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# Kinetics of Phenol Oxidation with Iron–Manganese Concretions

**O. V. Cheremisina, D. E. Chirkst, and M. A. Sulimova**

*St. Petersburg State Mining University, 21 liniya 2, Vasil'evskii Ostrov, St. Petersburg, 199106 Russia*
*e-mail: ovcheremisina@yandex.ru*

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**Abstract**—Kinetics of oxidation of phenols on the iron-manganese concretions in the temperature range 293–353 K at pH 5.5±0.5 was studied. Reaction of oxidation on the iron-manganese concretions has the second order by phenol. It is characterized by low activation energy, 17.5 kJ mol$^{-1}$, due to the catalytic action of iron(III) oxide. Lower rate of oxidation of phenols on the iron-manganese concretions is observed as compared to oxidation on the pyrolusite surface. It occurs because of the decrease in $MnO_2$ concentration in the iron-manganese concretions.

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The problem of decontamination of industrial waste waters from the dissolved organic compounds, in particular, of phenols, is one of the most important and at the same time of most complicated goals. Firstly, the diversity of chemical compositions of systems, of their formation and existence requires performing special studies for each case, which is not always possible. Secondly, the technology of the sufficiently complete decontamination of water requires as a rule the maintenance of special conditions, which as a rule can be hardly fulfilled in practice. And finally, many effective methods of deep decontamination need large economical and resource investments, using rare reagents with their subsequent regeneration, utilization or disposal of waste. That is why the search for new effective methods of decontamination of industrial waste waters is still actual.

Methods of decontamination of the phenol-containing waters may be classified as the regenerative and destructive. Destructive methods are used when isolation of phenols from waste waters is impossible or expensive. Main destructive methods of decontamination from the dissolved phenol are thermal oxidation, oxidation, electrochemical oxidation, and hydrolysis.

Using catalytic systems permits the decom-position of practically all organic substances which can be found in waste waters. Such treatment may cause deep oxidation of organic substances up to $CO_2$ and $H_2O$. Metals of varied valence, their oxides and salts, mainly the VIII group metals as well as copper, manganese, and their compounds are used as catalysts.

The liquid phase oxidation of phenol in water catalyzed with copper oxide applied on the active aluminum oxide at 130–145°C, 1.0–1.3 MPa pressure, and the contact time 45–90 min permitted to achieve its complete destruction [1].

Manganese dioxide is also used as the phenol oxidant [2-4]. At pH 9–10 it plays the role of catalyst, and $Mn^{2+}$ cations formed in the course of oxidation precipitate as the poorly soluble $Mn(OH)_2$ hydroxide on the surface of the mineral. Performing the oxidation process in the acidic medium at $pH < 4$ is not desirable due to the dissolution of manganese dioxide and the transfer of $Mn^{2+}$ ions in the solution. Their maximum permissible concentration is 0.1 mg l$^{-1}$ [5]. In [6] the oxidation of phenol with manganese dioxide at pH 5–6 was studied in the temperature range 323–393 K leading to formation of hydroquinone and *p*-benzoquinone. Their maximum permissible concentration is 0.2 mg l$^{-1}$ which is 200 times higher than that of phenol (0.001 mg l$^{-1}$). This oxidation is the second order reaction in the temperature range 393–323 K and proceeds in the kinetic regime with the activation energy 42.0 kJ mol$^{-1}$. In the temperature range 333–353 K the reaction proceeds according to the first order equation in the external diffusion regime with the activation energy 6.65 kJ mol$^{-1}$.

