MÖSSBAUER STUDY OF REACTION MECHANISMS OF FERRATES (Fe^{VI}, Fe^{V}, and Fe^{IV}): DETERMINATION OF EFFICIENCY IN WATER DECONTAMINATION

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Abstract

At present, treatment of surface, underground and waste water is viewed as a high priority and many studies deal with this issue. Water can be contaminated by organic pollutants, inorganic pollutants, toxic, heavy metals and their compounds, and many other substances that do not degrade to non-toxic compounds in natural waters. Therefore, it is necessary to prevent accumulation of these substances in water and remove them from environment.

In this respect, iron compounds in the high oxidation state (IV, V and VI), called ferrates, are very promising materials to water treatment. Especially, ferrates are able to remove hormones, such as estrogen, or medicines, for example antibiotics, from water. Reactions of ferrates with pollutants occur very quickly and thus, it is difficult to monitor the course of the reaction.

This study brings a deeper insight into the mechanism of ferrate reactions with pollutants because, thanks to Mössbauer spectroscopy, we are able to *in-situ* observe the course of the reaction. Moreover, analyzing the input materials, intermediates and also final products of reaction is possible once this technique is employed. In this regard, the application of Mössbauer spectroscopy for monitoring the reaction of ferrate(VI) with arsenic for removal of arsenic from environment is mentioned.

Keywords: Water treatment, ferrates, Mössbauer spectroscopy

1. INTRODUCTION

Currently, many studies are focused on cleaning and treatment of water. There is no wonder as, a large increase in human and industrial activity (i.e., industrial production, traffic, agriculture, extraction, chemical disasters, etc.) leads to increased contamination of groundwater and surface water. In this context, water can be contaminated by toxic, heavy metals and their compounds, organic pollutants (e.g., insecticides, herbicides, petroleum derivatives, solvents, medicaments, etc.) or inorganic pollutants (e.g., acids, ammonia, DDT, polychlorinated biphenyls, nitrogen, phosphorus, mercury, etc.). Many of these pollutants do not naturally decompose to non-toxic compounds in water. For this reason, a significant attention is currently devoted to the search for new methods and materials for the rapid, efficient and, as far as possible, a universal way of decontamination of water. Therefore, iron-based technologies still capture an eminent interest in the scientific community, especially, because they are environmentally friendly and use an Earth-abundant material. In addition, some materials containing iron are magnetic and their removing or recycling after culmination of the treatment process from environment is easier and less problematic. [1,2]

Iron occurs in several valence states (i.e., 0, II, III, IV, V and VI). In other words, it exists as metallic iron (Fe(0)), ferrous (Fe(II)), and ferric (Fe(III)) forms in the nature. Moreover, higher oxidation states of iron, such as +IV, +V and +VI, can be synthesized. These compounds of iron, where the Fe atom is in a higher oxidation state, with oxidation number +IV, +V or +VI, are generally called ferrates. These compounds comprise FeO_4^{4-} (Fe^{+IV}), FeO_4^{3-} (Fe^{+V}), and FeO_4^{2-} (Fe^{+VI}) ions. Recent studies have shown that ferrates are very promising materials for decontamination of water. They have a strong oxidation properties; in this respect, ferrate(VI) is the most powerful and most used agent. The stability and reactivity of the ferrates is dependent on pH and initial ferrate concentration of the solution, as well as on the presence of foreign ions in solution. Ferrates are the most stable in range of pH from 9.4 to 9.7. More dilute solutions of the ferrate ions are more stable, which means, that the stability of ferrates decreases with increasing concentration of ferrates solutions. Currently, a significant scientific interest is devoted to the +VI oxidation state of iron (Fe(VI)) because of its potential use as a "greener" oxidant for organic synthesis, a water oxidation catalyst and in treatment contaminants and toxins in water and wastewater. [1,3,4,5]

