Cobalt supported chitosan-derived carbon-smectite catalyst in Oxone® induced dye degradation

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ABSTRACT

Catalytic degradation of tartrazine in the presence of Oxone® activated by a catalyst constituted of cobalt supported on a nanocomposite of smectite with chitosan-derived carbon was investigated. The catalyst was synthesized using cobalt impregnation followed by carbonization at 773 K in an inert atmosphere. The synthesized catalyst was previously fully characterized using appropriate characterization methods, including XRPD, XPS, FTIR, HR-TEM, and low-temperature N_2-physisorption analysis. The catalytic experiments were performed by varying different experimental parameters (dye concentration, Oxone® concentration, temperature, and initial pH of the reaction solution). The kinetic and thermodynamic parameters were estimated from the experimental results. The kinetics data showed the best fit with the pseudo-first-order kinetics model. The activation energy of the investigated degradation process was calculated according to the Arrhenius equation. The catalyst showed excellent performance at low temperatures even at 298 K, and in the wide range of pH values.

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INTRODUCTION

The continuous increase in the human population on Earth, along with the improvement of living standards, has led to an increased demand for food and rapid growth of food processing industries [1]. Modern customers usually focus on color, aroma and taste when choosing food [2]. Therefore, the food processing industries use food additives for preservation, coloring, flavoring, and sweetening of products [3]. Food colorants as a significant member of food additives are widely used not only in the food industry (juices, sweets, puddings, chewing gums), but also in pharmaceutical and cosmetic industries (drugs and cosmetic products). The stability, strength, availability, and price are the main reasons why the synthetic dyes are frequently used in these industries. The synthetics food dyes are made up of complex aromatic molecular structures of azo and phenyl methane groups, which are xenobiotic compounds, resistant to environmental decomposition [4]. Because of uniform color, high solubility in water and high tolerance to oxidation and heating conditions, tartrazine (also known as E102, Acid Yellow 23, FD&C Yellow 5) is widely used in the food industry for achieving yellow shades [5] although some toxic and harmful effects of tartrazine were reported [6, 7]. Therefore, removal of this pollutant from wastewaters before discharge to the environment has become a real challenge. Currently, various methods were employed to remove tartrazine molecules from aqueous solutions including adsorption [8], ion-exchange [9], electrocoagulation [10], photocatalytic degradation [11], advanced oxidation processes [12, 13], etc. Nowadays, sulfate radical-based advanced oxidation processes with peroxymonosulfate (PMS) as source of reactive oxygen species (ROS) including the most reactive $SO_4^{.-}$ have attracted attention as solution for the removal of persistent pollutants from water [14]. Commonly as a source of PMS commercially available Oxone® is used [15, 16, 17]. PMS activation is necessary in order to operate at mild conditions, and different techniques were proposed including activation by cobalt cations, that has shown high activation efficiency [2, 18, 19]. However, the use of cobalt cations as homogeneous catalyst may result in secondary pollution which

2

restricts their practical application in wastewater treatment [20]. To address these issues, it is important to develop an environment-friendly heterogeneous cobalt-based catalyst. In the last decade, metal-containing carbon-based catalysts have been considered in PMS activation [14]. The carbon matrix can promote the uniform distribution of metal nanoparticles, increasing number of active sites, and thus improving the catalytic performance [21]. So far, various commercially available carbon-based catalysts including graphene and carbon nanotubes have been applied for PMS activation [14, 22]. However, the most of these materials are expensive. On the other hand, biowaste can be regarded as the most promising precursor of carbon as a green, sustainable, available, and adjustable resource. [23, 24, 25].

Biopolymer chitosan the second most abundant biopolymer in nature after cellulose can be obtained from the waste of crustaceans [26]. Because of its strong affinity toward transition metals including cobalt, chitosan was applied in the synthesis of catalysts [27, 28, 29, 30]. Furthermore, chitosan and clay minerals can be combined to form hybrid materials that benefit from synergy of properties of both components [31, 32, 33]. Our research group was the first who synthetized the carbonized Co/chitosan/smectite nanocomposite and applied it in the oxidative degradation of dye. In our previous work [34] local smectite clay from Bogovina (a coal mine in Serbia) was intercalated with biopolymer chitosan, impregnated with cobalt, and submitted to the carbonization process in the inert atmosphere at different temperatures. The best-performing catalyst was further investigated in this work. The obtained catalyst was evaluated in the oxidative degradation of food dye tartrazine with respect to degradation time and different experimental parameters (dye concentration, Oxone® concentration, temperature, and initial pH of the reaction solution).

