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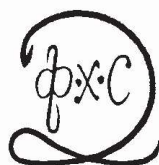
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PHYSICAL CHEMISTRY 2022

*16th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

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Serbia*

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and

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KINETIC AND THERMODYNAMIC STUDY OF THE OXIDATIVE CATALYTIC DEGRADATION OF TARTRAZINE IN THE PRESENCE OF OXONE[®] AND COBALT SUPPORTED CHITOSAN-DERIVED CARBON-MONTMORILLONITE

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ABSTRACT

Catalytic degradation of Tartrazine in the presence of Oxone[®] activated by Co-supported chitosan-derived carbon-montmorillonite as catalyst was investigated. The catalyst was synthesized using impregnation-carbonization method. The carbonization temperature was 500 °C. The catalytic experiments were performed at different temperatures in range from 25 °C to 40 °C in order to determine kinetics parameters. The kinetics data showed best fit with the first-order kinetics model. The activation energy of the investigated degradation process was calculated according to the Arrhenius equation.

INTRODUCTION

Dyes have been frequently applied in the industries of cosmetics, textile, manufacturing, and food. The synthetic food dyes are made up of complex aromatic molecular structures of azo and phenyl methane groups, which are recalcitrant xenobiotic compounds, that resistance to environmental decolorization process. 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]. Nowadays, sulfate radical-based advanced oxidation processes with peroxymonosulfate (PMS) as the oxidant have attracted attention as solution for the removal of persistent pollutants. Due to the chemical stability of PMS in mild conditions its activation is required. In this purpose different activation techniques were investigated and activation of PMS by cobalt cations has been widely used because of high activation efficiency of cobalt [2].

In this work domestic smectite clay from Bogovina was intercalated with biopolymer chitosan, impregnated with cobalt, and submitted to the carbonization process. The obtained catalyst was evaluated in the oxidative degradation of food dye Tartrazine with respect to degradation time and temperature. The kinetic and thermodynamic parameters were deduced from the catalytic tests. This data could be beneficial in elucidating the nature of the oxidative degradation process of the investigated catalytic system.

METHODS

Materials and catalyst synthesis

The Co(NO₃)₂·6H₂O (≥ 98 % purity) supplied by Centrohém Belgrade, high molar mass chitosan (deacetylated chitin or poly(D-glucosamine)) (av. MW = 342,500 g mol⁻¹), Oxone[®] (2KHSO₅·KHSO₄·K₂SO₄) and Tartrazine - C₁₆H₉N₄Na₃O₉S₂ was supplied by Sigma Aldrich were used as received.

The fraction below 2 μm of smectite-rich bentonite clay (Bogovina, Serbia) was submitted to the intercalation process by chitosan solution according to the previously described procedure [3]. The obtained material was impregnated by Co²⁺ ions using the incipient wetness impregnation method

[4]. The obtained sample was further submitted to the carbonization procedure at 500 °C in an N₂ atmosphere for 1h. The sample was denoted as Co/cCh-S. The microwave digestion of investigated sample and subsequent Inductively Coupled Plasma Optical Emission Spectrometry analysis were used for the determine the cobalt content. The amount of cobalt in Co/cCh-S was 6.11 mass %.

Catalytic tests

Catalytic tests were performed by stirring 10 mg of catalyst in 200 cm³ aqueous Tartrazine solution ($\gamma_0=50.0 \text{ mg dm}^{-3}$) in the presence of 0.130 mmol Oxone[®]. Catalytic reactions were conducted in a Pyrex reactor equipped with a mechanical stirrer and thermostated using a Julabo[®] circulating bath, at the following temperatures: 25 °C, 30 °C, 35 °C and 40 °C. The catalyst was added to the reaction mixture of Tartrazine and Oxone[®] and that 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. The solid and liquid phases were separated by centrifugation at 17000 rpm for 3 min. Characteristic Tartrazine UV absorption peak at 426 nm was used for degradation monitoring (Thermo Scientific, Evolution 220 UV–Visible Spectrophotometer).

Applied kinetic and thermodynamic models

The obtained catalytic data for each investigated temperature were treated with kinetic models of zero-order, first-order and second-order kinetics models. The first-order kinetics model was found to be the most appropriate. In (Eq. 1) this model is given in the linear form:

$$\ln C_t = \ln C_0 - k_1 t \quad (\text{Eq.1})$$

Where: C_0 and C_t are initial concentration of dye, and concentration in time t (mg L^{-1}), k_1 is the first-order rate constant.

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^{-1}), A is the Arrhenius factor, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K).

RESULTS AND DISCUSSION

The experimental data for catalytic decolorization of Tartrazine at different temperatures in the presence of the investigated catalyst and linear plots of applied first-order kinetics model at experimental catalytic data are given (**Figure 1.**).