As already mentioned, ferrate(VI) is the most widely used due to strong oxidizing properties. It exhibits a reduction potential of 2.2 V in acidic medium; the reduction potential decrease to 0.7 V in alkaline solution. Maximum performance is thus achieved in an acidic or a neutral environment. Ferrate(VI) can easily oxidize different organic contaminants and effectively inactive microorganisms or bacterial indicators. Ferrate(VI) can also remove metal and metalloid contaminants. Together with the reduction of Fe(VI) to Fe(III), coagulation and precipitation of certain pollutants is observed. The main advantage of the use of ferrates in water treatment is that ferrates have a disinfecting effect and the resulting reaction products are nontoxic. They have a versatile use, always combining several reaction processes. Ferrates remove also micropollutants, estrogens or antibiotics. Small doses of ferrates are enough for their application in water purification. [2,3,6]

Despite a very wide range of possible applications, the real utilization of ferrates in practice in greater amounts is hindered by their instability. Ferrate(VI) salts are comparatively stable for quite a long time in the case they are stored in a dry atmosphere. Otherwise, ferrates are very unstable in water, and ferrate(VI) is reduced to a compound containing iron in oxidation state +III (Fe^{+III}), which is much more stable. As already mentioned, ferrates are very promising materials, but for real application of these materials in water treatment and others, is necessary, at first, to understand the reaction mechanisms between these compounds and pollutants. Reactions between pollutants and ferrates are very fast and it is difficult to in-situ monitor their course. Fortunately, this obstacle can be overcome by ^{57}Fe Mössbauer spectroscopy. This contribution thus introduces ^{57}Fe Mössbauer spectroscopy as a powerful tool to describe and monitor the reaction mechanisms and also to analyze precursors and intermediate and final products. ^{57}Fe Mössbaeur spectroscopy is presented as a main technique for assessment of sample purity and identifying the intermediate states during transformation from Fe(VI) to Fe(III) as it provides distinguishing between various valence states of iron based on their Mössbauer hyperfine parameters. [3]

More specifically, the methodology of ^{57}Fe Mössbauer spectroscopy is described here for ferrate research. The Mössbauer parameters of oxidation states (+III, +IV, +V and +VI) of iron are also listed. Further, the preparation of ferrates and characterization of the precursors and reaction products are described. Finally, an example of ferrate(VI) application for removing arsenic from the environment is briefly outlined.

2. METODOLOGY OF MÖSSBAUER SPECTROSCOPY FOR INVESTIGATION OF FERRATES REACTION MECHANISM

2.1. Mössbauer spectrum and hyperfine parameters of ferrates

Mössbaeur spectroscopy represents a unique technique to distinguish different oxidation states of iron using the values of the isomer shift (δ). The δ values are very sensitive to the oxidation state of iron. Then, the differences in the position of the Mössbauer resonant lines of ferrates(IV, V, VI) and iron(III) in the velocity ranges are observed (**Figure 1a**).

The typical ^{57}Fe Mössbauer spectrum of iron(III), that is usually the final product of reactions of pollutants with ferrates, is shown in **Figure 1a)** on the top. The spectrum contains a doublet with the value of isomer shift δ = 0.35 ± 0.05 mm/s and the value of quadrupole splitting ΔE_Q = 0.70 ± 0.05 mm/s. For ferrate(IV), a doublet is typically observed with the value of isomer shift δ = - 0.25 ± 0.05 mm/s and the value of quadrupole splitting ΔE_Q = 0.20 ± 0.05 mm/s. Ferrate(V) also gives a doublet with the isomer shift δ = - 0.45 ± 0.05 mm/s and quadrupole splitting ΔE_Q = 0.80 mm/s and the ferrate(VI) exhibits singlet with the value of isomer shift δ = -0.90 ± 0.05 mm/s. In **Figure 1b)**, the diagram with ranges of the isomer shift values observed for iron-containing compounds is displayed. Information on the values of the Mössbauer hyperfine parameters for each oxidation state is necessary to know to subsequently determine a composition of a characterized compound.