**Table 1.** Chemical composition of concretions of the Finnish bay [7][a]

| Component | Average content, wt % | Limits of changes in content, wt % |
|---|---|---|
| $SiO_2$ | 17.87 | 9.91–26.43 |
| $TiO_2$ | 0.28 | 0.21–0.36 |
| Total Mn calculated on $MnO_2$ | 33.80 (35.87) | 15.51–53.43 |
| $Al_2O_3$ | 4.49 | 1.63–6.39 |
| $Fe_2O_3$ | 20.19 (36.23) | 10.31–33.98 |
| MgO | 1.59 | 0.94–2.14 |
| CaO | 1.41 | 0.93–2.21 |
| $Na_2O$ | 1.43 | 1.11–1.77 |
| $K_2O$ | 1.92 | 1.29–3.13 |
| $P_2O_5$ | 2.70 | 1.42–4.88 |
| Ba | 0.328 | 0.1–1.0 |
| Sr | 0.0027 (0.263) | 0.0005–0.0050 |
| V | 0.0076 | 0.0030–0.0120 |
| Co | 0.0067 | 0.0030–0.0120 |
| Cr | 0.0016 | 0.0012–0.0025 |
| Ni | 0.0134 | 0.0010–0.0500 |
| Y | 0.0015 | 0.0005–0.0025 |
| Mo | 0.0070 | 0.0020–0.0150 |
| Cu | 0.0034 (0.339) | 0.0020–0.0080 |
| Pb | 0.0034 (0.449) | 0.0001–0.0200 |
| Zn | 0.0057 (0.074) | 0.0005–0.0150 |

[a] Mass content of the elements defined in [12] by X-ray analysis is given in parentheses.

Analysis of reported data shows that natural minerals containing manganese dioxide have good adsorption properties and high catalytic ability while demonstrating the oxidative properties [2–4]. For the effective purification of the phenol-containing waste waters of chemical-metallurgical plants it is promising to use iron-manganese concretions. Mineral composition of iron-manganese concretions consists of todorokite, vernardite, pyrolusite, psilomelane, and ransierite [7]. Main mass of the ore part contains iron hydroxides in a form of hydrogetite FeO(OH) and double silicates with aluminum of ferrihydrite type $Fe_5Al_2(Al_2Si_6O_{22})(OH)_5$ and manganese(IV). But the kinetics of oxidation on natural minerals at high concentrations of phenols remains practically unstudied [8, 9].

Kinetics of oxidation of phenol in waste water with natural minerals of manganese(IV) oxide containing soft manganese mineral, rodochrosite, and hematite [10] was studied. The oxidation of phenol with starting concentrations 100–1000 mg $l^{-1}$ at different pH in the temperature range 293–333 K proceeds in the diffusion regime.

The catalytic activity of iron-manganese concretions would differ from the properties of pure $MnO_2$ and the minerals with its high content due to the presence of a significant amount of iron(III). It is presumable that $Fe_2O_3$ also exhibits the catalytic activity. The catalytic system described in [10] includes the activated carbon modified with the iron additives.

In the course of liquid phase oxidation in the boiling layer on this catalyst about 98% conversion of phenol was observed. Song et al. ascribe the observed results to the action of iron as the agent stabilizing the transition state of oxidized phenol molecules on the surface. Besides, it was reported lately [11] that the synthesis of heavy organic substances can take place in the course of oxidation of phenols in the presence of iron. That is why the establishment of the role of iron(III) in the course of oxidation of phenol is necessary.

We have studied kinetics of oxidation of phenol on iron-manganese concretions in the temperature range 293–353 K at the pH of water phase 5.5±0.5. The composition of the catalyst evaluated by means of X-ray luminescent method [14] is presented in Table 1.

Mass content of elements evaluated in [14] by means of the X-ray fluorescent methods is given in parentheses.

It was shown in [6] that at pH 5.5±0.5 the main product of oxidation of phenol with manganese dioxide is hydroquinone. *p*-Benzoquinone is formed in the yield less than 10 mol %. The absence of $Mn^{2+}$ cations in solutions is confirmed by the X-ray fluorescent data.

In Table 2 and in Fig. 1 the experimental dependences of concentration of phenol on the time of

