



PHYSICAL CHEMISTRY 2021

15th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

The Conference is dedicated to the

*30th Anniversary of the founding of the Society of Physical
Chemists of Serbia*

and

100th Anniversary of Bray-Liebhafsky reaction

**September 20-24, 2021
Belgrade, Serbia**

Title: Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8

Volume I: ISBN 978-86-82475-38-5

Editors: Željko Čupić and Slobodan Anić

Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: "Jovan", <Printing and Publishing Company, 200 Copies

Number of pages: 6+344, Format A4, printing finished in December 2021

Text and Layout: "Jovan"

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Organized by

*The Society of Physical Chemists of
Serbia*

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

*Borekov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences*

and

University of Belgrade, Serbia:

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KINETIC AND THERMODYNAMIC STUDY OF THE OXIDATIVE CATALYTIC DEGRADATION OF ACID ORANGE 10 IN THE PRESENCE OF OXONE® AND COBALT BASED CATALYST

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ABSTRACT

Catalytic degradation of Acid Orange 10 in the presence of Oxone® activated by Co-impregnated acid activated montmorillonite as catalyst was investigated. The catalytic experiments were performed at different temperatures in range from 303 to 333 K in order to determinate kinetics parameters. The kinetics data followed the first-order kinetics model. The activation energy of the investigated degradation process was calculated according to the Arrhenius equation.

INTRODUCTION

Degradation of pollutants present in effluents of textile industry received high attention since dyes and pigments from these effluents showed carcinogenic and mutagenic effects [1]. Most azo dyes have stable chemical structure, highly resistant to bio-treatment. Therefore, different physical-chemical methods such as adsorption or catalytic oxidative degradation have been employed in order to decrease concentration of pollutants in wastewaters of textile industry [1].

In this paper standard clay from Wyoming deposit with high content of montmorillonite was acid activated and then impregnated with cobalt, using incipient wetness impregnation method. The obtained catalyst was evaluated in oxidative degradation of Acid Orange 10 (AO10) with respect to degradation time and temperature. The kinetic and thermodynamic parameters were deduced from the catalytic tests. These data could be very useful in elucidating the nature of oxidative degradation process of investigated catalytic system.

EXPERIMENTAL

Materials

The sodium rich montmorillonite from Wyoming (MW) was supplied by The Clay Minerals Society repository (USA). MW was acid activated using HCl (35 wt. %, Lach-Ner). The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (≥ 98 % purity), Oxone® ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) and Acid Orange 10 (AO10, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$) were purchased from Sigma Aldrich. The AO10 was tested as model pollutant.

Catalyst synthesis

The acid activation of MW was performed using previously described method with 4.5 M HCl [2] in order to improve textural properties of raw clay. The cation exchange capacity (CEC) after activation was determined by standard ammonium acetate method [3]. The cobalt was introduced in the amount equal to CEC value, following procedure of wetness impregnation method ($1.0\text{Co}/\text{MW}_A$) [4].

Catalytic test

The catalytic degradation was carried out in thermostated reactor at temperatures: 303, 313, 323 and 333 K. The catalytic test was performed using 10 mg of catalysts in 200 cm^3 dye solution ($C_{\text{dye}}=50\text{ mg dm}^{-3}$) in the presence of Oxone® (0.2 g dm^{-3}) with respect to predetermined time (10, 20, 30, 60, 120 and 240 min). Solid and liquid phase were separated by centrifugation at 17000 rpm for 3 min,

and analyzed using a Thermo Electron Nicolet Evolution 500 UV–VIS spectrophotometer. Characteristic AO10 UV absorption peak at 478 nm was used for degradation monitoring.

Applied kinetic and thermodynamic models

The obtained catalytic data for each investigated temperature were treated with different kinetic models [5]. The first-order kinetics model was found to be the most appropriate. In (Eq. 1) this model is given in exponential form:

$$Y_t = Xe^{-kt} + E \quad (\text{Eq. 1})$$

Where: X is the amplitude, k is the first-order rate constant, and E is the endpoint.

Arrhenius relationship was used to evaluate the activation energy of adsorption:

$$\ln k_1 = \ln A - \frac{E_a}{RT} \quad (\text{Eq. 2})$$

Where: k_1 is first-order kinetics rate constant, E_a is the Arrhenius activation energy (kJ/mol), A is the Arrhenius factor, R is the gas constant (8.314 J/mol K) and T is the temperature (K).

RESULTS AND DISSCUSION

The catalytic data together with the first-order kinetics models are given in Fig. 1a. The calculated kinetic parameters are presented in Table 1. The obtained k values are used to construct Arrhenius plot (Fig. 1b).

