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Kinetics of Oxidation of Phenol with Manganese Dioxide

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Abstract—The kinetics of oxidation of phenol with manganese dioxide at pH 5.5±0.5 were studied. In the temperature range from 393 to 323 K the reaction is of second order, and it occurs in the kinetic mode with an energy of activation of 42.0 kJ/mol. In the temperature range from 333 to 353 K the reaction follows first-order equation and is controlled by external diffusion; the energy of activation is equal to 6.65 kJ/mol. The oxidation products are hydroquinone and 1,4-benzoquinone, the fraction of the latter being less than 10 mol %.

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Phenol is a component of wastewater in petrochemical, by-product-coking, and galvanic processes. Its concentration in waste water of a by-product coke plant may reach 1 g/l [1]. Meanwhile, phenol is one of the most hazardous pollutants. Its maximum allowable concentration (MAC) in basins for household water use is set at 0.001 mg/l [2]. In the course of wastewater treatment phenol is oxidized to hydroquinone or 1,4-benzoquinone for which MAC is 0.2 mg/l [2]. Purification to such concentration may be achieved by sorption methods.

Phenol can be oxidized by biochemical methods, ultrasonic treatment, and photocatalytic reactions; however, these procedures are not always effective but are expensive [3]. Therefore, manganese dioxide was proposed as oxidant [4–6]. In the pH range from 9 to 10 manganese dioxide acts as catalyst. Manganese(II) species formed as a result of oxidation of phenol deposit on the mineral surface as $Mn(OH)_2$ and are oxidized to MnO_2 with dissolved oxygen [7, 8]. However, in acid medium (pH < 4) dissolution of manganese dioxide and MnO_2-containing minerals is observed, and Mn^{2+} cations reside in solution [3, 9–11]. This is undesirable, for manganese(II) compounds are classed with toxicants (MAC 0.1 mg/l) [2]. Oxidation of benzenediols (hydroquinone [9] and pyrocatechol [10]) is described by Eq. (1).

$$C_6H_4(OH)_2 + MnO_2 + 2H^+ \rightleftarrows C_6H_4O_2 + Mn^{2+} + 2H_2O. \quad (1)$$

The oxidation products of benzenediols are the corresponding benzoquinones. The concentration of Mn^{2+} in solution is given by Eq. (2).

$$\log [Mn^{2+}] = \text{const} - 2\text{pH}. \quad (2)$$

Thus manganese(II) transfer to solution sharply decreases as pH rises, and it becomes harmless at pH > 5.6 [9]. Aqueous manganese dioxide oxidizes phenol to hydroquinone and 1,4-benzoquinone [11]. The mechanism of oxidation of benzenediols over MnO_2 surface was studied in [9, 10]. The process includes three steps:

(1) Formation of activated surface complex with Mn(IV)–O_{phenol} bonds; the complex is stabilized due to similarity of the Mn–Mn and O–O distances (277 and 285 pm or 554 and 570 pm for pyrocatechol and hydroquinone, respectively);

(2) Electron transfer;

(3) Decomposition of activated complex with formation of benzoquinone and manganese(II).

Taking into account the high energy of activation, 58.7±6.6 kJ/mol, the rate-determining step is the formation of activated surface complex; this reaction at pH 4 is of pseudofirst order with respect to pyrocatechol, and the rate constant *k* id equal to 5×10^{-3} s^{-1} [10].

Studies in the field of phenol oxidation with manganese dioxide extensively develop, for kinetic data on the oxidation process are important for the development of new methods for purification of phenol-containing wastewater. However, some discrepancies and unresolved problems should be noted. First of all, the available kinetic data were obtained at pH 4 [10] and 1.0–2.0 [3], whereas phenolic wastewaters are generally neutral. According to the data of [3], the reaction follows pseudosecond-order kinetics, and the rate-determining step is external diffusion with an energy of activation of 11.62 kJ/mol. Matocha et al. [10] reported that the order of the reaction is pseudofirst and that the rate-determining step is surface-chemical reaction. Therefore, in the present work we examined the kinetics of phenol oxidation with manganese dioxide in aqueous phase in the temperature range from 293 to 353 K at pH 5.5±0.5. The given pH value was selected taking into account that in this case the rate of phenol oxidation does not depend on the concentration of hydroxonium ions [10]. Insofar as the pK values for the surface $>\mathrm{Mn^{IV}(OH)_2}$ groups are pK_1 = 2.3 and pK_2 = 3.3, these groups dissociate almost completely at pH 5–6, whereas the degree of dissociation of phenolic hydroxy groups is negligible.