**Table 2.** Dependence of concentration of phenol on time

| *t*, min | *c*, M | | | | | | |
|---|---|---|---|---|---|---|---|
| | 293 K | 303 K | 313 K | 323 K | 333 K | 343 K | 353 K |
| 0 | 0.0137 | 0.0152 | 0.0146 | 0.0129 | 0.0126 | 0.0128 | 0.0171 |
| 2 | – | 0.0149 | – | 0.0130 | – | 0.0127 | 0.0152 |
| 5 | 0.0131 | 0.0147 | – | 0.0115 | – | 0.0120 | 0.0140 |
| 10 | 0.0128 | 0.0141 | 0.0141 | 0.0117 | 0.0119 | 0.0112 | 0.0130 |
| 15 | 0.0129 | 0.0135 | – | 0.0099 | – | 0.0105 | 0.0108 |
| 20 | – | – | 0.0134 | 0.0107 | 0.0114 | 0.0109 | 0.0113 |
| 25 | 0.0114 | 0.0132 | – | 0.0104 | 0.0105 | 0.0094 | 0.0109 |
| 30 | – | – | – | 0.0094 | – | 0.0098 | 0.0098 |
| 35 | 0.0114 | 0.0128 | 0.0130 | – | 0.0104 | 0.0094 | 0.0105 |
| 45 | – | – | – | – | 0.0094 | 0.0081 | 0.0090 |
| 50 | 0.0107 | – | – | | – | – | – |
| 60 | – | 0.0118 | – | 0.0080 | 0.0090 | 0.0081 | 0.0086 |
| 70 | – | – | 0.0104 | – | – | – | – |
| 90 | – | 0.0105 | – | – | 0.0088 | – | 0.0070 |
| 110 | 0.0097 | – | 0.0095 | – | – | – | – |
| 120 | – | 0.0096 | – | 0.0070 | – | 0.0063 | – |
| 130 | 0.0093 | – | – | – | – | – | – |
| 140 | – | – | – | 0.0065 | – | – | – |
| 150 | 0.0094 | – | 0.0080 | – | – | – | – |
| 160 | – | – | – | 0.0055 | – | – | – |
| 170 | 0.0082 | – | – | – | – | – | – |
| 180 | – | 0.0083 | 0.0071 | – | 0.0053 | 0.0058 | – |
| 200 | 0.0078 | – | – | 0.0063 | – | – | – |
| 210 | – | – | 0.0070 | – | – | – | – |
| 230 | 0.0070 | – | – | 0.0054 | – | – | – |
| 240 | – | 0.0071 | – | – | – | – | – |
| 300 | 0.0063 | – | – | – | – | 0.0036 | – |
| 320 | – | – | – | – | – | 0.0033 | – |

oxidation on iron-manganese concretions at pH 5.5±0.5, *V/m* ratio 20 ml $g^{-1}$ and 293, 303, 313, 323, 333, 343, 353 K are presented.

Treating the results of measurements in the temperature range 293–353 K showed that the dependences obtained are described by the kinetic equations of the second order reactions. Linear dependence of the value of reverse concentration on time is presented in Fig. 2. Linear trend equations and values of rate constants, evaluated from the slopes are listed in Table 3.

The value of activation energy calculated from the slope of linear trend $E_a = R|\tan \alpha|$ ($y = -2102.59x + 5.75$; $R^2 = 0.99$) presented in Fig. 3 was 17.48 kJ $mol^{-1}$.

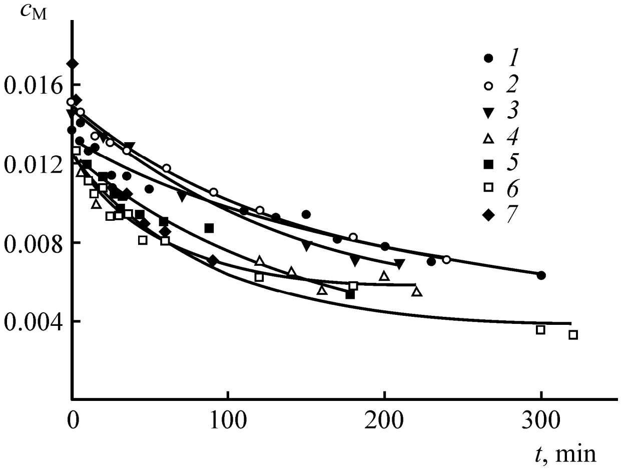

**Fig. 1.** Dependence of concentration of phenol on time at the temperature, K: (*1*) 292, (*2*) 303, (*3*) 313, (*4*) 323, (*5*) 333, (*6*) 343, and (*7*) 353.

