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Synthesis of Stable Alkaline Ferrates (VI) by Dry Process: Quantitative and Qualitative Assessment

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Abstract: This article presents a new process for synthesizing ferrate VI alkali K_2FeO_4 with high yield and purity of 98.3 to 99.1%, stable for 12 months at a temperature around 30°C, by heating the mixture of Potassium peroxide K_2O_2 and Fe_2O_3 with a K/Fe ratio = 4 at a temperature of 560°C for 5 hours under a current of oxygen, under the most favorable conditions. This is much better than that synthesized by deferent synthetic routes. The synthesis of VI ferrates was carried out under different experimental conditions (the K/Fe ratio varies from 1 to 6, T varies from 200 – 750°C, time varies from 6 to 17h and product storage temperature varies from 20 to 40°C) in order to obtain an optimal yield of ferrate VI stable and of high purity as well as to minimize the cost and to facilitate their storage and their transport. The presence and quality of iron VI was confirmed in the phase obtained by XRD, IR spectrometry, UV spectrophotometry and by the volumetric titration method quantitatively and qualitatively. The degradation rate of iron VI after 12 months of storage at around 30°C was observed and determined by Mossbauer spectrometer, UV spectrophotometry and by the volumetric titration method.

Keywords: Ferrate synthesis, Cathode, oxidant, coagulant, water treatment, Purity, Stability.

1. Introduction

Recently the iron of oxidation state VI ($Fe^{VI}O_4^{2-}$) has become an incredible Green Technology by their wide application as an environment-friendly oxidant, disinfectant and coagulant in water treatment, [1-9]. Several authors have shown the inactivation of microorganisms such as fecal and total coliforms, Escherichia coli, viruses as well as the oxidation of pharmaceuticals and organic products, personal care and the elimination of toxic metals [10-21]. However, the synthesis of ferrates (VI) turns out to be very delicate, this is due to the instability conferred on them by their high oxidizing power and their high production cost [22, 23], [24, 25]. Although the existence of alkaline ferrates has been cited for a century [26, 27], they have not been the subject of a considerable number of studies, this is due to the instability and difficulties encountered during their preparation.

The synthesis of iron (VI) has been studied by different authors [28-37]. But the importance of the reactions for the preparation of ferrates by the dry route lies mainly in their ability to produce alkali ferrates (IV) or directly from inexpensive and readily available starting materials (iron oxide), without complicated electrochemical procedures. Or preliminary preparation of reagents [38]. Martinez-Tamayo and al. [39] studied the behavior of the Na_2O_2-$FeSO_4$ system; these studies include the results obtained by the use of infrared spectrometry, X-ray diffraction and differential thermal analysis. They obtained ferrates (V) and (VI) whose nature depends on the molar ratio of the initial reactants. Kisselev and al [40] extensively studied the Na-Fe-O system and showed that one can prepare pure sodium ferrate (IV) with the formula Na_2FeO_3 and ferrate (VI) with the formula Na_4FeO_5, thus obtaining sodium ferrate Na_2FeO_3 by heating the mixture of Na_2O_2-Fe_2O_3 under oxygen at a temperature of 400°C, the Na/Fe molar ratio leading to the best results is 2.

Kopelev and al. [41] prepared the sodium ferrate Na_4FeO_5 and Na_2FeO_3 according to the procedure of Kisselev and al [40]. Ferrates (VI) were also prepared from galvanized waste [42], the waste was mixed with ferric oxide in an oven at 800°C, the sample was cooled and mixed with sodium peroxide solid then heated gradually for a few minutes. Among the wet and electrochemical synthesis methods, the dry method avoids the reaction of ferrates with water. This ferrate preparation process is considered a green technology by recycling various waste iron compounds [43]. Current research is limited to the laboratory and ferrate (VI) has not yet been implemented.

This work focuses on a new approach for the synthesis of stable and better-quality ferrate (VI) by dry process by optimizing the parameters influencing the synthesis yield and phase stability in order to reduce the cost, facilitate transport and storage for a long time.