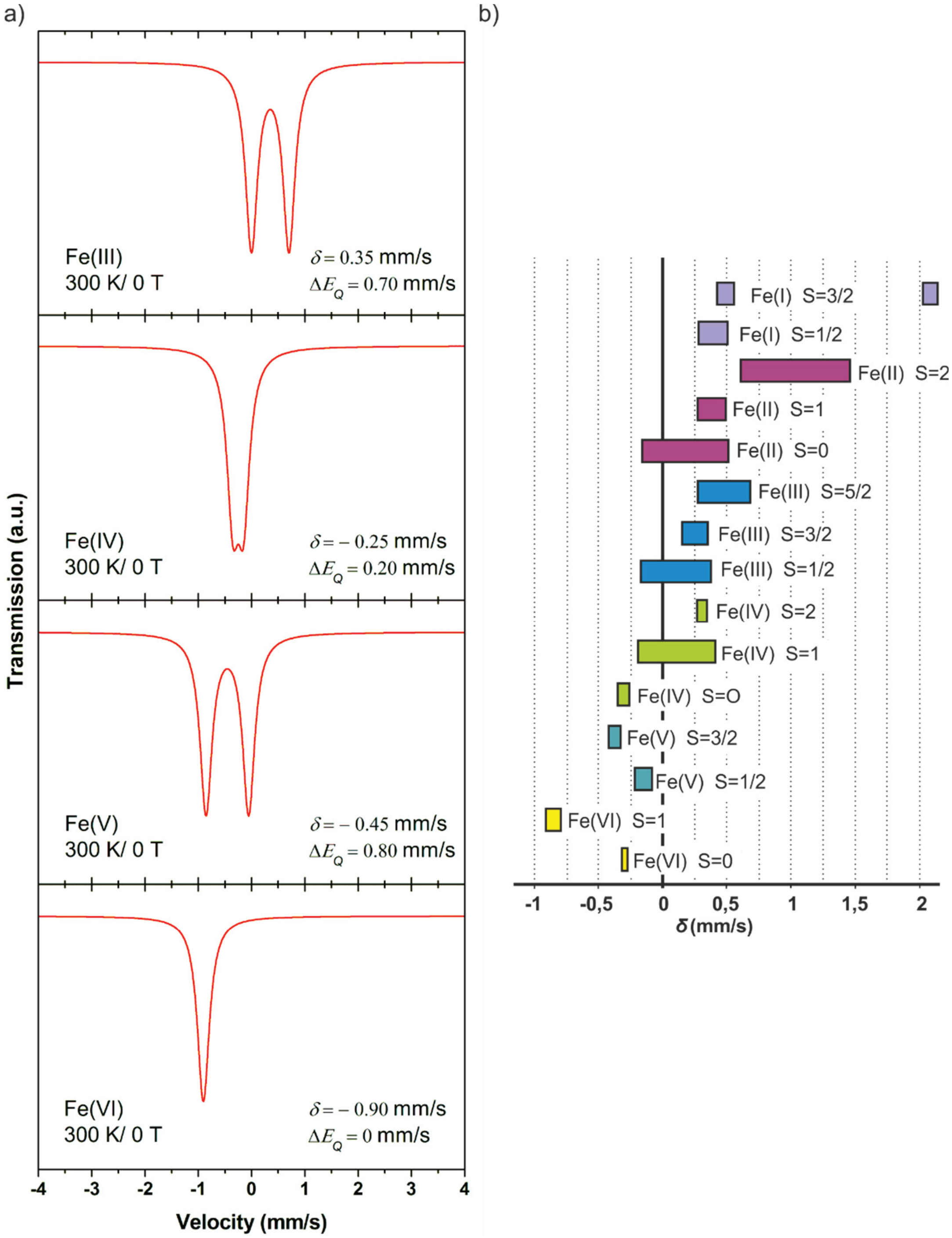

Figure 1 a) Representative ^{57}Fe Mössbauer spectrum of Fe(**III**), Fe(IV), Fe(V) and Fe(VI) at room temperature, without an external magnetic field. In the lower left corner, respective Mössbauer hyperfine parameters, such as isomer shift (δ) and quadrupole splitting (ΔE_Q) are displayed for each case. b) Diagram of isomer shift values observed for iron-containing compounds in various oxidation states at room temperature. The isomer shift values are referred to metallic α-Fe at room temperature. [8]