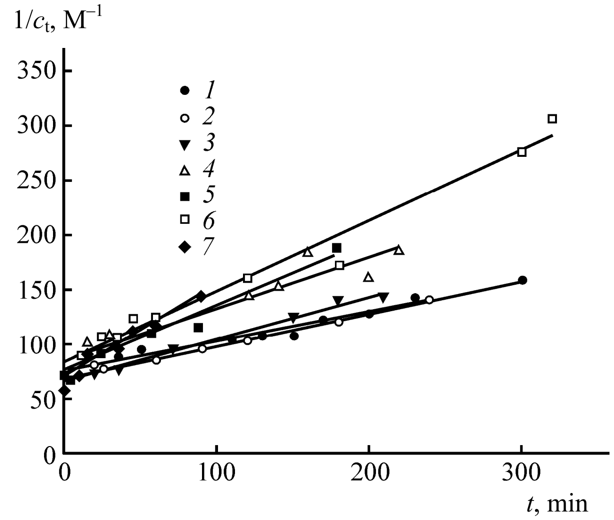

**Fig. 2**. Linear form of kinetic dependencies at the temperature, K: (*1*) 292, (*2*) 303, (*3*) 313, (*4*) 323, (*5*) 333, (*6*) 343, and (*7*) 353.

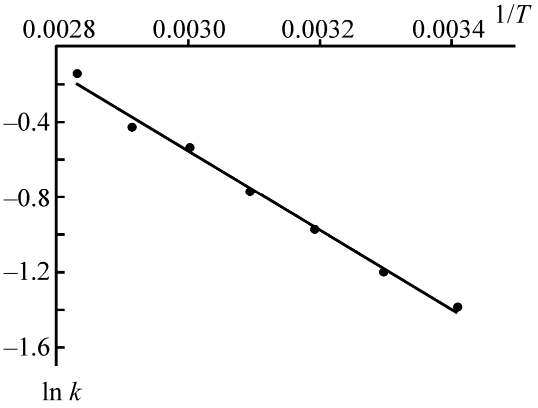

**Fig. 3.** Dependence of ln $k = f(T^{-1})$ in the temperature range 203–303 K.

**Table 3.** Kinetic characteristics of oxidation of phenol

| $T$, K | Trend equation | Rate constant $k$, $mol^{-1}$ l–1 $min^{-1}$ |
|---|---|---|
| 293 | $y = 0.271x + 75.43$; $R^2 = 0.97$ | 0.271 |
| 303 | $y = 0.301x + 67.35$; $R^2 = 0.99$ | 0.301 |
| 313 | $y = 0.378x + 66.93$; $R^2 = 0.99$ | 0.378 |
| 323 | $y = 0.465x + 86.03$; $R^2 = 0.94$ | 0.465 |
| 333 | $y = 0.583x + 77.26$; $R^2 = 0.96$ | 0.583 |
| 343 | $y = 0.652x + 81.91$; $R^2 = 0.98$ | 0.652 |
| 353 | $y = 0.864x + 68.55$; $R^2 = 0.95$ | 0.864 |

On the basis of the value $n = 2$ of the reaction order and the activation energy 17.48 kJ $mol^{-1}$ it may be suggested that in the temperature range 293–353 K the rate of oxidation is limited by the chemical reaction taking place on the surface. For the confirmation of nature of the limiting stage the experiment at the $V/m$ ratio 50 l $kg^{-1}$ was carried out. Obtained values of rate constants equal 0.269 mol $l^{-1}$ $min^{-1}$ at 293 K and 0.577 mol $l^{-1}$ $min^{-1}$ at 333 K and within the limits of experimental error they agree with the values of constants evaluated at $V/m$ 20 l $kg^{-1}$. The independence of the reaction rate constant from the phase ratio at 293 and 333 K contradicts the diffusive regime of oxidation.

Lower values of the rate of oxidation of phenol on the iron-manganese concretions as compared to pyrolusite [6] is due to the 3–4 times decrease in the $MnO_2$ content in iron-manganese concretions as compared to pyrolusite. From the data in [6] it follows that in the temperature range 293–333 K the values of rate constants of oxidation of phenol on pyrolusite vary from 0.314 to 1.556 mol $l^{-1}$ $min^{-1}$, and at 333 K the reaction goes over to the diffusive regime. Due to the low content of $MnO_2$ (35.87 wt %) in iron-manganese concretions the decrease in the rate of the chemical reaction occurs which limits the process of oxidation at the increase in temperature from 333 to 353 K in contrast to the oxidation on pyrolusite.

