

Research Article **Preparation and Application of Sustained-Release Potassium Ferrate(VI)**

Xuan Xu,^{1,2} Wei Wei,¹ Ping Tao,¹ and Yan Zhang¹

¹ Key Laboratory of Three Gorges Reservoir Region's Eco-Environment, Ministry of Education, Chongqing University, Chongqing 400045, China

² National Centre for International Research of Low-carbon and Green Buildings, Chongging University, Chongging 400045, China

Correspondence should be addressed to Xuan Xu; xuxuan@cqu.edu.cn

Received 30 December 2013; Revised 19 April 2014; Accepted 25 April 2014; Published 19 May 2014

Academic Editor: Yalei Zhang

Copyright © 2014 Xuan Xu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, a composite system for the sustained release of potassium ferrate(VI) (sustained-release K_2FeO_4) was prepared and applied for water treatment. The objective of this research was to maximize the effectiveness of K_2FeO_4 for water treatment by enhancing its stability using diatomite. The sustained-release K_2FeO_4 was characterized using X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. The results indicated that no new crystal phase was formed during the preparation and some K_2FeO_4 crystals entered the pores of the diatomite. From K_2FeO_4 release experiments, we found that the decomposition rate of K_2FeO_4 was obviously decreased, which greatly improved the contact rate between released K_2FeO_4 and pollutants. Via degradation of methyl orange, which was used as a model pollutant, the influential factor of K_2FeO_4 content within the complete sustained-release K_2FeO_4 system was studied. The optimal K_2FeO_4 content within the sustained-release K_2FeO_4 system was approximately 70%. In natural water samples, sustained-release K_2FeO_4 at a dosage of 0.06 g/L and with a reaction time of 20 minutes removed 36.84% of soluble microbial products and 17.03% of simple aromatic proteins, and these removal rates were better than those observed after traditional chlorine disinfection.

1. Introduction

Potassium ferrate(VI), with the formula K_2FeO_4 , as an environmentally friendly water treatment agent with strong oxidizing power, can not only sterilize natural water but also remove various organic and inorganic compounds [1–3]. In addition, its reduction by-product, Fe(III), is an effective flocculent that can absorb suspended solid and hazardous substances [4, 5]. More importantly, compared with chloric disinfection, no hazardous disinfection by-products (DBPs) are generated in K_2FeO_4 treatment of drinking water [6–8]. However, to date, K_2FeO_4 has not yet been widely applied as a replacement for chloric disinfectants in drinking water treatment, mainly due to the poor stability of concentrated K_2FeO_4 [9, 10]. The reduction potential of K_2FeO_4 varies from +0.7 V to +2.2 V in basic and acidic solutions, respectively [3]. The ferrate anion decomposes quickly during

the treatment process, resulting in low efficiency for water purification.

The stability of K_2FeO_4 is determined by its purity, the pH value of the solution, and various other factors [11]. Using a hypochlorite oxidation method, Hrostowski and Scott [12] successfully prepared K_2FeO_4 with a purity as high as 96.9%, which dramatically improved its stability during storage. However, this had little effect on the use of K_2FeO_4 given that its stability is still poor during the water treatment process. Wagner et al. [11] reduced the decomposition rate of K_2FeO_4 by controlling the solution pH value. In high pH solution, the concentration of hydrogen ions (H⁺) is low, leading to only weak catalytic decomposition. However, controlling pH is not commercially viable in practical water treatment processes.

In the present research, K_2FeO_4 crystals were absorbed into a porous media, diatomite, which has a highly porous structure and high surface area [13], enabling the subsequent slow release of K_2FeO_4 into water in order to prolong the reaction time and consequently improve the efficiency and purification effect of K_2FeO_4 . This method does not require a specific K_2FeO_4 purity or solution pH value, and, therefore, the technical difficulties and high cost of K_2FeO_4 preparation can be drastically reduced for the practical application of K_2FeO_4 in water purification processes.