2. Material and method

The synthesis of ferrates VI in particular K_2FeO_4 by dry process under the most favorable conditions is done by

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mixing pure potassium peroxide K_2O_2 and Fe_2O_3 (in order to avoid any secondary reactions) with a K/Fe ratio of 4, in a crucible of platinum, before placing it in an oven at a temperature of 560°C for a period of 5 hours under a stream of oxygen according to the reaction below (1). The molten mixture obtained is cooled in ball desiccators in order to avoid moisture absorption and above all we worked at a temperature of 560°C according to Jiang and Lloyd [44]. Dry synthesis at a temperature greater than or equal to 500°C seems unconvincing due to the explosiveness of the reaction medium and makes the high temperature synthesis process very dangerous. The phase found is ground using a mortar at a temperature of around 40°C (closed medium) and then stored in an oven at a temperature of 30°C.

The synthesis reaction:

$$\mathbf{Fe_2O_3 + 3K_2O_2 \rightarrow 2K_2FeO_4 + K_2O} \qquad (1)$$

The product obtained was analyzed by IR spectrometry, XRD, UV spectrophotometry and by the volumetric titration method as well as by Mossbauer spectrometry after 12 months storage. The high-value product obtained according to the analyzes carried out is stored at T= 30°C to monitor its degradation over time (test their stability) by measuring the optical density at the wavelength of 507 nm and at a pH greater than 10 using UV spectrophotometry, according to the method of tsapin and al [45]. Each month determines the monthly degradation rate of ferrate VI (%) during 12 months of storage. However, the accuracy of the real degradation rate of ferrate VI of the synthesized phase after one year of storage is done by volumetric titration and by Mossbauer spectrometry.

We have widely used in this study the analysis by UV spectrophotometry to test the effect of different parameters essential to the production of ferrates VI by dry process such as the temperature, the drying time and the K/Fe ratio, knowing that the peak characteristic of iron (VI) comes out at this wavelength, according to the method of tsapin and al [45]. For reasons of reliability, ease and availability of the device in our laboratories in order to avoid the problem of waiting. However, the best result found under the most favorable conditions was analyzed and confirmed by the IR and DRX spectrometer as well as the volumetric titration method. Titration of the synthesized product by the volumetric method based on the oxidation of a chromites salt with ferrate VI determines the purities of K_2FeO_4 between 96.3 to 98.1% according to the reaction below (2).

$$\mathbf{Cr(OH)_4^- + FeO_4^{2-} + 3\,H_2O \rightarrow Fe(OH)_3.(H_2O)_3 + CrO_4^{2-} + HO^-} \qquad (2)$$

The resulting chromate is titrated with ferrous salt solution and sodium diphenylamine sulfonate as an indicator [44].

The FTIR, XRD and Mossbauer spectra of our samples were performed at the Regional University Interface Center (CURI) in Fez, Morocco.

3. Results and discussion

1. Effect of K/Fe ratio

The measurement of the optical density of the solution of ferrate (VI) of the synthesized phase K_2FeO_4 at a wavelength of 507 nm as a function of the K/Fe ratio, gives an idea of the evolution of the reaction of synthesis and optimize the K/Fe ratio from potassium peroxide K_2O_2 and Fe_2O_3 (fig.1).

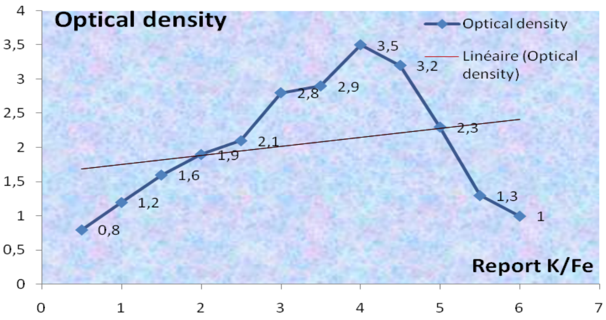


Fig. 1: Variation of the optical density of the solution of ferrate (VI) (K_2FeO_4) synthesized at 507 nm as a function of the K/Fe ratio (t= 5 h, T=560°C).

According to the curve, it can be seen that the optical density of the ferrate (VI) obtained increases as a function of the K/Fe ratio up to the value 4, of which D.O = 3.50, which implies a change in the yield of the ferrate (VI) in function of the K/Fe ratio and this confirms the result of Martinez-Tamayo et al who approve the interest of the molar ratio of the initial reagents in the synthesis of ferrates VI by dry process [39].

