Synthesis and characterization of Lepidocrocite and its potential applications in the adsorption of pollutant species

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Abstract. In this work, we report some results with reference to the synthesis and structural characterization (DRX) of the lepidocrocita ($\gamma$-FeOOH). The synthesis of this solid is reviewed very carefully since it is known that the reaction mechanism is by no means unique. This work is intended to put forward an updated study of this type of surface in connection with the adsorption of some inorganic pollutants which are most likely to be present in a variety of industrial procedures such as the area of the metallurgic and also in pigment additives and in the wood manufactures. We have focused this particular study to those species derived from chromium (VI), which is known to be toxic in character. Some previous studies performed by other authors suggest that some oxyhydroxides of iron such as the $\alpha$–FeOOH solid may give rise to interactions with this pollutant. Also, its action upon the chromium (VI) species has not yet been reported. In this current experimental study, we report the synthesis and an updated DRX-powder pattern for this solid.

1. Introduction

1.1. Synthesis and characterization of lepidocrocite – a brief Review.

The formation mechanisms of iron oxides and oxyhydroxides (Fe-OOH) had been carefully studied and reported in the literature \cite{1,2} since this compounds whether in amorphous or crystalline form are present in phenomena like atmospheric oxidation, sea corrosion and pasivation on iron surface.

Published database provides information such as thermochemical data and Pourbaix diagrams in the 25 – 300 °C range, for iron species in solid and aqueous solutions. Over 32 species are mentioned in literature but only those which show presence of iron hydroxides and oxyhydroxides are tackled in this study.

To have a better understanding, the information available to rationalize the synthesis of our compound $\gamma$–FeOOH, is a matter of academic debate regarding the proposed reaction mechanisms, since they are not unique. Similarly, to obtain a unique phase has a major importance when considering the different iron species present in aqueous phase (depending operation conditions, pure lepidocrocite can be obtained by precipitation). The crystalline structure of this compound is given in detail \cite{1,2} but the synthetic way is not conclusive. Regarding formation or transformation kinetics of iron oxyhydroxides, the data available is not clearly reported due to the high complexity in the formation of this type of compounds. Therefore, small variations in operation conditions (pH, stirring method, temperature and pressure) could lead us to one or several known species, which are currently present in aqueous solution.
In atmospheric conditions, conformations of iron structures are mostly non – stoichiometric, which makes this field attractive since this inherent complexity can explain, in principle, the high reactivity of this minerals.

A thorough literature research suggests that a stable phase of iron is hematite (\( \alpha \)-Fe\(_2\)O\(_3\)), in presence of water or humid air \([3]\). Along this view and depending upon the exposure conditions, meta – stable products could be formed. The relative stability of each phase is given by the activation energy necessary to form a phase which is more stable from a thermodynamic point of view. Also, there are information related to Pourbaix diagrams for iron ionic species generated from compounds such as FeCl\(_2\) and FeSO\(_4\).

This allows in a sensible form to understand the presence of species related with ferrous ion (Fe\(^{+2}\)) in the graphic of pH as a function of potential gradient (electromotive force). These diagrams suggest different synthetic methods for lepidocrocite; hence they are a useful and effective tool for these experimental studies. This information has been reported in detail in the literature \([4]\) and will not be repeated here.

In the diagram of reference \([4]\), the series of reactions are labeled using positive integers. In this study, special interest is given to equation 17 for our synthesis \([4]\):

\[
Fe^{+2} + 2H_2O \leftrightarrow FeOOH + 3H^+ + 1e^- \quad E^n = E^0 + 0.17745 \ pH + 0.05915 \log[Fe^{+2}]
\]

Values for \(E^n\) are 0.89 V and 0.99 V for phases \(\alpha - FeOOH\) and \(\gamma - FeOOH\), respectively. This half - reaction, illustrates the mechanism to obtain the lepidocrocite from the oxidation of the Fe\(^{+2}\) ions. Similarly, the Nernst equation shows that pH must be controlled, either by addition of a base or an acid – base buffer.

Information given above allows us to justify the synthetic methods which will be illustrated in the following sections of this paper.

