Catalytic Properties of Fe-containing Layered Aluminosilicates in Photo-oxidation of Dye “Methyl Green”

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Abstract. The iron-containing materials with an iron content of 40 mg/g and 52.5 mg/g, a specific surface area of 107 m$^2$/g and 96 m$^2$/g are developed on the basis of natural layered aluminosilicate (montmorillonite) and polyhydroxo complexes of iron. It is shown that the materials exhibit high catalytic activity in the photo-oxidation of dye “Methyl Green”. The influence of physicochemical parameters (loading of the catalyst, a ratio of initial concentrations [H$_2$O$_2$]/[MG] on the efficiency of the dye photo-oxidation was established. The optimum conditions, which made it possible to achieve high mineralization and 100 % the dye oxidation efficiency were determined: the catalyst loading equal to 1.0 g/l and the ratio of [H$_2$O$_2$] and [MG] equal to stoichiometric ratio (55 mol/mol). The decrease of the total organic carbon content after photo-oxidation reaction was 56.5%. The average value of the quantum yield of the dye photo-oxidation was 0.30 mol/Einstein. The results of the conducted research show that the developed iron-containing materials are the promising catalysts for photo-Fenton processes of oxidative degradation of organic compounds. The materials are of interest for use in wastewater treatment processes from toxic organic pollutants.

1. Introduction

It is well known that clean water and air are the source of life and health of mankind. At the same time, water and air, without changing externally, their parameters may contain unacceptably large amounts of toxic substances and pathogenic microorganisms, causing a slow poisoning or disease outbreaks.

Currently intensive researches on the purification of water and air are conducted in many countries [1,2]. The most effective ways of wastewater treatment from organic pollutants are the "advanced oxidation processes", in which the oxidation of organic substances is carried out by a highly active oxygen-containing particles or radicals generated from H$_2$O$_2$, O$_2$ and O$_3$ [3]. These technologies include Fenton and photo-Fenton Fe-peroxide systems (Fe$^{2+}$/H$_2$O$_2$, Fe$^{3+}$/H$_2$O$_2$, Fe$^{3+}$/(H$_2$O$_2$,UV)), with which deep oxidation of organic compounds occurs to carbon dioxide, water and inorganic ions [4-7].

The generation of hydroxyl radicals proceeds through the reactions [8,9]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + ^{\cdot}OH + HO^- \quad (1)$$
\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (2)
\]

Hydroxyl radicals have high oxidation potential \((E^0 = 2.32 \text{ V})\) and quickly oxidize organic compounds.

\[
'\text{OH} + R \rightarrow R_i \quad (3)
\]

Fenton processes occurring under the influence of light are called photo-Fenton processes [10]. Their high efficiency is associated with the photolysis of the cation \(\text{Fe}^{3+}\) according to the reaction [11,12]:

\[
\text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{OH}^- \quad (4)
\]

This reaction represents an additional source of highly reactive hydroxyl radicals compared to the traditional Fenton process [13].

The studies conducted in the current decade, show that the effective Fenton-type catalysts are Fe-containing materials obtained by fixation of iron oxides on aluminosilicate matrix of clay minerals [14]. These materials have a large specific surface area and high iron content, and are of great interest as Fenton and photo-Fenton catalysts for processes of wastewater treatment. Their use in heterogeneous photo-Fenton system is considered as the reaction of oxidation for wastewater treatment. Specific attention is given to the basic operating conditions of the process, namely the wavelength and light source power, the initial and final concentration of \(\text{H}_2\text{O}_2\), catalyst loading, pH and temperature [15].

The aim of this work is to obtain iron-containing layered aluminosilicate and to study their catalytic properties in the photo-oxidation of the dye "Methyl Green".