2. Effect of temperature

The results of the study made on the effect of the calcinations temperature on the yield of the reaction of potassium peroxide and Fe_2O_3 are illustrated in figure 2 below at different temperatures (200 – 750°C).

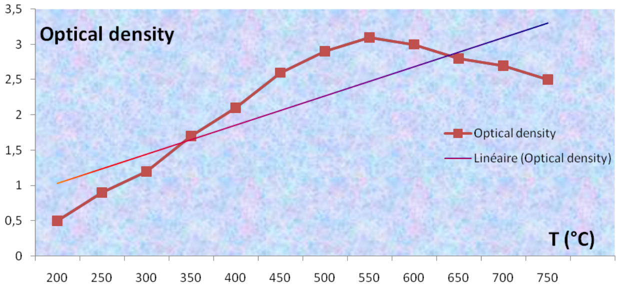


Fig. 2: Variation of the optical density of the solution of ferrate (VI) (K_2FeO_4) at 507 nm as a function of temperature (K/Fe =4, t = 5 h).

It is found that the optical density of ferrate (VI) increases with temperature up to 560°C as an optimum temperature for the production of stable ferrate (VI) with high yield whose optical density of the solution measured at 507 nm is of the order of 2.60, which means that the temperature has a negative influence on the yield and the quality of the synthesized phase in certain ranges.

3. Effect of calcinations time

The experimental evaluation concerning the influence of the drying time on the yield of the ferrate VI synthesis reaction by dry route under exclusive conditions leads to the results represented in Figure 3.

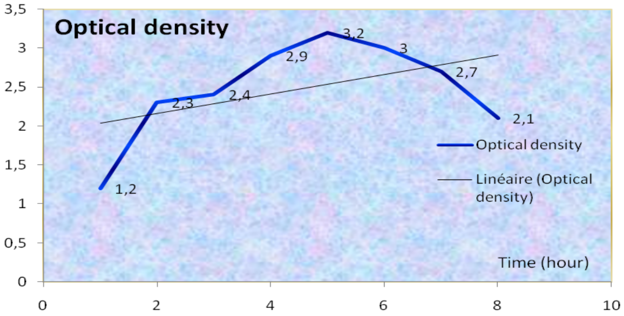


Fig. 3: Variation of the optical density of the solution of ferrate (VI) (K_2FeO_4) at 507 nm as a function of time (T=560°C and K/Fe = 4).

The optical density reaches its maximum at a value of 3.21 for duration of 5 hours of heating and beyond this time, it begins to decrease, which means that the yield of the iron VI synthesis reaction reached is maximum at around 5 o'clock. Therefore, the interest of optimization of time during the synthesis of ferrates VI by dry process.

4. Stability of ferrate as a function of time

The results of monitoring the degradation of ferrate as a function of time are drawn up in figure 4.

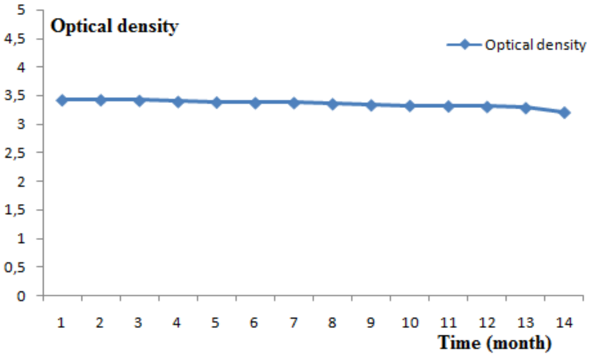


Fig. 4: Variation of the optical density of the solution of ferrates VI (K_2FeO_4) at 507 nm as a function of months of storage at a temperature of 30°C.

According to the curve (fig.4), it is observed that the optical density measured each month after storage at a temperature around 30°C varies very slightly does not exceed 0.01%, which means that the rate of degradation of the iron VI is very low in different months. Indeed, this result presents a progress in the synthesis of ferrate VI stable at a temperature around 30°C, such that one of the tricks related to iron VI is due to their instability [22, 23].

