



EFFECT OF TEMPERATURE AND DRYING TIME ON THE SYNTHESIS OF STABLE K_2FeO_4 BY WET METHOD

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ABSTRACT

Fe (VI) as an oxidant has a higher oxidation potential than ozone, hydrogen peroxide, permanganate or chlorine. Demanding environmental regulations encourage the use of ferrate as a decontaminating agent of choice. Thus, the purpose of this work is to identify and optimize the time and drying temperature of stable to ambient K_2FeO_4 by wet means facilitating their storage and transport. Wet synthesis is performed by attacking ferric sulfate $FeSO_4 \cdot 7H_2O$ by ClO^- hypochlorite with a chlorometric degree of $50^\circ F$ in a concentrated medium KOH, at a temperature of $55^\circ C$. The drying time is of the order of 12 hours at a temperature of $120^\circ C$. The obtained result was characterized by UV spectrophotometer by measuring the optical density at a wavelength of 507 nm.

Keywords: Ferrate, Bactericidal, Antioxidant, Flocculant, Coagulant, Water treatment, Electrochemical, Cathode.

1. INTRODUCTION

Iron compounds in oxidation degree (VI) have the advantage of being powerful oxidants and bactericides [1] which explains their particular interest in water treatment.

The synthesis of ferrates (VI) has been studied by various authors [2-14] Despite the improvement, it remains limited. Hrostowski and Scott [15] proposed a potassium ferrate synthesis method with a yield of 10 to 15% of ferrate. One year later, Ockerman, et al. [16], Schreyer, et al. [17] showed that the protocols of precipitation, washing and drying are required to achieve a stable and solid product.

Williams and Riley [18] have provided an advance in the ferrate preparation protocol (VI) by replacing sodium hydroxide by KOH. However, for the environment in which operate Hrostowski and Scott [15] in this case very concentrated KOH, K_2FeO_4 is assumed to be very soluble whereas KCl precipitates in the solution, which then makes possible a separation by filtration.

The wet method considered the most convenient is, however, very expensive Lee, et al. [19]. Deininger [20] deposited a patent for an economical process for the preparation of large-scale potassium ferrate from three compounds: potassium hydroxide, chlorine and ferric salt.

2. MATERIAL AND METHOD

Hydrated iron sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is mixed with bleach (ClO^- hypochlorite) at 50°C (French chlorometric degree) in a concentrated medium of KOH. The mixture is stirred for one hour at a temperature of 55°C according to the following reaction:



Recovering K_2FeO_4 is performed by vacuum filtration. This phase is dried at 120°C for 12 hours and then put into a ball desiccator. The resulting phase was analyzed and monitored over time with UV spectroscopy by measuring the optical density at 507 nm.

According to Tsapin, et al. [21] measuring the optical density of the solution of ferrate (VI) is done at a wavelength of 507 nm with a pH greater than 10. The characteristic peak of iron (IV) appears at this wavelength.

3. RESULTS

The measurement of the optical density of the solution of ferrate (VI) of the phase synthesized at 507 nm gives an idea about the evolution of the performance and stability of iron (VI).