2. Materials and Methods

2.1. Chemicals. The following chemicals were of analytical reagent grade and used without further purification: ferric nitrate (Sigma Aldrich Reagent Co., Ltd.), calcium hypochlorite (Shun Chemical Reagent Co., Ltd.), potassium hydroxide (Chongqing Chuandong Reagent Co., Ltd.), and methyl orange (ChengDu Kelong Chemical Co., Ltd.). Diatomite (Chinasun Specialty Products Co., Ltd.) was of chemically pure grade and was used without further purification.

2.2. Preparation of Sustained-Release K_2 FeO₄. A paste of 15 g of Ca(ClO)₂ and 25 mL of 13 mol/L KOH solution were added to a 100 mL beaker. After mild stirring, the mixture was filtered using an 800-eye filtering cloth and then 20 mL saturated KOH solution was added to the filtrate. The mixture was filtered again using 800-eye filtering cloth and 8g of Fe(NO₃)₃·9H₂O, which had been ground fully immediately prior to use, was slowly introduced to the filtrate in the ice water bath five times. After 1 hour of continued stirring in an agitator, diatomite was added to the mixture. To achieve samples with different K_2 FeO₄ content, 6.92 g, 11.87 g, 18.46 g, 27.69 g, or 41.54 g of diatomite was added to individual samples. Each mixture was stirred for 5 additional minutes, followed by a 30-minute precipitation step in an ice bath. After filtration of the mixture, the filter cake was collected as the sustained-release K₂FeO₄ sample. The theoretical weight of K2FeO4 in each sustained-release K2FeO4 sample was 27.69 g. The sustained-release K₂FeO₄ samples were labeled as Fe₈₀, Fe₇₀, Fe₆₀, Fe₅₀, and Fe₄₀ based on the theoretical mass fraction of K₂FeO₄ in each sample. For example, Fe₈₀ indicates that the theoretical mass fraction of K₂FeO₄ in the composite was 80%. When diatomite was not added, the sample contained only K_2 FeO₄.

2.3. Characterization of Sustained-Release K_2FeO_4 . The X-ray diffraction (XRD) patterns of the sustained-release K_2FeO_4 samples were obtained using a Shimadzu XRD-6000 diffractometer using Cu K α radiation (40 kV, 30 mA). Data were recorded over the range from 10° to 80° (2 θ) with a scan rate of 4° min⁻¹. Fourier transform infrared spectroscopy (FT-IR) patterns were obtained using a Shimadzu IRPrestige-21 infrared spectrometer with the frequency ranging from 500 to 2000 cm⁻¹. Scanning electron microscopy (SEM) images were obtained using a FEI Quanta 450 scanning electron microscope.

2.4. Ferrate Release Rate of Sustained-Release K_2FeO_4 . To control the decomposition rate of Fe(VI), the release rate experiment of sustained-release K_2FeO_4 was carried out in



FIGURE 1: XRD patterns of Fe_{70} , Fe_{60} , K_2FeO_4 , and diatomite samples.

an ice water bath. First, 0.1g pure K₂FeO₄ or a sample of each sustained-release K₂FeO₄ composite was added to a 250 mL beaker containing 250 mL water. The solution was then agitated at 60 rpm for 30 min in the ice water bath, and, finally, the concentration of Fe(VI) in solution was determined according to the adsorption at 510 nm using a spectrophotometer.

2.5. Degradation of Methyl Orange. Eight test solutions of 20 mg/L methyl orange were prepared by dissolving methyl orange granules in deionized distilled water. Then, 0.125 g Fe_{80} , 0.143 g Fe_{70} , 0.167 g Fe_{60} , 0.200 g Fe_{50} , 0.250 g Fe_{40} , 0.100 g K₂FeO₄, 0.043 g diatomite, and a simple mixture of 0.100 g K₂FeO₄ and 0.043 g diatomite were added individually to these test solutions. The theoretical weight of K_2FeO_4 in all seven K_2FeO_4 -containing samples was 0.100 g. Each test solution was stirred rapidly and then allowed to stand for 20 min. The methyl orange degradation rate was calculated according to the concentration of methyl orange. The concentration of methyl orange was determined by fluorescence spectrophotometry using a Hitachi F-7000 fluorescence spectrophotometer, because methyl orange is a fluorescent substance [14]. The fluorescence intensity varied linearly with methyl orange concentration in the range of 5-20 mg/L, with a correlation coefficient of 0.998. Therefore, the concentration of methyl orange could be calculated using the fluorescence intensity value through a linear regression equation.