The decrease in the activation energy from 42.0 to 17.5 kJ $mol^{-1}$ at the transfer from pyrolusite to iron-manganese concretions can be attributed to the catalytic action of iron(III) oxide whose content is comparable with the content of $MnO_2$ (Table 1). For the confirmation or rejection of this assumption we carried out the oxidation of phenol on the surface of pure $Fe_2O_3$ and on a mixture of $Fe_2O_3$ and $MnO_2$ in 1:2 molar ratio characteristic of iron-manganese concretions and at the ratio of volume of the liquid phase to the mass of solid *V/m* 20 l $kg^{-1}$ and 323 K.

Results of this experiment are presented in Table 4 and Fig. 4.

Dependences of concentration of phenol on the time of oxidation on the surfaces of $Fe_2O_3$ and of the mixture of $Fe_2O_3$ and $MnO_2$ are described by the kinetic equations of the second order reaction. In Fig. 5 linear dependences of the reverse concentration on time are presented. In Table 5 equations of linear trends and the rate constants evaluated from the slopes for $Fe_2O_3$ and $Fe_2O_3$–$MnO_2$ mixture are listed. Analogous values for pure $MnO_2$ were taken from [6].

In the kinetics of the liquid phase heterogenic catalysis a significant role is played by the surface concentration of catalyst because the liquid phase oxidation of phenol takes place on the surface of solid catalyst. That is why for evaluation of the real rate constants of the process the values of specific surfaces of iron-manganese concretions, of pyrolusite, and of $Fe_2O_3$ were measured. Results of these evaluations are as follows.

| Mineral | Iron-manganese concretions | $MnO_2$ | $Fe_2O_3$ |
|---|---|---|---|
| Specific surface, $m^2\ g^{-1}$ | 35.39 | 40.34 | 9.67 |

As the rate of heterogenic catalytic and heterogenic reactions are referred to the unit of surface of catalyst or the solid phase, the real rate constant of oxidation $k_r$ can be calculated from the experimental value $k_{exp}$ according to Eq. (3).

$$k_r = k_{exp}/c_s. \quad (3)$$

Here $c_s$ is the surface concentration of solid phase, mol $m^{-2}$ calculated according to the formula (4).

$$c_s = 1/(S_s M). \quad (4)$$

Here *M* is the molecular mass of $MnO_2$ or $Fe_2O_3$.

Calculated $k_r$ values for the oxidation at 323 K on the surface of pure $Fe_2O_3$ and $MnO_2$ were $4.94\times10^5$ $m^{-1}$ $min^{-1}$ and $5.6\times10^6$ $m^{-1}$ $min^{-1}$ respectively.

While studying the process on the surface of the mixture of $Fe_2O_3$ and $MnO_2$ in 1:2 molar ratio the value of the experimental rate constant was 0.997 mol $l^{-1}$ $min^{-1}$. Within the limits of experimental error it coincides with the value calculated from the separate experimental rate constants of the reaction on the surface of $MnO_2$ and $Fe_2O_3$ considering the molar

**Table 4.** Dependence of concentration of phenol on the time of oxidation on the surface of $Fe_2O_3$ and a mixture of $Fe_2O_3$ and $MnO_2$ at 323 K

| *t*, min | *c*, M | |
|---|---|---|
| | $Fe_2O_3$ | $Fe_2O_3 + MnO_2$ |
| | 333 K | 333 K |
| 0 | 0.0157 | 0.0155 |
| 2 | 0.0155 | 0.0151 |
| 5 | 0.0155 | 0.0149 |
| 10 | 0.0149 | 0.0137 |
| 15 | 0.0144 | 0.0126 |
| 20 | 0.0137 | 0.0099 |
| 25 | 0.0136 | 0.0111 |
| 30 | 0.0131 | 0.0094 |
| 35 | 0.0131 | 0.0094 |
| 45 | 0.0123 | 0.0086 |
| 60 | 0.0120 | 0.0090 |
| 90 | 0.0115 | 0.0064 |
| 120 | 0.0112 | 0.0066 |
| 180 | 0.0109 | 0.0070 |
| 240 | 0.0105 | 0.0062 |
| 300 | 0.0101 | 0.0040 |
| 315 | 0.0101 | 0.0034 |