EXPERIMENTAL

Materials and catalyst synthesis

The catalyst was synthesized using <2µm of smectite-rich bentonite clay (Bogovina, Serbia), chitosan (deacetylated chitin or poly(D-glucosamine), av. MW=342,500 g mol^{-1}), and $Co(NO_3)_2·6H_2O$ ($\geq$ 98 % purity) according to the previously described procedure [34]. After intercalation of chitosan into the smectite structure, impregnation with Co^{2+},

the carbonization at 773 K in N_2 atmosphere for 1h was performed [34]. The sample was denoted as Co/cCh-S.

Characterization of catalyst

The content of the C and N was determinated by elemental analysis. The cobalt content was measured using inductively coupled plasma method (ICP-OES). Besides, X-ray powder diffractometry (XRPD), Fourier-transform infrared spectroscopy (FTIR), textural analysis based on N_2 physisorption at -196 ⁰C, high resolution transmission electron microscopy (HR-TEM), and photoelectron spectroscopy (XPS) were also applied as characterization techniques.

The complete results of characterization of Co/cCh-S were presented in our previous article [34], while selected characterization results are summarized and listed in Table I.

Table I

The XRPD revealed that the interlamellar spacing of 1.32 nm corresponds to the monolayer graphene-like structure formed between lamellas of smectite. The FTIR spectrum of the Co/cCh-S confirmed presence of hydroxyl, alkyl, and carbonyl functional groups. The vibrations of organic phase were mostly overlapped with those originated from smectite structure. HR-TEM showed that the sample has a layered structure with well-dispersed and incorporated small spherical cobalt-containing formations, while XPS analysis confirmed the presence of cobalt in the Co^{III} and Co^{II} oxidation states. In addition, the XPS analysis confirmed the existence of Co^{II} / Co^{III} / Co^{II} redox cycle during the PMS activation [34].

Catalytic tests

In catalytic tests the source of ROS was Oxone® ($2KHSO_5·KHSO_4·K_2SO_4$), while tartrazine - $C_{16}H_9N_4Na_3O_9S_2$, supplied by Sigma Aldrich, was used as model pollutant dye.

The catalytic activity of the Co/cCh-S in terms of tartrazine degradation via Oxone®️ activation was evaluated by a series of batch experiments as a function of the: (i) tartrazine concentration, (ii) Oxone®️ concentration, (iii) temperature of the catalytic reaction, and (iv) the initial pH of the reaction solution (pH$_i$).

All catalytic experiments were carried out in a Pyrex reactor. The reaction system was homogenized by mechanical stirring. The constant temperature was maintained by Julabo®️ circulating bath. The 10 mg of the catalyst was added to the 200 cm^3 of tartrazine solution. In each series of experiments one parameter was varied, while other parameters were kept constant. The concentration of the tartrazine was investigated in the range 30 mg dm^{-3}- 60 mg dm^{-3}, and Oxone®️ concentration in range (100 – 250) mg dm^{-3}. The effect of temperature and pH$_i$ was investigated in range from 298 K to 313 K and from 2 to 9, respectively. The pH of native tartrazine / Oxone®️ mixture was 3.7. After the catalytic reaction, the catalyst was removed by centrifugation. The concentration of the undegraded dye was measured using a UV-Vis spectrophotometer (Thermo Scientific, Evolution 220), at λ_{max} =426 nm.

In order to determinate the amount of tartrazine removed due to the adsorption process, the adsorption test was performed under following experimental conditions: γ_{tart}=50 mg dm^{-3}; V_{tart}= 200 dm^{-3}; m_{ads} =10mg; T=30 °C and unadjusted pH.

Kinetic and thermodynamic models

The obtained catalytic data for each experiment were fitted with different kinetic models (zero-order, pseudo-first-order, and pseudo-second-order kinetics models). The square of the coefficient of correlation (R^2) of the zero-order kinetic model (ZO), pseudo-first-order kinetic model (PFO), and pseudo-second-order kinetic model (PSO) for different reaction parameters were presented in Table II.

Table II

Based on the obtained R^2 values, the pseudo-first-order kinetics model was found to be the most appropriate for the investigated reaction system. In (*Eq.* 1) this model is given in the linear form:

$$\ln C_t = \ln C_0 - k_1 t \tag{1}$$

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

Arrhenius relationship was used to evaluate the activation energy of the catalytic process:

$$\ln k_1 = \ln A - \frac{E_a}{RT} \qquad (2)$$

Where: k_1 is the pseudo-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 J mol^{-1} K^{-1}) and T is the temperature (K).

RESULTS AND DISCUSSION

Influence of the initial concentration of tartrazine

The influence of initial tartrazine concentration (γ_{Tar}) on the efficiency of Co/cCh-S catalyst in degradation of tartrazine was investigated in the range from 30 mg dm^{-3} to 60 mg dm^{-3} at 303 K, pH 3.7, and Oxone® concentration (γ_{Ox}) of 200 mg dm^{-3}. The results are presented in Fig. 1a. In addition, the rate constants based on the first-order kinetic model are shown in Fig. 1b.

