Heterogeneous catalytic system "Fe -aluminosilicate / hydrogen peroxide" for liquid-phase oxidation of phenol

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Abstract. The kinetic regularities of phenol oxidation with hydrogen peroxide in the presence of a Fe-aluminosilicate catalyst (Fe ASK) obtained by introducing a mixed Fe/Al (1/12) polyhydroxocomplex into montmorillonite were studied. It was established that the rate of phenol oxidation depends on the reaction conditions (pH, hydrogen peroxide concentration, phenol concentration, catalyst content and temperature). The maximum reaction rate leading to 100% phenol conversion is observed at a pH of 3.7. The stability of the catalyst to leaching iron ions increases with increasing pH. The oxidation rate of phenol increases with increasing initial concentrations of hydrogen peroxide and phenol and with increasing catalyst content. The reaction orders for the reagents and the effective activation energy are determined. The kinetic equation of the reaction is obtained. The optimal conditions for the phenol oxidation in the heterogeneous catalytic system “Fe-aluminosilicate / hydrogen peroxide”, under which 100% phenol conversion is achieved, the catalyst is stable and water pollution by iron ions is excluded, are determined. Due to its high efficiency, this system is of interest for use in the processes of wastewater purification from phenols.

1. Introduction
Nowadays the current problem of environmental protection is the pollution of natural water bodies with toxic organic compounds, in particular phenol and its derivatives. Phenols entering the reservoirs have a different origin. Natural phenols that make up plants, organic matter of soil, peat, sapropel, coal and brown coal and shale, can be released into the environment as a result of biochemical decomposition of plant residues, as well as during the processing of mineral organic minerals. The main sources of water pollution with phenols are industrial enterprises. The chemical industry produces phenol and its derivatives in large quantities. In 2008, the world produced more than 7.3 million tons of phenol and the amount of phenol produced annually increases by about 0.5 million tons [1]. Most of the phenol produced is used in the production of plastics (carbonate plastics, epoxy and phenol-formaldehyde resins) and artificial fibers. Phenol is consumed in large quantities in the production of antioxidants, synthetic surfactants, drug stabilizers, antiseptics, pesticides, as well as building materials. Hydrolysis and pulp and paper industry, coke-chemical plants and other chemical enterprises supply very large amounts of phenol-containing wastes [2].

Phenol is a highly hazardous substance, the toxic effect of which is already apparent at very low concentrations. The high toxicity of phenol and its derivatives is due to the presence in their structure of a hydroxyl group associated with the aromatic ring, as well as other groups that can actively react
with enzymes, proteins, and other cell components of living organisms, deforming their structure and biological functions. The maximum content of phenols in the water of fishery bodies of water should not exceed the sanitary norm - 0.001 mg l⁻¹ [3-5].

An effective method of purification of phenol-containing wastewater is the process of deep catalytic oxidation using environmentally friendly oxidizing agents such as ozone, oxygen, hydrogen peroxide, or their combination [6]. The advantages of catalytic liquid-phase oxidation compared with such methods of industrial wastewater treatment as biodegradation and adsorption are the possibility of neutralizing a wide range of phenolic compounds and the high rate of the process at low temperatures. Oxidation processes with the use of hydrogen peroxide provide the ability to treat wastewater in a wide range of concentrations, temperatures and pH, and do not require sophisticated technological equipment. Hydrogen peroxide is an environmentally friendly oxidizing agent, since the main products of oxidation processes occurring with its participation are carbon dioxide and water, and it is becoming more and more widely used in the practice of wastewater treatment. The combination of hydrogen peroxide with a catalyst increases the reaction rate and allows you to achieve a high oxidation depth of toxic organic compounds at low temperature and pressure. Due to their high activity and lower cost, water-soluble iron compounds Fe (II) and Fe (III) are most often used as catalysts (Fenton and Raff homogeneous oxidative systems). The high efficiency of these systems is due to the formation of hydroxyl radicals directly during the oxidation reaction as a result of the catalytic decomposition of hydrogen peroxide [7-8]:

\[
\begin{align*}
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + OOH + H^+, \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH + OH^-
\end{align*}
\]

The hydroxyl radical is one of the most powerful oxidizing agents and is able to easily oxidize numerous organic compounds. The widespread use of homogeneous oxidizing systems in water treatment processes requires solving the problem of separation of the catalyst from the aqueous solution and its subsequent regeneration, which leads to significant economic costs. Therefore heterogeneous systems, in which the catalysts are water-insoluble transition metal compounds or their ions deposited on various porous supports are more preferred for industrial processes. As such carriers can be used natural aluminosilicates (zeolites and clay minerals), which are characterized by a large specific surface area, and are available, cheap and environmentally friendly materials [9-15]. The development of catalytic methods for the deep oxidation of organic compounds requires a detailed study of both the properties of catalysts and the kinetics and mechanism of catalytic reactions.