2.2. Preparation of ferrates

In general, three methods are often used to synthesize ferrates. The first method involves dry oxidation by heating a mixture of iron(**III**) oxides under strongly alkaline conditions and in the presence of oxygen. For example, adopting this strategy K_2FeO_4 (i.e., ferrate(VI)) can be prepared using heating of iron(**III**) oxides and potassium nitrate over 1100 °C. To synthesize Na_2FeO_4 (i.e., ferrate(VI)), a protocol involving heating of iron(**III**) oxides and sodium peroxide at 600 °C can be exploited. Then, the Na_4FeO_4 (i.e., ferrate(IV)) can be obtained by heating of iron(**III**) oxide and sodium peroxide at 370 °C. Generally, dry methods involve mixing ferric salt, often iron oxide, with alkali peroxide (Na_2O_2, K_2O_2) at high temperatures. Depending on the composition of the reaction mixture (Fe, Na, and O_2) and temperature, ferrate(IV), ferrate(V) or ferrate(IV) can be prepared. The second method to synthesize ferrates is based on wet oxidation, when iron(**III**) oxides or their salts are oxidized by an oxidant (e.g., potassium hypochlorite, sodium hypochlorite, ozone, etc.) in strong alkaline environment. Na_2FeO_4 can be synthesized using sodium hydroxide. K_2FeO_4 can be then precipitated from the solution by subsequent adding of potassium hydroxide to the Na_2FeO_4 solution. Using dry methods, various ferrates(VI) can be prepared, such as Cs_2FeO_4, $RbFeO_4$, $BaFeO_4$, $SrFeO_4$, and others. Third strategy for preparation of ferrates involves electro-chemical methods of anodic oxidation. Iron or iron salts are selected as an anode and sodium or potassium hydroxides are used as an electrolyte. The advantage of this approach for the synthesis of ferrates is often connected with the efficiency and quality, i.e., the yield of the reaction and the phase purity of the final products. The drawbacks include the complexity of the method and financial costs. [1,7]

Based on the study [9] (see the experimental section there for more details) Na_4FeO_4 - Fe(IV) and K_3FeO_4 - Fe(V) salts were prepared and the reproducibility of the solid state synthesis has been verified by ^{57}Fe Mössbauer spectroscopy and X-ray powder diffraction. The following values are referred to metallic α-Fe at room temperature. At first, ferrate(IV), Na_4FeO_4, was synthesized following the reaction **Equation 1**, i.e.,

$$8Na_2O_2 + 2Fe_2O_3 \rightarrow 4Na_4FeO_4 + 3O_2 \qquad (1)$$

The reaction took place in a glovebox, where Na_2O_2 was grinded to a powder. Then, Fe_2O_3 was added to Na_2O_2 and homogenized and heated to 400 °C for hour. After cooling down to room temperature, analyzes were performed. The room-temperature ^{57}Fe Mössbauer spectrum of Na_4FeO_4 features a doublet with the isomer shift $\delta = -0.23 \pm 0.05$ mm/s and the quadrupole splitting $\Delta E_Q = 0.41 \pm 0.05$ mm/s. Based on the results from ^{57}Fe Mössbauer spectroscopy, the amount of Fe(IV) was 94 at.% and Fe(III) 6 at.%. The X-ray powder diffraction determined the purity of the sample, i.e., the amount of Fe(IV), higher than 90 at.% in accordance with ^{57}Fe Mössbauer spectroscopy measurements. At the top of **Figure 2**, ^{57}Fe Mössbauer spectrum (a)) and X-ray diffraction pattern (b)) of synthesized Na_4FeO_4 are shown. To prepare Fe(V), the two-steps reaction process was performed (reaction **Equation 2** and **Equation 3**).