The kinetic experiments were performed as follows. A cell maintained at a constant temperature was charged with 800 ml of an aqueous solution of phenol with a concentration of about 1 g/l, 40 g of manganese dioxide of chemically pure grade was added, and the mixture was stirred at a speed of 400 rpm. Samples of the reaction mixture with a volume of 15 ml were withdrawn at definite time intervals and analyzed for phenol, hydroquinone, and benzoquinone. All reagents were of chemically pure grade.

The concentration of phenol was determined by spectrophotometry, by measuring absorbance in the UV region at λ 235 nm [12–16]. Alkaline solutions (pH 13) of phenol and its derivatives are characterized by red shift of the absorption maxima relative to those observed in neutral solution (pH 7) due to formation of phenoxide ion. The absorbance in alkaline medium is proportional to the concentration of both major component and impurities, whereas the absorbance of the same solution neutralized to pH 7 originates only from impurities. The concentration of phenol is then given by the difference between in the optical densities at pH 13 and pH 7: $\Delta D = D_{\mathrm{pH\,13}} - D_{\mathrm{pH\,7}}$. Analysis of the electronic absorption spectra of reference aqueous solutions of phenol, hydroquinone, pyrocatechol, and resorcinol with a concentration of 5 mg/l at pH 7 showed that only phenol solution did not absorb at λ 235 nm.

The concentration of phenol was determined as follows. A 1-ml sample of a solution containing 1–0.1 g/l of phenol was transferred into a 100-ml volumetric flask, and the volume was adjusted to 100 ml by adding a 0.1 M solution of sodium hydroxide. Two 5-ml samples were withdrawn from the resulting solution. The fist sample was placed into a volumetric flask and adjusted to a volume of 10 ml by addition a solution of sodium hydroxide, and the optical density of the resulting solution at λ 235 nm was measured against 0.1 M NaOH. The second sample was diluted to a volume of 10 ml with 0.1 M hydrochloric acid, and the optical density was measured at the same wavelength relative to a neutralized sodium hydroxide solution. The optical density was linearly related to the phenol concentration up to 10 mg/l; detection limit 0.5 mg/l. Determination of phenol was possible in the presence of nitrogen and sulfur oxides, hydrogen sulfide, aldehydes, ketones, alcohols, and benzene and its homologs. Amines exhibiting an analogous red shift interfered with phenol determination.

Taking into account that phenol molecule possesses a nucleophilic center in the *para* position with respect to the hydroxy group (due to mesomeric effect), hydroquinone and 1,4-benzoquinone were presumed as oxidation products [11]. The concentration of hydroquinone was determined from the difference $D_{\mathrm{pH\,13}} - \Delta D$. The concentration of 1,4-benzoquinone was determined by spectrophotometry after oximation with hydroxylamine hydrochloride [17]. For this purpose, 0.25 ml of a solution of hydroxylamine hydrochloride with a concentration of 2 g/l was added to 2–6 ml of a solution to be analyzed, the mixture was kept for 5 min, 0.2 ml of 25% aqueous ammonia was added, and the mixture was diluted with water and alcohol (for 6-ml samples, only with alcohol) to a volume of 8 ml. The colored solution was analyzed by spectrophotometry in a 1-cm cell at λ 436 nm; the optical density was measured relative to a blank solution. The concentration of benzoquinone in 200–250 min increased to 40–50 mg/l, and the sum of the phenol, hydroquinone, and benzoquinone concentrations was equal to the initial phenol concentration. Thus the oxidation product of phenol is hydroquinone with an impurity of 1,4-benzoquinone (<10 mol %). The low oxidative power of manganese dioxide may be attributed to relatively high pH value.