2.6. Degradation of Fluorescent Substances in Natural Water. Water samples were collected before and after liquid chlorine disinfection in a water supply network in Shapingba, Chongqing, China for comparative studies. The water in this network was treated for coagulation, sedimentation, and sand filtration before liquid chlorine disinfection. First, 0.015 g Fe₇₀ was added to 250 mL water samples and then the changes in the three-dimensional fluorescence patterns were analyzed



FIGURE 2: SEM images of Fe_{70} , Fe_{60} , K_2FeO_4 , and diatomite samples ((a) K_2FeO_4 ; (b) diatomite; (c) F_{60} ; and (d) F_{70}).

after a 20-minute reaction time. The resulting changes in fluorescence in the water samples were compared to those after the liquid chlorine disinfection process. Three-dimensional fluorescence patterns were obtained using a Hitachi F-7000 fluorescence spectrophotometer. The concentrations of soluble microbial products and simple aromatic protein also were determined according to the linear regression method used to determine the methyl orange concentration.

3. Results and Discussion

3.1. XRD Analysis of Sustained-Release K_2FeO_4 . The XRD patterns of Fe_{70} , Fe_{60} , K_2FeO_4 , and diatomite samples are shown in Figure 1. It can be seen that diatomite had two sharp diffraction peaks at $2\theta = 21.82^{\circ}$ and 36.00° . K_2FeO_4 had only one sharp diffraction peak at $2\theta = 29.72^{\circ}$. Other diffraction peaks belonged to the residual crystals of KOH and KNO₃ in the samples. The three sharp diffraction peaks of sustained-release K_2FeO_4 were at $2\theta = 21.82^{\circ}$, 29.72°, and 36.00° . Basically, the sharp diffraction peaks of Fe₇₀ and Fe₆₀ coincided with those of K_2FeO_4 and diatomite. In other words, no new crystal was generated during the preparation.

Therefore, the XRD analysis indicates that K_2FeO_4 and diatomite were combined by physical adsorption, which is beneficial to prevent the loss of K_2FeO_4 reactivity.

3.2. SEM Analysis of Sustained-Release K₂FeO₄. Figure 2 shows SEM representative images of Fe70, Fe60, K2FeO4, and diatomite samples. The particle size of K₂FeO₄ was roughly $2 \mu m$. Due to its poor dispersion, an aggregation phenomenon was observed. The particle size of diatomite was approximately $35 \,\mu$ m, and void spaces (i.e., pores) between the particles were obvious. SEM images demonstrated that the voids in the diatomite were filled with K₂FeO₄ crystals, which even covered the surfaces of the diatomite. The particle size of K₂FeO₄ in the Fe₇₀ samples was nearly the same as that of the pure K_2FeO_4 sample. Nevertheless, the dispersion of K₂FeO₄ particles in the Fe₇₀ samples was much better than that of the pure K₂FeO₄ samples. Obvious aggregation of K₂FeO₄ particles was also visible in the Fe₆₀ samples, with K₂FeO₄ crystals covering the diatomite surfaces. The K₂FeO₄ crystals covering the diatomite surfaces can dissolve in the water instantly and participate in the reaction, whereas the K₂FeO₄ crystals contained in the diatomite pores will dissolve

K₂FeO₄

Diatomite

Fe₇₀

Fe₆₀

1750

1500

2000

Wave number (cm^{-1}) FIGURE 3: FT-IR spectra of Fe₇₀, Fe₆₀, K₂FeO₄, and diatomite samples.

1250

1000

750

500

825.03 808.17 619.15



FIGURE 4: Ferrate release rate from sustained-release K_2 FeO₄ samples. (Experimental conditions: ice water bath, 60 rpm agitation, and initial pH = 7.4~7.6.)

slowly and continuously and then react with substances in solution. Therefore, the SEM analysis indicates that a K_2FeO_4 proportion of 70% in the sustained-release K_2FeO_4 composites is appropriate for continued release of K_2FeO_4 .

