Degradation of endocrine disrupting chemicals in aqueous solution by Interaction of photocatalytic oxidation and ferrate (VI) oxidation

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Abstract In this study, the degradation of bisphenol A in aqueous suspension by interaction of photocatalytic oxidation and ferrate(VI) oxidation was investigated under different conditions. The results indicate that the formation of Fe(V) and Fe(IV) is in the photocatalytic reduction of Fe(VI) by electron (e_{cb}^-) on the surface of TiO_2. The oxidation efficiency of the photocatalytic oxidation in the presence of Fe(VI) was much greater than that without. In addition, the decomposition of Fe(VI) under different conditions was also investigated. The results indicate that the Fe(VI) reduction was accelerated by photocatalytic reaction and the adsorption capacity of Fe(VI) on TiO_2 surface decreased as pH increased. The characteristics of solid potassium ferrate prepared were investigated by X-ray diffraction. It was found that the potassium ferrate solid has a tetrahedral structure with a space group of D2h (Pnma) and a = 7.705 Å, b = 5.863 Å, and c = 10.36 Å.

Keywords BPA, Endocrine Disrupting Chemicals, Potassium Ferrate, Photocatalytic Oxidation

Introduction

Due to the shortage of water supply sources, reclaimed water for indirect potable water reuse has been explored in many regions. A major concern has been of residual pollutants existing in the effluents from sewage treatment works. With the rapid development of analytical techniques, it has been reported that many of these effluents contained low concentration of endocrine disrupting chemicals (EDCs) (Kimura et al., 2004). It is well known that bisphenol A (BPA) as one of EDCs has an estrogenic effect, causing an abnormal increase in the growth of yeast cells in polycarbonate flasks. Moreover, BPA contributes significantly to the environmental problem as evidenced by a number of recent studies (Inoue et al., 2003). Hence, the necessity to explore new technologies for degrading these EDCs within the effluents for water reuse is quite significant.

Titanium dioxide (TiO_2) photocatalysis has been extensively studied to remove organic and inorganic chemicals from water and wastewater. As electrons (e_{cb}^-) move from the valence band to the conduction band of TiO_2 in the primary step of the photocatalytic process, the valence band holes (h_{vb}^+) act as a very strong oxidizing agent. However, there are still some fundamental problems concerning the efficiency of photocatalysis. TiO_2 photoreaction usually has a low rate of electron transfer to oxygen and a high rate of recombination between electron (e_{cb}^-)/hole (h_{vb}^+) pairs that result in a low quantum yield of < 5%.

Potassium ferrate (K_2FeO_4) has been well known as a very strong oxidizing agent for a long time. Recent research indicates that the ferrate oxidation reaction from Fe(VI) to Fe(III) is not a single step reaction, which includes two sequential intermediates of Fe(V) and Fe(IV) (Johnson and Sharma, 1999; Chenthamarakshan et al., 2000). The studies demonstrated that Fe(V) is 10^3-10^5 times more reactive with compounds than Fe(VI), which means the reduction from Fe(VI) to Fe(V) is a critical rate-determining step in the whole reaction and ferrate oxidation efficiency can be enhanced by one-electron-reducing agents such as the conduction band electrons (e_{cb}^-).

$$FeO_4^{2-} + e_{cb}^- \rightarrow FeO_4^{3-}$$

In this study, Fe(VI) was used to capture the electrons from TiO_2 photocatalysis to form Fe(V), while preventing the recombination of electron (e_{cb}^-)/hole (h_{vb}^+) pairs during photocatalytic reaction. Fe(VI) reduction and BPA degradation in aqueous solution were studied under different conditions.

Methodology

Materials

BPA chemical (99%) from Aldrich was used as a model EDC. Solid potassium ferrate was prepared in our laboratory with high purity (99%) by oxidation of ferric nitrate with hypochlorite.

Characterization of solid potassium ferrate

X-ray diffraction (XRD) analysis was carried out to study the composition of solid potassium ferrate, in which XRD patterns were obtained by using a Philips recording diffractometer with the filtered CuKα reaction. Data were recorded over the range from 10^o to 60^o (2θ) at a recording speed of 1^o min^{-1}.

Equipment

A cylindrical photoreactor used in the study has an effective volume of 250 ml and is surrounded with a circulating water jacket for temperature control. A 6-W UV lamp with a main emission at 365 nm is equipped in the middle of the photoreactor as illustrated by Figure 1.

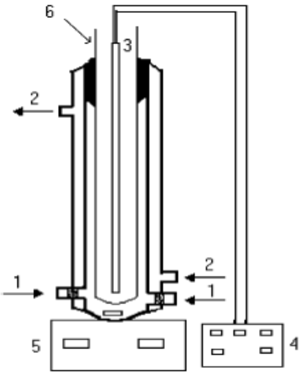

Figure 1 Schematic diagram of the photoreactor system (1: air; 2: water; 3: UV lamp; 4: timer; 5: stirrer; and 6: quartz jacket).