In addition, we determined the concentration of manganese in solution using a Spectroscan-U X-ray fluorescent crystal diffraction spectrometer. When the reaction time was 300 min and longer, the concentration of manganese in solution did not exceed its detection limit equal to 4 mg/l. Insofar as stoi-

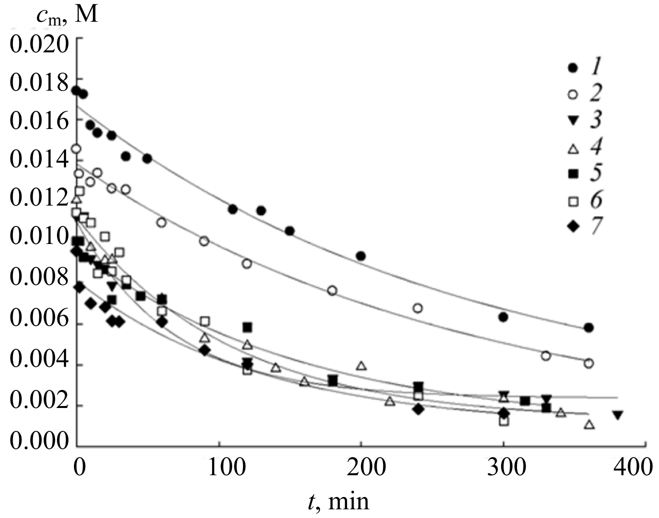

Fig. 1. Kinetic curves for the oxidation of phenol (c_m) with manganese dioxide (V/m = 20 ml/g) at (*1*) 293, (*2*) 303, (*3*) 318, (*4*) 323, (*5*) 333, (*6*) 343, (*7*) 353 K.

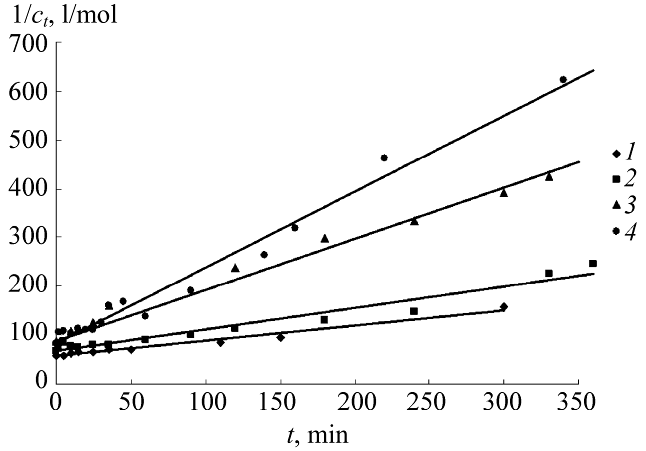

Fig. 2. Linearized kinetic dependences for the oxidation of phenol with manganese dioxide (V/m = 20 ml/g) at (*1*) 293, (*2*) 303, (*3*) 318, and (*4*) 323 K.

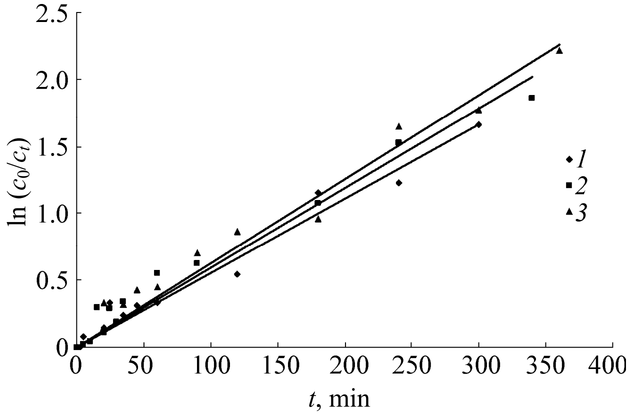

Fig. 3. Linearized kinetic dependences for the oxidation of phenol with manganese dioxide (V/m = 20 ml/g) at (*1*) 333, (*2*) 343, and (*3*) 353 K.

chiometry of a reaction analogous to reaction (1) requires the concentration of Mn^{2+} to exceed 500 mg/l, we can conclude that manganese(II) is not transferred to solution at pH > 5.