3.3. FT-IR Analysis of Sustained-Release K_2FeO_4 . Figure 3 shows the transmittance FT-IR spectra of Fe_{70} , Fe_{60} , K_2FeO_4 , and diatomite samples. The IR absorption spectrum of the K_2FeO_4 sample includes a primary peak at 825.53 cm⁻¹, which can be recognized as the characteristic peak of FeO_4^{2-1} and is attributed to the stretching vibrations of the Fe–O

FIGURE 5: Removal rate of methyl orange using different treatments. (Experimental conditions: methyl orange concentration = 20 mg/L, solution volume = 500 mL, and reaction time = 20 min.)

bond [15, 16]. Other peaks may be the result of impurities in the K_2FeO_4 samples. The absorption peaks of the diatomite sample at 619.15 cm⁻¹ and 808.17 cm⁻¹ can be assigned to the stretching vibration of SiO–H. Both Fe–O and SiO–H bonds were detected in Fe₇₀ and Fe₆₀ samples, demonstrating the existence of K_2FeO_4 and diatomite in the composite samples.

3.4. Ferrate Release Rate from Sustained-Release K_2 FeO₄ Samples. Figure 4 shows the changes in Fe(VI) concentration in solution after the addition of various sustained-release K₂FeO₄ composite samples. The figure shows that when pure K₂FeO₄ was added to the aqueous solution, the Fe(VI) concentration rapidly increased, reaching the maximum concentration within 2 min before beginning to decrease rapidly and showing complete degradation after 10 min. After addition of the sustained-release K2FeO4 samples in the aqueous solution, the Fe(VI) concentration was maintained at higher levels for longer periods, and the Fe(VI) decomposition rate was slower than that observed for pure K₂FeO₄. Specifically, for the Fe_{70} , Fe_{60} , Fe_{50} , and Fe_{40} samples, the Fe(VI) concentration increased within 5 min, and the highest concentration from Fe70 samples reached 99.47 mg/L. These results demonstrate that sustained release of K₂FeO₄ was achieved from the diatomite pores observed in Figure 2. When sustained-release K₂FeO₄ was added to the water, K₂FeO₄ dissolved gradually starting from the outside of the samples and later from the inside of the diatomite pores, releasing Fe(VI) slowly and maintaining a higher concentration of Fe(VI) in solution. Such sustained, continuous release can reduce the decomposition rate of Fe(VI) and thereby improve the probability of interaction between Fe(VI) and pollutants, thus improving the effectiveness of Fe(VI) for water purification.

3.5. Degradation of Methyl Orange. Figure 5 presents the removal rate of methyl orange using different treatment agents. It is evident from this figure that the removal

FIGURE 6: Three-dimensional fluorescence patterns demonstrating the removal of soluble organics by Fe_{70} and liquid chlorine. ((a) Water sampled before chlorine disinfection; (b) water sampled after chlorine disinfection: chlorine dosage = 1.5 mg/L, and reaction time = 30 min; (c) water treated by Fe_{70} : dosage = 0.06 g/L, and reaction time = 10 min; and (d) water treated by Fe_{70} : dosage = 0.06 g/L, reaction time = 20 min.)