The relation which makes it possible to calculate the percentage of degradation of Iron (VI) is given by the following formula:

$$\textbf{\% degradation of iron (VI)} = D.O_i - D.O_f / D.O_i$$

$D.O_i$ and $D.O_f$: Optical densities of iron (VI)

The calculation of the rate of degradation between the months, as well as the state of production of ferrate VI and the different months of storage is represented in the following table.

Table 1: Variation in the optical density of ferrate VI of the synthesized phase K_2FeO_4 as a function of the rate of degradation between the initial state of production and different months of storage of ferrate VI (%) as well as a function of the rate of degradation between months of ferrate VI storage (%).

t (Month)	The degradation rate between the initial state of production and different months of storage of ferrate VI (%)	The monthly degradation rate of ferrate VI (%)
1	0.01	0.01
2	0.01	0.01
3	0.04	0.03
4	0.05	0.01
5	0.07	0.02
6	0.07	0.00
7	0.08	0.01
8	0.09	0.02
9	0.10	0.01
10	0.11	0.03
11	0.13	0.03
12	0. 14	0.01

According to these results, we note that the rate of degradation of iron (VI) remains very low until it is canceled as a function of time and varies in a different way from one month to another during storage at 30°C. This low degradation may be due to the low level of impurity detected in the synthesized phase, however the rate of degradation observed between the different months of storage at a temperature around 30°C does not exceed 0.01 % and it is limited to 0.07% in the first six months, thus making it possible to solve the problem of stability of ferrate VI, at a well-determined temperature, despite studies on the synthesis of ferrate VI by dry process remaining insufficient compared to where d other synthesis methods which makes negative on the improvement of this type of synthesis, which is useful to the environment because it can be considered as a green technology for the recycling of various waste iron compounds as well as to reduce the cost of Synthesis of this super oxidant directly from inexpensive and readily available starting material (iron oxide) and especially iron VI presents the future of water treatment as a coagulant and disinfectant as well as used as a battery cathode thanks to their high potential and their capacity to store electrical charges. However, the problem of explosiveness remains a barrier that requires developing it and especially in the dry process when working at a high temperature above 400°C which can make it explosive according to Kisselev and al [40].

4. Characterizations and analysis of the phase synthesized by the dry method

1. Diffraction by RX (DRX)

The diffractometer used is the computer-controlled XPERT-PRO with a K-α copper cathode (λ = 1.5405980 Å). The scan adopted with a step of 0.06682° and a time/step of 1s. The measuring angle range is 10° to 90°. Figure 5 shows the X-ray diffractogram obtained on potassium ferrate powder for a ratio of (K/Fe =2, 3, 4) and calcined at 560°C for 5 hours. The X-ray diffractogram shows a mixture of reflection peaks characteristic of ferrate (VI) (Licht and al) [30] of different purity depending on the ratio (K/Fe) used. In addition, certain peaks present phases that can be assimilated to intermediate compounds of iron IV or V for the K/Fe ratios = 2 or 3 located around 2 thetas equal to 32, such that the angle of these peaks do not represent iron III used at the start. However, it is noted that the characteristic peaks of iron VI are sharp at 2 thetas equal to 20.8; 25.8; 30.1; 34.8; 45.5 and 53.5 for the K/Fe ratio = 4 (fig.5) which is compatible with those found by various authors [34-37]. The minor deviations observed for some peaks can be attributed to the sample preparation and calibration procedure as well as to the types of reagents used. Indeed, the result observed in XRD confirms the degree of purity obtained by UV spectrometer and by volumetric titration.