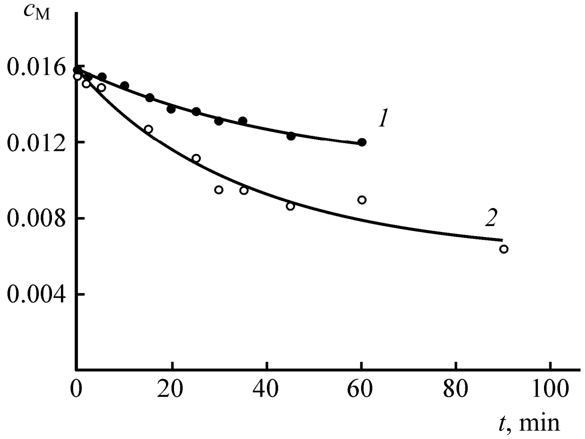

**Fig. 4.** Dependence of concentration of phenol on the time of oxidation at 333 K. (*1*) on $Fe_2O_3$ surface and (*2*) on the surface of a mixture of $Fe_2O_3$ and $MnO_2$.

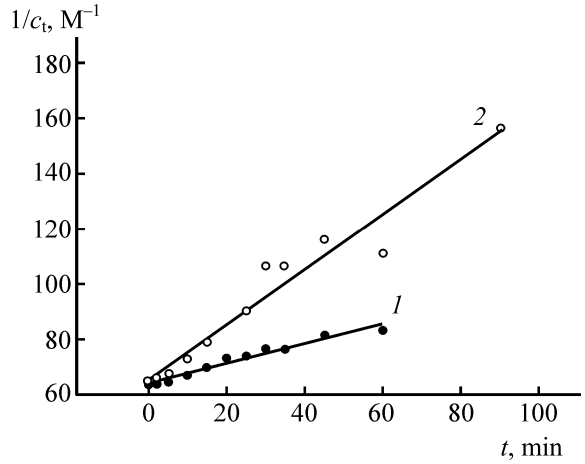

**Fig. 5.** Linear form of kinetic dependencies at 323 K. (*1*) Oxidation on $Fe_2O_3$ surface and (*2*) oxidation on a surface of $Fe_2O_3$–$MnO_2$ mixture.

parts of oxides ω in the mixture [Eq. (5)] which is equal to 1.160 mol $l^{-1}$ $min^{-1}$

$$k_{\mathrm{exp}} = k_{\mathrm{exp}}^{\mathrm{MnO_2}}\,\omega_1 + k_{\mathrm{exp}}^{\mathrm{Fe_2O_3}}\,\omega_2\,. \qquad (5)$$

According to the data of Table 1 the molar part values $\omega_1$ are 0.67 and 0.33 respectively. From the calculated $k_r$ values at 323 K on the surfaces of pure oxides $Fe_2O_3$ and $MnO_2$ considering the given molar ratio 1:2 $k_{exp}$ the value equal to 0.427 mol $l^{-1}$ $min^{-1}$ was evaluated. It agrees with the experimental value 0.465 mol $l^{-1}$ $min^{-1}$ measured in the process of oxidation on the surface of iron-manganese concretions.

Hence, the process of oxidation of phenols on the iron-manganese concretions proceeds slower as compared to pyrolusite which can be ascribed to the decrease in concentration of $MnO_2$ in iron-manganese concretions. Nevertheless, the presence of iron(III) oxide in the iron-manganese concretions contributes to the value of rate constant of the surface chemical reaction and significantly decreases the activation barrier.

**Table 5.** Kinetic characteristics of oxidation of phenol on the surface of minerals at 323 K

| Oxidants | Trend equation | Rate constant *k*, $mol^{-1}$ l–1 $min^{-1}$ |
|---|---|---|
| $Fe_2O_3$ | $y = 0.356x + 64.18$; $R^2 = 0.97$ | 0.356 |
| $Fe_2O_3 + MnO_2$ | $y = 0.997x + 65.42$; $R^2 = 0.95$ | 0.997 |
| $MnO_2$ | $y = 1.556x + 82.91$; $R^2 = 0.98^a$ | 1.556 |

[a] Linear trend equation and value of the rate constant on $MnO_2$ surface at 323 K were evaluated in [6].