The purpose of this work is to study the kinetic regularities of phenol oxidation by hydrogen peroxide in the presence of a Fe-containing aluminosilicate catalyst and to determine the optimal conditions of phenol oxidation in water solutions.

2. Materials and methods

2.1. Materials
Phenol, 30% hydrogen peroxide, FeCl₃·6H₂O, AlCl₃·6H₂O, NaOH were purchased from Aldrich.

2.2. Preparation and characterization of the catalyst
To obtain a Fe-containing aluminosilicate catalyst (Fe ASK) layered aluminosilicate montmorillonite, which was isolated from bentonite clay from the Mukhorthala deposit (Republic of Buryatia, Russia), was used as a porous support. The montmorillonite fraction of clay had a chemical composition (wt.%): SiO₂ - 65.50, Al₂O₃ - 14.50, Na₂O - 0.16, K₂O - 0.17, MgO - 1.36, CaO - 1.06, Fe₂O₃ - 1.07, H₂O 16.16 [9]. Iron ions were introduced into the aluminosilicate as a complex ion [Fe₆Al₉O₂₂(OH)₂₄(H₂O)₁₂]³⁺, which was obtained by hydrolyzing a
mixture of aqueous solutions of FeCl₃ and AlCl₃ by adding a NaOH solution to them. The catalyst was synthesized according to the procedure described in [16].

The textural characteristics of Fe ASK were determined by the method of low-temperature nitrogen adsorption on the ASAP-2400 Micromeritics unit according to the standard procedure [17]. The total Fe ASK specific surface area was 195 m²·g⁻¹, the pore volume was 0.270 cm³·g⁻¹, and the average pore diameter was 5.5 nm. To determine the iron content, leaching of iron ions into an aqueous solution was carried out by treating Fe ASK with concentrated hydrochloric acid. The concentration of iron ions in the solution was determined by the reaction of formation of a colored complex with o-phenanthroline [18]. The optical density of the solution was measured on an Agilent-UV/Vis spectrophotometer at a wavelength of 490 nm. The Fe content in the catalyst was 1.5%. The concentration of an aqueous solution of hydrogen peroxide was determined by permanganometric titration [18].

2.3. Kinetic experiments
The phenol oxidation reaction was carried out in a thermostatically controlled reactor equipped with a magnetic stirrer and reflux condenser, under the conditions: T = 50°C, pH = 4, [phenol] = 1 mM, [hydrogen peroxide] = 14 mM, [Fe ASK] = 1 g·l⁻¹. An aqueous solution of phenol with a given concentration was loaded into the reactor, a calculated volume of hydrogen peroxide solution and a weight of catalyst were introduced. After a certain period of time, a sample was taken, which was diluted with distilled water and centrifuged to separate the catalyst. The concentration of phenol in the reaction mixture was determined by the optical density of the solution, which was determined on an Agilent-UV/Vis spectrophotometer at a wavelength of maximum phenol absorption (274 nm). Phenol conversion was calculated by the formula: Conversion (%) = (C₀ - C) / C₀)·100%, where C₀ is the initial concentration of phenol, C is the concentration of phenol at a given time. The initial reaction rate (W) was calculated by the equation: W = 0.5·C₀ / t₅₀%, where t₅₀% is the time of 50% phenol conversion.

3. Results and discussion
The oxidation of phenol by hydrogen peroxide proceeds according to the stoichiometric equation:

\[ C₆H₄OH + 14H₂O₂ → 6CO₂ + 17H₂O \]

(3)

In the presence of iron-containing catalysts, the reaction rate increases significantly due to the fact that iron ions interact with hydrogen peroxide and lead to the formation of active hydroxyl radicals (equations 1.2), which quickly oxidize phenol [19]. The amount of hydrogen peroxide, which is necessary for the complete oxidation of phenol to carbon dioxide and water, is 14 moles per 1 mole of phenol.

Figure 1 shows the absorption spectra of an aqueous solution of phenol at different periods in the oxidation reaction with hydrogen peroxide in the presence of Fe ASK. During oxidation, a decrease in the intensity of the characteristic absorption bands of phenol is observed at 253, 274 and 280 nm, up to their complete disappearance, which indicates a 100% conversion of phenol.