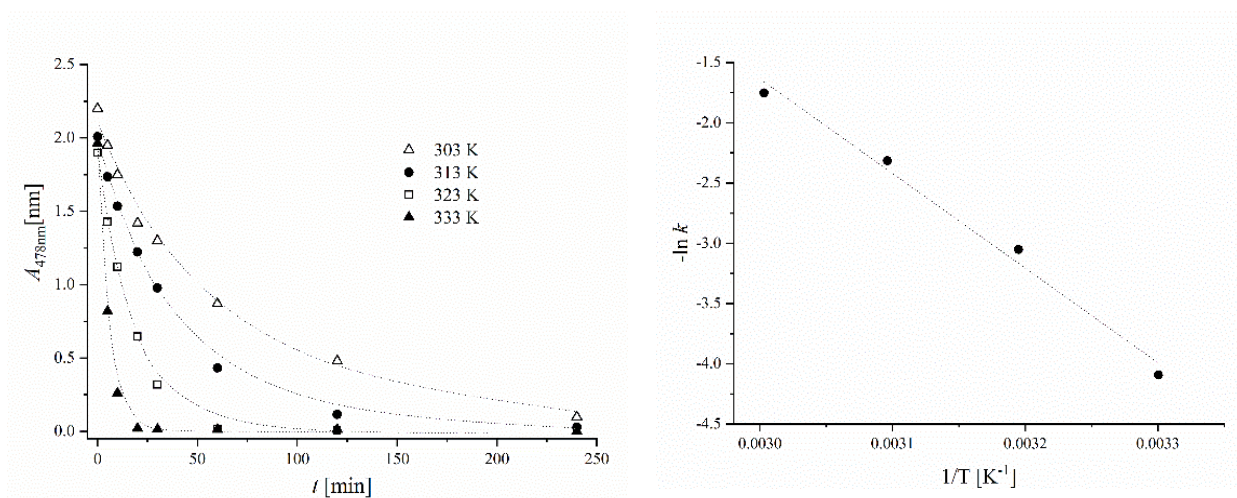


Figure 1. a) Experimental data and the first-order fitting curves for reaction of catalytic degradation of AO10 in the presence of 1.0Co/MW_A catalyst and Oxone® at different temperatures; b) Arrhenius plot of investigated process.

Table 1. Parameters calculated by fitting experimental data of catalytic degradation of AO10 with exponential fit (Eq. 1)

T [K]	k [min ⁻¹]	X [arb. unit]	E [arb. unit]	R^2	$\Sigma\sigma_i$
303	$1.67 \cdot 10^{-2} \pm$ $2.2 \cdot 10^{-3}$	$2.005 \pm$ 0.096	$0.099 \pm$ 0.022	0.989	$4.39 \cdot 10^{-2}$
313	$0.0251 \pm$ $7 \cdot 10^{-4}$	$1.972 \pm$ 0.022	$0.018 \pm$ 0.008	0.999	$2.72 \cdot 10^{-3}$
323	$0.0551 \pm$ $2.1 \cdot 10^{-3}$	$1.918 \pm$ 0.029	$0.0143 \pm$ 0.0083	0.998	$5.15 \cdot 10^{-3}$
333	$0.186 \pm$ $8 \cdot 10^{-3}$	$1.973 \pm$ 0.034	$0.001 \pm$ 0.0001	0.998	$4.87 \cdot 10^{-3}$

Where: X - amplitude of absorbance, E – endpoint of absorbance, k – first-order rate kinetics constant, R^2 – square of the coefficient of correlation, and $\Sigma\sigma_i$ – sum of squared deviations.

The process kinetics showed good agreement with the exponential fit with the squares of coefficients of correlation of ≥ 0.989 . Thus, the first-order kinetics for the investigated process was confirmed. Along with the increase of temperature of degradation process, the value of the first-order rate kinetics constant increased.

The activation energy E_a , obtained from slope of $\ln k_1$ plotted versus $1/T$ (Fig. 1b) has value of 1.16 kJ mol⁻¹. The obtained result was much lower than those previously reported in literature for similar processes of catalytic degradation of dyes [6].

CONCLUSION

The catalyst obtained by cobalt impregnation of acid activated montmorillonite was used for oxidative degradation of Acid Orange 10 dye in the presence of Oxone® at different temperature (303K - 333K). It was estimated that catalytic data obeyed first-order kinetics model, while calculated first-order rate constant (k_1) increased with temperature. The activation energy (E_a) for AO 10 degradation was evaluated using the k_1 values for investigated temperatures and Arrhenius equation. The obtained value for E_a of 1.16 kJ mol⁻¹ was much lower than those previously reported in literature for similar processes of catalytic degradation of dyes.

Acknowledgement

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2020-14/200026).

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