Figure 1 shows the experimental plots of phenol concentration versus time in the oxidation with manganese dioxide at pH 5.5±0.5 (V/m = 20 ml/g) at 293, 303, 318, 323, 333, 343, and 353 K. The plots obtained in the temperature range from 293 to 323 K were found to be approximated by second-order kinetic equations. Figure 2 shows the linear plots of reciprocal phenol concentration versus time. At 333–353 K, a different mechanism of the reaction is observed, and the dependences of the phenol concentration upon time fit first-order kinetic equations. The plots $\ln (c_0/c_t) = f(t)$ are given in Fig. 3, and the linear trend equations and rate constants determined from the slopes are presented in Table 1.

The dependences $\ln k = f(T^{-1})$ shown in Fig. 4 are described by linear equations $y = -5052x + 15.988$ ($R^2 = 0.98$) in the temperature range from 293 to 323 K and $y = -800.12x - 2.795$ ($R^2 = 0.98$) at 333–353 K. The energies of activation calculated from the slopes of the linear trends ($E_a = R\tan\alpha$) are given in Table 1.

Change of the reaction kinetics in the temperature range from 323 to 333 K indicates change of the rate-determining step. On the basis of the reaction order (n = 2) and energy of activation (42.0 kJ/mol) we presumed that the rate-determining step at 293–323 K is the formation of activated complex on the solid phase surface, as in the oxidation of pyrocatechol over birnessite surface [10]. The energy of activation determined in the present work is lower than the value 58.7±6.6 kJ/mol reported in [10]. This may be due to formation of pyrocatechol activated complex with more sophisticated structure (coordination of two functional groups to manganese). The different orders of the reaction may be rationalized by the fact that manganese(IV) is reduced to Mn^{2+} with stable $3d^5$ electron configuration. Manganese(III) lacks one electron to fill the $3d$ sublevel by half and is unstable. Pyrocatechol molecule donates two electrons to manganese(IV) atom; therefore, the surface reaction is of first order. On the other hand, the reduction of Mn^{4+} to Mn^{2+} requires two phenol molecules, so that the rate-determining step is bimolecular, and the order of the reaction is equal to 2.

The above assumptions were confirmed by analysis of the kinetic dependence at 318 K and at a V/m ratio

Table 1. Kinetic parameters for the oxidation of phenol with manganese dioxide at V/m = 20 ml/g

T, K	Reaction order n	Trend equation	Rate constant k, mol l^{-1} min^{-1}	E_a, kJ/mol
293	2	$y = 0.314x + 57.48$; R^2 0.98	0.314	42.0
303	"	$y = 0.440x + 68.75$; R^2 0.95	0.440	"
318	"	$y = 1.047x + 88.80$; R^2 0.98	1.047	"
323	"	$y = 1.556x + 82.91$; R^2 0.98	1.556	"
333	1	$y = 0.0055x$; R^2 0.97	0.0055[a]	6.65
343	"	$y = 0.0060x$; R^2 0.96	0.0060[a]	"
353	"	$y = 0.0063x$; R^2 0.97	0.0063[a]	"

[a] min^{-1}.

equal to 50 ml/g. The experimental data are collected in Table 2, and linearized kinetic dependence in the coordinates c^{-1}—$f(t)$ is shown in Fig. 5.

The linear trend is described by the equation $y = 1.050x + 58.28$ with a reliability factor R^2 of 0.99. The rate constant at V/m = 50 ml/g, k_{45} = 1.050 l mol^{-1} min^{-1}, coincided with the value obtained V/m = 20 ml/g, k_{45} = 1.047 l mol^{-1} min^{-1} (Table 1). The fact that the rate constant does not depend on the ratio V/m indicates kinetic control of the process, where the rate-determining step is surface reaction. By analogy with the data of [10], the following reaction mechanism may be proposed.

