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Ferrate(VI): Green chemistry oxidant for degradation of cationic surfactant

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Abstract

Iron in its familiar form exists in the +2 and +3 oxidation states, however, higher oxidation state of iron +6, ferrate(VI) ($Fe^{VI}O_4^{2-}$) can be obtained. The high oxidation power of ferrate(VI) can be utilized in developing cleaner ("greener") technology for remediation processes. This paper demonstrates the unique property of ferrate(VI) to degrade almost completely the cationic surfactant, cetylpyridinium chloride ($C_5H_5N^+(CH_2)_{15}CH_3 \cdot H_2O\ Cl^-$, CPC). The Rate law for the oxidation of CPC by ferrate(VI) at pH 9.2 was found to be: $-d[Fe(VI)]/dt = k[Fe(VI)][CPC]^2$. Ferrate(VI) oxidizes CPC within minutes and molar consumption of ferrate(VI) was nearly equal to the oxidized CPC. The decrease in total organic carbon (TOC) from CPC was more than 95%; suggesting mineralization of CPC to carbon dioxide. Ammonium ion was the other product of the oxidation. This is the first report in which $Fe^{VI}O_4^{2-}$ ion opens the pyridine ring and mineralizes the aliphatic chain of the organic molecule giving inorganic ions.

Keywords: Cationic surfactant; Ferrate(VI); Oxidation; Cetylpyridinium chloride; Degradation

1. Introduction

Surface-active agents, commonly called surfactants, contain a group of organic compounds that have both a hydrophobic group (e.g. alkyl chain) and a hydrophilic group (e.g. ammonium ion). Surfactants impact on all aspects of our daily life either directly in household detergents and personal care products or indirectly in the production and processing of materials that surround us. Domestic products pertain to household, pharmaceuticals, food, textiles and cosmetics is predominant among the surfactant applications. Therefore, it is possible to speculate that the environmental pollution by surfactants is increasing due to daily life applications (Horvath and Huszank, 2003). Surfactants are not directly toxic, but they inhibit both the settlement of floating particles and the dissolution of atmospheric oxygen into natural waters.

The major concern arising from the wastewater treatment plant is caused by some of the surfactants, especially cationic surfactants that are not biodegraded completely and contaminate the aquatic environment (Garcia et al., 2000). The study of Schroder et al. (1999) showed that the elimination of anionic surfactants was efficient in a wastewater treatment technology using a combination of adsorption and biological processes.

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The biodegradation of surfactants is usually slow; therefore, advanced oxidation techniques have been applied to completely eliminate them from the effluents (Hidaka et al., 1990; Schroder et al., 1999; Sanz et al., 2003). The photodegradation of surfactants in heterogeneous TiO_2 has been studied in detail (Avranas et al., 1993; Hidaka et al., 1995; Ohtaki et al., 2000). The role of hydroxyl radical in degradation of surfactants was also studied by using Fe(III)-photoinduced oxidation process (Horvath and Huszank, 2003). Over the past decade, there has been an increasing interest in ferrate(VI) ($Fe^{VI}O_4^{2-}$) because of its potential in remediation processes as a green chemical (Sharma, 2002, 2004; Sharma et al., 2005). Due to the green chemistry of ferrate(VI), its use in environmentally friendly "super iron" batteries (Licht and Tel-Vered, 2004) and in cleaner technology for organic synthesis has also been suggested (Delaude and Laszlo, 1996).

Potassium salt of ferrate(VI), K_2FeO_4, has a reduction potential of 0.7 V in basic and of 2.2 V in acidic solution, respectively (Wood, 1958).

In acidic media:

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \quad E^0 = 2.2\ V \qquad (1)$$

In basic media:

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \quad E^0 = 0.7\ V \qquad (2)$$

The oxidizing power of ferrate(VI) is higher than those of the common oxidants such as permanganate, ozone, and hypochlorite (Jiang and Lloyd, 2002; Sharma, 2002). The spontaneous decomposition of Fe(VI) in water forms molecular oxygen (Eq. (3)).