1.2. Lepidocrocite obtention (\(\gamma - FeOOH\))

Formation of \(\gamma - FeOOH\) in aqueous solutions is restricted to ferrous iron and Fe(II), Fe(III) intermediaries’ oxidation in neutral or slightly acid solutions. As a first approximation, is not possible to obtain the compound directly from ferric solutions. In figure 2, information concerning a probable reaction mechanism is given.

\[
Fe(OH)_2 \rightarrow \text{green rusts I y II}
\]

![Figure 1. Probable reaction mechanism for lepidocrocite](image_url)

2. Experimental results

2.1. Synthesis of Lepidocrocite from ferrous chloride (FeCl\(_2\))

Synthesis of Lepidocrocite substrate was achieved, using tetra – hydrated ferrous chloride (FeCl\(_2\) \cdot 4H\(_2\)O) as starting reactive, proceeding as follows:

A 0.2 M of FeCl\(_2\) \cdot 4H\(_2\)O solution was prepared in 200 mL of distillated water with initial pH of 3.2. The solution is diluted with 200 mL of water in order to have an initial pH value of 3.4.
Afterwards, 5mL of NaOH 0.1M was added (rapidly) rising pH up to 6.5. Solution is stirred and air is pumped at the rate of 500 [mL/min] during 4 hours. Subsequently, NaOH 1.0 M (approximately 100 mL) is added to solution maintaining a pH of 6.5, for a time interval of 4 hours. Finally the product is filtered, washed, and dried at 60ºC under atmospheric pressure for 6 hours.

Figure 2.

2.2. Characterization of Lepidocrocite

Structural characterization of lepidocrocite (\(\gamma – FeOOH\)) was realized by powder X-ray diffraction (PXRD). A Siemens D5000 X-ray diffractometer (sample’s fixed position) was used, which has a built-in graphite monochromator, divergence diaphragms and variable dispersion. Experimental measure conditions with this equipment were 30 mA and 40 kVotlt. Samples were analyzed using a copper anode source and nickel filter, with wavelengths \(\lambda_{\alpha_1} = 1,5406\)Å and \(\lambda_{\alpha_2} = 1,5444\)Å. A surface of 20 mm was exposed to radiation with absolute precision not greater than 0.005 º with reproducibility of 0.0005 º (\(\theta\) and 2\(\theta\)). In figure 2, a diffractogram (PXRD) of lepidocrocite is given in the range between 10 º and 70 º (2\(\theta\)). Experimental evidence suggests formation of lepidocrocite, after optimization of sample’s crystallinity as a consequence of the following factors: (a) Greater reaction time. 4 hours instead of 2 hours proposed in literature [2], (b) Rigorous control of thermochemical variables such as initial pH followed by a rapid change from pH 3.4 to 6.5 in a few minutes, (c) Higher reaction yield. 90% against 40% reported in literature [2] and (d) Use of a sophisticated drying method.

Some data of interest are the following: Orthorhombic crystalline system, spatial group \(D_{2h}^{17} (Cmcm)\), packing sequence ABC, parameters: \(a = 3,88\)Å, \(b = 12,54\)Å, \(c = 3,07\)Å, \(\alpha = \beta = \gamma = 90^\circ\) [1,5]. It is important to mention that diffraction intensities do not coincide with previous reported works [5]. In addition, a complete assignment of all crystalline planes has not yet been made, and therefore it does seem necessary to do further studies, employing optimization procedures such as Rietveld type if one wishes to find solid and consistent explanation for these intensity differences.
2.3. Thermoanalysis

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) was performed to lepidocrocite sample using NETZSCH STA 409C DTA/TGA equipment. Experimental conditions are the following: air atmosphere, 19.54 mg of Alumina (Al₂O₃) reference mass, 8.43 mg of sample mass (lepidocrocite), initial temperature 20 °C, final temperature 600 °C and heating speed 10 °C/min.

Thermoanalysis results show two regime of mass loss. First regime is between 240 °C and 300 °C associated with a mass loss of 16.02%, due to surface water loss. Second region is an exothermic reaction at 472 °C, with a mass loss of 3.02% associated with removal of structural hydroxyl groups and chloride ions. Over this temperature mass remains constant suggesting formation of lepidocrocite. In addition, BET measurements indicated 25.3[m²/g] of surface area.