$$Fe^{III}O_x\left(OH\right)_y + KNO_3 \rightarrow KFeO_2 + NO_x \qquad (2)$$

$$KFeO_2 + 2KNO_3 \rightarrow K_3FeO_4 + 2NO_2 \qquad (3)$$

At first, homogenized mixture of KNO_3 and $Fe^{III}O_x(OH)_y$ was heated up to 950 °C for 30 minutes. After cooled down, the $KFeO_2$ was observed and then, in the second step, the $KFeO_2$ was added to KNO_3. This mixture was again homogenized and heated up to 1000 °C in presence of nitrogen. After that, the prepared K_3FeO_4 was frozen using liquid nitrogen. The room-temperature ^{57}Fe Mössbauer spectrum of K_3FeO_4 shows a doublet with the isomer shift $\delta = -0.52 \pm 0.05$ mm/s and the quadrupole splitting $\Delta E_Q = 0.88 \pm 0.05$ mm/s. In the middle of **Figure 2**, the ^{57}Fe Mössbauer spectrum (c)) and X-ray diffraction pattern (d)) of synthesized K_3FeO_4 are displayed. The X-ray powder diffraction again determined the purity of the sample, i.e. the amount of Fe(V), higher than 90 at.%. Based on the analysis of the respective ^{57}Fe Mössbauer spectrum, the amount of Fe(V) was 93 at.% and the amount of Fe(III) was 7 at.%. Using ^{57}Fe Mössbauer spectroscopy, it is also feasible to check the quality of potassium ferrate(VI), with declared purity higher than 95 %, from Sigma-Aldrich. This ferrate is usually used in applications for water treatment. At the bottom of the **Figure 2**, the ^{57}Fe Mössbauer spectrum (e)) and X-ray diffraction pattern (f)) of K_2FeO_4 are shown. The respective ^{57}Fe Mössbauer spectrum of K_2FeO_4 features a singlet with the isomer shift δ = - 0.89 ± 0.05 mm/s. The X-ray powder diffraction and also ^{57}Fe Mössbauer spectroscopy determined 96 at.% of Fe(VI) and 4 at.% of Fe(III). [9]

