RESEARCH ARTICLE (Open Access)

Valorization of industrial wastes *via* chemical preparation of the environmentally friendly oxidants

NDUE KANARI[1*], SEIT SHALLARI[2], FREDERIC DIOT[1], ERIC ALLAIN[1], JACQUES YVON[1]

[1]Université de Lorraine, UMR 7359 CNRS, CREGU, GeoRessources Laboratory, 2, rue du doyen Roubault, BP 10162, 54505 Vandoeuvre-lès-Nancy, France

[2]Agriculture University of Tirana, Faculty of Agriculture and Environment, 1029, Tirana, Albania

*Corresponding author; E-mail: ndue.kanari@univ-lorraine.fr

Abstract

Extraction of several non-ferrous metals generates large amounts of solid wastes leading to a serious environmental threat, causing significant and lasting damage to flora and fauna. With the tight environmental regulations and embracing the concept of the "sustainable development" in the environmental strategy, research centers in collaboration with industrial sectors have to develop new approaches for the treatment of the already generated and stored wastes. The aim of this work is to chemically transform this ironbased wastes into green, sustainable and high added value materials having iron in hexavalent state Fe(VI), known as alkali ferrates [(Na, K)$_2$Fe^{VI}O$_4$] and appreciated for their strong oxidation capacity and multifunctional properties. The experimental tests consist of simultaneous reactions of two solids (hydrated ferrous sulphate and alkali hydroxide) and one gaseous oxidant (diluted chlorine) at room temperature. Scanning electron microscope (SEM), X-ray diffraction (XRD) and chemical analyses are used to determine the composition of the starting samples and the solid reaction products. The oxidation state of iron [Fe(II), Fe(III) and Fe(VI)] is mostly determined by Mössbauer spectroscopy (MS) technique. The effects of several parameters on the transformation yield of Fe(II) into Fe(VI) are systematically investigated in order to optimize the synthesis process. A comparison of ferrates preparation process developed here, with principles of the "green chemistry" suggests that numerous points such as: prevention, atom economy, less hazardous chemical synthesis, design for energy efficiency, lead to consider this process as "green chemistry" and the obtained ferrates as environmentally friendly oxidants.

Keywords: industrial waste, ferrates synthesis, green oxidant.

1. Introduction

With a mass content of about 5 %, iron is one the most common elements of the earth's crust. Its compounds are present in most of the nonferrous metals deposits where these metals represent often a small fraction. Although a part of ferrous components is separated during mining and primary mineral processing, a large part of iron goes to the extractive processes of these metals. Further, the iron is sometimes present in the natural mineral bodies [e.g. $FeTiO_3$, $CuFeS_2$, $(Ni,Fe)_9S_8$, etc.] of the target metals that can be separated necessarily during the primary metal extraction. Therefore, huge amounts of iron bearing wastes are inevitably generated from both hydro- and pyro-metallurgical operations on raw materials. Their inappropriate disposal and management has a significant impact on public health, plants and animals. One of these typical industrial wastes is iron sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) generated during titanium oxide (TiO_2) manufacture by the sulphate process [1]. A part of this by-product is used as anti-moss, essentially for agriculture, the rest has to be disposed as a waste. It was often dumped in the sea, leading to the medium acidification *via* the simplified oxidation/hydrolysis scheme [$Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(OH)_3$]. Recently, ferrous sulphate appeared to be an excellent material for the synthesis of powerful oxidants, alkali ferrates "AF" ($A_2Fe^{VI}O_4$, A = Na, K) having iron in hexavalent state [1-4] and frequently noted as [Fe(VI)]. The ferrate ion (FeO_4^{-2}) is mainly appreciated for its strong oxidizing ability [$E°(FeO_4^{-2}/Fe^{3+} = 2.2$ V)], which is significantly higher than those corresponding to the current used oxidants. As shown by Eq. (1), the reduction of ferrate ion (FeO_4^{2-}) in aqueous solution generates both ferric hydroxide precipitate and nascent oxygen.

