



**PHYSICAL CHEMISTRY 2022**

16<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

Proceedings  
Volume I

**September 26-30, 2022**  
**Belgrade, Serbia**

**Title:** PHYSICAL CHEMISTRY 2022, 16<sup>th</sup> International Conference of Fundamental and Applied Aspects of Physical Chemistry (Proceedings) **ISBN** 978-86-82475-41-5

**Volume I:** ISBN 978-86-82475-42-2

**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, Ilije Đuričića 19, 200 Copies

**Number of pages:** 6+320, Format A4, printing finished in December 2022.

Text and Layout: "Jovan"

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

200 - *Copy printing*



# PHYSICAL CHEMISTRY 2022

*16<sup>th</sup> International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*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:*

*Faculty of Physical Chemistry  
Institute of Chemistry, Technology and Metallurgy  
Vinča Institute of Nuclear Sciences  
Faculty of Pharmacy*

*and*

*Institute of General and Physical Chemistry, Belgrade, Serbia*

## International Organizing Committee

**Chairman:** S. Anić (Serbia)

**Vice-chairman:** M. Gabrovska (Bulgaria)

A. A. Vedyagin (Russia)

S. N. Blagojević (Serbia)

**Members:** N. Cvjetičanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), A. Ivanović-Šašić (Serbia), D. Jovanović (Serbia), N. Jović-Jovičić (Serbia), M. Kuzmanović (Serbia), S. Maćešić (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović Bijelić (Serbia), B. Simonović (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia),

## International Scientific Committee

**Chairman:** Ž. Čupić (Serbia)

**Vice-chairman:** V. Bukhtiyarov (Russia)

S. Todorova (Bulgaria)

B. Adnađević (Serbia)

**Members:** S. Anić (Serbia), A. Antić-Jovanović (Serbia), A. Azizoglu (Turkey), R. Cervellati (Italy), A. Clayton (Australia), A. Cristina Silva (Portugal) G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), R. Faria (Brasil), M. Fronczak (Poland), I. Grinvald (Russia), P. Humpolíček (Czech), M. Jeremić (Serbia), I. Kiss (USA), E. Kiš (Serbia), A.V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), T. Kowalska (Poland), G. Kyzas (Greece), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), N. Ostrovski (Serbia), V. Parmon (Russia), J. Pérez-Mercader (USA) Z. Petkova Cherkezova-Zheleva (Bulgary), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), D. Stanisavljev (Serbia), N. Stepanov (Russia), Zs. Szakacs (Romania), Z. Šaponjić (Serbia), Á. Tóth (Hungary), M. Trtica (Serbia), H. Varela (Brasil), V. Vasić (Serbia), Nadezda Vasilyeva (Russia), D. Veselinović (Serbia), V. Vukojević (Sweden), A. De Wit (Belgium)

## Local Executive Committee

**Chairman:** S. N. Blagojević

**Vice-chairman:** A. Ivanović-Šašić

**Members:** M. Ajduković, I. N. Bubanja, D. Dimić, J. Dostanić, D. Drakulić, S. Jovanović, Z. Jovanović, D. Lončarević, J. Krstić, B. Marković, J. Maksimović, S. Marinović, D. Milenković, T. Mudrinić, M. Pagnacco, N. Potkonjak, B. Stanković, I. Stefanović, A. Todorović, M. Vasić, F. Veljković, M. Pejčić, G. Stevanović, H.Šalipur.K. Milošević, S. Pavlović, V. Kostić, B. Milovanović.

## CATALYTIC PROPERTIES OF COBALT-DOPED ALUMINA CATALYST IN OXONE<sup>®</sup> ACTIVATED DEGRADATION OF ORANGE G

S. Marinović, T. Mudrinić, M. Ajduković, N. Jović-Jovičić, P. Banković and T. Novaković

*University of Belgrade, Institute of Chemistry, Technology and Metallurgy  
Njegoševa 12, 11000 Belgrade, Serbia.  
(sanja.marinovic@ihtm.bg.ac.rs; sanja@nanosys.ihtm.bg.ac.rs)*

### ABSTRACT

Cobalt-doped alumina catalyst was synthesized using the sol-gel method, gelled and calcined at 500 °C. The synthesized material was previously fully characterized. Cobalt-doped alumina was tested as catalysts in an Orange G degradation in the presence of Oxone<sup>®</sup>. Oxone<sup>®</sup> is a precursor of radicals and the role of the investigated catalyst was to activate its decomposition. Sulfate ion radicals act as oxidizing species in dye degradation reaction. The influence of the mass of the catalyst and the reaction temperature was investigated. The catalyst mass and temperature increase were beneficial for the dye degradation rate. The pseudo-first order kinetic model was found to be the most appropriate fit for experimentally obtained data. The adsorption of the dye on Co-doped alumina was also tested, and it was found to be negligible. The investigated catalyst was found to be effective for Orange G degradation in the presence of Oxone<sup>®</sup>.

