



SYNTHESIS PROCESS OF STABLE BaFeO_4 BY DRY METHOD

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ABSTRACT

Ferrate (VI) alkalis are the best known and best studied. The importance of their study is due to their increasingly diverse and innovative applications. The aim of this work is to prepare stable at ambient BaFeO_4 , to study and optimize the key parameters influencing the performance of the oxidation of iron (III) into iron (VI) and to monitor its degradation over time in order to minimize the cost and improve the production of ferrate (VI) for their interest in the water treatment.. the synthesis of the phase was carried out by dry processing, using the reaction $\text{Ba}_3(\text{Fe}(\text{OH})_6)_2, \text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2$ at a temperature of 850°C under flowing oxygen for a period of 12 hours with a ratio of $\text{Ba} / \text{Fe} = 3$. The result was characterized by UV spectrophotometer, measuring the optical density at the wavelength of 507 nm.

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

1. INTRODUCTION

The development of iron synthesis processes (VI) is very difficult due to its oxidizing power. Of all the oxidants/disinfectant practically used in water and pollutants treatment [1], the ferrates are in high demand because they have a standard potential $\text{FeO}_4^{2-}/\text{Fe}^{3+} = 2.2 \text{ V}$. The evolution of water pollution shows very dangerous statistics because of the emergence of new pollutants.

Although the existence of alkali ferrates has been cited for a century [2-10], currently, there is a need for research and innovation to improve the existing methods of preparation and to develop new methods that would aim to increase the stability and performance of the latters, reducing, thus, the cost of the production and the responsiveness of ferrates with the contaminant [1]. The synthetic iron (VI) has been studied by various authors [11-21]. But the importance of the reactions for the preparation of dry ferrates lies mainly in their ability to produce alkali ferrate (VI) directly from the starting inexpensive and readily available material (iron oxide), without complicated procedure or electrochemical preliminary preparation of reagents [22].

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Scholder, et al. [23] advocated two methods of synthesis of M_2FeO_4 if M is a divalent element (Ba^{2+} , Sr^{2+}) from Fe (III) or from metaferrate corresponding alkaline earth metal.

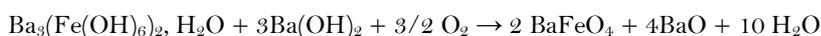
Martinez-Tamayo, et al. [24] studied the behavior of the Na_2O_2 - $FeSO_4$ system. Their study includes the results obtained from the use of infrared spectroscopy, X-ray diffraction and differential thermal analysis. They obtained Ferrate (V) and (VI) whose nature depends on the molar ratio of the initial reactants. Kisselev, et al. [25] have extensively studied the Na-Fe-O system and have shown that we could prepare ferrate (IV) of pure sodium of formula Na_2FeO_3 and ferrate (VI) of formula Na_4FeO_5 . In their study, they could get the Na_2FeO_3 sodium ferrate by heating the mixture of Na_2O_2 - Fe_2O_3 in oxygen at a temperature of 400 ° C, the molar ratio Na / Fe bringing the best results is 2. Kopelev, et al. [26] have prepared sodium ferrate Na_4FeO_5 and Na_2FeO_3 according to the procedure used by Kisselev, et al. [25] Ferrates (VI) were also prepared from galvanized waste [27]. The waste was mixed with ferric oxide in an oven at 800 ° C. The sample was then cooled and mixed with sodium peroxide solid and then gradually heated for a few minutes. Unlike methods of synthesis by wet and electrochemical means, the dry method avoids the ferrate reaction with water. This ferrates preparation process is considered a green technology by recycling various waste iron compounds. Lee, et al. [28]

During recent years, a growing number of investigations about the preparation, physicochemical characterization and detailed performance of some ferrates (VI), such as $SrFeO_4$, $BaFeO_4$, Na_2FeO_4 , Rb_2FeO_4 and Cs_2FeO_4 , have appeared in the literature [29-32]. The solubility of $BaFeO_4$, a commonly studied salt as a super oxidizing iron [33], has also been extensively studied.

2. MATERIAL AND METHOD

$Ba_3(Fe(OH)_6)_2$, H_2O and $Ba(OH)_2$ were mixed in a pure platinum crucible to avoid side reactions. The resulting mixture was placed in an oven at a temperature of 850 ° C under flowing oxygen for a period of 12 hours with a ratio of Ba / Fe = 3. The resulting molten mixture is cooled in a ball desiccator in order to avoid moisture absorption as we especially worked at a temperature of 850 ° C according to Jiang and Lioyd [34]. Synthesis by dry means at a temperature above or equal to 500 ° C seems unconvincing due to the explosion of the reaction mixture and makes the process of synthesis at high temperature very dangerous. The measured phase was analyzed and monitored over time with UV spectrophotometry by measuring the optical density at 507 nm. According to Tsapin, et al. [35], measuring the optical density of the solution of ferrate (VI) is performed at a 507 nm wavelength with a pH greater than 10. The characteristic peak of iron (VI) is achieved at this wavelength.

The synthesis reaction is as follows:



3. RESULTS

Measuring the optical density of the solution of ferrate (VI) of the synthesized $BaFeO_4$ phase at a wavelength of 507 nm as a function of the Ba / Fe ratio gives an idea about the evolution of the synthesis reaction (Figure 1).