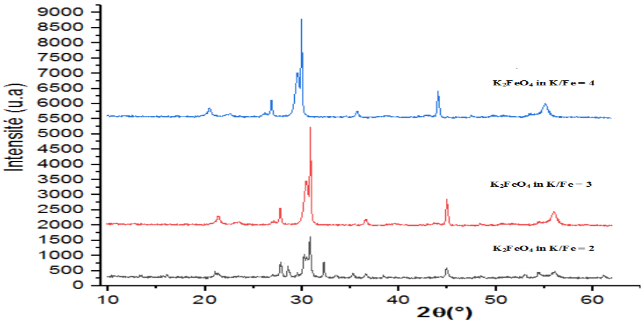


Fig. 5: XRD spectra of three samples of K_2FeO_4 synthesized with a K/Fe ratio = 2, 3 and 4

2. Spectrometry IR

IR spectroscopy is a quantitative method to prove the existence of Iron (VI) in the synthesized phase. Because the appearance of the spectra is linked to the symmetry of the molecule or of the FeO_4^{2-} groups (tetrahedral structure), the IR spectrum of the potassium powders calcined at 560°C for 5 hours was also recorded in a length interval of wave ranging from 500 cm^{-1} to 1600 cm^{-1}. The IR spectra of the raw powders (Fig. 6) presents a series of absorption bands marked by absorption bands located at: 767,781, 790, 807, 912 and 1001 cm^{-1} characteristic of ferrate (VI) and presents a great similarity to those found by the authors C. Li and al. [36]; W. Griffith [46]; P. Tarte and al. [47]. However, the vibration band located at 1500 cm^{-1} can be attributed to K_2O groups of the phase, thus confirming the results obtained by XRD.

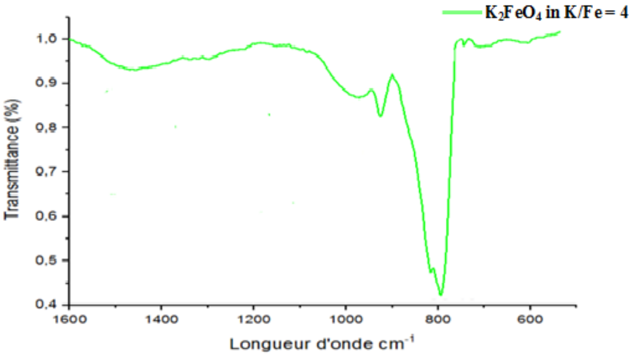


Fig. 6: IR spectrometer of K_2FeO_4 synthesized with a K/Fe ratio = 4.

3. Volumetric titration method

The purity of K_2FeO_4 was determined by chromites analysis according to the method of Lee Y.H. et al [43] who determined the synthesized phase of potassium ferrate for a K/Fe ratio = 4 and calcined at 560°C for 5 hours is 98.3% to 99.1% pure on the basis from the redox state and the remaining iron is in a lower valence state. Although at these relatively low concentration levels, the specific nature of this ferric impurity is difficult to distinguish, it can be attributed to intermediate compounds of iron IV or V. Because the absorption bands observed on the IR spectrometer do not represent any symmetry of the molecule which exhibits the degree III iron used in the initial reagents. Indeed, this result agrees with those obtained by IR spectroscopy, XRD and UV spectrophotometer. Anyway, we can suppose that the excess of iron, existing in several forms of amorphous ferric salts can be generalized in the form of an impurity of the intermediate compounds of iron IV or V at 1.7%.

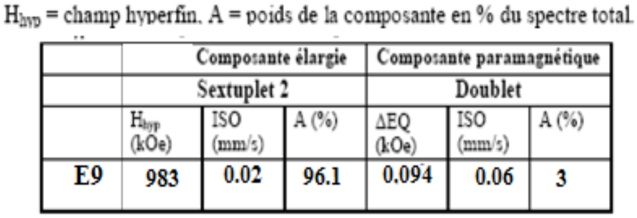
4. Mossbauer spectroscopy

Mossbauer spectroscopy in particular allows a quantitative analysis of the oxidation states of iron, because it is very sensitive to the environment of the resonant nucleus and also makes it possible to highlight the existence of a magnetic order at low temperature, by generating six transitions which gives rise to a sextuplet in the case of iron [29], [48,49].

The characterization of K_2FeO_4 by Mossbauer spectroscopy after twelve months of storage at a temperature around

30°C reveals a degradation of Iron (VI) over time (fig. 7). Indeed, the spectrum is in the form of a magnetic broadened component which was calculated by the superposition of the sextuplet and a paramagnetic component adjusted by a paramagnetic doublet. The hyperfine parameters deduced from the calculation of the spectrum are grouped together in the table below.