### INTRODUCTION

Alumina is a material with unique catalytic, adsorption, optical, and electronic properties [1]. For these reasons, it can be used in a variety of applications such as catalyst support material, because of its high chemical inertness, high specific surface area, and crystalline structure [2]. In metal-doped alumina small amounts of a doping agent (metal) are added during the synthesis of alumina. This type of synthesis provides uniform dispersion of the doping metal in the aluminum matrix [3].

Oxone<sup>®</sup> (2KHSO<sub>5</sub>×KHSO<sub>4</sub>×K<sub>2</sub>SO<sub>4</sub>) is a mixed salt with peroxymonosulfate (PMS) as active component. It can be used as a precursor of sulfate ion radicals. Without outer activation, PMS's decomposition is very slow [4]. Among different activation techniques, activation of PMS by transition metal cations has attracted much attention because of high activation efficiency of transition metals. Cobalt has shown the best performance of all transition metals and it has been largely used as oxidation catalyst in numerous environmental applications [5].

Orange G (OG) is a synthetic, anionic, mono azo-dye soluble in water and stable at any pH. It is used in textile and printing industries as a coloring agent. OG dye has a hazardous and harmful effects on aquatic species and the entire water environment. Its toxic, carcinogenic and teratogenic effects to the living organisms have been attributed to the azo group in its chemical structure. The exposure of humans to OG may result in irritation of the gastrointestinal and respiratory tract [6].

In this work cobalt-doped alumina catalyst (CoA-500) was investigated in Oxone<sup>®</sup> activated degradation of Orange G. The influence of different reaction parameters on the catalytic activity was followed.

### EXPERIMENTAL

Aluminum isopropoxide was used as a precursor in the synthesis of cobalt-doped alumina by the sol-gel method. Freshly prepared boehmite sol was mixed with Co-nitrate solution in order to obtain a homogeneous Co (II)-doped boehmite sol with Co<sup>2+</sup>/Al<sup>3+</sup> molar ratio of 0.4. The doped boehmite sols were then gelled and subsequently calcined at 500 °C [7]. The obtained material was previously fully

characterized using X-ray powder diffraction (XRPD), temperature programmed reduction (TPR), and low-temperature N<sub>2</sub> physisorption analysis [7].

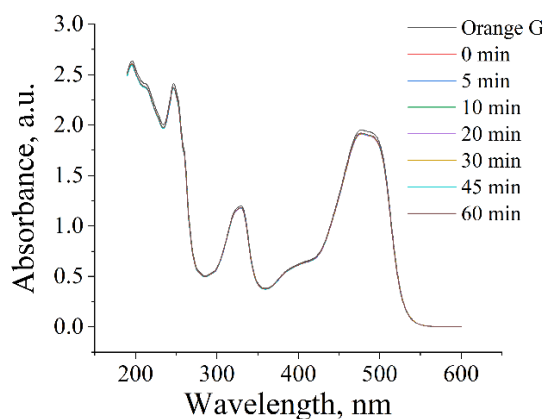
Catalytic tests were conducted in a 500 cm<sup>3</sup> Pyrex reactor thermostated using a Julabo MC 4 circular heater and equipped with a mechanical stirrer. Aqueous solution of Orange G (C<sub>0,OG</sub> = 50 mg dm<sup>-3</sup>) was stirred in the presence of 0.130 mmol Oxone<sup>®</sup>. In all experiments, the catalyst was added to the reaction mixture 5 min after the Oxone<sup>®</sup> was introduced into the OG solution. This moment was taken as the initial (0 min) moment of the reaction. With the respect to this moment aliquots were taken at predetermined periods of time. Supernatant solutions were separated from the solid phase by centrifugation at 17000 rpm for 3 min and analyzed using UV–Vis spectrophotometry (Thermo Scientific, Evolution 220 UV–Visible Spectrophotometer). The following experimental parameters were investigated. The effect of the mass of the catalyst was investigated in the range from 10 mg to 100 mg and for reaction temperature 30 °C. The effect of temperature was monitored in the range from 30 °C to 60 °C. The mass of catalysts was 10 mg, and the solution volume was 200 dm<sup>3</sup>. The peak at 478 nm indicating decolorization of the reaction solution was monitored and analyzed.

