Catalytic purification of aqueous solutions of synthetic dyes using modified forms of bentonite

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Abstract. Fe- and mixed Fe / Al - Bentonites (Bent) were prepared from naturally occurring montmorillonite and Fe and mixed Fe / Al containing polyoxocations. The samples were characterized by chemical analysis and low temperature adsorption of nitrogen. The Fe content was 15.5-36.0 mg g$^{-1}$. Surface area $S_{BET}$ was equal 118-219 m$^2$ g$^{-1}$. The catalytic wet peroxide oxidation of diazo dye Direct Blue using the obtained solids was studied. It was established that Fe / Al -Bent was the most active and stable in color and COD removals of Direct Blue. The important factors affecting catalyst activity and color removal have been studied i.e. the influence of pH, temperature, catalyst amount, $H_2O_2$ concentration. The best results for color and COD removals and low Fe leaching were obtained when operated at pH = 4.6, $t = 40^\circ$C, 1.0 g·l$^{-1}$ catalyst and molar ratio $[2H_2O_2]/[dye] = 70$.

1. Introduction
Nowadays, the wastewater purification from toxic organic compounds is one of the actual problems. Modern synthetic dyes have complex chemical structure and are resistant to biochemical degradation in water systems. The catalytic methods using ecologically pure oxidant hydrogen peroxide and Fe$^{2+}$ are the most effective for sewage treatment from organic compounds (advanced oxidation processes (AOPs)). The effectiveness of AOPs is caused by the generation of active and non-selective $\cdot OH$-radicals, able to oxidize many organic compounds including dyes. But homogeneous Fenton process has some disadvantage, that limit its industrial application [1]. The limit range of pH for operation and the necessity of a post-treatment to remove the iron ions are the major drawbacks of this technology. These drawbacks can be overcome using solid catalysts [2]. The materials, obtained by incorporating Fe and Cu ions into porous support such as zeolite [3] and clays are used as active catalysts for the decomposition of hydrogen peroxide for the oxidative degradation of organic compounds. In recent years pillared clays are considered as promising catalysts in numerous areas because of the particular structure, high thermal and chemical stability, ecological safety and low cost of natural clay minerals [4,5]. Recently Fe-, and Cu -containing pillared clays are successfully used in wet peroxide oxidation of phenol [6-10] and some dyes [11-15].

In this study catalytic wet peroxide oxidation of diazo dye Direct Blue (DB) was carried out using Fe - and mixed (Fe–Al) clays as catalysts and the influence of the variables of the reaction conditions on the catalytic activity was investigated.
2. Materials and methods

2.1. Materials

The reactive diazo dye Direct Blue (DB) is a commercially available dye having the following chemical formula $\text{C}_{34}\text{H}_{24}\text{N}_6\text{Na}_3\text{O}_{16}\text{S}_4$, molecular weight 992. It was used without further purification.

2.2. Preparation of the catalysts

The natural clay used to prepare the Fe-, Fe/Al- samples (Fe-, FeAl-Bent) was obtained from a bed located in Mukhor-Tala (Russia) and purified by conventional methods. Its total composition, expressed in wt.% of oxides was the following: $\text{SiO}_2$, 65.50; $\text{Al}_2\text{O}_3$, 14.30; $\text{Fe}_2\text{O}_3$, 1.78; $\text{MgO}$, 1.42; $\text{CaO}$, 1.08; $\text{K}_2\text{O}$, 0.20; $\text{Na}_2\text{O}$, 0.10; $\text{FeO}$, 0.22; $\text{MnO}$, 0.02; $\text{TiO}_2$, 0.19; $\text{P}_2\text{O}_5$, 0.03; $\text{H}_2\text{O}$, 15.16. For the synthesis of catalysts a clay fraction of 20-40 μm was used. The clay consists of montmorillonite (about 90 %) and of cristobalite as a small impurity [10].

FeAl - Bent-1 was prepared by using a standard procedure [10]. First, the modifying solution of FeAl was prepared by mixing appropriate volume of aqueous 0.1 M Fe and 0.1 M Al chlorides with 0.1 M Na$_2$CO$_3$ to obtain a final solution with a molar ratio of Fe/Al =1/10 and final pH of 4.2). The modifying solution was aged during 2 week and was heated at 95°C during 36 h, then added under stirring to the clay suspension preliminary processed by ultrasound 22kHz (3 min). After storage for 24 h, the modified clay was washed until total elimination of chloride ions, dried at room temperature and finally calcined at 500°C during 2 h. Fe/Al - Bent -2 was prepared by the same way as FeAl - Bent -1, but a molar ratio of Fe/Al was 1/1. Fe - Bent was prepared by the following method: the modifying solution of Fe was obtained by hydrolysis of 1M FeCl$_3$ with 1 M NaOH (a molar ratio OH$^-$/Fe$^{3+}$ of 1.5) at stirring vigorously and aging for 24 h (a final pH of 1.8-2.0). Preliminary the clay suspension was also treated by ultrasound before the addition of the modifying solution. Then modifying solution of Fe was introduced to the clay suspension at stirring and was storage over 24 h. Fe - Bent was washed until total elimination of chloride ions, dried at room temperature and finally calcined at 500°C during 2 h.