rate of the simple mixture roughly equates the sum of the removal rate of K_2FeO_4 and diatomite. No synergistic effect was observed with the simple mixture of K_2FeO_4 and diatomite. The removal rates of methyl orange by sustainedrelease K_2FeO_4 samples were all higher than that using only K_2FeO_4 . However, considering that the diatomite within the sustained-release K_2FeO_4 samples could also absorb methyl orange, only the performances of Fe_{70} and Fe_{60} samples were better than those of the simple mixture. Specifically, 0.143 g of Fe_{70} and 0.167 g of Fe_{60} removed 6.49 mg (removal rate of 64.86%) and 4.11 mg (removal rate of 41.08%) of methyl orange, respectively. The removal efficiency of Fe_{70} was as 2.2 times that of the simple K_2FeO_4 and diatomite mixture. Potassium ferrate formed a good Fe(VI) sustainedrelease structure, allowing Fe(VI) to be slowly released into the solution and thus reducing the decomposition rate of Fe(VI). As a result, the contact probability between Fe(VI) and methyl orange was increased and thus the removal rate of methyl orange was improved. For the simple mixture of K₂FeO₄ and diatomite, K₂FeO₄ quickly dissolved in the water, and most of the Fe(VI) failed to react with methyl orange. Therefore, the methyl orange removal rate with the simple mixture was significantly less than the rates achieved by the Fe₇₀ and Fe₆₀ samples. These results are consistent with those from the experiment determining the ferrate release rate from sustained-release K₂FeO₄ samples (Figure 4). A possible reason for the reduced methyl orange removal rate at K_2FeO_4 mass fractions below 60% may be that the dosage of diatomite was high enough to cause an increase in the degradation rate of K_2FeO_4 . When the K_2FeO_4 mass fraction was above 70%, the crystal shape of the sustainedrelease K_2FeO_4 sample was approximately the same as that of the K_2FeO_4 sample and most of the K_2FeO_4 crystals failed to be absorbed into the pores of diatomite, which corresponded with a much lower removal rate of methyl orange.

In the process of sample preparation, the actual concentration of K_2FeO_4 is less than the theoretical value. We tested the purity of the prepared K_2FeO_4 and found that it was about 97%, which is close to the theoretical value. However, we could not determine the purity of the sustainedrelease K_2FeO_4 . However, the preparation time of sustainedrelease K_2FeO_4 is longer, and thus, the actual concentration of K_2FeO_4 in the sample may be significantly less than the theoretical value. For the degradation of methyl orange, the degradation effect is better after adding the theory amount K_2FeO_4 . This concluded that the degradation effect is better after adding the real amount of K_2FeO_4 .

3.6. Degradation of Fluorescent Substances in Natural Water. Figure 6 shows the three-dimensional fluorescence patterns of water samples treated by traditional chlorine disinfection in a water network and Fe₇₀. Two fluorescence peaks were observed in these patterns at $\lambda_{ex}/\lambda_{em} = 275 \text{ nm}/305 \text{ nm}$ and $\lambda_{\rm ex}/\lambda_{\rm em} = 225 \,\rm nm/330 \,\rm nm$. These peaks represent soluble microbial products and simple aromatic protein [17]. After traditional chlorine disinfection, the fluorescence intensity at 275 nm/305 nm was reduced by 11.86%, but the fluorescence intensity at 225 nm/330 nm remained almost unchanged. The intensities of the two fluorescence peaks were reduced by 31.58% and 16.67%, respectively, after a 10 min treatment with Fe₇₀, and by 36.84% and 17.03%, respectively, after a 20 min treatment with Fe70. The results indicate that the released K₂FeO₄ removed more soluble organic matter from the water samples than liquid chlorine. Thus, treatment with sustainedrelease K₂FeO₄ may improve the quality of purified drinking water.

4. Conclusions

In this study, a novel encapsulation method using hypochlorite oxidation to prepare sustained-release K_2FeO_4 was presented. The Fe(VI) release experiments demonstrated that diatomite as an encapsulation material affords the slow release of K_2FeO_4 into solution, which greatly increases the contact probability between released K_2FeO_4 and pollutants. The optimal mass fraction of K_2FeO_4 in the sustainedrelease K_2FeO_4 , among those tested, was found to be 70%. A maximum methyl orange removal rate of 64.86% was achieved with 0.3 g/L Fe₇₀ and a reaction time of 20 min, for an initial methyl orange concentration of 20 mg/L. With an Fe₇₀ dosage of 0.06 g/L and reaction time of 20 min, 36.84% of soluble microbial products and 17.03% of simple aromatic protein were removed from natural water samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

Financial support from the National Natural Science Foundation of China (no. 51108483), the Natural Science Foundation Project of CQ CSTC (no. cstcjjA20002), the 111 Project (no. B13041), and the Fundamental Research Funds for the Central Universities (no. 106112013CDJZR210002) is gratefully acknowledged.