We carried out experiments on the effect of the pH of the reaction mixture on the oxidation rate of phenol at initial pH values of 2.5, 3.0, 3.7, 4.0 and 5.0. Figure 2 shows the conversion of phenol in 60 minutes of reaction and the degree of leaching of iron ions from the catalyst into an aqueous solution at different pH values. The results show that, in contrast to the homogeneous Fenton system, the heterogeneous system “Fe ASK/H₂O₂” is quite active even at pH 5.0. The maximum reaction rate leading to maximum conversion is observed at a pH of 3.7. The change in pH in the direction of decreasing and increasing leads to a decrease in conversion. The stability of the catalyst to the leaching of iron ions increases with increasing pH. To select the optimum pH value, it is necessary to take into account not only the activity of the catalyst, but also its stability under the conditions of the
oxidation reaction. Taking into account both these factors, it can be concluded that the most optimal pH value is in the range of 3.7–4.0 (Figure 2), at which the degree of conversion of phenol was above 85%, and the degree of leaching of iron ions was 0.1–0.2%, which indicates on the high stability of Fe ASK.

Figure 1. Changes in the absorption spectrum of a phenol solution during its oxidation (reaction time 0-100 min).

Figure 2. Phenol conversion and iron leaching at various pH (50 °C, [phenol] 1 mM, [H₂O₂] 14 mM, [Fe ASK] 0.5 g·l⁻¹).

Experiments on the effect of hydrogen peroxide concentration on the kinetic of phenol oxidation were carried out at 50 °C, pH = 4.0, catalyst content 1.0 g·l⁻¹, phenol concentration 1.0 mM and various initial concentrations of hydrogen peroxide (3.5, 7.0, 10.0, 14.0, 25.0 mM). As the hydrogen peroxide concentration increases from 3.5 to 14.0 mM, the reaction rate increases significantly, which
can be judged by the initial reaction rate (W) and a decrease in the time of 50% phenol conversion (Table 1).

Table 1. Kinetics of phenol oxidation in the presence of FeASK at various concentrations of H$_2$O$_2$

| [H$_2$O$_2$] (mM) | [H$_2$O$_2$]/[Phenol] (mole/mole) | W (M·min$^{-1}$) | Time of 50% conversion (min) | Time of 100% conversion (min) |
|-----------------|----------------------------------|-----------------|-----------------------------|-----------------------------|
| 25              | 25                               | 1.79·10$^{-5}$  | 28                          | 100                         |
| 14              | 14                               | 1.67·10$^{-5}$  | 30                          | 100                         |
| 10              | 10                               | 1.04·10$^{-5}$  | 48                          | 120                         |
| 7.0             | 7.0                              | 8.62·10$^{-6}$  | 58                          | 180                         |
| 3.5             | 3.5                              | 6.58·10$^{-6}$  | 76                          | >210                        |

With an increase in the peroxide concentration from 14.0 to 25.0 mM, the increase in the reaction rate is not so significant in that with an excess of hydrogen peroxide its decomposition increases as a result of side reactions [15]. The time of 100% conversion of phenol also decreases with increasing concentration of hydrogen peroxide from 3.5 to 14.0 mM and then ceases to depend on the concentration of hydrogen peroxide (Table 1). When the concentration of hydrogen peroxide is 3.5 mM, which is 4 times less than the stoichiometric amount required for the complete oxidation of phenol according to equation (3), the conversion of phenol is only 77.6% in 210 minutes, which is caused by a lack of hydrogen peroxide. According to the kinetic data given in the table, an increase in the concentration of hydrogen peroxide leads to an increase in the initial rate (W) of phenol oxidation and a decrease in the time of 50% and 100% conversion of phenol.

Experiments to study the effect of the initial concentration of phenol on its oxidation rate were carried out at 50°C, pH = 4.0, Fe ASK content 1.0 g·l$^{-1}$, hydrogen peroxide concentration 14.0 mM, and phenol concentrations were 0.25, 0.5, 1.0, 2.0 and 4.0 mM. The results are shown in Table 2. The effect of phenol concentration is observed in the initial period of the oxidation reaction, leading to an increase in the initial reaction rate with increasing phenol concentration. The time of 100% conversion of phenol increases from 80 minutes to 90 minutes with an increase in the concentration of phenol from 0.25 to 0.5 mM and does not change in the range of 0.5 - 2.0 mM. However, a further increase in the concentration of phenol to 4.0 mM leads to an increase in the time of 100% conversion of phenol. At a concentration of phenol of 4.0 mM, 100% conversion of phenol can not be achieved even after 150 min of the reaction. The conversion of phenol becomes 70% after 60 min from the start of the reaction and does not change further, which is caused by the complete consumption of hydrogen peroxide because lack the ratio [H$_2$O$_2$]/[Phenol] is only 3.5 in this experiment.

