 \mu\text{M}$; $\text{TiO}_2 = 0.066 \text{ gL}^{-1}$; $\text{Intensity} = 1.62 \times 10^{-6} \text{ einstein s}^{-1}$.

of aqueous ammonia have been conducted to seek ammonia removal from waters [38–41]. Photocatalytic oxidation of aqueous ammonia was not observed at $\text{pH} < 5$. However, significant degradation of ammonia was noticed in alkaline media [41]. In our study, the photocatalytic oxidation of ammonia was found to be approximately three times faster in the presence of Fe(VI) than with no Fe(VI) in the solution mixture (Figure 5). The photoreduction rate of Fe(VI) also increased in the presence of ammonia in the solution (Figure 5).

3.2.2 Cyanate

The oxidation of cyanides by chemical, electrochemical, and biochemical methods usually results in the formation of cyanate [42–47]. Although cyanate is much less toxic than cyanide, it is chemically unstable and may have an adverse effect on the natural environment. It is therefore important to convert the cyanate into other stable inert end products. The photocatalytic oxidation of cyanate on TiO₂ surfaces may be a viable method for decontamination of cyanate into nitrate [48–50]. The enhancement of the photocatalytic reduction of Fe(VI) in the presence of cyanate was observed in preliminary experiments (Figure 6). It is likely that Fe(VI) increases

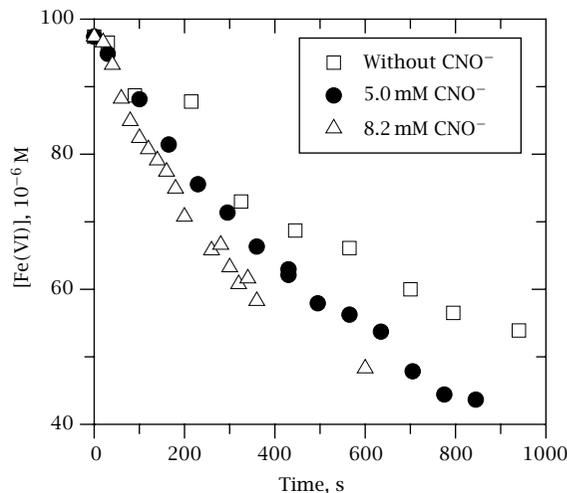


Figure 6. Photocatalytic reduction of Fe(VI) in presence of cyanate. $[\text{Fe(VI)}] = 100 \mu\text{M}$; $\text{TiO}_2 = 0.066 \text{ gL}^{-1}$; $\text{Intensity} = 1.40 \times 10^{-7} \text{ einstein s}^{-1}$.

the rate of photocatalytic oxidation of cyanate. Nitrite and nitrate were the only products observed in the photocatalytic oxidation of cyanate in the presence of a strong oxidant, H₂O₂ [50]. Similar products may also be formed in the photocatalytic oxidation of cyanate by Fe(VI) in our suspensions.

3.2.3 Fulvic Acid

In recent years, there has been increasing interest in natural organic matter (NOM) present in potable surface and ground water supplies. One reason for concern is related to the formation of disinfection byproducts (DPB's) from the treatment of water by chlorination methods [51]. Oxidation of NOM by chlorination produces chlorinated hydrocarbons, many of which are known or suspected carcinogens. Alternative methods such as photoinduced reactions in the presence of the semiconducting TiO₂ catalyst may control formation of DPB in drinking water treatment processes [52–54]. Studies on the photocatalytic oxidation of fulvic acid (FA) in water in aqueous Fe(VI) solutions have been initiated. Fulvic acid was selected because it is a major constituent of NOM. Concentrations of Fe(VI) were monitored during photocatalytic experiments on TiO₂ suspensions in the absence and presence of fulvic acid (Figure 7). A higher reduction rate of Fe(VI) was noted in the presence of fulvic acid. Future experiments will include the measurement of fulvic acid concentrations in the experiment to confirm the oxidation of fulvic acids.

3.2.4 Mechanism

The enhancement in Fe(VI) reduction and ammonia oxidation can be explained by the suggested reactions

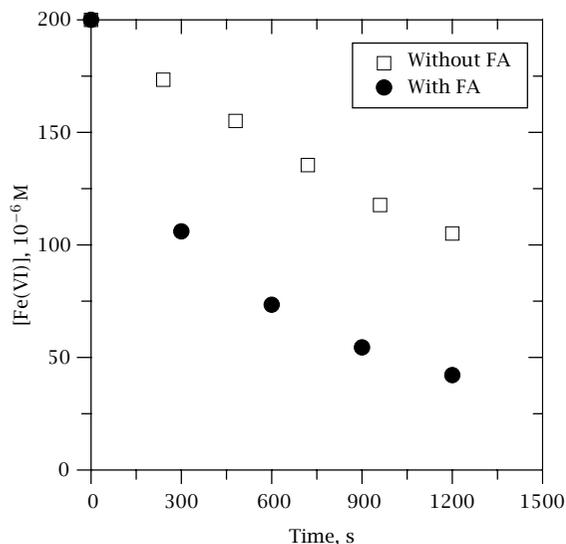
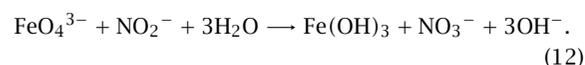
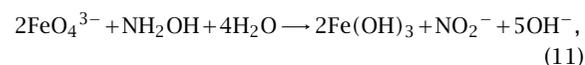
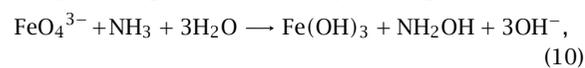
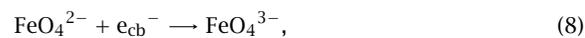