Data [12] show that chemosorption of two-atomic and more complex molecules proceeds monomolecularly or dissociatively. Molecular chemisorptions proceeds with the preservation of bonds in the adsorbed molecule. It is caused by the coordinational interaction of adsorbate and adsorbent.

$$> {}^{\delta+}\mathrm{Mn}^{\mathrm{IV}} < (2\mathrm{O}^-) + 2^{\delta-}\mathrm{C_6H_5OH}$$
$$\rightleftarrows [> {}^{\delta+}\mathrm{Mn}^{\mathrm{IV}} < (2\mathrm{O}^-)] \cdots\cdots (2^{\delta-}\mathrm{C_6H_5OH}), \qquad (6)$$

$$> {}^{\delta+}\mathrm{Fe}^{\mathrm{III}}\text{—}(\mathrm{O}^-) + {}^{\delta-}\mathrm{C_6H_5OH}$$
$$\rightleftarrows [> {}^{\delta+}\mathrm{Fe}^{\mathrm{III}}\text{—}(\mathrm{O}^-)] \cdots\cdots ({}^{\delta-}\mathrm{C_6H_5OH}). \qquad (7)$$

The specific feature of molecular chemisorptions is also the low value of activation energy as was demonstrated in the process of oxidation of phenol on the surface on iron-manganese concretions. The interaction of the charged forms of oxygen in metal oxides with the oxidized substance is accompanied by the electron transfer to the catalyst.

$$[> {}^{\delta+}\mathrm{Mn}^{\mathrm{IV}} < (2\mathrm{O}^-)] \cdots\cdots (2^{\delta-}\mathrm{C_6H_5OH})$$
$$\rightarrow > {}^{\delta+}\mathrm{Mn}^{\mathrm{II}} \cdots\cdots (2\mathrm{O}^-) \cdots\cdots (2^{+}\mathrm{C_6H_5OH}), \qquad (8)$$
$$[> {}^{\delta+}\mathrm{Fe}^{\mathrm{III}}\text{—}(\mathrm{O}^-)] \cdots\cdots ({}^{\delta-}\mathrm{C_6H_5OH})$$
$$\rightarrow > {}^{\delta+}\mathrm{Fe}^{\mathrm{II}} \cdots\cdots (\mathrm{O}^-) \cdots\cdots ({}^{+}\mathrm{C_6H_5OH}). \qquad (9)$$

The presence of electron transfers in the intermediate interaction explains the exclusive role of the transition metal compounds as the oxidation catalysts. High catalytic activity of compounds of the transition *d*-metals is caused by the comparatively low energy of valence alterations of their ions, which facilitates the electron transfer. A significant role belongs also to the ability of formation of coordination compounds. The electron transfer is the quick stage of oxidation. The rate of the process would be limited by chemimolecular adsorption [reactions (1), (2)] and the stability of activation complexes $[>^{\delta+}\mathrm{Mn}^{\mathrm{IV}}<(2\mathrm{O}^-)]\cdots(2^{\delta-}\mathrm{C_6H_5OH})$ and $[>^{\delta+}\mathrm{Fe}^{\mathrm{III}}<(\mathrm{O}^-)]\cdots({}^{\delta-}\mathrm{C_6H_5OH})$.

The activated complex with iron oxide is less stable. This statement is based on the lower value of energy of the iron-oxygen bond as compared to the energy of manganese-oxygen bond [12]. The activetion energy of oxygen desorption is the sum of values of the metal-oxygen bond energies and the activation energies of oxygen adsorption. For the iron and manganese oxides these values are comparable.

The cleavage of activated complexes does not lead to the formation of $Mn^{2+}$ and $Fe^{2+}$ cations in solution as show the X-ray fluorescent analysis data. Evidently these ions remain on the surface of the solid phase and then according to [8, 13] are oxidized with air oxygen to form FeO and MnO.

Summary equations of the reactions may be represented as follows:

$$MnO_2(s) + 2\ C_6H_5OH(sol) + H_2O(l) \rightleftarrows MnO(s) + 2\ HO\text{–}C_6H_5\text{–}OH(sol) + 2\ H^+_{aq},$$

$$Fe_2O_3(s) + 2\ C_6H_5OH(sol) + H_2O(l) \rightleftarrows 2FeO(s) + 2\ HO\text{–}C_6H_5\text{–}OH(sol) + 2\ H^+_{aq}.$$

Hence, the oxidation of phenol on iron-manganese concretions in the temperature range 293–353 K has the second order by phenol and is characterized by low value of activation energy (17.5 kJ mol$^{-1}$) due to the catalytic action of iron(III) oxide. The lower rate of oxidation of phenol on iron-manganese concretions as compared to the rate on the surface of pyrolusite originates from the decrease in $MnO_2$ concentration in iron-manganese concretions.