3. Stability of γ−FeOOH substrate

Our results emphasize the stability of the substrate in the process of adsorption of an inorganic pollutant Cr(VI), which has being studied under adverse environments compared with its ideal conditions, i.e.: pH = 6.50, temperature 20 °C. In the same manner, employing cyclic voltammetry, the iron content in the liquid was studied which contains the substrate and in this way to observe a possible release of ferric iron (Fe⁺³) into the solution. In the pH range of 4.0 – 8.0 and temperature range of 10 °C – 60°C it is possible to conclude the substrate is stable (no release of Fe⁺³ to the solution). On the other hand, outside the previously mentioned ranges, substrate is soluble in the liquid and loses its properties as pollutant adsorber.

| Essay number | Lepidocrocite mass (g) | Pollutant concentration (mg/L) | Amount of filtered pollutant (mL) | Final pollutant concentration (mg/L) |
|--------------|------------------------|-------------------------------|----------------------------------|------------------------------------|
| First        | 0.2                    | 0.4                           | 15                               | 0.02                               |
| Second       | 0.6835                 | 0.5                           | 100                              | 0.02                               |
| Third        | 0.700                  | 5.0                           | 20                               | 0.02                               |
| Fourth       | 0.700                  | 5.0                           | 40                               | 0.02                               |
| Fifth        | 0.700                  | 5.0                           | 60                               | 0.5                                |

3.1. Adsorption of Cr (IV) by γ−FeOOH

Lepidocrocite γ−FeOOH has also been the target of some additional research studies so as to search for its apparent capacity to adsorb pollutant derived from As(IV), [6]. Following, the study of a possible adsorption of Cr (VI) species on lepidocrocite surface is made. Synthetic samples of Cr (VI), in different concentrations, were prepared from potassium dichromate (K₂Cr₂O₇). At this point, it may be illuminating to observe that a burette contains the pollutant liquid and lepidocrocite is located in a small Teflon tube, acting as a filter adsorbing the pollutant compound. Some additional detail may be obtained upon request to RA. Regarding determination of Cr (VI) a first semi – quantitative measure was realized using a colorimetric kit, whose concentration values are previously established. In table 1, experimental results are shown with respect to adsorption of Cr (VI) on lepidocrocite. The fifth essay’s operation conditions were chosen for the study of the adsorption of Cr (VI) in solution. Initial conditions are: pollutant concentration 5.0 mg/L and lepidocrocite mass 0.70 g, the last acting as a filter or adsorber for Cr (VI). Table 2 shows adsorption data for Cr (VI) with lepidocrocite.
Table 2

| Consumption range (mL) | Final pollutant concentration (mg/L) |
|------------------------|--------------------------------------|
| 0                      | [inaccurate]                         |
| 12                     | 0.02                                 |
| 22                     | 0.02                                 |
| 33                     | 0.10                                 |
| 44                     | 0.50                                 |

4. Conclusions
We have obtained iron species $\gamma – FeOOH$ using a rather special synthetic routes, improving reaction yield previously reported up to 90% of initial precursor mass (FeCl$_2$).

This type of compound has been shown to be stable in a wide range of temperature and pH. Furthermore, regarding the adsorption of Cr (VI); the first test had being done, showing positive results. In future studies, using proper methodologies we should be able to determine the adsorption capacity of this type of surfaces. Moreover, with the aid of chemical and physical techniques we may reveal how the adsorption process takes place. These results require further experimental analysis in order to make a full discussion, nevertheless we observe that an increase in the Cr (VI) concentration, the support reaches saturation, hence there are no adsorption sites available to the pollutant. This may be taken as evidence which shows that the adsorption of Cr (VI) is indeed feasible by the lepidocrocite. At this stage of the study, our principal aim was to have an idea on whether the lepidocrocite interacts with chromium (VI), and the results already obtained though preliminary, show that the assumptions are correct and further experimental studies are needed to reach more conclusive results.

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