Table.2: Hyperfine parameters deduced from the calculation of the spectrum after twelve months of storage at a temperature around 30°C.



H_{hyp} = champ hyperfin. A = poids de la composante en % du spectre total

	Composante élargie			Composante paramagnétique		
	Sextuplet 2			Doublet		
	H_{hyp} (kOe)	ISO (mm/s)	A (%)	ΔEQ (kOe)	ISO (mm/s)	A (%)
E9	983	0.02	96.1	0.094	0.06	3

The hyperfine parameters deduced from the calculation of the spectrum after twelve months of storage at a temperature around 30°C, makes it possible to visualize the degree of oxidation of the iron and to know the evolution of the rate of iron (VI) with the time, because the trick linked to ferrate VI is due to its instability over time.

According to the results (Tableau.2 and fig.7), it can be seen that the degradation of iron VI is reflected on the spectrum by an isomeric shift of 0.02 mm /s for the sextuplet which presents iron (VI) and which comes out in the vicinity of -1 [29], [48,49]. This confirms the result found by XRD, IR spectrometer, chromites analysis and UV spectrometer. This isomeric shift is due to a low degradation of iron (VI) to iron (III) linked to the production method or where a low percentage of impurity which remains in the sample, and which is limited by the chromites analysis to 1.3 %.

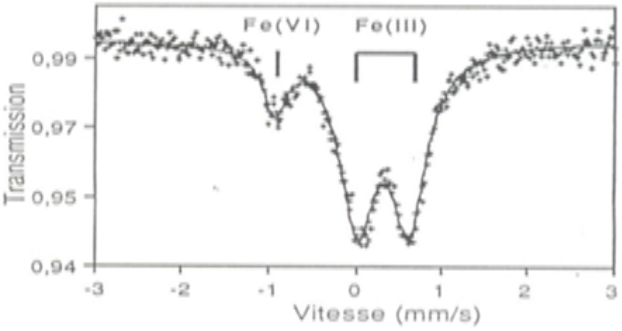


Fig. 7: Mossbauer spectrometer of K_2FeO_4 after twelve months of storage at a temperature of 30°C

The results observed by Mossbauer spectrometer and UV spectrophotometry after 12 months of storage at a temperature around 30°C have been confirmed by the volumetric titration method, the rate of degradation of iron VI of which does not exceed 3% at most. This result is a progress for the synthesis of stable iron VI by dry process in order to facilitate its storage and its transport. As well as the dry synthesis remains easy, without electrochemical complication and preparation of reagents because it is based only on the recycling of waste iron which is rather available and less expensive.

5. Discussions

According to our results, the ratio of K/Fe = 4 (Fig. 1) is necessary for the synthesis of iron (VI) in particular K_2FeO_4 by dry process stable for one year of storage at a temperature of 30°C and of purity varying between 98.3 to 99.1% under the most favorable conditions (T= 560°C for 5 hours of drying) under a stream of oxygen (fig. 2, 3, 4). This is compatible with the results of the various preliminary studies [39, 40], showing the effect of the ratio of reagents on the synthesis of iron (VI) by the dry route.

A preliminary study by Kopelev and al [41] showed the effect of the heating temperature of the reaction mixture on the yield and purity of the phase synthesized by the dry route by mixing the waste with ferric oxide in a furnace at 800°C, which is compatible with our results obtained at a temperature of 560°C. As well as Martinez-Tamayo and al [39] studied the behavior of the Na_2O_2-$FeSO_4$ system by heating it to a temperature of 400°C and under a stream of oxygen to synthesize pure ferrate VI. However, this view is only suitable for drying in a temperature range less than or equal to 400°C, because in reality and at temperatures above 400°C, K_2O_2 is better for the preparation of Fe(VI) by the dry process. Under a current of oxygen and with a molar ratio K/Fe= 4 than Na_2O_2.

Despite the studies made on the synthesis of ferrates by dry process, they remain insufficient until now because of the use of a high temperature which can lead to explosiveness. While this method is better for the ability to produce alkali ferrates (VI) or directly from inexpensive and readily available starting material (iron oxide), without complicated electrochemical procedures or preliminary preparation of reagents [38].