Figs. 1a, 1b

Tartrazine degradation efficiency declined with the increase of initial concentration of tartrazine (Fig. 1a) due to insufficiently of ROS. Since experiments were carried out using 10 mg of Co/cCh-S, and γ_{Ox} = 200 mg dm^{-3} a higher concentration of tartrazine would require prolonged time to attain the same removal as lower concentrations. For instance, for tartrazine concentrations (γ_{Tar}) of (30, 40, and 50) mg dm^{-3} maximal tartrazine degradation was reached after (25, 30, and 60) min, respectively (Here the maximal tartrazine degradation is associated with total disappearance of 426 nm peak). The removal of tartrazine was ascribed to the oxidative degradation process, since the adsorption test revealed that the investigated materials was not able to adsorbed tartrazine. Maximal degradation of dye was not reached when concentration of

6

tartrazine was 60 mg dm^{-3}. Furthermore, generated organic intermediates might compete for the availability of ROS.

As shown in Fig. 1b, the pseudo-first-order rate constants (k_1) decreased with the increase of initial concentration of tartrazine. The k_1 decreased 1.75, 3.48, and 3.76 times when the initial concentration of tartrazine increased from 30 mg dm^{-3} to 40 mg dm^{-3}, 50 mg dm^{-3} and 60 mg dm^{-3}, respectively. For further investigation, the initial concentration of tartrazine of 50 mg dm^{-3} was chosen and in this manner the monitoring of the kinetic of the investigated reaction could be possible.

Influence of Oxone® concentration

The influence of Oxone® concentration on the degradation of tartrazine ($\gamma_{Tar} = 50$ mg dm^{-3}) was investigated in the range from 100 mg dm^{-3} to 250 mg dm^{-3} at 303 K, and pH_i 3.7. The results are presented in Fig. 2a, while the rate constants based on the pseudo-first-order kinetic model were shown in Fig. 2b.

Figs. 2a and 2b

For all investigated concentrations of Oxone®, degradation of tartrazine was ≈ 98% after 60 min of reaction, except for 100 mg dm^{-3} when degradation reached 90.7%. Differences in efficiency of tartrazine degradation were more apparent for the first 30 min of the reaction. Fig. 2a revealed that the reaction slightly accelerated from 64.6% to 77.2% with the increase of γ_{Ox} from 100 mg dm^{-3} to 200 mg dm^{-3} while increasing up to 250 mg dm^{-3} enhanced tartrazine degradation efficiency to 88.5% for 30 min. It can be inferred that the excessive amount of Oxone® could generate more ROS i.e., enhanced degradation of tartrazine. Moreover, the $k_1 = 0.0799$ min^{-1} for $\gamma_{Ox} = 250$ mg dm^{-3} was approximately twice as high as k_1 for $\gamma_{Ox} = 100$ mg dm^{-3} (0.0402 min^{-1}). However, in the initial period of reaction (10 min) degradation was similar for $\gamma_{Ox} = 200$ mg dm^{-3} and for the $\gamma_{Ox} = 250$ mg dm^{-3}. For further investigations, the $\gamma_{Ox} = 200$ mg dm^{-3} was chosen.

Influence of the temperature

The experimental data for catalytic degradation of tartrazine at pH_i 3.7 at different temperatures in the presence of the investigated catalyst is presented in Fig. 3a. The temperature increase was beneficial for the tartrazine degradation (Fig. 3a). For all investigated temperatures maximal tartrazine degradation was reached after 60 min of reaction, except for 298 K (84.2 %). Additionally, the time required for the maximal degradation was shorter at higher temperatures, *i.e.,* the maximum was achieved after only 30 min at 313 K. Furthermore, k_1 values had almost linear increase with the increase of temperature (Fig. 3b). Nevertheless, high degradation degree even for the lowest investigated temperature (298 K) indicated excellent efficiency of the tested catalyst.

Figs. 3a and 3b

The obtained k_1 values are used in Eq. (2) to estimate the activation energy of investigated catalytic process (Fig. 4.).

Fig. 4

The calculated values for k_1 were used for the Arrhenius plot and the linear fit of $\ln k_1$ versus $1/T$ was obtained with $R^2 = 0.979$. The activation energy (E_a) of 79.23 kJ mol^{-1} was obtained from the slope of this fit (Fig. 4). The E_a value is in agreement with literature data for similar systems of oxidative catalytic degradation of dyes [5, 35].

Influence of initial pH of the reaction solution

The influence of the initial pH of the reaction solution (pH_i) on tartrazine degradation was investigated with respect to reaction time and presented in Fig 5a. The reaction was conducted in the pH range from 2 to 9, including native pH (3.7). The influence of pH_i on rate constants obtained for the pseudo-first-order kinetic model is given in Fig. 5b.