### 2. Experimental

#### 2.1. Synthesis of the Fe-containing materials (Fe-MM)

To get a catalyst we used clay mineral montmorillonite as a silica-alumina matrix [16,17]. The chemical composition of the clay mineral montmorillonite (wt.%): \(\text{SiO}_2\) - 65.6, \(\text{Al}_2\text{O}_3\) - 15.4, \(\text{Fe}_2\text{O}_3\) - 2.0, \(\text{FeO}\) - 0.08, \(\text{MnO}\) < 0.01, \(\text{MgO}\) - 1.42, \(\text{CaO}\) - 1.18, \(\text{Na}_2\text{O}\) - 0.02, \(\text{K}_2\text{O}\) - 0.06, \(\text{P}_2\text{O}_5\) < 0.03, \(\text{TiO}_2\) - 0.16, \(\text{H}_2\text{O}\) - 14.31 [18]. The synthesis of Fe-MM was performed according to the procedure presented in [18]. The Fe-modifying solutions were prepared by alkaline hydrolysis of 0.1 M solutions of \(\text{FeCl}_3\), by adding to them 0.1M \(\text{NaOH}\) until reaching the \(\text{OH/Fe}\), equal to 2.0 mol/mol under stirring. Then the modifying solutions (MS) were held at room temperature for 24 hours. Afterwards, Fe-containing MS were added to a water suspension of Na-MM and a mixture was allowed to stand at a room temperature for 24 hours. Then the solid phase was separated from the liquid by centrifugation. The resulting material was washed with distilled water and was calcined at 500°C for 2 hours. The conditions of MS preparation and the obtaining of Fe-MM are shown in Figure 1 [18].

![Figure 1. The scheme of Fe-MM obtaining.](image-url)
2.2. The characterization of the prepared catalysts

The iron content in the material was determined by the photometric method by reaction with o-phenanthroline. The iron was transformed into solution in the form of Fe$^{3+}$ ions by storage of Fe-MM in the concentrated HCl for 24 hours. The content of iron in the aqueous solutions was determined by atomic absorption analysis (AAS Solaar M 6 spectrometer, Thermo Electron Corporation, UK) [20]. The specific surface of the materials was determined by low-temperature adsorption/desorption of nitrogen on the installation Thermosorb LP (Katakan, Novosibirsk, Russia) [21]. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method [19].

2.3. The photo-oxidation tests

The testing of catalytic properties of materials was conducted in reaction of photo-oxidation of dyes such as Bromphenol blue (BphB) C$_{19}$H$_{10}$Br$_4$SO$_5$, Methyl green (MG) C$_{25}$H$_{30}$N$_3$Cl$_2$, Methylene blue (MB) C$_{16}$H$_{18}$N$_3$SCl with hydrogen peroxide in aqueous solutions [20]. The decrease of dyes concentration in the reaction was fixed by changing the optical density of the solution, which was measured for UV-Vis spectrophotometer Agilent 8453 (Agilent Technologies, USA) at the maximum absorption wavelength.

The conditions of testing dye: 10 ml of 10mg/l of dye; 3 g/l of catalyst; H$_2$O$_2$ concentration 1*10$^{-5}$M; UV irradiation time 15 min (UV 15 W).

2.4. The determination of the total organic carbon and radiation intensity

The determination of total organic carbon (TOC) was performed on the analyzer Shimadzu TOC-L [21]. The TOC in the original dye solution and the reaction solution was determined after 2 hours of reaction. To assess the efficiency of use of light energy radiation intensity was determined with chemical actinometer K$_3$[Fe(C$_2$O$_4$)$_3$]·3H$_2$O [22].