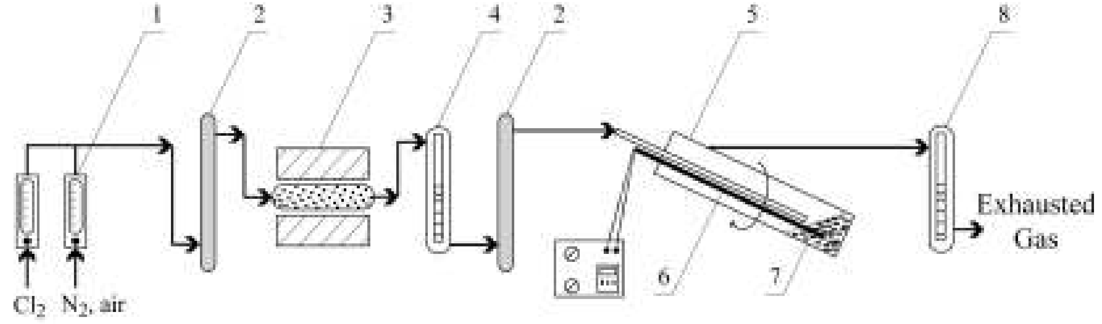
$$2[FeO_4]^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 4OH^{-} + 3O^{\bullet} \qquad (1)$$

Ferrate is used for water treatment due to its powerful oxidizing capacity (oxidation of organics and mineral materials, biocide agent) and to the flocculating property of the resulting ferric hydroxide. Further, the decomposition of the ferrate generates a basic media favoring the precipitation of heavy metals as hydroxides. Note also that $Fe(OH)_3/Fe_2O_3$, issued from ferrate reduction, is considered as an environmentally friendly product. These properties make the ferrate an ongoing material particularly interesting and valuable for waters, wastewaters and effluents treatment. Some studies on the applications of ferrates, cited here [5-13], are part of the numerous research reports found in the literature. However, most of them are performed at laboratory scale due to the difficulties for Fe(VI) preparation and its stability as well as to high investment and operations costs for an industrial purpose. In addition, the drawback of the methods known for the metal ferrate synthesis is their preparation in aqueous solutions. These methods required pure chemicals and many operations for ferrates manufacturing. Note also that the water reacts with ferrate ion (Eq. 1) causing the rapid reduction of Fe(VI), resulting to low efficiency for the conversion of [Fe (II, III) to Fe (VI)].

Therefore, this research work aims at overcoming the difficulties related with ferrates preparation and to summarize several features of the synthesis process. The methods described here are performed by dry route under atmospheric conditions allowing the simultaneous reaction of the wasted iron salts (e.g. $FeSO_4{\cdot}xH_2O$), the alkali hydroxides (KOH & NaOH) and gaseous chlorine (Cl_2).

2. Material and Methods

The different industrial samples of ferrous sulphate heptahydrate are mainly used as iron salt for the synthesis of ferrates. Scanning electron microscope (SEM), X-ray diffraction (XRD), and chemical analyses are used to determine the composition of these ferrous sulphate samples. The oxidation state of iron [Fe(II) and Fe(III)] of the samples was determined by Mössbauer spectroscopy (MS). The chemical analyses revealed that the collected samples contain close to 20 % iron and 35 % sulphate (theoretical composition of $FeSO_4{\cdot}7H_2O$ is 20.09 % iron and 34.55 % sulphate) confirming that used samples were almost pure. The quasi totality of iron was found to be in divalent state and the main phase was $FeSO_4{\cdot}7H_2O$. Potassium hydroxide pellets (KOH) having a diameter of about 5 mm and containing about 15 % H_2O (in weight) are employed as alkali medium, whilst sodium hydroxide is used as pearls of about 1 mm containing 99 % NaOH. The gaseous reagents (Cl_2, N_2, O_2) had a purity higher than 99 % and air is supplied by a compressor. The main apparatus assembly intended for the alkali ferrates synthesis is schematized in Figure 1. The gas humidity of the gaseous mixture was decreased by their passing through P_2O_5 and H_2SO_4 columns. If necessary, a carbon furnace heated at 800 °C can be used for eliminating any trace of oxygen contained in nitrogen and chlorine. The reactor consists of a glass rotary one (5) with adjustable rotation speed.



1. Flowmeter
2. P_2O_5 columns
3. Carbon furnace
4. H_2SO_4 column
5. Rotary reactor
6. Thermocouple
7. Sample
8. NaOH column

Figure 1. Schematic representation of the experimental setup used for ferrate synthesis in rotary reactor.