According to our results, 5 hours of heating the reaction mixture of K_2O_2 with Fe_2O_3 were sufficient at a temperature of 560°C, under a stream of oxygen to reach the maximum yield of the synthesis reaction of 99.1% pure ferrate VI and stable at 30°C. This time means that the synthesis reaction goes through several stages in order to stabilize the Iron VI, the iron III used as starting reagents can go through several intermediate compounds of oxidation state IV and V in order to reach oxidation state VI. This is consistent with studies done by Martinez-Tamayo and al [39] and Kisselev and al [40]. These studies have shown that we can obtain ferrates (V) and (VI) whose nature depends on the molar ratio of initial reagents, as well as Cici and al [42] arrived at the synthesis of ferrate VI by heating the mixture of ferric oxide and sodium peroxide for a few minutes at 800°C in several phases.

Several previous studies present the process of synthesis of ferrate VI by dry route as a green technology for the recycling of various waste iron compounds and the most advantageous compared to other methods of synthesis, to avoid the procedural complications of using the electrochemical route and preliminary products as well as avoiding the reaction of ferrates with water, in addition to their ability to produce ferrates VI in quantity to meet the growing global demand. The availability of iron oxides as a starting material that can be found easily and inexpensively, which makes the cost of synthesis positive and raises the requirement on a global scale [38], [43].

According to our results, the phase synthesized by dry process of K_2FeO_4 was analyzed by XRD, IR spectrometer, UV spectrometry to quantify the degree of oxidation of iron existing in this phase in a quantitative and qualitative way. Therefore, the results found by XRD (fig. 5), represent the VI ferrate peaks compatible with those found by different authors [34-37], with some minor deviations that may be due to the difference in the sample preparation and calibration procedure. This result was confirmed by the IR spectrometer (fig. 6), which presents absorption bands characteristic of the symmetry of the molecule or of the FeO_4^{2-} groups (tetrahedral structure), which presents a great similarity with that of the previous authors Li and al. [36]; Griffith [46]; Tarte and al. [47]. However, the tests carried out under the different experimental conditions (K/Fe = 1 – 6, T = 200 – 750°C, t = 6 –17h and at the product storage temperature (T = 20 - 40) are carried out at using a UV spectrometer by measuring the optical density of the solution of ferrate (VI) at the wavelength of 507 nm which determines the existence of iron VI according to the method of tsapin and al [45]. UV was used extensively in this work due to its availability and efficiency, to confirm the favorable results by XRD, IR spectrometer and volumetric titration analysis (% of phase purity found).

The Mossbauer spectrometer was used only to confirm the existence of iron VI after 12 months of storage at a temperature of 30°C (fig. 7), based on its reliability in revealing the different degrees of iron oxidation that exists in the phase, therefore, to give a further idea about the rate of degradation of iron VI and the type of iron thus formed.

The degradation rate of synthesized VI ferrates does not exceed 3% after one year of storage, is attributed to the low impurity observed or to the sample preparation and calibration method.

And finally, the synthesized phase presents an important progress in the synthesis of ferrate VI by a dry and easy to elaborate way without preparation of the reagents, nor electrochemical complications. able to meet the growing demand for requirements on VI ferrates, thanks to the availability of different sources of ferric oxides (galvanized waste, ferric oxides, etc.) as a starting product that can be found easily and inexpensively, which makes positive on the cost of synthesis and raises the requirement on a global scale [38], [43].

6. Conclusion

In this study, we arrived at the most suitable method for the synthesis of ferrate (VI), in particular K_2FeO_4 stable at a storage temperature of 30°C by dry process, using the direct reaction of the mixture of Fe_2O_3 with K_2O_2 in the most favorable experimental conditions to date (K/Fe ratio = 4, a temperature of 560°C for 5 hours under a current of oxygen).

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

These results showed that the synthesis of ferrate VI by the dry route remains the cheapest compared to other synthesis methods, thanks to the availability of iron oxides as a starting product which can be found easily and inexpensively, which makes it positive on the synthesis cost and lifts the requirement on a global scale. Because iron VI has become an incredible green technology through their wide application as an environmentally friendly oxidant, disinfectant and coagulant in water treatment.

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