Fe-Montmorillonites in the Reaction of Organic Dyes Oxidation

S. TS. KHANKHASAEVA[1], L. V. BRYZGALOVA[1], E. TS. DASHINAMZHILOVA[1] and A. A. RYAZANTSEV[2]

[1]*Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, Ul. Sakh'yanovoy 8, Ulan Ude 670047 (Russia)*

E-mail: shan@bsc.buryatia.ru

[2]*Siberian Transport University, Ul. D. Kovalchuk 191, Novosibirsk 630049 (Russia)*

E-mail: raastu@irs.ru

Abstract

Regularities in catalytic oxidation of "Acid chrome dark blue" dye in water solutions are studied under the effect of Fe-montmorillonite catalyst obtained by intercalation of iron polyhydroxocomplexes into the montmorillonite clay from Mukhortalinskoye deposit (Buryatia). An impact of the initial concentrations of reagents, temperatures, and pH on the reaction rate is studied. The outcomes of organic dyes oxidation bear witness to the possibility of practical application of Fe-montmorillonite catalyst in the processes of sewage decontamination from dyes.

INTRODUCTION

Presently, one of the topical environmental problems remains the neutralization of sewage from various pollutants, in particular from dyes. More than 80 % of synthetic dyes show carcinogenic, mutagen, and allergic effect with respect to living organisms. The maximum permissible concentration of dyes in the sewage discharged into the water bodies depends on the dye type and can amount from 0.05 to 0.5 mg/l; meanwhile their content in the sewage of many manufactures is as great as 5–10 mg/l [1].

The catalytic methods using ecologically clean oxidizers, specifically, ozone, oxygen, and hydrogen peroxide are most advantageous for sewage decontamination from dyes. Hydrogen peroxide possesses a number of technological benefits over ozone and oxygen, and finds ever-widening applications in practice of sewage decontamination from organic compounds [2]. Owing to their high activity, iron ions Fe^{2+} and Fe^{3+} (Fenton and Raff systems) [3] are most often used as catalysts. The need for the subsequent additional treatment of water solutions to remove iron ions from them and activity of the specified systems in the limited range of pH stimulate a search for heterogeneous catalysts based on iron compounds [4, 5]. The layer-columnar structured pillar materials obtained on the basis of natural layered silicates and on the basis of hydroxocations of transition elements, in particular iron, attract great interest for their use as catalysts, since their catalytic properties in water solutions are practically unstudied. Previously we have examined textural and adsorption properties of such materials obtained on the basis of montmorillonite (MM) and polyhydroxocomplexes of iron (III) [6], and showed the possibility of their application as oxidation catalysts of phenols in water solutions [7].