It is designed in manner that its rotation does not disturb the input and the output of the gases. Reactors having volumes from 0.15 L to 2.5 L are mainly used for the experimental tests. The solid sample ($FeSO_4 \cdot xH_2O$+AOH) was placed in the reactor, since then, a given gas mixture containing chlorine was circulated into the reactor allowing the ferrate synthesis by the contact of the two solid phases with the gas mixtures (air+Cl_2, N_2+O_2+Cl_2 and/or N_2+Cl_2). The spent gases are purified by NaOH solution before their release to the atmosphere. A thermocouple (6) was placed into the sample to measure the temperature increase due to exothermic nature of the synthesis reactions. The synthesis products were subjected to Mössbauer spectrometry and chemical analysis to determine the Fe^{VI} efficiency of the synthesis process.

To explore new developments for the preparation of metal ferrates, the fluidized bed reactor with the temperature-regulated water system is also checked. The experimental procedure as well as the features for this synthesis method are already described elsewhere [14, 15].

3. Results and Discussion

The overall reaction for the potassium ferrate synthesis can be represented by Eq. (2). It should be analogue for the synthesis of the Na-ferrate, although its exact formula is still doubtful. In both the cases, the water is released according to Eq. (2) coming from the iron sulphate, from the synthesis reactions and from KOH in the case of the K-ferrate (K_2FeO_4). This suggests that the amount of water released during the synthesis is high and consequently, it can react with the product and decrease the Fe^{VI} efficiency. For these reasons, it was suggested to use the ferrous sulphate monohydrate ($FeSO_4 \cdot H_2O$) for the synthesis of potassium ferrate. It can be obtained by dehydration of $FeSO_4 \cdot 7H_2O$ at temperatures lower than 150 °C [1, 2].

$$FeSO_4 \cdot xH_2O + 2Cl_2 + 8KOH \leftrightarrow K_2FeO_4 + K_2SO_4 + 4KCl + (x+4)H_2O \qquad (2)$$

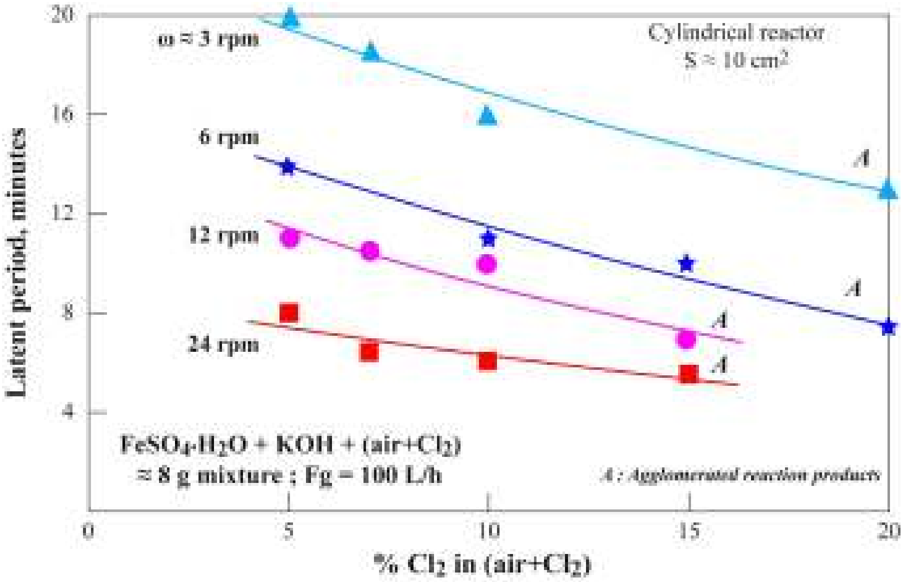


Figure 2. Evolution of starting time of intensive reaction as a function of % Cl_2 and rotation speeds of the reactor during potassium ferrate synthesis.

The first experimental tests for the K_2FeO_4 synthesis are performed with 8 grams of solids in a 0.15 L rotary reactor of cylindrical shape. The typical purple colour of the synthesis product, water and heat release are the obvious evidences of the ferrates. These phenomena indicate that an intensive reaction takes place after a latent period. Figure 2 describes the evolution of this latent period as a function the rotation speed (ω) of the reactor and the chlorine content in the gas mixture (air+Cl_2) having a total flow rate (F_g) of 100 L/h. The latent period, for a fixed chlorine content in the gas mixture, decreases as the rotation speed of the reactor increases. Products obtained during the treatment using 10 % Cl_2 were not agglomerated whatever is the reactor rotation speed between 3 and 24 rpm. Chlorine contents equal to and higher than 15 % led to full agglomeration of the reactions products and to the decomposition of the synthetized ferrates into iron (III) components.