2.3. Characterization of the catalysts

BET specific surface areas were determined by adsorption of nitrogen at 77 K, by using Micromeritics ASAP-2400. Elemental chemical analyses were performed to determine the composition of natural clay and the content of iron in the catalysts, by using atomic absorption spectroscopy (Solaar 6 M).

2.4. Reaction procedures and analysis

Chemical oxidation of dye DB was carried out in a glass thermostated reactor equipped with a stirrer and a reflux condenser. The solid catalyst (1.00 - 4.00 g·l$^{-1}$) was put into 25 ml of an aqueous dye solution (0.1 mmol·l$^{-1}$) under continuous stirring at 40, 50, 60°C and pH 2.5-5.2. $\text{H}_2\text{O}_2$ concentration was varied 3.5-9.0 mmol·l$^{-1}$. The stoichiometric quantity of hydrogen peroxide needed to total transformation of DB into CO$_2$ is equal (68 moles of H$_2$O$_2$ per mole of DB).The samples of the reaction mixture taken along time were centrifuged before measurement of absorbance. The conversion of dye in the solution was determined by the absorbance measurements at 590 nm (Agilent 845 UV–VIS spectrometer).

The chemical oxygen demand (COD) of the dye solutions after reaction oxidation was determined by the bichromatic method [16].

3. Results and discussion

3.1. Characterization of catalysts
The textural characteristics the natural clays and catalysts obtained from nitrogen adsorption-desorption isotherms are given in the Table 1. The sample FeAl - Bent -1 had a mixed structure with the presence of both mesopores and micropores. All other solids had a mesoporous structure [17, 18]. FeAl - Bent -1 was characterized by the highest BET specific surface area of 219 m²·g⁻¹. The iron content of the solids was 15.5–36.0 mg·g⁻¹, while in the initial clay it was 8 mg·g⁻¹.

| Catalyst                  | Content of Fe, (mg·g⁻¹) | S_BET, (m²·g⁻¹) | V_pore, (cm³·g⁻¹) | D_pore, (Å) | V_µ, (cm³·g⁻¹) |
|---------------------------|--------------------------|-----------------|-------------------|-------------|---------------|
| Natural Bent air-dry      | 8.0                      | 119             | 0.271             | 91          | 0.004         |
| FeAl - Bent -1 - 500°C    | 15.5                     | 219             | 0.268             | 78          | 0.050         |
| FeAl - Bent -2 - 500°C    | 33.6                     | 118             | 0.212             | 72          | 0.001         |
| Fe - Bent - 500°C         | 36.0                     | 128             | 0.274             | 85          | 0.001         |

3.2. Catalytic oxidation

Catalytic experiments were performed using a 0.1 mmol·l⁻¹ (100 mg·l⁻¹) solution of DB, which is in the range of diazo dyes concentrations usually found in industrial waste streams. In aqueous solutions Fe-containing catalysts cause the decomposition of hydrogen peroxide with formation hydroxyl radicals which are strong oxidizers of dyes of various types. The results presented in Figure 1, confirmed that among the obtained Fe-containing materials a catalyst FeAl - Bent -1 had the most catalytic activity in color removal of dye DB. The degree of its discoloration reached 99%. It was also the most stable to leaching of iron ions during the oxidation of dye. The amount of Fe ions leached into solution was equal to 0.23 ppm for FeAl - Bent -1. The catalysts Fe - Bent and FeAl - Bent -2 are less stable to leaching due to low dispersion of Fe and a significant amount of iron associated with each other [10]. So the kinetics of the catalytic oxidation of DB with hydrogen peroxide were studied in detail in the presence of FeAl - Bent -1. The effects of the initial pH, the catalyst load, concentration of H₂O₂ were investigated.

![Figure 1. Color removal during the oxidative degradation of DB in the presence of the catalysts: ■ - natural Bent; ● - Fe - Bent; ▲ - FeAl -Bent -2; ♦ - FeAl - Bent-1 ([dye]=0.1 mmol·l⁻¹, [H₂O₂]=7 mmol·l⁻¹, [catalyst]=3 g·l⁻¹, t=40°C; pH = 4.6).](image-url)
3.2.1 The influence of pH on catalytic oxidation

The influence of pH on diazo dye DB removal using FeAl - Bent-1 and $H_2O_2$ was studied at initial values of pH 2.5, 3.8, 4.6, 5.2. In Figure 2 the results obtained for dye removal as a function of the initial pH of the solution at various reaction times were presented. The differences in color removal between the different pH values were great during the early stages of the reaction. But after 300 min of reaction color removal was almost complete independent of pH due to a drop of pH and acceleration of the reaction because of the fragmentation of dye molecule into organic acids [2]. The activity of catalyst at pH 5.2 could be explained by the high surface acidity of FeAl - Bent-1 as it was assumed in [10, 13]. The iron leaching depended strongly on pH and was more significant at pH 2.0. Such results were also obtained by Ramires et al [15] using Fe-containing heterogeneous catalysts based on saponite clay in oxidation of Orange II solutions. The leaching of Fe ions decreased at high pH values. At initial pH > 3.8 the catalyst was enough stable, because the amount of Fe dissolved was less 0.3 ppm.