The purpose of this work is studying the regularities of catalytic oxidation of anionic organic dyes by hydrogen peroxide under the effect of Fe-montmorillonite.
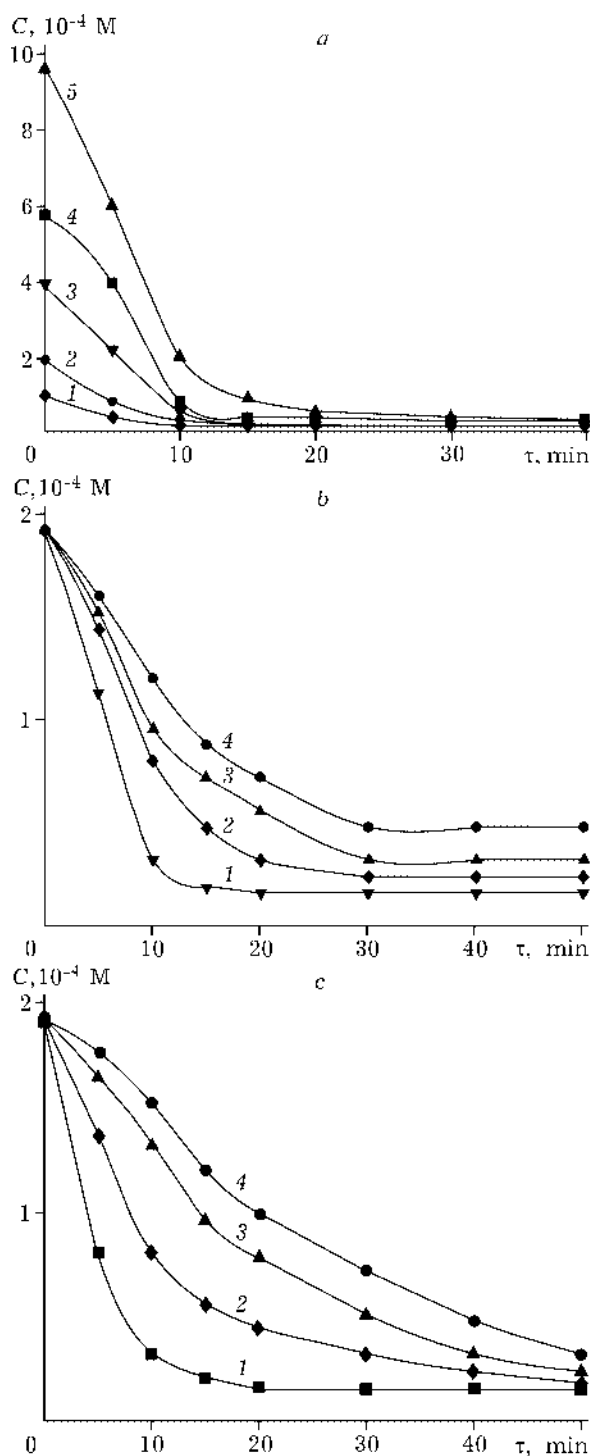
Fig. 1. Dependence of ACDB concentration on time at different initial concentrations of dye (*a*), hydrogen peroxide (*b*) and catalyst (*c*) (pH 2.0, $t = 40\,^{\circ}C$): *a* – [ACDB], 10^{-3} mol/l: 9.6 (*1*), 19.3 (*2*), 38.6 (*3*), 57.8 (*4*), 96.4 (*5*); [Fe-MM] = 5.0 g/l, [H_2O_2] = 2.0 M; *b* – [H_2O_2], 10^{-3} mol/l: 50 (*1*), 6.9 (*2*), 3.45 (*3*), 1.72 (*4*), [Fe-MM] = 5.0 g/l, [ACDB] = 1.92 10^{-4} M; *c* – [Fe-MM], g/l: 5.0 (*1*), 2.5 (*2*), 1.0 (*3*), 0.5 (*4*), [H_2O_2] = 0.05 M, [ACDB] = 1.92 10^{-4} M.

EXPERIMENTAL

To yield Fe-montmorillonite (Fe-MM) catalyst, the clay from Mukhortalinskoye deposit (Buryatia) presented predominantly by montmorillonite (90 %) has been used. The natural mineral (composition, mass fraction, %: SiO_2 65.5, Al_2O_3 14.3, Fe_2O_3 1.8, CaO 1.5, MgO 1.1, K_2O 0.2, Na_2O 0.1, H_2O 15.5) was suspended in the distilled water, levigated, and fine-dispersed fraction was separated by centrifugation. The catalyst was obtained with the method described in [6] and exposed to heat treatment at 500 °C within 2 h. Unlike [6], suspension of clay prior to sol introduction was treated with ultrasound of frequency 22 kHz for 5 min.

Iron content of the obtained catalyst was determined photometrically with *ortho*-phenanthroline [8] upon the catalyst standing in concentrated HCl during 1 day. Iron content of Fe-MM specimen was 37.5 mg/g.

Textural characteristics of Fe-MM were determined similar to [6]. Specific surface of the catalyst comprised 121.68 m^2/g, average diameter of pores 89.3 Å, total pore volume was 0.28 cm^3/g.

Azo dye "Acid chrome dark blue" (ACDB) of composition $C_{16}H_9O_9Na_2ClS_2N_2$ was used in the work. Kinetic experiments were conducted in the temperature-controlled reactor with stirring by a magnetic stirrer. Kinetics of dye oxidation was studied from changing of optical density of the dye solution in time. The density was measured in spectrophotometer Agilent 8453 UV-VIS at $\lambda_{max} = 590$ nm. Dye concentration was determined from the calibration plot of optical density of dye solution versus dye concentration. Dye concentration in the solution varied in the range from 9.6 10^{-5} to 9.64 10^{-4} M, that of hydrogen peroxide, from 1.72 10^{-3} to 2.0 M, concentration of catalyst, from 0.5 to 5.0 g/l; pH changed from 2.0 to 5.0. The degree of dye oxidation was determined from the ratio of the quantity of the reacted dye to its initial quantity multiplied by 100 %.