(1) Formation of activated complex via reaction of manganese(IV) at nucleophilic center of the phenol molecule in the *para* position with respect to the hydroxy group. The $>Mn^{IV}(OH)_2$ groups undergo dissociation, while protons do not participate in the reaction at pH 5.5±0.5. The rate-determining step is bimolecular in phenol;

$$>\overset{\delta+}{Mn}{}^{IV}(2O^-) + 2\,\overset{\delta-}{C}{}_6H_5OH \rightleftarrows [>\overset{\delta+}{Mn}{}^{IV}(2O^-)] \cdots\cdots (2\,\overset{\delta-}{C}{}_6H_5OH)$$

(2) Electron transfer is a fast step;

$$[>\overset{\delta+}{Mn}{}^{IV}(2O^-)] \cdots\cdots (2\,\overset{\delta-}{C}{}_6H_5OH)$$

$$\rightarrow\ >\overset{\delta+}{Mn}{}^{II} \cdots\cdots (2O^-) \cdots\cdots (2\,\overset{+}{C}{}_6H_5OH)$$

(3) Decomposition of the activated complex with formation of products. Manganese(II) species are not transferred to solution, and they reside on the solid phase surface. According to [7, 8], Mn^{2+} species are then oxidized to MnO_2 with dissolved oxygen. The major oxidation product is hydroquinone, whereas less than 10% of phenol is oxidized to 1,4-benzoquinone.

The overall reaction equation with account taken of preliminary hydrolysis of surface groups and dissociation of $Mn^{IV}(OH)_2$ groups looks as follows.

$$MnO_2\ (\text{solid}) + 2\ C_6H_5OH\ (\text{solution}) + H_2O\ (\text{liquid})$$
$$\rightleftarrows MnO\ (\text{solid}) + 2\ HOC_6H_4\text{–}OH\ (\text{solution})$$
$$+\ 2\ H^+\ (\text{hydrated})$$

Table 2. Dependence of the concentration of phenol on time at V/m = 50 ml/g

Time, min	c, M	
	318 K	343 K
0	0.0141	0.0172
2	0.0139	0.0159
5	0.0136	0.0141
10	0.0132	0.0144
15	0.0129	0.0143
25	0.0127	0.0140
35	0.0125	0.0102
60	0.0121	0.0086
90	0.0100	0.0063
120	0.0089	0.0059
180	0.0078	0.0042
240	0.0063	0.0033
300	–	0.0028
330	0.0043	–
360	–	0.0024

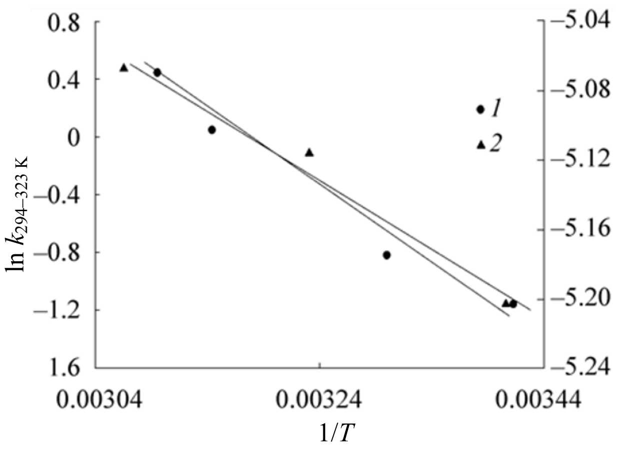

Fig. 4. Plots of ln*k* vs. reciprocal temperature in the temperature ranges (*1*) 333–353 and (*2*) 293–323 K.