More advanced experimental tests showed that this latent period can be avoided by mixing the solids ($FeSO_4 \cdot H_2O$ and KOH) in absence of the reactive gases. This is probably due to the formation of K_2SO_4, produced by the reaction of $FeSO_4 \cdot H_2O$ with KOH, that acts as nuclei for the potassium ferrate synthesis. Note that K_2FeO_4 and K_2SO_4 have the same structure and lattice parameters. Further, in order to avoid secondary reactions, especially the reaction of KOH with chlorine giving potassium chloride as final product, the premixing of the potassium hydroxide with iron sulphate, is preferentially performed in most experimental tests. The rest of the unreacted iron sulphate is reused for a new synthesis test. The synthesis products manufactured by using the fresh iron sulphate and recycled iron sulphate are subjected to the Mössbauer spectroscopy; the obtained results are depicted in Figure 3. Clearly, the Fe^{VI} yield of the synthesis using fresh iron sulphate (Fig. 3-*a*) and reused iron sulphate (Fig. 3-*b*) are similar indicating the possible recycling of the iron salts in the synthesis process.

The effects of a good number of the experimental parameters (summarized below) on the potassium ferrate synthesis are tested in order to find the best conditions for a high Fe^{VI} efficiency of the process. Nearly, similar variables are also checked for the synthesis of the sodium ferrate.

- type of iron salt ($Fe^{II}SO_4 \cdot H_2O$, $Fe^{III}SO_4 \cdot OH$),
- (K, Na)/Fe ratio of solids,
- flow rate of gases (from 40 to 700 L/h),
- type of diluting gas (air and/or N_2),
- chlorine content in the gas mixtures (2 to 20 % Cl_2),
- residence time (30 to 120 minutes),
- reactor shape and volume (from 0.15 to 2.5 L),
- solids loading mode as the reaction progresses, etc.

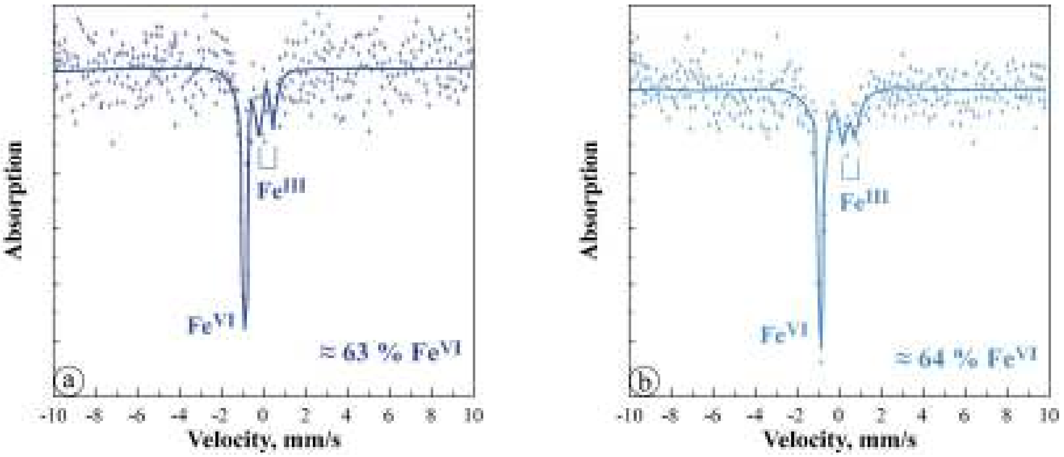


Figure 3. Mössbauer spectrum of product obtained from the reaction: ($FeSO_4 \cdot H_2O$) + (air+7 % Cl_2) + KOH *(a)* and ($FeSO_4 \cdot H_2O$ reused) + (air+7 % Cl_2) + KOH *(b)*.