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe^{3+} + 3/2O_2 + 10OH^- \qquad (3)$$

Ferrate(VI) as an oxidant for nitrogen and sulfur-containing pollutants has given a convincing result in water and wastewater treatment (DeLuca et al., 1983; Sharma, 2002). Moreover, it can also inactivate microorganisms (Murmann and Robinson, 1974; Waite, 1979). The reaction of ferrate promotes the coagulation process, and subsequently forms a ferric hydroxide gel that greatly enhances the aggregation and settling process (Jiang and Wang, 2003). Fe(VI) ion, as a coagulant, in the physicochemical treatment of combined industrial wastewaters, has proven effective for removing organic matter, nutrients, and some metals, at low levels. More recently, ferrate(VI) has shown its effectiveness in oxidizing emerging pollutants, estrogens and pharmaceuticals in water (Hu et al., 2004; Jiang et al., 2005; Li et al., 2005; Sharma and Mishra, in press; Sharma et al., in press) Such advantageous properties of ferrate(VI) with a non-toxic by-product, Fe(III), make ferrate(VI) a green chemical in oxidation, coagulation, and disinfection for water and wastewater treatment.

In the present work, we have determined the rate-law, stoichiometry, and products of the reaction of ferrate(VI) with a cationic surfactant, cetylpyridinium chloride (CPC) to seek degradation of the surfactant in the aquatic environment. CPC has a large molecular structure, $C_5H_5N^+(CH_2)_{15}CH_3 \cdot H_2O\ Cl^-$, containing a nitrogen-containing six-member ring and a long aliphatic chain attached to a nitrogen atom of the molecule. We report for the first time that ferrate(VI) completely degrades CPC by attacking the hydrophobic alkyl chain and opening the aromatic ring of the molecule.

2. Experimental methods

2.1. Materials and methods

CPC was obtained from Aldrich Chemical Company. Potassium ferrate(VI) (K_2FeO_4, 98%+ purity) was prepared using Thompson et al. (1951) method. Orange II (C.I. 15510, acid orange 7) was obtained from Sigma Chemical Co. Other chemicals, sodium chloride (99.5%), acetic acid (100%), sodium acetate (99%), and chloroform (99.4%) were purchased from MERCK. All chemicals were used without further purification. Solutions were prepared in ultrapure water (18 MΩ) purified with a PURELAB Maxima ELGA system.

Ferrate(VI) solutions were prepared by dissolving a desired amount of ferrate(VI) salts into a 1.7 mM borate/8 mM phosphate buffer solution at pH 9.2, where ferrate(VI) is most stable. The phosphate serves as a complexing agent for the Fe(III) produced, which otherwise precipitate as a hydroxide would accelerate the decomposition of ferrate(VI). The concentration of ferrate(VI) was measured based on the absorbance by a Shimadzu UV-1601PC spectrophotometer at 510 nm wavelength. A molar absorption coefficient, $\varepsilon_{510\ nm} = 1150\ M^{-1}\ cm^{-1}$ was used for calculating $[FeO_4^{2-}]$ at basic media (Bielski and Thomas, 1987).

Analysis of CPC was performed using a dye extraction procedure for cationic surfactants (Hidaka et al., 1990; Singhal et al., 1997). Briefly, Orange II (0.1%, 1.5 ml) solution, sodium chloride (2.5 g) and CH_3COOH/CH_3COONa buffer solution (5 ml, pH 3.45) were first added to the experimental sample solution (5 ml) of a cationic surfactant. The well-mixed solution was then extracted with chloroform (10 ml) by vigorous shaking for about 3 minutes. The chloroform layer containing CPC was separated and the absorbance (at 486 nm) of this sample solution was measured using the Shimadzu UV-1601PC Spectrophotometer, which gives the amount of surfactant in the sample solution.

The oxidation experiments were conducted by mixing ferrate(VI) with CPC at pH 9.2. The concentration of CPC was kept constant at 83.7 μM and varying the ferrate(VI) concentration from 19.8–177 μM. The solutions were magnetically stirred along the reaction time. The temperature and the pH of the solution were recorded