The experiments of Fe(VI) reduction and BPA degradation in aqueous solution were carried out under different reaction conditions. During each reaction, water samples were collected at different time intervals. At each sampling time, sodium sulphite solution was added immediately to the sample when it was taken to stop any further reaction. The samples were then centrifuged at 4000 rpm for 15 min before analysis.

The concentration of Fe(VI) was determined by UV/vis spectroscopy. K_2FeO_4 dissolved as FeO_4^{2-}, has a distinctive UV/Vis spectrum with a maximum absorbance at 510 nm. The molar absorptivity at 510 nm has been determined as 1150 M^{-1} cm^{-1} by Bielski and Thomas in 1987. The concentration of BPA was determined by high performance liquid chromatography (HPLC Finnigan LCQ DUO) with a high pressure pump (Spectrasystem P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). In the HPLC analysis, a Pinnacle II C18 column (5 µm particle size, 250 mm length, and 4.6 mm inner diameter) was employed and a mobile phase of acetonitrile/water (7:3, v/v) was provided at a flowrate of 0.8 ml min^{-1}. An injection volume of 20 µl was used and the concentration of BPA was determined by the UV detector at 278 nm.

Results and discussion

Characteristics of solid potassium ferrate

The solid potassium ferrate was prepared in our lab and its purity was determined to be of 99%. To further determine its characteristics, the solid potassium ferrate sample was examined by XRD analysis. The analytical results are shown in Figure 2. It can be seen in the XRD pattern that four peaks of 002, 111, 211, and 013 correspond to potassium ferrate and the main peak (013) at 30.1° (2θ) is very sharp and strong, representing high purity. The XRD result also indicates that the prepared potassium ferrate sample has a tetrahedral geometrical structure with a space group of D_{2h} (Pnma) and a = 7.705 Å, b = 5.863 Å, and c = 10.36 Å.

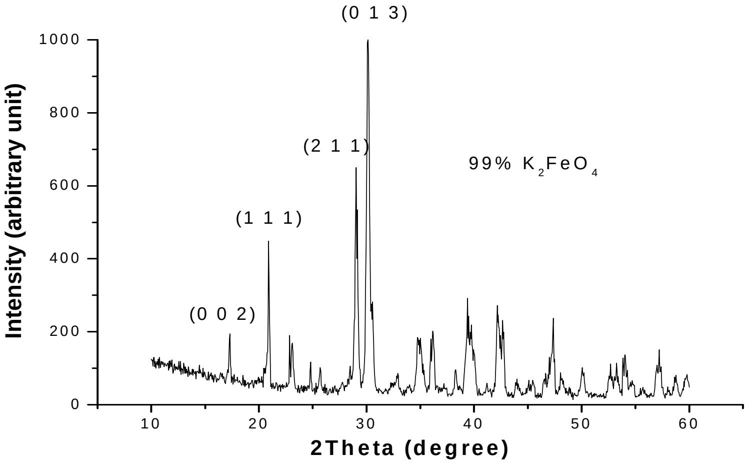

Figure 2 The XRD pattern of potassium ferrate sample

Reduction of Fe(VI)

A set of experiments was carried out to study the reduction of Fe(VI) in aqueous K_2FeO_4 solution with an initial concentration of 0.1 mM at pH 9.0 under different conditions: (i) Fe(VI) only in the dark; (ii) Fe(VI) with UV; (iii) Fe(VI) + TiO_2 without UV; and (iv) Fe(VI)

+ TiO_2 with UV. The temporal change in Fe(VI) concentration up to 20 min reaction was measured by UV/Vis spectrometry. The experimental results are shown in Figure 3.

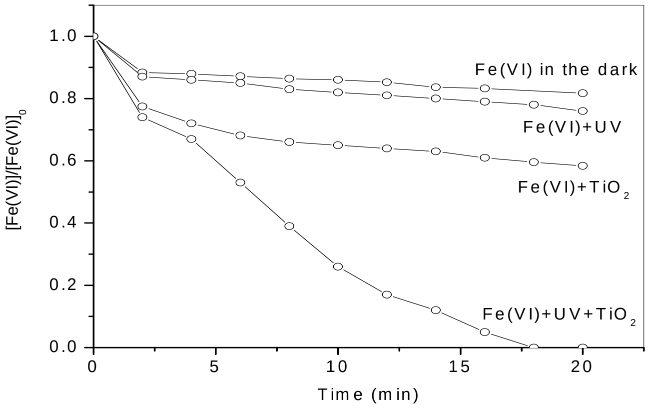

Figure 3 Reduction of Fe(VI) vs. time ($[Fe(VI)]_0 = 0.1$ mM and $[TiO_2] = 1$ g l^{-1}).