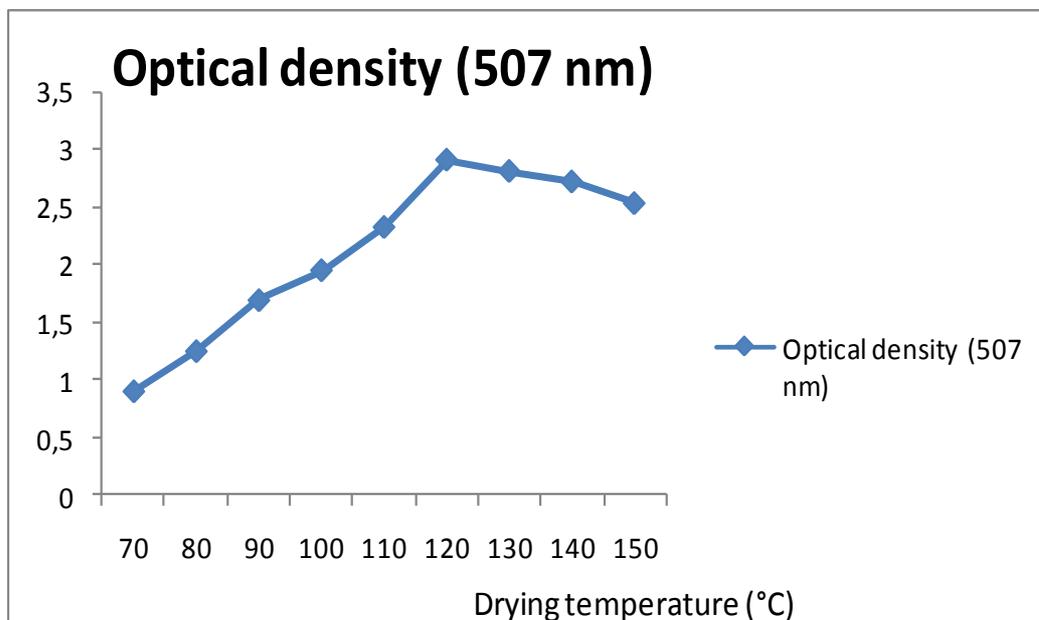


Figure-1. Optical Density of the solution of ferrate (VI) (K_2FeO_4) at 507 nm as a function of the drying temperature for a period of 12 hours.

The curve (Fig. 1) shows that the optical density of ferrate (VI) increases with the temperature up to 120°C which is an optimum temperature for the production of stable at ambient ferrate (VI) with a high yield whose optical density is of the order of 2.911.

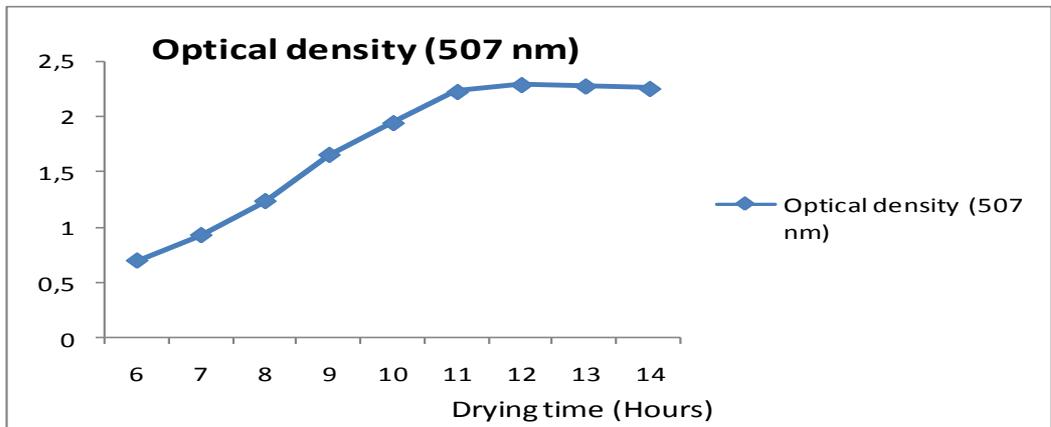


Figure-2. Optical density of the solution of ferrate (VI) (K_2FeO_4) at 507 nm as a function of the drying time at a temperature of 120 °C.

According to these results (Fig. 2), the optical density peaks at 2286 for a period of 12 hours, which explains the impact of the drying time on the production and yield of stable at ambient iron (VI).

5. MONITORING OF THE DEGRADATION OF THE FERRATE OVER TIME.

Monitoring the results of degradation (K_2FeO_4) shows that the storage period goes up to 12 months with a degradation rate limited to 30.61% in the first six months. The results of calculating the rate of degradation between the months and between the state of production of ferrate (VI) and the different months of storage is given in Table 1.