Table 2. Kinetics of phenol oxidation at various concentrations of phenol in the presence of Fe ASK.

| [Phenol] (mM) | [H$_2$O$_2$]/[Phenol] (mole/mole) | W (M·min$^{-1}$) | Time of 50% conversion (min) | Time of 100% conversion (min) |
|--------------|----------------------------------|-----------------|-----------------------------|-----------------------------|
| 0.25         | 56                               | 2.60·10$^{-6}$  | 48                          | 80                          |
| 0.5          | 28                               | 6.25·10$^{-6}$  | 40                          | 90                          |
| 1.0          | 14                               | 1.67·10$^{-5}$  | 30                          | 90                          |
| 2.0          | 7.0                              | 3.33·10$^{-5}$  | 30                          | 90                          |
| 4.0          | 3.5                              | 6.05·10$^{-5}$  | 33                          | >150                        |
To study the effect of catalyst content on the reaction rate of phenol oxidation, experiments were performed at 50 °C, pH = 4.0, phenol concentration of 1.0 mM, hydrogen peroxide concentration of 14.0 mM and Fe ASK content of 0.5, 1.0, 3.0 and 5.0 g·l⁻¹. An increase in the catalyst content leads to a reduction in the time of 50% and 100% phenol conversion (Table 3). In this case, the initial oxidation rate of phenol also increases, which is caused by an increase in the number of catalytic centers interacting with hydrogen peroxide according to reactions (1, 2).

| Content of Fe ASK (g·l⁻¹) | W (M·min⁻¹) | Time of 50% conversion (min) | Time of 100% conversion (min) |
|---------------------------|-------------|-----------------------------|-----------------------------|
| 5.0                       | 2.27·10⁻⁶   | 22                          | 40                          |
| 3.0                       | 2.00·10⁻⁵   | 25                          | 50                          |
| 1.0                       | 1.67·10⁻⁵   | 30                          | 90                          |
| 0.5                       | 1.04·10⁻⁵   | 48                          | 140                         |

The effect of temperature on the oxidation rate of phenol was studied at temperatures of 40, 50, 60 °C (pH=4, [Phenol] = 1 mM, [H₂O₂] = 14 mM, [FeASK] = 1 g·l⁻¹). With increasing temperature, a decrease in the time of 50% and 100% conversion of phenol and an increase in the reaction rate are observed (Table 4). The effective activation energy was calculated by the Arrhenius equation \( \ln W = f \left( \frac{1}{T} \right) \), where \( T \) is the absolute temperature of the reaction [20], and was 49 ± 5 kJ·mol⁻¹.

| Temperature (°C) | W (M·min⁻¹) | Time of 50% conversion (min) | Time of 100% conversion (min) |
|-----------------|-------------|-----------------------------|-----------------------------|
| 40              | 9.80·10⁻⁶   | 51                          | 140                         |
| 50              | 1.67·10⁻⁵   | 30                          | 90                          |
| 60              | 2.78·10⁻⁵   | 18                          | 60                          |

The reaction orders for the reagents (hydrogen peroxide, phenol) and catalyst were determined using the dependences \( \lg W = f \cdot (\lg C_o) \), where \( C_o \) is the initial concentration of the reactants or the content of the catalyst. The resulting kinetic equation of the reaction had the form \( W = k \cdot [\text{Phenol}]^{1.1} \cdot [\text{H}_2\text{O}_2]^{0.6} \cdot [\text{FeASK}]^{0.4} \), where \( k \) – effective rate constant.

On the basis of the obtained data, the optimal conditions for the phenol oxidation reaction in the heterogeneous catalytic system Fe-aluminosilicate / hydrogen peroxide were: \( T = 40-50 \) °C, pH = 3.7-4.0, [hydrogen peroxide]/[phenol] = 14 mole/mole, [Fe ASK] = 1-3 g·l⁻¹. Under these conditions, a sufficiently high oxidation rate of phenol was achieved and the catalyst was stable.

4. Conclusion
The kinetic regularities of phenol oxidation with hydrogen peroxide in the presence of a Fe-aluminosilicate catalyst (Fe ASK) obtained by introducing a mixed Fe/Al (1/12) polyhydroxocomplex into montmorillonite were studied. The dependence of the phenol oxidation rate on the reaction conditions (pH, hydrogen peroxide concentration, phenol concentration, catalyst content and temperature) was established. The optimal conditions for the reaction of phenol oxidation
in the heterogeneous catalytic system “Fe-aluminosilicate / hydrogen peroxide”, under which phenol oxidation proceeds quickly, the catalyst is stable and water is not contaminated with iron ions were determined: T = 40-50 °C, pH = 3.7-4.0, [hydrogen peroxide] / [phenol] = 14 mole / mole, [Fe ASK] = 1-3 g·l⁻¹. The results obtained in this work showed a high efficiency of the catalytic system “Fe-aluminosilicate / hydrogen peroxide” for the oxidation of aqueous solutions of phenol, which makes it possible to recommend this system for use in the processes of purifying wastewater from phenols.

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