Figure 7. Photocatalytic reduction of Fe(VI) in presence of fulvic acid (FA). $[\text{Fe(VI)}] = 200 \mu\text{M}$; $[\text{FA}] = 0.045 \text{ gL}^{-1}$; $\text{TiO}_2 = 0.066 \text{ gL}^{-1}$; $\text{Intensity} = 1.40 \times 10^{-6} \text{ einstein s}^{-1}$.

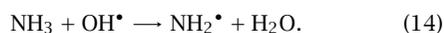
in Scheme I. The following assumptions were made in Scheme I: (1) equilibrium exists between species of ammonia and Fe(VI) in the bulk solution and at TiO_2 surfaces, and (2) rates of reduction or oxidation of species are not limited by their transport from the bulk solution to TiO_2 surfaces.

Scheme I

Reduction of Fe Species



Oxidation of Nitrogen Species



In this scheme, OH^\bullet radical preferentially reacts with ammonia (eq. (14)) rather than dimerizing to form hydrogen peroxide. The rate constant for OH^\bullet dimerization ($k = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) is greater than $k_{14} = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [55, 56]. However, the ammonia concentration, $9.4 \times 10^{-4} \text{ M}$, is 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. Reaction (13) will

inhibit the recombination of electrons and holes and thus increase the photocatalytic reduction of Fe(VI). Acceleration of the photocatalytic reduction of metal ions has been reported when organic substrates scavenge the valence-band holes [3, 57, 58].

Scheme I involves Fe(V), a highly reactive species which is produced by (a) reduction of Fe(VI) by conduction-band electrons (reaction (8)); (b) amino radical reduction of Fe(VI) (reaction (9)). The formation of an intermediate Cr(V) in the heterogeneous photocatalytic reduction of Cr(VI) using TiO_2 in the presence and absence of ethylenediaminetetraacetic acid (EDTA) was directly obtained by EPR spectroscopy [59]. These results support the occurrence of reaction (8) in Scheme I.

In homogeneous solution, the rates of Fe(VI) reduction by amino acid radicals [18] are of the order of $10^9 \text{ M}^{-1}\text{s}^{-1}$ and it is assumed that the rate constant for reaction (9) will be fast. The amino radical in the proposed Scheme I results from the reaction of ammonia with a hydroxyl radical, $k = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; $\text{pH} = 11.4$ (reaction (14)) [60]. Since Fe(V) reacts 3-5 orders of magnitude faster than Fe(VI) [18, 33, 61], Fe(V) will react with ammonia to give hydroxylamine (reaction (10)). The possibility of forming hydroxylamine through a reaction, $\text{NH}_2^\bullet + \text{OH}^\bullet \rightarrow \text{NH}_2\text{OH}$, $k = 9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [62], as an alternative to eq. (10) is ruled out because of the much higher concentrations of Fe(VI) ($5.6 \times 10^{-4} \text{ M}$) than the steady state concentration of OH^\bullet in the reaction mixture. The further reactions of Fe(V) with intermediates, hydroxylamine and nitrite, will result in the production of nitrate (reactions (12)). Recent work also suggests the formation of nitrate as a product in a similar study using Cr(VI) [10].

4. CONCLUSIONS

The laboratory studies were made in deoxygenated phosphate and buffer solutions to elucidate the mechanism of photocatalytic oxidation reactions involving Fe(VI) in reaction mixtures. Results suggest the potential role of a powerful oxidant, Fe(V), in oxidizing less reactive nitrogen-containing pollutants and fulvic acid by TiO_2 photocatalysis in the presence of Fe(VI). Future experiments that monitor the concentrations of reactants and products at different time intervals during the reactions under different concentrations of Fe(VI), TiO_2 , light intensity, and a selected pollutant will unravel the steps in the reaction mechanism of the photocatalytic oxidation of pollutants and NOM in the presence of Fe(VI).

The studied process can be applied to decontamination of wastewater. The controlled parameters in the present study such as buffers and removal of oxygen are not necessarily required in any real environment applications. The suggested pH range, 8.5-10.0, in the technique can be easily achieved by adding

either NaOH or HCl, depending on the initial pH of the contaminated water. Fe(III) hydroxide produced from Fe(VI) acts as a coagulant for removal of pollutants [63]. The expected competing reaction between inherent oxygen and conduction band electrons can be minimized extensively by applying excess Fe(VI) to the contaminated water. Consequently, Fe(VI) will preferentially react with e_{cb}^- to give Fe(V). A combination of the oxidant Fe(VI) and the photocatalyst TiO_2 therefore has potential in environmentally friendly remediation processes.

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