3. Results and discussion

3.1. The Physico-chemical properties of materials

In the obtained samples, we determined and specific surface area. The results of determination of the iron content in the samples of obtained materials are listed in the Table 1. The iron content in the samples obtained by method I, in which the concentration of FeCl$_3$ in the modifying solution was 1.0*10$^{-5}$ M, was higher than in the samples prepared by method II using modifying solution with the concentration of FeCl$_3$ 5.0*10$^{-6}$ M.

| Marking          | MS composition, ml | OH/Fe | Parallel samples | $\chi$, mg/g | $\chi$, mg/g | $S_{sp}$, m$^2$/g |
|------------------|--------------------|-------|------------------|--------------|--------------|------------------|
| Fe-MM(I)$_{\text{calcined}}$ | 0.1M FeCl$_3$ - 100 0.1M NaOH - 200 | 2.0   | 1                | 50           | 52.5         | 107              |
|                  |                    |       | 2                | 55           |              |                  |
| Fe-MM(II)$_{\text{calcined}}$ | 0.1M FeCl$_3$ – 50 0.1M NaOH - 100 | 2.0   | 1                | 40           | 41.7         | 96               |
|                  |                    |       | 2                | 45           |              |                  |
|                  |                    |       | 3                | 40           |              |                  |

This material is also characterized by a greater specific surface: for material Fe-MM(I) the surface is equal to 107 m$^2$/g, and for material Fe-MM(II) - 96 m$^2$/g.

3.2. The catalytic properties of materials

The results of testing of the catalytic properties of Fe-MM(I)$_{\text{calcined}}$ are given in the Figure 2.
The dye discoloration did not occurred during the dark the oxidation reaction. The efficiency of oxidation when exposed to daylight amounted to 26.1% for BPhB, 8.3% for MG and 8.1% for MB. The introduction of the catalyst in the reaction mixture and UV-irradiation caused an increase in the efficiency of 1.2 times for BPhB, 1.5 times for MG and 1.3 times for MB compared to non-catalytic reaction. It was caused by the hydroxyl radicals formation through the (2), the photolysis of Fe$^{3+}$cations proceeds (4), as well as the photolysis of hydrogen peroxide molecules occurs by the reaction: $\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot\text{OH}$.

The increase in the number of hydroxyl radicals, which rapidly interact with dye molecules, leads to an increase in the rate of their oxidation reaction [20].

For further study we used the dye MG (Figure 3), in the oxidation of which was observed the highest catalytic effect by of Fe-MM.

The complete mineralization of the MG according as a result of oxidation proceeds to this equation:

$$25\text{C}_2\text{H}_3\text{NCl} + 55\text{H}_2\text{O}_2 \rightarrow 25\text{CO}_2 + 57\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} + \text{HNO}_3$$

The results of experiments on the oxidation of the dye MG at the stoichiometric ratio of hydrogen peroxide and dye in the presence of different catalysts are shown in the Table 2.

| Sample           | The efficiency of oxidation dye+cat+H$_2$O$_2$+UV, % | Leaching of Fe$^{3+}$, (% of total content) |
|------------------|-----------------------------------------------------|--------------------------------------------|
| Fe-MM(I)$_{\text{calcined}}$ | 90.5                                                | 0.12                                       |
| Fe-MM(II)$_{\text{calcined}}$ | 83.3                                                | 0.15                                       |

Thus, the catalyst Fe-MM(I)$_{\text{calcined}}$ is the most active and stable. It is characterized by the greatest iron content and minimum leaching of Fe$^{3+}$ (0.12%), and also has a large specific surface area. The efficiency of UV oxidation of dye MG amounted to 90.5% in the presence of this catalyst.
3.3. The influence of conducting on the efficiency of the oxidation

The results of dye oxidation experiments with various loading (0.5, 1.0 and 1.5 g/l) and the molar ratio \([\text{H}_2\text{O}_2]/[\text{MG}]\) equal to 13.75 are shown in the Table 3.