The presence of iron(III) oxide in iron-manganese concretions contributes to the value of the rate constant of the surface-chemical reaction and significantly decreases the activation barrier.

## EXPERIMENTAL

Experiments were carried out in the temperature-controlled vessel loaded with 800 ml of aqueous phenol solution with the concentration about 1 g l$^{-1}$ and 40 g of iron-manganese concretions of the granulometric composition 1.0–2.0 mm. The vessel content was stirred at a rate 400 rpm. After the definite time intervals 15 ml aliquots were taken and the content of phenol [15, 16] and manganese cations was analyzed in them.

The content of $Mn^{2+}$ cations in solution was evaluated by means of the X-ray fluorescent analysis using the Spectroscan-U crystal diffraction spectrometer.

The phenol content was evaluated by the absorption in the UV spectrum at 235 nm. For this purpose the 1 ml aliquots of analyzed solution with the phenol content 1–0.1 g l$^{-1}$ were placed in the 100 ml measureing flask, and 0.1 M sodium hydroxide solution was added to the completion of the flask volume. From the solution thus obtained two 5 ml aliquots were taken. The first one was diluted in the measuring flask to 10 ml with NaOH solution and optical density of the solution obtained was measured on the wavelength 235 nm against the 0.1 M NaoH solution. The second aliquot was diluted in the measuring flask up to 10 ml with 0.1 N hydrochloric acid and its optical density was measured at the same wavelength against the neutralized solution of sodium hydroxide.

Linear dependence of optical density on concentration is observed in the range up to 10 mg l$^{-1}$, evaluation limit is 0.5 mg l$^{-1}$. The evaluation of phenol is possible in the presence of nitrogen and sulfur oxides, hydrogen sulfide, aldehydes, ketones, alcohols, benzene and its homologs, but it is impeded by the presence of amines exhibiting the same red shift [15, 16].

In alkaline medium at pH 13, the light absorption is proportional to the content of phenol and its derivatives, while at pH 7 it is caused only by the presence of impurities. Absorption spectra of water solutions of phenol, hydroquinone, pyrocatechol, and resorcinol in the concentration 5 mg l$^{-1}$ at pH 7 showed that no light absorption takes place only in the case of phenol. Selectivity of evaluation is achieved due to the red shift of the absorption bands in the alkaline solutions of phenol and its derivatives as compared to neutal ones (pH 7) caused by the formation of phenolates. The content of phenol was found from the difference of optical densities of solutions measured at pH 13 and pH 7.

In the course of our work specific surfaces of iron-manganese concretions, of pyrolusite, and of pure iron(III) oxide were measured. The specific surface was evaluated by means of sorption of methylene blue from water solution [17]. A batch of the air dry sample, 5 g, was placed in a 100 ml Erlenmeyer flask and 50 ml of 0.01 N methylene blue solution was added by means of a pipette. The resulting mixture was shaken and left for 12–14 h. The colored suspension was twice filtered through the blue band filter. First portions of filtrate (~10 ml) were thrown away because of sorption of the methylene blue with filter. Aliquots of filtrate and starting solution (1 ml) were diluted to 100 ml with water and optical densities of these solutions at 665 nm were measured. From the value of calculated concentration of methylene blue in filtrate the capacity was evaluared by means of formula (1) with the accuracy 0.1 meq.

$$E = (\Delta c V \times 10^{-3})/m\ (\text{eq g}^{-1}). \qquad (1)$$

Here $\Delta c$ is the difference in concentrations of starting and equilibrium solutions of methylene blue, eq l$^{-1}$; $V$ is the volume of starting methylene blue solution, cm$^3$; $m$ is the mass of mineral batch, g.

From the value of exchange capacity and the dimensions of the area, occupied by one methylene blue cation equal to $95.6\times10^{-20}$ m$^2$ according to X-ray measurements specific surface was calculated. As the maximum amount of the adsorbed methylene blue corresponds to the monomolecular layer of dye, specific surface value can be found by means of formula (2).

$$S = EN_AW_0\ (\text{m}^2\ \text{g}^{-1}). \qquad (2)$$

Here $E$ is the value of capacity of adsorbent with respect to methylene blue, eq g$^{-1}$; $N_A$ is the Avogadro constant, $W$ is the area occupied by one methylene blue cation.

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