One of the most important items for the alkali ferrate synthesis is the control of the highly exothermic reactions. Temperatures as high as 175 °C are recorded when 10 grams of the solids are mixed in presence of chlorine at room temperature [1]. Note that high temperatures in the reaction zone cause the agglomeration of the synthesis product, promote the secondary reactions and are responsible for the ferrates decomposition. In this optic, attempts are made to design a process that is controllable and easy to apply on a larger scale. One possibility to synthesize high amount of K-ferrate in the same reactor was to load periodically the solids in the reactor. Figure 4 represents the obtained results during the synthesis of K-ferrate in a reactor of 2.5 L by using 5-6 % Cl_2 in the gas mixture of (N_2+Cl_2).

About 115 grams of solids ($FeSO_4 \cdot H_2O$ + KOH) were loaded in the reactor before the gas mixture was introduced. The temperature increased up to 55 °C and when the temperature started to decrease, a second lot of about 70 grams was put in the reactor. Load of other lots of solids is made periodically each 20 minutes. Total of solids introduced in the reactor was about 460 grams and the maximum temperature did not exceed 65 °C. The synthesis product contained about 50 % of iron at hexavalent state.

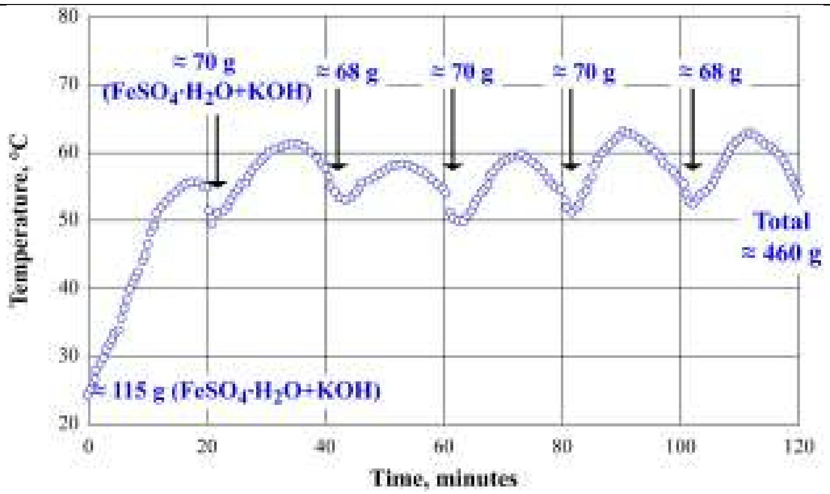


Figure 4. Synthesis of K-ferrate loading periodically the solids (N_2+Cl_2 = 700 L/h, ≈ 5-6 % Cl_2, ω = 5 rpm).

Use of a fluidized bed for the alkali ferrate synthesis was also tried and considered as a promising choice. It is well known that the fluidized beds could efficiently overcome the difficulties of mass and energy transfer, especially in case of heterogeneous reaction systems. In the present case of alkali ferrates synthesis, it is expected that fluidized bed would increase the efficiency of Fe^{II} to Fe^{VI} conversion and enhance the reaction kinetics. However, the great difference in particle sizes between iron sulphate (< 50 µm) and NaOH (≥ 1 000 µm) was the real difficulty for the synthesis of sodium ferrate in fluidized bed. An enhanced process is already invented [15] to overcome this difficulty. It included two main steps, i.e., (i) premixing of NaOH with iron sulphate (solid-solid reactions) leading to a single solid, and (ii) fluidization of the obtained mixture in diluted chlorine (gas-solid reactions). The synthesis process is an exothermic one, and it is accomplished within few minutes. Heat and water were rapidly evacuated from the reaction zone leading to a dried Na-ferrate. Although this process described essentially the synthesis of Na-ferrate using NaOH and iron sulphate, it could be also extended for the others alkali and/or alkaline ferrate synthesis and using various iron bearing compounds. For instance, KOH with a well-defined size could be also used instead of NaOH for the premixing with iron salts.

An environmental assessment of this research work should be perceptibly deduced by comparing the obtained results with the well-known principles of green chemistry [16]. Several criteria (prevention, atom economy, less hazardous chemical syntheses, design for energy efficiency, use of renewable feedstocks, design for degradation, etc.) make the ferrates green and environmentally friendly compounds. Further, this investigation is a good example showing the possibility to transform a waste ($FeSO_4·H_2O$) into a useful value-added product (alkali ferrates).