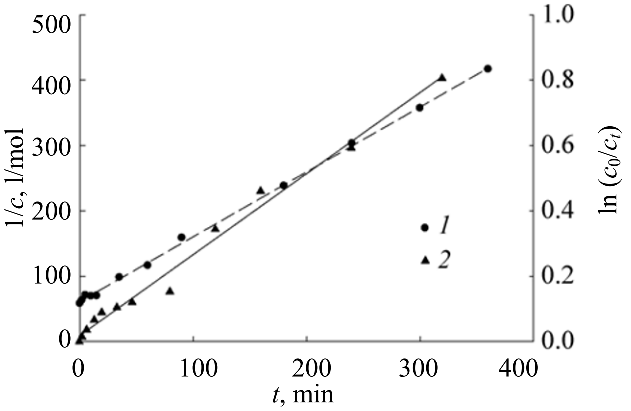

Fig. 5. Linearized kinetic dependences for the oxidation of phenol with manganese dioxide (*V*/*m* = 50 ml/g) (*1*) at 318 K in the coordinates 1/*c*—*f*(*t*) and (*2*) at 343 K in the coordinates ln (c_0/c_t)—*f*(*t*).

$$>\overset{\delta+}{\mathrm{Mn}}{}^{\mathrm{II}}\cdots\cdots(2\mathrm{O}^-)\cdots\cdots(2\,\mathrm{C}_6\overset{+}{\mathrm{H}}_5\mathrm{OH}) \rightarrow\ >\overset{\delta+}{\mathrm{Mn}}{}^{\mathrm{II}} + 2\,\mathrm{HO–C_6H_5–OH}$$

The reaction rate rapidly increases as the temperature rises, and at 333–353 K the process is controlled by external diffusion. Here, the rate-determining step is stationary convective diffusion of phenol molecules in the Nernst layer. This is consistent with pseudofirst order of the reaction and low energy of activation, 6.65 kJ/mol. An additional support to the above assumption was obtained by analysis of the kinetic dependence at 343 K at a *V*/*m* ratio of 50 ml/g. The experimental data are given in Table 2, and the kinetic dependence linearized in the coordinates ln (c_0/c_t)—*f*(*t*) is shown in Fig. 5. The linear trend is described by the equation $y = 0.0035x$ with a reliability factor R^2 of 0.99. The rate constant at *V*/*m* = 50 ml/g is k_{70} = 0.0035 min^{-1}, which is lower than at *V*/*m* = 20 ml/g, k_{70} = 0.0060 min^{-1}. The fact that the rate constant depends on the ratio *V*/*m* suggests that the reaction rate is limited by external diffusion. The oxidation of pyrocatechol was studied in [10] at lower temperatures (283–298 K); therefore, the process occurred in the kinetic mode. The oxidation of phenol at 293–333 K [3] was found to be controlled by external diffusion with an energy of activation of 11.62 kJ/mol. However, the kinetic region was not identified. A probable reason is that the reaction was studied in [3] at low pH values (1–2) at which manganese dioxide possesses a higher oxidation potential. According to the Nernst equation, $\varphi(\mathrm{MnO_2, H^+/Mn^{2+}, H_2O}) = 1.23 - 0.118\,\mathrm{pH}$.

At pH < 2, $\mathrm{Mn^{IV}(OH)_2}$ groups on the solid phase surface almost do not undergo dissociation, the $\mathrm{MnO_2}$ surface has no negative charge, and the reaction with nucleophilic centers in phenol molecules is facilitated. Therefore, the surface reaction in acid medium is faster, and the overall rate of the process is limited by diffusion.

Thus the major oxidation product of phenol at pH 5.5±0.5 is hydroquinone; 1,4-benzoquinone is formed in an amount of less than 10 mol %, and $\mathrm{Mn^{2+}}$ species are not transferred to solution. In the temperature range from 293 to 323 K the reaction is characterized by second order with respect to phenol, the energy of activation is 42.0 kJ/mol, and the rate-determining step is surface chemical reaction. The reaction at 333–353 K follows pseudofirst-order kinetics with an energy of activation of 6.65 kJ/mol, the rate-determining step being external diffusion.

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