**Table 3. The influence of catalyst content**

| Time, min | 0.5 g/l | The efficiency of oxidation, % | 1.0 g/l | 1.5 g/l |
|-----------|---------|--------------------------------|---------|---------|
| 10        | 14.3    |                               | 33.3    | 32.0    |
| 20        | 62.0    |                               | 76.2    | 75.0    |
| 30        | 97.0    |                               | 98.0    | 97.1    |

The maximum efficiency of oxidation (98.0 %) is observed when the content of the catalyst is equal to 1.0 g/l. It is known that the rate of side reaction between Fe\(^{3+}\) ions and hydrogen peroxide with the formation of hydroperoxide radical and molecular oxygen increases at high iron content in Fenton systems and their activity in the oxidation of organic compounds is much less than that of the hydroxyl radical [22]:

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (5)
\]

\[
\text{Fe}^{3+} + \text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad (6)
\]

The existence of an optimal dose of the catalyst in photo-Fenton systems is explained by an increase in the turbidity of suspensions, which causes radiation scattering. This leads to a reduction in the radiation dose available for photo-Fenton processes. Also this can be caused by diffusion limitations that cause a decrease in the quantity of available active sites on the catalyst surface.

The experiments were conducted in which the mole ratio of \([\text{H}_2\text{O}_2]/[\text{MG}]\) varied from 0.5 to 1.75 to study the effect of the concentration of hydrogen peroxide on the efficiency of dye. The results of the oxidation experiments with various mole ratio \([\text{H}_2\text{O}_2]/[\text{MG}]\) are given in the Figure 4.

**Figure 4. The dependence of the efficiency of oxidation from the molar ratio \([\text{H}_2\text{O}_2]/\text{MG}\)**

The initial reaction rate and the oxidation efficiency of MG increase with an increase of the molar ratio of \(\text{H}_2\text{O}_2\) and MG from 0.5 to 1.0. This is caused by an increase in the rate of formation of hydroxyl radicals. The oxidation efficiency of the dye decreases with an increase in the molar ratio higher than 55 mol/mol. This is due to the occurrence of side reactions of hydroxyl radicals with an excess of peroxide, which lead to the formation of low-activity hydroperoxide radicals and molecular oxygen [22]:
The highest oxidation rate of the dye is observed at optimum ratio of [H$_2$O$_2$] and [MG], which is equal to stoichiometric ratio (55 mol/mol). The oxidation efficiency is 100% at optimum ratio for 120 minutes of reaction. This is confirmed by the change of the electron absorption spectra of the dye solution in the course of reaction (Figure 5).

The value of the total organic carbon (TOC) in the initial solution was determined as 11.19 mg/l and TOC was 4.87 mg/l in the reaction solution. The TOC reduction was 56.5% for 2 hours of the oxidation.

The quantum yield of the photo-destruction of the MG was determined to estimate the efficiency of the light energy use. We have calculated the quantum yield of the reaction at the content of catalyst 1.0 g/l and a stoichiometric ratio [H$_2$O$_2$]/[MG]. The quantum yield amounted to 0.26, 0.31 and 0.33 mol/Einstein for 10, 20 and 30 minutes of reaction, respectively. The average value of the quantum yield equal to 0.30 mol/Einstein.

4. Conclusion
Two samples of the Fe-containing materials with an iron content of 40 mg/g and 52.5 mg/g, a specific surface area of 107 m$^2$/g and 96 m$^2$/g are obtained from a natural layered aluminosilicate (montmorillonite).

It is shown that the most active and stable catalyst in the photo-oxidation of the dye “Methyl Green” is the material that contains the largest amount of iron and has the largest specific surface.

The influence of the main factors (loading of the catalyst, a ratio of initial concentrations [H$_2$O$_2$]/[MG]) on the dye photochemical oxidation efficiency was established. Thus, the optimum conditions allowing to achieve a 98-100 % oxidation efficiency are the catalyst loading equal to 1.0 g/l. The ratio of [H$_2$O$_2$] and [MG] equal to stoichiometric ratio (55 mol/mol).

The reduction of the total organic carbon was 56.5% for 2 hours of the dye oxidation reaction. The average value of the quantum yield of the reaction of dye photo-oxidation equal to 0.30 mol/Einstein.

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