It is seen that the decrease of Fe(VI) concentration in aqueous solution without TiO_2 was insignificant. It was also found that the Fe(VI) concentration in aqueous TiO_2 suspension was decreased more significantly than that in absence of TiO_2 due to adsorption by TiO_2 particles in the dark. Under UV illumination, the Fe(VI) concentration in aqueous TiO_2 suspension was decreased greatly. It is believed that the reduction of Fe(VI) under this condition resulted mainly from photocatalytic reduction reaction. The photocatalytic reduction of Fe(VI) to Fe(III) on the TiO_2 surface can be expressed by the following reactions:

$$FeO_4^{2-} + e_{cb}^- \rightarrow FeO_4^{3-}$$
$$FeO_4^{3-} + e_{cb}^- \rightarrow FeO_4^{4-}$$
$$FeO_4^{4-} + 4H_2O + e_{cb}^- \rightarrow Fe(OH)_3 + 5OH^-$$

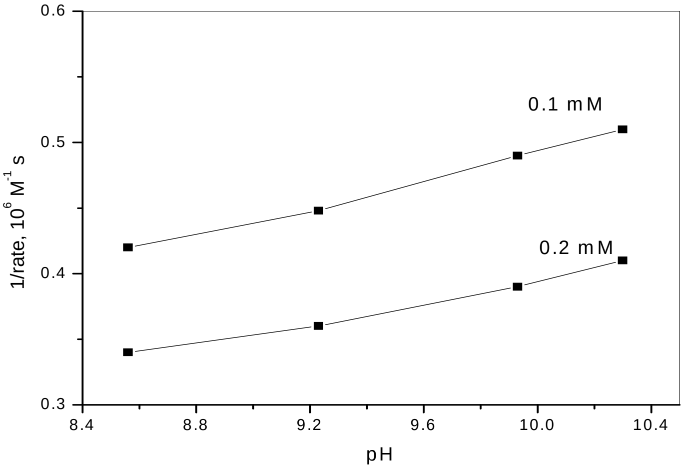

Figure 4 Reduction rate of Fe(VI) vs. pH under UV illumination ($[TiO_2] = 1$ g l^{-1}).

More experiments were performed to study the reduction of Fe(VI) in the TiO_2 suspension under UV illumination at different pH. According to the experimental data, the initial rates of Fe(VI) reduction were determined from the slopes of the linear relationship between log concentration of Fe(VI) versus reaction time at different pH and are presented in Figure 4. Two sets of experiments with the initial Fe(VI) concentrations of 0.1 mM and 0.2 mM demonstrated that the higher reduction rates occurred at higher pH.

Langmuir-Hinshelwood (L-H) model has been applied to describe the kinetics of heterogeneous reactions such as photocatalytic reaction in aqueous TiO_2 suspension by many researchers successfully (Alekabi et al., 1989; Turchi and Ollis, 1989; Lin et al., 1993; Ooka et al., 1999; Sharma et al., 2003). Since the photocatalytic reduction of Fe(VI) in the TiO_2 suspension is also a heterogeneous reaction, the L-H equation below would be a suitable model to describe the photocatalytic reduction of Fe(VI) in aqueous TiO_2 suspension under UV illumination:

$$\frac{1}{rate} = \frac{1}{k} + \frac{1}{kK[substrate]}$$

Where *k* is the reaction rate constant and K is the apparent binding constant.

By applying the above equation to fit the experimental data obtained in this study, the rate constant *k* and apparent binding constant K for the reduction of Fe(VI) at different pH were determined and are compared in Table 1.

Table 1 Rate constant (*k*) and apparent binding constant (K) at different pH

pH	*k* ($\times 10^{-6}$ M s^{-1})	K ($\times 10^{4}$ M^{-1})
8.56	3.85	1.55
9.23	3.68	1.45
9.93	3.45	1.36
10.3	3.23	1.30

It is seen from Table 1 that the values of both *k* and K decreased with increased pH. They had the lowest values at the highest pH in the range of 8.56 - 10.3. The main reason for the decrease of the adsorption capacity on the TiO_2 surface is that Fe(VI) has different forms at different pH as shown below:

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \qquad pK_a = 1.6 \pm 0.2$$ (Licht et al., 2001)

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \qquad pK_a = 3.5$$ (Licht et al., 2001; Sharma, 2002)

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \qquad pK_a = 7.3 \pm 0.1$$ (Licht et al., 2001; Sharma, 2002)

According to the above pK_a values, the fractions of each form ($H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}) against pH can be calculated and are shown in Figure 5. It is seen from Figure 5 that FeO_4^{2-} is dominant at pH 10.3. Therefore, the reaction rate and binding constant are smaller at pH 10.3 than that at lower pH, because there is a greater electrostatic repulsion force between FeO_4^{2-} and the negatively charged surface of TiO_2 particles.