![Figure 2. The influence of pH on the color removal (\([\text{dye}]=0.1 \text{ mmol}\cdot\text{l}^{-1}, \ [H_2O_2]=7 \text{ mmol}\cdot\text{l}^{-1}, \ [\text{catalyst}]=3 \text{ g}\cdot\text{l}^{-1}, \ t=40 \text{ °C}).\)]](image)

![Figure 3. The influence of catalyst concentration on color removal (\([\text{dye}]=0.1 \text{ mmol}\cdot\text{l}^{-1}, \ [H_2O_2]=7 \text{ mmol}\cdot\text{l}^{-1}, \ [\text{catalyst}]=3 \text{ g}\cdot\text{l}^{-1}, \ t=40 \text{ °C}; \ pH = 4.6).\)]](image)

3.2.2. The influence of catalyst concentration on catalytic oxidation

The influence of catalyst concentration on color removal of DB solutions versus time is presented in Figure 3. The initial pH was equal to 4.6, the hydrogen peroxyde concentration 7 mmol⋅l⁻¹, t = 40°C. After 300 min of oxidation with a dose of 1.0 g⋅l⁻¹ FeAl - Bent-1 the color removal was 86 %. By increasing the dose of catalyst to 3.0 g⋅l⁻¹ the color removal increased to 99 %. Further increasing the catalyst amount to 4.0 g⋅l⁻¹ only a slight increase in color removal was observed, after 300 min of reaction. However by increasing the amount of catalyst used the concentration of dissolved iron ions in solution increased to 0.4 ppm. So the amount of 1.0 g⋅l⁻¹ catalyst was selected for further experiments.

3.2.3. Influence of hydrogen peroxyde concentration on catalytic oxidation

The results of kinetic of catalytic oxidation of DB with different hydrogen peroxyde concentrations are presented in Figure 4. The increase in hydrogen peroxyde concentration led not only to acceleration of DB decolorization but also fuller mineralization of intermediate products, as it observed from COD values in Figure 5. This could be caused by additional amount of $\cdot\text{OH}$ radicals will be formed. The increase of $H_2O_2$ concentration above 7.0 mmol⋅l⁻¹ led to insignificant increase of color removal and
COD removal. It is known [19,20] that hydroxyl radicals in the presence of excess of H$_2$O$_2$ produce hydroperoxy radicals which are less active than hydroxy radicals in oxidative degradation of organic compounds.

Figure 4. The influence of hydrogen peroxide concentration on color removal ([dye]=0.1 mmol·l$^{-1}$, [catalyst]=3 g·l$^{-1}$, t=40°C, pH = 4.6).

Figure 5. The influence of H$_2$O$_2$ concentration on COD removal ([dye]=0.1 mmol·l$^{-1}$, [catalyst]=3 g·l$^{-1}$, t=40°C pH = 4.6).

3.2.4. The influence of temperature on catalytic oxidation

The results obtained for DB decolorization at three different temperatures (40, 50 and 60°C) showed that the initial reaction rate increased when the temperature increased as it was expected due to Arrhenius law. However the color removal of DB after 120 min of oxidation was similar at 50 and 60°C, and after 300 min it was similar at 40, 50 and 60°C. The temperature 40°C was chosen as optimal taking into account the process cost.

3.2.5. Stability and recycling of the catalyst

The stability of the catalyst is one of major characteristics for its practical application. To investigate the stability of FeAl-Bent-1 with respect to Fe leaching and catalytic performance the catalyst was used in four consecutive runs. For subsequent cycles the filtered catalyst was dried at 100°C for 2 h. The results of color removal and Fe leaching in consecutive runs on dye oxidation are shown in Figure 6.

Figure 6. Results of dye oxidation at reusability of catalyst ([dye]=0.1 mmol·l$^{-1}$, [H$_2$O$_2$]=7 mmol·l$^{-1}$, [catalyst]=3 g·l$^{-1}$, t=40°C; pH = 4.6).
A slight decrease in activity of catalyst was observed after third run. Also the amount of dissolved Fe ions increased in 4th run. Thus the catalyst FeAl- Bent-1 exhibited not only good activity but also a low small leaching during 20 h of oxidative reaction.

4. Conclusion
Fe- and mixed FeAl - Bentonites were proved as good catalysts for wet peroxide oxidation of diazo dye Direct Blue. The method of iron insertion into clay essentially influenced on the leaching of iron ions from FeAl - and FeAl - Bentonites. It was established that FeAl - Bent-1 is the most active and stable in color and COD removals of Direct Blue. The most important factors having a significant influence on the catalytic oxidation were the catalyst amount, hydrogen peroxide concentration, temperature and pH. The range of pH value for which Fenton-type oxidation occurred was broadened from pH 2.5 to 5.2. The best results for color and COD removals and low FeAl leaching were obtained when operated at pH = 4.6, 40°C, 1.0 g · l⁻¹ catalyst and molar ratio [H₂O₂]/[DB] = 70.

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