The relation used to calculate the percentage degradation of Iron (VI) is given by the following formula:

$$\% \text{ Degradation of the iron (VI)} = (D.O_i - D.O_f) / D.O_i$$

D.O_i: Optical densities of the iron (VI) respectively in the initial state

D.O_f: Optical Densities of iron (VI) in the final state

Tables-1. Optical density of the solution Ferrate (VI) K_2FeO_4 of the synthesized phase as a function of the degradation rate between the initial state of the production and storage of ferrate VI over different months (%) and as a the rate of degradation between the months of storage of ferrate VI (%).

t (Months)	The rate of deterioration from baseline in the production and storage of different months of ferrate VI (%)	The monthly rate of degradation ferrate VI (%)
1	0.37	0.37
2	4.08	3.72
3	11.19	7.41
4	21.39	11.48
5	27.89	8.26
6	30.61	3.77
7	41.15	15.19
8	48.29	13.81
9	55.10	13.15
10	61.90	15.15
11	68.36	16.96
12	75.17	21.50

According to our results (table 1), synthesized iron (VI) may withstand up to 12 months of storage at room temperature, as iron degradation rate (VI) in the first six months does not exceed 30.61%.

Note that the K_2FeO_4 degradation rate remains variable over time and varies differently from one month to another during storage. Climate change plays a very vital role in the degradation rate of ferrate (VI) due to changes in humidity.

6. DISCUSSION

As our results show, the drying temperature and drying time needed for the production of stable at room K_2FeO_4 with a high yield are respectively of the order of 120 °C and 12 hours, which is an encouraging step for the development of new industrial processes for the production of ferrate VI. This result confirms the studies done by [Hrostowski and Scott \[15\]](#) and [Wang, et al. \[12\]](#); [Ockerman, et al. \[16\]](#).

Monitoring the degradation of synthesized K_2FeO_4 show the stability of this phase up to 12 months of storage with a degradation rate in the first six months that does not exceed 30.61%. Climate variation impacts the degradation of ferrates by changes in humidity.

7. CONCLUSION

This manuscript reviews the most appropriate method for the production of K_2FeO_4 stable at ambient from the reaction of hydrated iron sulfate $FeSO_4 \cdot 7H_2O$ and bleach (hypochlorite the ClO^-) at 50°F (French chlorometric degree) in a concentrated medium KOH for one hour. Comparing the synthesis results of the obtained stable K_2FeO_4 with that of the literature, we notice that we obtained, for the first time, a relatively high yield of stable at ambient ferrate (VI) with wet method processing during 12 months. This represents a significant advance in the field of synthetic iron (VI) at laboratory scale. This result is very encouraging for mass production of ferrate (VI) at industrial scale.

RÉFÉRENCES

- [1] M. Abdellatif EL, Z. Abdelaziz, I. Mustapha, and B. Kawtar FIKRI, "The role of ferrates (VI) as a disinfectant: Quantitative and qualitative evaluation for the inactivation of pathogenic bacteria," *African Journal of Microbiology Research*, vol. 7, pp. 3690-3697, 2013.
- [2] A. Hooker, "Hipocloritos". *Chem. and Met. Eng.*, vol. 23, p. 961, 1920.
- [3] G. W. Thompson, L. T. Ockerman, and J. M. Schreyer, "Preparation and purification of potassium ferrate VI," *J. Am. Chem. Soc.*, vol. 73, pp. 1379-1381, 1951.
- [4] R. Scholder, H. Bunsen, F. Kin, W. Zeiss, and Z. Anorg, "Zur kenntnis der ferrate(VI)," *Zeitschrift für Anorga- Nische und Allgemeine Chemie*, vol. 282, pp. 268-279, 1955.
- [5] G. Hoy and M. Corson, "Critical slowing down of spin fluctuations in K_2FeO_4 ," *J. of Magnetism and Magnetic Materials*, vol. 15, pp. 627-628, 1980.
- [6] F. Menil, "Systematic trends of the ^{57}Fe mössbauer isomer shifts in (FeO_n) and (FeF_n) polyhedra. Evidence of a new correlation between the isomer shift and the inductive effect of the competing bond T-X ($\rightarrow Fe$) where X Is O or F and T any element with a formal positive charge," *J. Phys. Chem. Solids*, vol. 46, pp. 763-789, 1985.