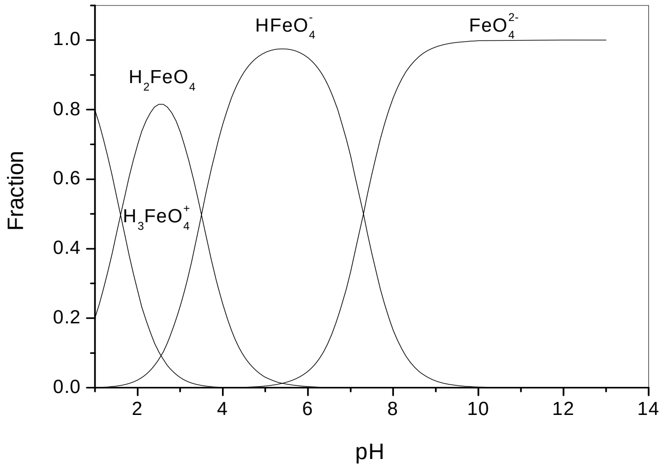

Figure 5 Fraction of Fe(VI) at different pH (Delaude and Laszlo, 1996).

Degradation of BPA

A set of experiments under different conditions was performed to study the degradation of BPA with an initial concentration of 0.1 mM together with: (i) Fe(VI) only, (ii) Fe(VI) + TiO_2, (iii) TiO_2 + UV, and (iv) TiO_2 + Fe(VI) + UV. The experimental results are shown in Figure 6.

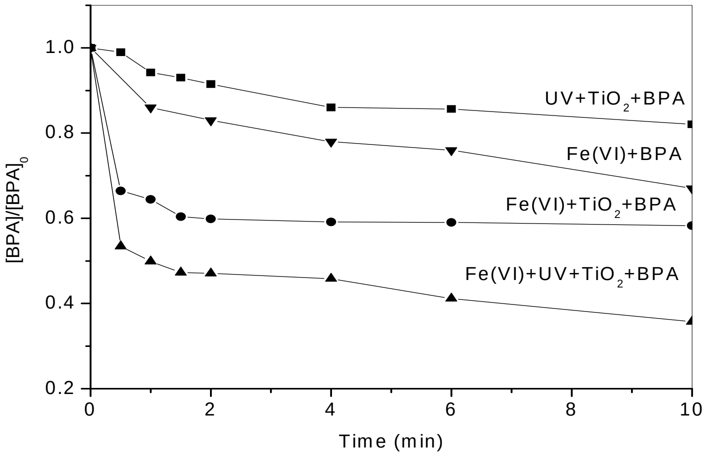

Figure 6 Degradation of BPA vs. time
($[Fe(VI)]_0 = 0.1$ mM, $[BPA]_0 = 0.1$ mM, $[TiO_2] = 1$ g l^{-1}).

It is seen from Figure 6 that the BPA concentration after 10 min reaction was decreased by 18% with TiO_2 and UV, resulting from photocatalytic oxidation alone, and decreased by 33% with Fe(VI) only in the dark, resulting from ferrate oxidation alone. Under UV illumination together with TiO_2 and Fe(VI), the BPA concentration was greatly reduced by 65% after 10 min. resulting from the interaction of photocatalytic oxidation and ferrate (VI) oxidation. These results indicate that the photocatalytic oxidation of BPA in the presence of

Fe(VI) was found to be approximately 2.5 times faster than that without Fe(VI). Alternatively, we may say that the ferrate oxidation of BPA was enhanced by 2 times due to the presence of TiO_2 and UV illumination.

In such an interactive reaction, BPA was quickly oxidized by several oxidants including hydroxyl radicals, Fe(VI) and also Fe(V), since Fe(V) reacts 3-5 orders of magnitude faster than Fe(VI) (Sharma et al., 1991; Rush and Bielski, 1994). Meanwhile, this interactive reaction can inhibit the recombination of electron/hole pairs and also generate Fe(V) to accelerate the degradation of BPA in aqueous solution simultaneously.

Conclusions

The experimental results indirectly confirmed the formation of Fe(V) in the photocatalytic reduction of Fe(VI) by e_{cb}^- on the TiO_2 surface, and also indicated that the reduction rate of Fe(VI) is dependent on pH significantly. The experiments demonstrated that the photocatalytic oxidation of BPA in the presence of Fe(VI) was found to be approximately 2.5 times faster than that without Fe(VI). Not only Fe(VI) can oxidize BPA, but also effectively inhibit the recombination of electrons and holes in the photocatalytic process. Therefore, the combination of ferrate oxidation and photocatalytic oxidation may have good potential for application in environmental remediation processes.

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