To determine the order of a reaction in respect to components of the reaction mixture (Fe-MM, H_2O_2, ACDB, H^+), the experiments were performed where the concentrations of three components were kept constant, and the

concentration of the fourth one varied. The order of a reaction in respect to components was determined with the method of initial velocities [9]. To determine activation energy, the reaction of dye oxidation was conducted at the temperatures of 25, 40, and 45 °C.

RESULTS AND DISCUSSION

According to the experimental data, dye oxidation rate depends on the initial concentrations of ACDB, H_2O_2, and Fe-MM catalyst (Fig. 1, a–c). Experimental order of a reaction in respect to ACDB dye was equal to 0.5, in respect to the catalyst, 0.6. Reaction order in respect to hydrogen peroxide at initial concentrations of the latter of $1.72 \cdot 10^{-3}$ M comprised 0.5; at higher values, the order is close to zero. Reaction rate of ACDB oxidation depends not only on the initial concentration of reagents, but also on pH (Fig. 2): it decreases, as pH increases from 2.0 to 5.0. Reaction order in respect to H^+ ions concentration was 0.83.

Dye oxidation rate increases with an increase in the reaction temperature from 25 to 45 °C. Activation energy of the reaction of ACDB oxidation in the presence of Fe-MM, determined from the logarithmic form of the Arrhenius equation, comprised 37.4 kJ/mol. The obtained value of activation energy is in a good agreement with the values characteristic of radical-chain reactions in water solutions.

Since the conditions of the reaction in acidic medium make possible washing out of iron ions from the catalyst, we performed the experiments on determination of the concentration of iron ions in the solution. Table 1 presents data on the kinetics of iron ions washout from a specimen of Fe-MM catalyst at various temperatures and pH. It is evident that the degree of washing out of iron ions from Fe-MM catalyst increases with increasing temperature and with decreasing pH. The highest degree of washing out of iron is evidenced at pH 2.0 and comprises 0.7 % at 25 °C and 6.6 % at 40 °C that is considerably lower than the degree of washing out of active metal for known iron-bearing catalysts [4]. The data obtained suggest that the reaction of ACDB oxidation at low pH values proceeds through a homogeneous-heterogeneous
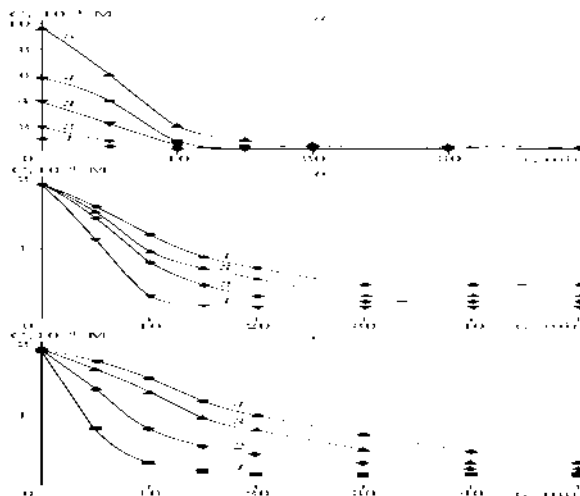

Fig. 2. Dependence of ACDB concentration on time at various pH: 2.0 (1), 3.0 (2), 4.0 (3), 5.0 (4); [Fe-MM] = 5.0 g/l, $[H_2O_2]$ = 2.0 M, [ACDB] = $1.92 \cdot 10^{-4}$ M, t = 40 °C.