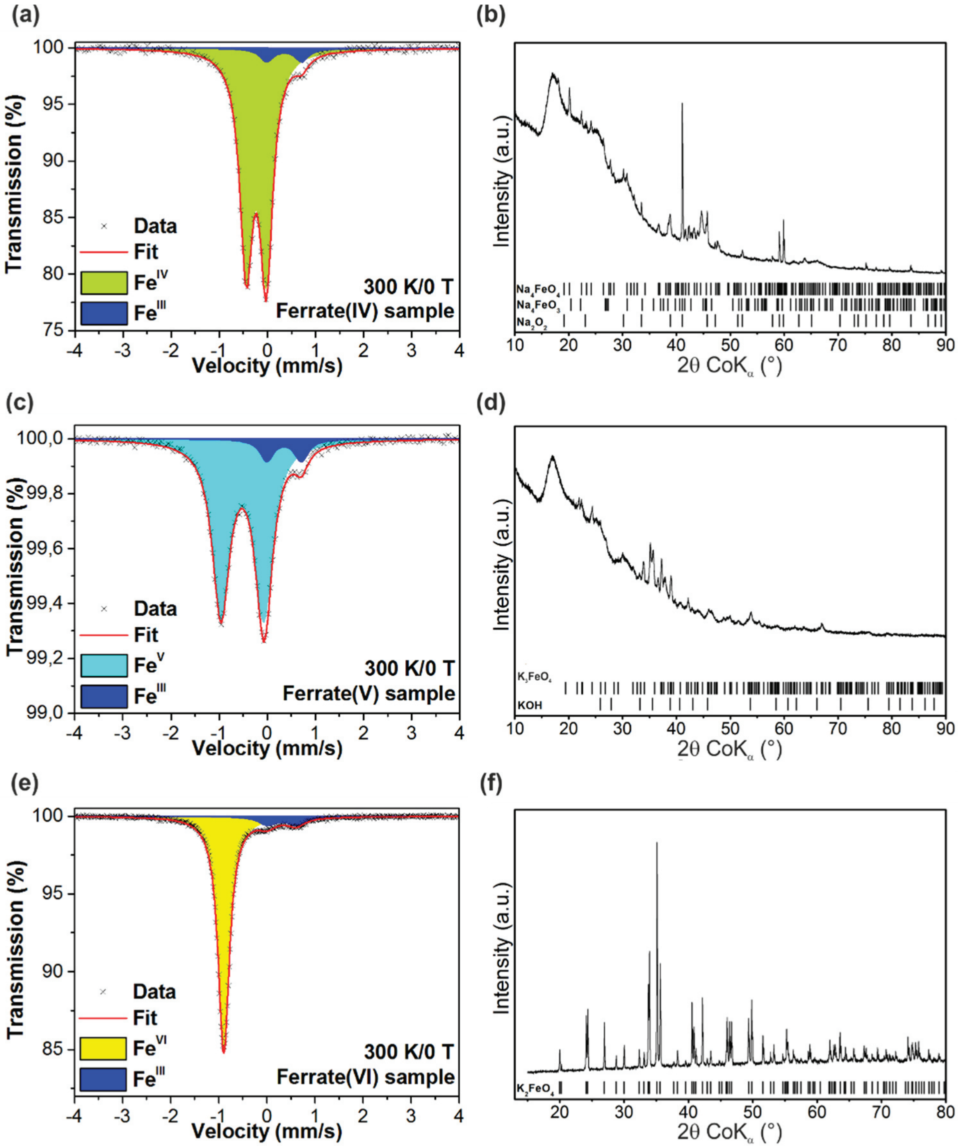

Figure 2 a) ^{57}Fe Mössbauer spectrum of Na_4FeO_4 - Fe(IV), b) X-ray diffraction pattern of synthesized Na_4FeO_4, c) ^{57}Fe Mössbauer spectrum of K_3FeO_4 - Fe(V), d) X-ray diffraction pattern of synthesized K_3FeO_4, e) ^{57}Fe Mössbauer spectrum of K_2FeO_4 - Fe(VI), f) X-ray diffraction pattern of synthesized K_2FeO_4. [9]

2.3. Reactions of ferrates

As already mentioned, ferrates have a high reduction potential. Thus, they are equipped with powerful oxidation properties; among them ferrate(VI) is the most strongest oxidant. Due to this feature, ferrate(VI) is the most used agent from group of ferrates. Ferrate(VI) has a reduction potential of 2.2 V in acidic medium and the reduction potential equals to 0.7 V in alkaline medium. Below, the equations of reactions of ferrate(VI) in the alkaline solution (**Equation 4**) and in the acidic solution (**Equation 5**) are listed. [1,6,7]

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \tag{4}$$

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \tag{5}$$

Thus, in water, ferrate(VI) immediately decomposes to stable oxidation state of Fe^{III}. When an electron is gained in water, ferrate(VI) is reduced to intermediate products, i.e., high valence states of iron, Fe(V) and Fe(IV), through 1-e^- and 2-e^- transfer processes. Simultaneously, the final iron-containing compound with iron in oxidation state Fe^{III} is also observed. Proof of the formation of intermediate iron species, Fe(V) and Fe(IV), during decomposition of Fe(VI), can be performed by fast freezing of reaction solution and subsequent characterization using ^{57}Fe Mössbauer spectroscopy (see **Figure 3**). The reaction rate is always based on pH, the concentration of the solution and the presence of foreign ions. The resulting products of ferrate(VI) decomposition in water are always iron(III) oxides or hydroxides (e.g., Fe_2O_3, Fe_3O_4, FeOOH, $Fe(OH)_3$). The decomposition is accompanied by a change of color from black-purple to sorrel. Once the color is changed, the substances are no longer usable. [1,10,11]