References

- R. K. Murmann and P. R. Robinson, "Experiments utilizing FeO₄²⁻ for purifying water," *Water Research*, vol. 8, no. 8, pp. 543–547, 1974.
- [2] K. S. Kim, Y. K. Chang, S. K. Bae, and C. S. Hahn, "Selective oxidation of allylic and benzylic alcohols using potassium ferrate under phase-transfer catalysis condition," *Synthesis*, vol. 10, pp. 866–868, 1984.
- [3] V. K. Sharma, "Potassium ferrate(VI): an environmentally friendly oxidant," *Advances in Environmental Research*, vol. 6, no. 2, pp. 143–156, 2002.
- [4] J.-Q. Jiang and B. Lloyd, "Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment," *Water Research*, vol. 36, no. 6, pp. 1397– 1408, 2002.
- [5] Q. Han and W. Y. Dong, "Progress in development of potassium ferrate as new, highly efficient water treatment agent," *Environmental Science and Technology*, vol. 35, no. 12, pp. 200–205, 2012 (Chinese).
- [6] J. S. Mattice and H. E. Zittel, "Site specific evaluation of power plant chlorination," *Journal of the Water Pollution Control Federation*, vol. 48, no. 10, pp. 2284–2308, 1976.
- [7] M. J. Nieuwenhuijsen, M. B. Toledano, N. E. Eaton, J. Fawell, and P. Elliott, "Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review," *Occupational and Environmental Medicine*, vol. 57, no. 2, pp. 73– 85, 2000.
- [8] J.-Q. Jiang, S. Wang, and A. Panagoulopoulos, "The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment," *Chemosphere*, vol. 63, no. 2, pp. 212– 219, 2006.
- [9] L. Delaude and P. Laszlo, "A novel oxidizing reagent based on potassium ferrate(VI)¹," *The Journal of Organic Chemistry*, vol. 61, no. 18, pp. 6360–6370, 1996.
- [10] J. H. Qu, S. Lin, and L. L. Wang, "Aquatic stability of ferrate and its application in water treatment," *Acta Scientiae Circumstantiae*, vol. 21, pp. 106–109, 2001 (Chinese).
- [11] W. F. Wagner, J. R. Gump, and E. N. Hart, "Factors affecting the stability of aqueous potassium ferrate(VI) solutions," *Analytical Chemistry*, vol. 24, no. 9, pp. 1497–1498, 1952.
- [12] H. J. Hrostowski and A. B. Scott, "The magnetic susceptibility of potassium ferrate," *The Journal of Chemical Physics*, vol. 18, no. 1, pp. 105–107, 1950.
- [13] J. F. Lemonas, "Diatomite," American Ceramic Society Bulletin, vol. 76, no. 6, pp. 92–95, 1997 (Chinese).

- [14] L. Yu, J. Xi, H. T. Chan, T. Su, D. L. Phillips, and W. K. Chan, "The degradation mechanism of methyl orange under photocatalysis of TiO₂," *Physical Chemistry Chemical Physics*, vol. 14, no. 10, pp. 3589–3595, 2012.
- [15] W. He, J. Wang, H. Shao, J. Zhang, and C.-N. Cao, "Novel KOH electrolyte for one-step electrochemical synthesis of high purity solid K₂FeO₄: comparison with NaOH," *Electrochemistry Communications*, vol. 7, no. 6, pp. 607–611, 2005.
- [16] Z. Xu, J. Wang, H. Shao, Z. Tang, and J. Zhang, "Preliminary investigation on the physicochemical properties of calcium ferrate(VI)," *Electrochemistry Communications*, vol. 9, no. 3, pp. 371–377, 2007.
- [17] Y. Han, X. J. Zhou, D. C. Peng, and X. C. Wang, "Effect of chlorination disinfection on three dimension fluorescence characteristic of DOM in secondary effluent," *Chinese Journal* of Environmental Engineering, vol. 6, no. 7, pp. 2226–2230, 2012 (Chinese).

International Journal of Medicinal Chemistry

International Journal of Analytical Chemistry

Advances in Physical Chemistry