mechanism. To estimate the contribution of homogeneous reaction, we performed additional experiments on ACDB oxidation in the presence of $FeCl_3$ solution. The strength of $FeCl_3$ solution in homogeneous reaction has been calculated based on the degree of washing out of iron from the catalyst at various temperatures for 60 min. Data on kinetics of ACDB homogeneous oxidation suggest that the contribution of homogeneous reaction to the total reaction rate is 8.3 % at pH 2.0 and 25 °C. As the temperature increases, the contribution of homogeneous reaction grows according to an increase in quantity of iron ions passing into solution. As is suggested by data from Table 1, the degree of iron washing out from catalyst at pH > 3.0 is insignificant and the reaction proceeds through a heterogeneous mechanism. This is supported by the circumstance that the re-
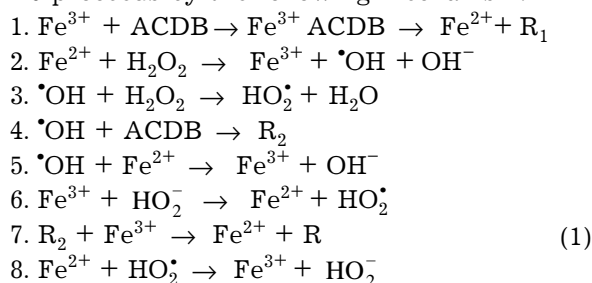
TABLE 1

Kinetics of washing out of iron ions from Fe-MM at various temperatures and pH

pH	Degree of washing out (%), at a temperature of							
	25 °C				40 °C			
	during a period of τ, min							
	10	20	30	60	10	20	30	60
2.0	0.4	0.6	0.7	0.7	3.0	3.5	3.9	6.6
3.0	0.2	0.3	0.3	0.3	1.0	1.5	1.8	2.3
4.0	<0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.5

action does not run in the mixture filtered off from the catalyst.

Literature data on the mechanism of ACDB dye oxidation under the effect of heterogeneous iron-bearing catalysts are rather scarce; therefore, we performed a correlation of the obtained kinetic data with the mechanism of ACDB oxidation under the effect of iron ions in water solutions. It is known [3] that ACDB oxidation by hydrogen peroxide under the effect of Fe^{3+} ions generates $^{\bullet}OH$ and HO_2 radicals, and reaction of ACDB oxidation at pH 2.0 proceeds by the following mechanism:

1. $Fe^{3+} + ACDB \rightarrow Fe^{3+} ACDB \rightarrow Fe^{2+} + R_1$
2. $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$
3. ${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$
4. ${}^{\bullet}OH + ACDB \rightarrow R_2$
5. ${}^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$
6. $Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2^{\bullet}$
7. $R_2 + Fe^{3+} \rightarrow Fe^{2+} + R$ (1)
8. $Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^-$

where R, R_1, R_2 are the radicals being formed in ACDB oxidation.

For the homogeneous ACDB oxidation rate (W), the steady-state concentration method at pH 2.0 gives an expression [3], $W = k_{exp}[Fe^{3+}]_0[H_2O_2]_0^{0.5}[ACDB]_0^{0.5}$, where k_{exp} is an effective kinetic constant of ACDB oxidation under the effect of iron ions [see the scheme (1)]. The kinetic equation obtained by us for ACDB oxidation under the effect of Fe-MM at pH 2.0 is of the following form: $W = k_{exp}[Fe^{3+}]_0^{0.6}[H_2O_2]_0^{0.5}[ACDB]_0^{0.5}$, where k_{exp} is an experimental kinetic constant of ACDB oxidation under the effect of Fe-MM. At rather high $[H_2O_2]$, when $^{\bullet}OH$ is consumed predominantly by the reaction with hydrogen peroxide (see the scheme (1), the stage No. 3), ACDB oxidation rate is independent of $[H_2O_2]$; the similar dependence is observed also in the case of Fe-MM catalyst, when $[H_2O_2]$ is higher than 0.05 M.

The experimental kinetic equation of ACDB oxidation obtained by us under the effect of Fe-MM is similar to that for ACDB oxidation under the effect of iron ions, thus we can make a conclusion that ACDB oxidation in the system Fe-MM−H_2O_2 may proceed through the mechanism similar to the scheme (1). The set of the kinetic data obtained allows thus far making only qualitative remarks on the mechanism of heterogeneous oxidation of dyes in the presence of Fe-MM. A detailed determination of the reaction mechanism invites further investigations.