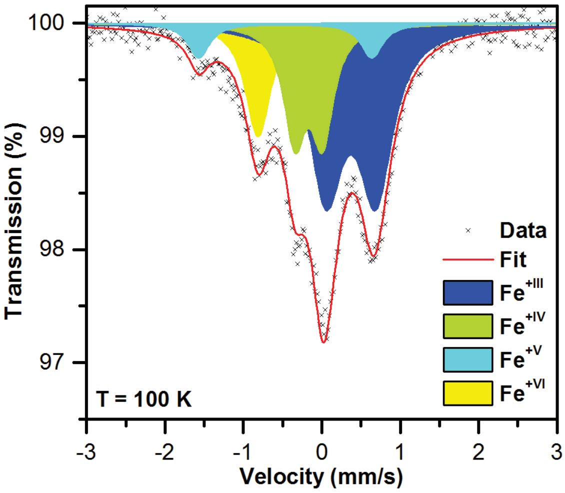

Figure 3 ^{57}Fe Mössbauer spectrum of the sample taken during decomposition of Fe(VI) to Fe(III) and characterized using ^{57}Fe Mössbauer spectroscopy. All possible oxidation states of iron are observed. [9]

2.4. Example of application ^{57}Fe Mössbauer spectroscopy in the removal of arsenic from environment using ferrate(VI)

In aerobic surface water, primarily arsenate ($As^VO_4^{3-}$, As(V)) occurs. Then, arsenite ($As^{III}O_3^{3-}$, As(III)) predominantly exists in anaerobic environment. However, arsenite (As(III)), that is more toxic than arsenate (As(V)), oxides to arsenate under aerobic conditions. One of the arsenic removal options is to use a sorbent, where arsenic is bonded either on the surface or into the sorbent pores. Current technologies are limited by a low sorption capacity of sorbents. The ratio between sorbent and arsenic is usually in the ranges from 1000:1 to 100:1 in weight fraction. The second restriction of available technologies bonding arsenic onto the surface sorbent lies in release of arsenic back to environment due to leaching effect. Thus, exploitation of ferrate(VI) combines the properties of an oxidant, used to oxidizing of As(III) to As(V), and efficient sorbent with a low sorbent/As ratio. More specifically, here we mention an example of removal of arsenic from environment using K_2FeO_4, with concentration of iron equal to 0.5 g/L (see more details in study [13]). As sources of As(III) and As(V), $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ were used, respectively, with a final concentration of arsenic of 100 mg/L. Then, the ratio between Fe:As is 5:1. Three studied samples are shown in **Figure 4**. The "blank" sample was prepared by adding of ferrate(VI) to deionized water, at the "ex-situ" sample was at first added ferrate(VI) to deionized water and subsequently As-containing compound. At the third "in-situ" sample was simultaneously added ferrate(VI) and also As-containing compound to deionized water.