- [7] S. Licht, V. Naschitz, L. Halperin, N. Halperin, L. Lin, J. Chen, S. Ghosh, and B. Liu, "Analysis of ferrate (VI) compounds and super-iron Fe (VI) battery cathodes: FTIR, ICP, titrimetric, XRD, UV/VIS, and electrochemical characterization," *J. Power Sources*, vol. 101, pp. 167–176, 2001.
- [8] S. Licht, R. Tel-Vered, and L. Halperin, "Direct electrochemical preparation of solid Fe (VI) ferrate, and super-iron battery compounds," *Electrochem. Commun.*, vol. 4, pp. 933–937, 2002.
- [9] H. Weichun, W. Jianming, S. Haibo, Z. Jianqing, and C. Chu-nan, "Novel KOH electrolyte for one-step electrochemical synthesis of high purity solid K₂FeO₄: Comparison with NaOH," *Electrochemistry Communications*, vol. 7, pp. 607–611, 2005.
- [10] X. Zhihua, W. Jianming, S. Haibo, T. Zheng, and Z. Jianqing, "Preliminary investigation on the physicochemical properties of calcium ferrate (VI)," *Electrochemistry Communications*, vol. 9, pp. 371–377, 2007.
- [11] J. Híveša, M. Benová, K. Bouzek, J. Sitek, and V. K. Sharma, "The cyclic voltammetric study of ferrate (VI) formation in a molten Na/K hydroxide mixture," *Electrochimica Acta*, vol. 54, pp. 203–208, 2008.
- [12] Y. L. Wang, S. H. Ye, Y. Y. Wang, J. S. Cao, and F. Wu, "Structural and electrochemical properties of a K₂FeO₄ cathode for rechargeable Li Ion batteries," *Electrochimica Acta*, vol. 54, pp. 4131–4135, 2009.
- [13] M. Zuzana, K. Bouzek, J. Híveš, V. K. Sharma, J. T. Raymond, and J. C. Baum, "Research progress in the electrochemical synthesis of ferrate (VI)," *Electrochimica Acta*, vol. 54, pp. 2673–2683, 2009.
- [14] A. Jain, V. Sharma, and M. Mbuya, "Removal of arsenite by Fe (VI), Fe (VI)/ Fe(III), and Fe(VI)/Al(III) salts: Effect of pH and anions," *J. Hazard. Mater.*, vol. 169, pp. 339–344, 2009.
- [15] H. J. Hrostowski and A. B. Scott, "The magnetic susceptibility of potassium ferrate," *J. Chem. Phys.*, vol. 18, pp. 105–107, 1950.
- [16] L. T. Ockerman, J. M. Schreyer, and G. W. Thompson, "Preparation and purification of potassium ferrate VI," *J. Am. Chem. Soc.*, vol. 73, pp. 1379–1381, 1951.
- [17] J. M. Schreyer, G. W. Thompson, and L. T. Ockerman, "Potassium ferrate (VI)," *Inorganic Synthesis*, vol. 4, pp. 164–169, 1953.
- [18] D. H. Williams and J. T. Riley, "Preparation and alcohol oxidation studies of the ferrate (VI) ion FeO₄²⁻," *Inorg. Chim. Acta*, vol. 8, pp. 177–183, 1974.
- [19] Y. H. Lee, M. Cho, J. Y. Kim, and Yoon., "Chemistry of ferrate (Fe(VI)) in aqueous solution and its application as a green chemical," *J. Ind. Eng. Chem.*, vol. 10, pp. 161–171, 2004.
- [20] J. P. Deininger, "Process for preparing potassium ferrate K₂FeO₄," Brevet Européen, No.0082590, Date De Publication: 29 Juin 1983, 1983.
- [21] A. I. Tsapin, M. G. Goldfeld, G. D. McDonald, K. H. Neilson, B. Moskovitz, P. Solheid, W. Klemner, S. D. Kelly, and K. A. Orlandini, "Iron (VI): Hypothetical candidate for the Martian oxidant," *Icarus*, vol. 147, pp. 68–78, 2000.

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