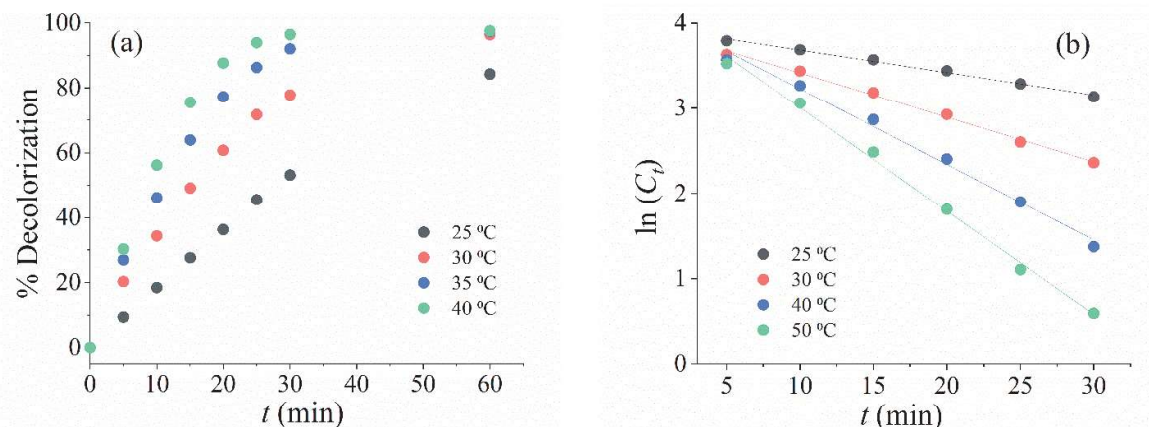


Figure 1. (a) Catalytic decolorization of Tartrazine in the presence of Co/cCh-S-500 catalyst monitored at 426 nm for temperature range from 25 °C - 40 °C ($m_{\text{cat}}=10.0$ mg, $V_0=200$ cm³, $C_0=50.0$ mg dm⁻³; 0.130 mmol of Oxone[®]); (b) The linear plots of first-order kinetics model applied at experimental catalytic data of Tartrazine decolorization.

It was found that raising the temperature has a positive impact on the decolorization of Tartrazine (**Figure 1a**). The total decolorization was achieved for the reaction conducted at a temperature range 30 - 40 °C for the investigated period of time. Additionally, the time required for the decolorization was shorter at higher temperatures, *i.e.*, 98% of decolorization was achieved only in 30 min at 40 °C. High degradation degree (84 %) even for lowest investigate temperature (25 °C) indicates the excellent efficiency of the tested catalyst.

Furthermore, it was found that the first-order kinetic model can be successfully used for the interpretation of kinetics data, and linear fits for each temperature are given (**Figure 1b**). The calculated kinetic parameters are presented (**Table 1.**).

T [°C]	25	30	35	40
k_I [min ⁻¹]	0.0265	0.0522	0.0886	0.1213
R^2	0.993	0.994	0.990	0.995

The linear fit of the the first-order kinetic model (**Figure 1b**) shows good agreement with experimental catalytic data with the squares of coefficients of correlation of ≥ 0.993 .

The calculated values of the first-order rate constant (**Table 1.**) increased with the increases in temperature. The obtained k_I values are used to construct the Arrhenius plot (**Figure 2.**).

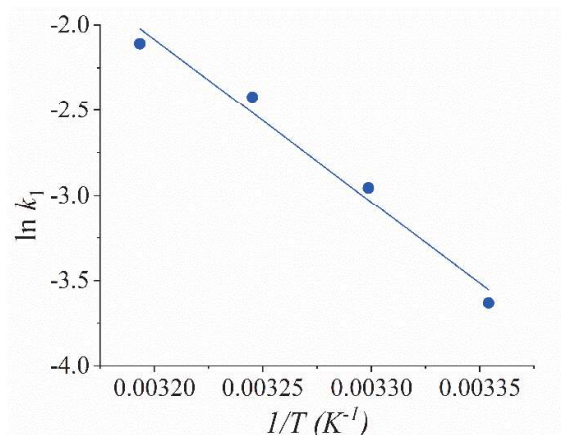


Figure 2. Arrhenius plot of Tartrazine decolorization in the presence of Co/cCh-S-500.

The Arrhenius plot shows a good linear relationship existed in the plots of $\ln k_1$ versus $1/T$ ($R^2 = 0.979$). The activation energy E_a was obtained from the slope of linear fit (**Figure 2.**), and has a value of $79.23 \text{ kJ mol}^{-1}$. The obtained result is in agreement with literature data found for similar systems of oxidative catalytic degradation of dyes [5].

CONCLUSION

The catalyst obtained by cobalt impregnation of chitosan-smectite composite and further carbonization at $500 \text{ }^\circ\text{C}$ was used for decolorization of Tartrazine in the presence of Oxone[®] at different temperatures ($25 \text{ }^\circ\text{C} - 40 \text{ }^\circ\text{C}$). The results of a study on the kinetics and thermodynamics of the Tartrazine decolorization by the peroxymonosulfate oxidation process was discussed. The influence of temperature has been studied. In the given conditions, total decolorization was achieved within only 30 min at $40 \text{ }^\circ\text{C}$. The kinetic studies showed that the decolorization of Tartrazine followed the first-order kinetics. In addition, it was found that the rate constants of the first-order chemical reaction increased with the increase of reaction temperature. Under the investigated catalytic conditions, the activation energy (E_a) for decolorization of Tartrazine by the peroxomonosulfate was determined to be $79.23 \text{ kJ mol}^{-1}$. High degradation degree even for lowest investigate temperature ($25 \text{ }^\circ\text{C}$) indicates the excellent efficiency of the tested catalyst.

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