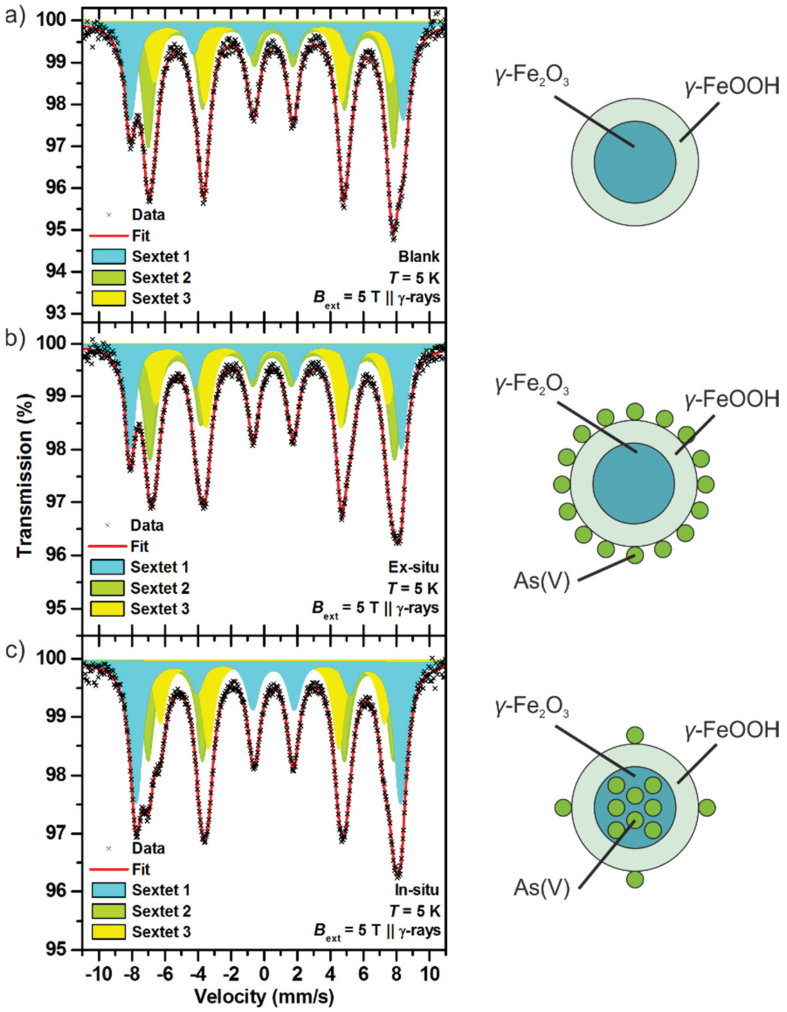

Figure 4 ^{57}Fe Mössbauer spectra collected at a temperature of 5 K and in a field of 5 T for a) “blank” sample (sample of ferrate(VI) added to deionized water), b) “ex-situ” sample (As(V)-containing compound was added to mixed deionized water with ferrate(VI)) and c) “in-situ” sample (simultaneously addition of ferrate(VI) and also As(V)-containing compound to deionized water). On the left side, the embedding of As(V) onto the surface nanoparticle (panel (b)), and primarily into the structure of nanoparticle and subsequently onto the surface (panel (c)) is illustrated. [13]

The experiment is based on forming γ-Fe_2O_3 nanoparticles, which can be after the completion of the treatment process, very easily removed from environment using an external magnet. As seen in **Figure 4 c)**, the uniqueness of using ferrate(VI) in water treatment is that arsenite is "in-situ" structurally embedded into the tetrahedral sites of γ-Fe_2O_3 nanoparticles formed during reaction with water and the pollutant. Thus, As(V) ions are not released back to the environment and they are firmly bonded into the structure of nanoparticles. Moreover, using ^{57}Fe Mössbauer spectroscopy, the amount of As(V), which are embedded in the nanoparticles (x in **Equation 6**) is possible to determine based on the evaluation of spectral ratio of the components belonging to the tetrahedral and octahedral sites in the γ-Fe_2O_3 crystal structure, i.e.,

$$\left[Fe^{3+}_{1-x} As^{5+}_{x} \right]^{T} \left[Fe^{3+}_{5/3-y} o_{1/3+y} \right]^{O} O_4 \qquad (6)$$

In the "blank" sample, the spectral ratio between tetrahedral (T) and octahedral (O) sites is T:O ~ 0.65, in the "ex-situ" sample, T:O ~ 0.7 and in the "in-situ" sample, T:O ~ 1.22. Based on these values, the amount of As(V) in the nanoparticles was estimated to be approximately 25 at.%. [13]

3. CONCLUSION

This study highlighted the significance of ^{57}Fe Mössbauer spectroscopy for studying reaction mechanism of ferrates with pollutants. Ferrates, particularly ferrate(VI) and their preparation and reaction mechanism were described in more details. Finally, the experiment presenting an unique properties of ferrate(VI) for removing of arsenic from environment was reviewed.

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