## RESULTS AND DISCUSSION

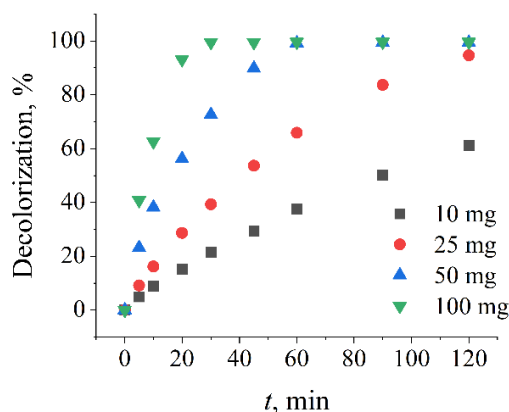
The XRPD confirmed the main phase is a type of cobalt spinel (Co<sub>3</sub>O<sub>4</sub>, CoAl<sub>2</sub>O<sub>4</sub> or Co<sub>2</sub>AlO<sub>4</sub>) and the second phase was identified to be  $\gamma$ -alumina. H<sub>2</sub> TPR confirmed the presence of Co<sub>3</sub>O<sub>4</sub> in CoA-500 as a dominant phase. The N<sub>2</sub> adsorption-desorption isotherm expressed the IVa isotherm type behavior, according to the IUPAC, and was reversible at lower equilibrium pressures. The total pore volume was determined to be 0.196 cm<sup>3</sup>g<sup>-1</sup> and the specific surface area was 133 m<sup>2</sup>g<sup>-1</sup> [7].

Prior to catalytic tests, the adsorption test was performed using CoA-500 as adsorbent. The adsorption was monitored using the UV–Vis spectrophotometry. The amount of Orange G, adsorbed onto the investigated sample under the same conditions applied for the catalytic test (200 cm<sup>3</sup> of 50 mg dm<sup>-3</sup> Orange G solution, 40 mg of Oxone<sup>®</sup> (0.131 mmol), 10 mg of catalyst, 30 °C, 60 min) was less than 3%.

(Figure 1).



**Figure 1.** Adsorption test with Orange G

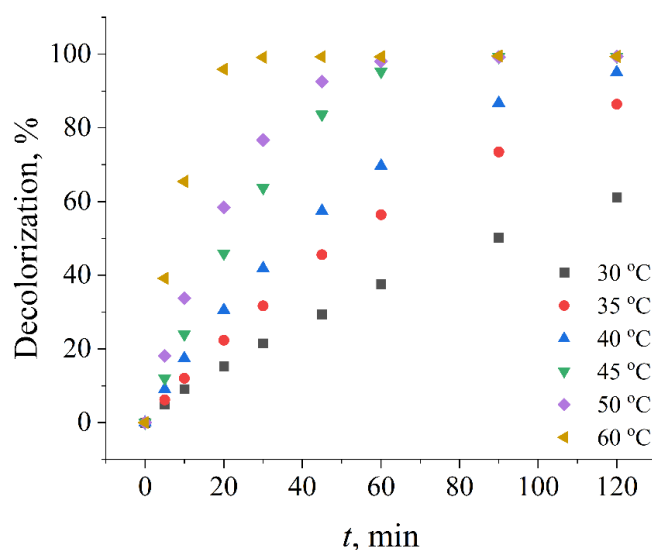


**Figure 2.** Influence of mass of catalyst CoA-500 on decolorization of Orange G

The influence of the mass of the catalyst was investigated for CoA-500 in the mass range from 10 mg to 100 mg (200 cm<sup>3</sup> of 50 mg dm<sup>-3</sup> Orange G solution; 40 mg of Oxone<sup>®</sup>; T=30 °C, reaction time of up to 120 min) (Figure 2.). Decolorization was monitored through the changes of the absorbance at  $\lambda_{\text{max}} = 478$  nm. With the increase of the mass of the catalyst the degree of decolorization increased. For the mass of 100 mg a plateau, related to nearly 100% of decolorization, was reached after 20

minutes. On the other hand, for the lowest mass, the total decolorization was not reached within the investigated time (120 minutes). For further investigations, a lower mass of catalyst was chosen so the monitoring of the kinetic of the investigated reaction could be possible.