We performed the experiments to evaluate the degree of oxidation of ACDB dye ($1.9 \ 10^{-4}$ mol/l) by hydrogen peroxide in the presence of Fe-MM (5.0 g/l) with the various pH and temperatures. Oxidation was carried out for 110 min. The obtained results are presented in Table 2. It is evident that the degree of dye oxidation grows with an increase in temperature and concentration of hydrogen peroxide up to 0.05 M. Further increase in the concentration of hydrogen peroxide has practically no effect on the change of the degree of dye oxidation owing to the consumption of $^{\bullet}OH$ radicals by the reaction with H_2O_2. The catalyst is active throughout the entire studied range of pH (2.0−6.2). The greatest degree of dye oxidation (99.8 %) is evidenced at pH 2.0 under conditions when the reaction proceeds by a homogeneous-heterogeneous mechanism. However, as is suggested by data of Table 2, in conditions when washing out of iron ions from the catalyst is insignificant and the reaction proceeds by a heterogeneous mechanism (pH ≥ 3.0), the degree of dyes oxidation remains rather high too. With the re-use of the catalyst at pH 3.2, a decrease

TABLE 2

Outcomes of ACDB dye oxidation in water solutions in the presence of Fe-MM

Experiment No.	t, °C	pH	$[H_2O_2]$, mol/l	Degree of oxidation, %
1	40	2.0	0.01	83.8
2			0.02	98.5
3			0.05	99.8
4			0.10	99.6
5			0.20	99.5
6			2.00	99.3
7		3.0	2.00	99.1
8		4.0		91.8
9		5.0		62.5
10	25	2.0	0.05	89.6
11		3.2		85.1
12*		3.2		84.7

*The catalyst was re-used upon washing with water and drying at 160 °C for 2 h.

in the degree of ACDB dye oxidation was insignificant (0.4 %), which confirms the evidence on stability of the catalyst at pH ≥ 3. Based on the above data on the impact of the reaction conditions on the degree of dyes oxidation and stability of the catalyst, the optimum conditions for the reaction to carry out may be considered the following: pH ≥ 3, concentration of hydrogen peroxide 0.05 M, the temperature $25-40\ ^{\circ}C$.

CONCLUSIONS

Kinetic regularities in oxidation of "Acid chrome dark blue" dye in water solutions under the effect of Fe-MM catalyst obtained through intercalation of iron polyhydroxocomplexes into the montmorillonite clay from Mukhortalinskoye deposit are explored. An effect of the initial concentration of reagents, of temperature, and pH on the reaction rate is studied. The optimum conditions of the reaction are determined, which make it possible to attain a high degree of dye oxidation and stability of the catalyst. The results on oxidation of the organic dyes, the use of which is made in textile manufactures, bear witness to the possibility of practical application of Fe-MM catalyst in the oxidation processes of dyes solutions.

Acknowledgement

REFERENCES

1 S. V. Kholodkevich, G. G. Yushina, E. S. Apostolova, *Ekol. Khim.*, 5 (1996) 75.
2 L. V. Panov, V. P. Panov, *Zh. Prikl. Khim.*, 73 (2000) 615.
3 A. Ya. Sychev, V. G. Isak, Gomogenny kataliz soyedineniyami zheleza, Shtiintsa, Kishinev, 1988.
4 O. P. Pestunova, O. L. Ogorodnikova, V. N. Parmon, *Chemistry for Sustainable Development*, 11 (2003) 227. http://www-psb.ad-sbras.nsc.ru
5 K. Fajerwerg, H. Debellefontaine, *Appl. Catal. B: Environmental*, 10 (1996) 229.
6 M. A. Shchapova, S. Ts. Khankhasaeva, A. A. Ryazantsev et al., *Chemistry for Sustainable Development*, 10 (2002) 347. http://www-psb.ad-sbras.nsc.ru
7 M. A. Shchapova, S. Ts. Khankhasaeva, A. A. Ryazantsev, *Ekologiya Prom-st Rossii*, 6 (2001) 15.
8 Yu. Yu. Lurie, Analiticheskaya khimiya promyshlennykh i stochnykh vod, Khimiya. Moscow, 1984.
9 I. V. Berezin, A. A. Klesov, Prakticheskiy kurs khimicheskoy i fermentativnoy kinetiki, Izd-vo MGU, Moscow, 1976.