4. Conclusions

Industrial waste containing Fe(II) and/or Fe(III) can be converted into alkali ferrates having iron at hexavalent state. The synthesis process is achieved by dry route in rotary reactor and fluidized bed without external energy supply.

The synthesis of the alkali ferrates is a very sensitive process depending strongly on the water content and heat released from the exothermal reactions synthesis. The slow-down of the reactions kinetics and the process control can be realized by loading periodically the solids and/or by increasing the Fe/K ratio. The Fe(VI) efficiency is near to 65 % in the case of K-ferrate.

Best results are obtained during sodium ferrate synthesis in fluidized bed. The process is based on two steps starting by premixing of NaOH with iron sulphate leading to a single solid and followed by fluidization of the obtained mixture in diluted chlorine. The conversion of Fe (II, III) into Fe (VI) is about 55 % and the process is easy to transpose at larger scales.

The synthesis of alkali ferrates, as described here, is a clean process and can be considered as belonging to “green chemistry” by certificating most of its principles.

References

1. Kanari N.: **Contribution to chlorine chemistry and its applications: Synthesis of alkali ferrates (VI); A study of the kinetics of chlorine-solid reactions**. Habilitation Diploma. Institut National Polytechnique de Lorraine, Nancy, France. 2000.
2. Kanari N, Ostrosi E, Ninane L, Neveux N, Evrard O: **Synthesizing alkali ferrates using a waste as a raw material**. JOM 2005, **57**(8): 39-42.
3. Kanari N, Filippova I, Diot F, Mochón J, Ruiz-Bustinza I, Allain E, Yvon J: **Utilization of a waste from titanium oxide industry for the synthesis of sodium ferrate by gas-solid reactions**. Thermochimica Acta 2014, **575**: 219-225.
4. Ninane L, Kanari N, Criado C, Jeannot C, Evrard O, Neveux N.: New processes for alkali ferrate synthesis. In: Ferrates: VK Sharma; 2008: 102-111.
5. Jiang J-Q, Zhou Z, Patibandla S, Shu X: **Pharmaceutical removal from wastewater by ferrate(VI) and preliminary effluent toxicity assessments by the zebrafish embryo model**. Microchemical Journal 2013, **110**: 239-245.
6. Licht S, Wang B, Gosh S, Li J, Naschitz, V: **Insoluble Fe(VI) compounds: effects on the super-iron battery**. Electrochemistry Communications 1999, **1**: 522-526.
7. Sharma VK: **Potassium ferrate(VI): an environmentally friendly oxidant**. Advances in Environmental Research 2002, **6**: 143-156.
8. Sharma VK: **Ferrate(V) oxidation of pollutants: a premix pulse radiolysis study**. Radiation Physics and Chemistry 2002, **65**: 349-355.
9. Lee Y, Um I-H, Yoon J: **Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation**. Environmental Science & Technology 2003, **37**: 5750-5756.
10. Jiang JQ: **Research progress in the use of ferrate(VI) for the environmental remediation**. Journal of Hazardous Materials 2007, **146**: 617-623.
11. Jain A, Sharma VK, Mbuya OS: **Removal of arsenite by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: Effect of pH and anions**. Journal of Hazardous Materials 2009, **169**: 339-344.
12. Jiang J-Q, Zhou Z, Sharma VK: **Occurrence, transportation, monitoring and treatment of emerging micro-pollutants in waste water - A review from global views**. Microchemical Journal 2013, **110**: 292-300.
13. Yang X, Gan W, Zhang X, Huang H, Sharma VK: **Effect of pH on the formation of disinfection by-products in ferrate(VI) pre-oxidation and subsequent chlorination**. Separation and Purification Technology 2015, **156**: 980-986.
14. Kanari N, Ostrosi E, Diliberto C, Filippova I, Diot F, Allain E, Yvon J.: **Green process for the chemical conversion of an industrial waste into useful materials**. Proceedings of the 5th International Conference on Engineering for Waste and Biomass Valorisation 2014, 1810-1825.
15. Kanari N.: **Method of producing ferrates (VI)**. French patent, publication date: 14 Mars 2008, n° 2 905 609. Extension at international level: 13 Mars 2008, n° WO 2008/029046.
16. Anastas PT., Warner JC: **Green chemistry: Theory and practice**, Oxford University Press, New York; 1998.