The influence of temperature was investigated in the (30–60) °C temperature range during 120 min. The mass of the catalysts was 10 mg. (**Figure 3.**). Temperature increase was beneficial for the dye decolorization rate. Under the investigated conditions, the total decolorization was achieved in the case of the reaction conducted at 50 °C and 60 °C. The decolorization at 30 °C was much slower, and only 61% of decolorization was obtained.



**Figure 3.** Influence of reaction temperature on decolorization of Orange G

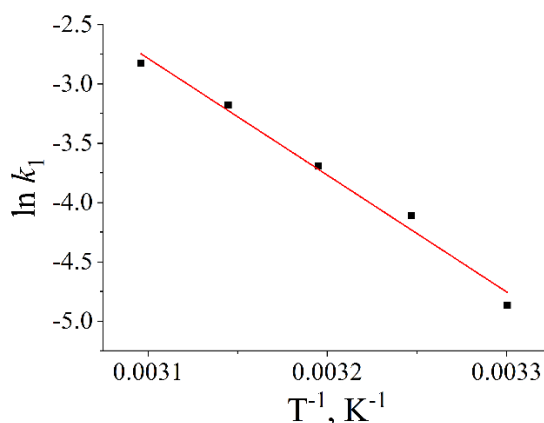
Different kinetic models were tested, but the pseudo-first order kinetic model was found to be applicable for all selected temperatures (**Table 1**). The pseudo-first order rate constant ( $k_1$ ) increased with increasing reaction temperature.

**Table 1.** Pseudo-first order kinetic parameters

Temperature, °C	$k_1$ , min <sup>-1</sup>	$R^2$
30	0.0077	0.9999
35	0.0164	0.990
40	0.0249	0.986
45	0.0418	0.987
50	0.0594	0.985

$k_1$ -pseudo-first order rate constant,  $R^2$ - square of coefficient of correlation

The Arrhenius equation was applied for obtained kinetic data:  $\ln k_1 = \ln A - E_a (RT)^{-1}$ ; A – constant related to the geometry,  $E_a$  – activation energy (J mol<sup>-1</sup>), and T – thermodynamic temperature (K) and R – universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). The activation energy was found to be:  $E_a = 9850$  J mol<sup>-1</sup> (**Figure 4.**).



**Figure 4.** The Arrhenius equation graph

## CONCLUSION

The cobalt-doped alumina was synthesized using sol-gel method, gelled and calcined at 500 C. The obtained material was tested as a catalyst in Orange G solution degradation. The dye degradation was performed in the presence of Oxone as a source of  $SO_4^{\cdot -}$  ion radicals. Without the catalyst the degradation was insignificant due to the slow Oxone self-decomposition. Also, adsorption of the dye on the investigated material was less than 3%. The influence of the CoA-500 mass and reaction temperature was investigated. The increase of the mass of the catalyst and temperature was beneficial for the reaction. The reaction was found to be very fast in the presence of CoA-500 as the catalyst. The pseudo-first order kinetic model was found to be applicable for all investigated temperatures. The cobalt-based alumina was found to be a promising catalyst in Oxone<sup>®</sup> initiated Orange G degradation.

## Acknowledgment

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract 451-03-68/2022-14/200026).

## REFERENCES

- [1] Y. Li, J. Su, R. Li, Microporous Mesoporous Mater. 243 (2017) 9–15.
- [2] K. Paranjpe, Pharm. Innov. J. 6 (11) (2017) 236–238.
- [3] C. Maldonado, J. Rivera De la Rosa, C.J. Lucio-Ortiz, A. Hernandez-Ramírez, F. F. Castillon Barraza, J.S. Valente, Materials 7 (2014) 2062–2086.
- [4] J.D. Chen, Y. Yongjian, G. Show, H. Wang, Water Sci Technol 78 (2018) 2338–2348.
- [5] P. Hu, M. Long, Appl. Catal. B Environ. 181 (2016) 103–117.
- [6] S. Imam, A. Muhammad, H. Babamale, Z. Zango, J. Environ. Treat. Tech. 9 (2021) 318–327.
- [7] S. Marinović, T. Mudrinić, B. Dojčinović, T. Barudžija, P. Banković, T. Novaković, J. Environ. Chem. Eng. 9 (2021) 106348.