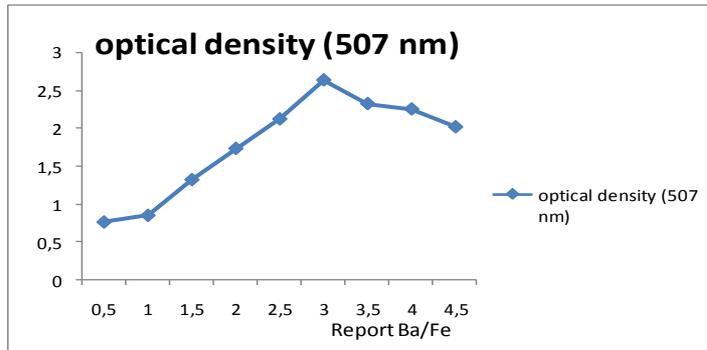


Figure-1. Optical density of the solution of ferrate (VI) BaFeO₄ at 507 nm as a function of Ba / Fe (t = 12 h, T = 850 ° C).

According to the curve (Fig. 1), the optical density of the obtained ferrate (VI) increases with the ratio of Ba / Fe until the value 3 of OD = 2.633, implying a change in the performance of ferrate (VI) as a function of Ba / Fe ratio.

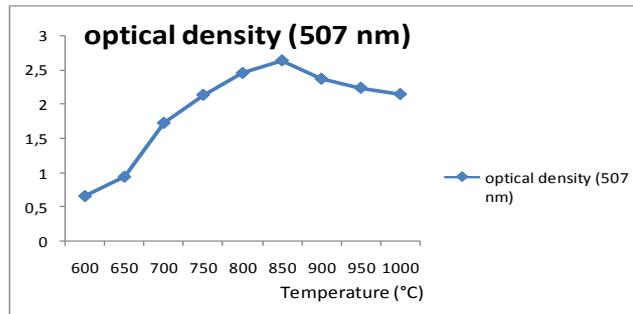


Figure-2. Optical density of the solution of ferrate (VI) BaFeO₄ at 507 nm as a function of the temperature (Ba / Fe = 3, t = 12 h).

From the curve (Fig. 2), we deduce that the optical density of ferrate (VI) increases with temperature up to 850°C which is an optimum temperature for the production of stable at ambient ferrate (VI) with an important synthesis reaction yield and an optical density of the order of 2.635.

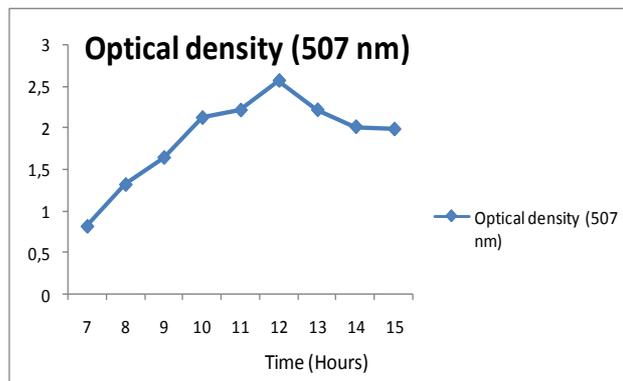


Figure-3. Optical density of the solution of ferrate (VI) BaFeO₄ at 507 nm over time (T = 850 ° C and Ba / Fe = 3).

According to these results (Fig. 3), the optical density reaches its maximum at 2,569 for a period of 12 h, which explains the impact of the reaction time on the production of stable at ambient iron (VI) as well as on the importance of the resulting product.

4. MONITORING FERRATE DEGRADATION OVER TIME

BaFeO₄ degradation monitoring results show that the storage period goes up to 12 months with a degradation rate limited to 29.98% during the first six months.

The results of calculating the rate of degradation between the months and between the state of production and ferrate (VI) and different months of storage are given in Table 1.

The relation used to calculate the percentage of 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 of ferrate (VI) of BaFeO₄ synthesized phase as a function of the degradation rate between the initial state of the production and the storage of ferrate VI during different months (%) and also as a function of the degradation rate between the months of storage of ferrate VI (%).

t (Months)	The rate of deterioration from baseline in the production and storage of ferrate VI during different months (%)	The monthly rate of degradation of ferrate VI (%)
1	3.91	3.91
2	12.25	8.68
3	15.48	3.67
4	19.81	5.11
5	27.47	9.55
6	29.98	3.45
7	34.26	6.12
8	42.50	12.52
9	49.94	12.93
10	61.59	23.27
11	65.27	9.58
12	72.29	20.21

From these results (table 1), we see that the rate of degradation of iron (VI) remains variable over time and varies differently from one month to another during storage, which means that the climate variations influence the degradation rate of ferrate (VI) due to changes in humidity.

5. DISCUSSION

The Ba / Fe ratio necessary for the synthesis of stable at ambient iron (VI) for a high yield is of the order of 3 (Figure 1) This is consistent with the results of various preliminary studies [15], [29], [30], [31], [32], which showed that the Ba / Fe ratio ideal for the dry synthesis of iron (VI) is greater than 2.

The optimum temperature ($T = 850\text{ }^{\circ}\text{C}$) for the synthesis of ferrate (VI) (Fig. 2) is a positive step forward for the development of industrial production processes of ferrate (VI). This result confirms the studies done by Scholder [8].

The synthesis reaction time ($t = 12\text{ h}$) is an important parameter to produce stable at ambient ferrate (VI) by dry method [15]. Climate change also affects the degradation rate and the duration of storage of ferrate (VI) at room temperature.

6. CONCLUSION

This manuscript reviews the most appropriate method for the synthesis of BaFeO_4 alkaline stable at ambient ferrate (VI) from the reaction $\text{Ba}_3(\text{Fe}(\text{OH})_6)_2$, H_2O and $\text{Ba}(\text{OH})_2$, with the ratio $\text{Ba} / \text{Fe} = 3$ at a temperature of $850\text{ }^{\circ}\text{C}$ and a reaction time of about 12 hours.

The dry synthesis process of ferrate (VI) is a very easy and very promising method, although there is still need more technical and economic development for efficient industrial application.

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