Figs. 5a and 5b

For all investigated pH_i except for strongly acidic (pH 2) the maximal tartrazine degradation occurred. The low degradation efficiency of investigated catalyst at pH 2 is in agreement with previously published literature data [17, 25]. In strongly acidic conditions, the H_2SO_5 becomes the main species present in the solution, forming a strong hydrogen bond leading to the high Oxone® stability. Also, the scavenging effects of proton at low pH values on radicals might be the reason for dramatic drop of catalytic performance in highly acidic conditions [17, 25].

Differences in reaction rates in pHi range from 3.7 to 9.0 were noticeable in the first 30 min of the reaction. It can be observed that the optimal performance was exhibited for neutral and close to neutral environment (pH_i 6–8), which is consistent with previous findings for Co-based catalysts [34, 36]. The maximal tartrazine degradation at pH_i 7 was achieved after 20 min, while for pH_i 6 and pH_i 8 tartrazine 25 min was needed. For 25 min of reaction at pH_i 2, 3.7, and 9 only 10.8%, 69.3%, and 48.2% of tartrazine was degraded, respectively.

The changes in pH during the catalytic reaction were observed [34]. When the pH_i was in the range from 6–9, the pH of the solution dropped significantly during the catalytic reaction. After 60 min of reaction the pH was approx. 3.7 for (pH_i 6–8) and 4.7 for pH_i 9. On the other hand, for pH_i 2.0 and 3.7, the pH values during the reaction slightly varied after 60 min 2.2 and 3.2, respectively.

The highest k_1 value was obtained for pH_i 7 (0.1925 min^{-1}), while for pH_i 6 and pH_i 8 k_1 values were slightly lower (0.1592 min^{-1} and 0.1515 min^{-1}, respectively). Probably, as a consequence of pH change during the reaction at pH_i 9, three different stages of the reaction were observed. In the first stage (up to 15 min of reaction) the reaction was moderate, followed by a dramatic decrease in the second stage occurring from 15 min up to 30 min, and finally in the third stage being faster than in the first stage. The rate constants were 0.0370 min^{-1} and 0.0091 min-1, for the first and second stages respectively. Nevertheless, the Co/Ch-S was found to be efficient in a broad pH_i range from native up to 9.

CONCLUSION

The catalyst was synthesized by cobalt impregnation of chitosan-smectite nanocomposite and further carbonized at 773 K in the inert atmosphere. The catalyst was tested in Oxone® (source of reactive oxygen species) induced degradation of tartrazine. The influence of different experimental parameters (dye concentration, Oxone® concentration, temperature, and initial pH of the reaction solution - pH_i) on the rate of catalytic reaction was investigated. Tartrazine degradation efficiency decreased with the increase in tartrazine concentration. The increase in Oxone® concentration and the increase in reaction temperature were beneficial for the degradation rate. On the other hand, the catalyst was found to be efficient in a broad pH_i range i.e. from native (3.7) up to 9, while the pH optimum for the catalytic reaction was found to be 7. The kinetic studies showed that the degradation of tartrazine followed the pseudo-first-order kinetics. Under the investigated catalytic conditions, the activation energy (Ea) was determined to be 79.23 kJ mol^{-1}. High degradation degree even for the lowest investigated temperature (298 K) indicated the excellent efficiency of the tested catalyst.

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Tables

Table I Summarized results of Co/cCh-S characterization [34]

Method		Properties / Results
XRPD	*Smectite d_{001}*(nm)	1.32 Graphene-like structure incorporated in form of monolayer in smectite structure.
Elemental analysis [mass%]	C	8.2
	N	1.2
ICP-OES [mass%]	Co	6.1
N_2 physisorption	S_{BET}(m^2g^{-1})	73.2
XPS	State of elements	Co^{II}, Co^{III} sp^2 carbons hybridized structures
FTIR	Position of vibration bands ascribed to the functional groups	3420 cm^{-1} -OH group
		2920/ 2850 cm^{-1} -CH alkyl structures
		1639 cm^{-1} -C=O structures
		1029 cm^{-1} Si-O-Si overlapped with C-O-C structures
HR-TEM	Morphological properties	~1.34 nm distance between smectite lamellae ~ 3 nm cobalt-containing spherical particles, well dispersed

Where: d_{001}- basal spacing of smectite; S_{BET} – specific surface area

Table II The square of the coefficient of correlation (R^2) of the zero-order kinetic model (ZO), pseudo-first-order kinetic model (PFO), and pseudo-second-order kinetic model (PSO)

Reaction parameter	R^2 (ZO)	R^2 (PFO)	R^2 (PSO)
Tartrazine concentration	$\geq$0.730	$\geq$0.961	$\geq$0.901
Oxone® concentration	$\geq$0.978	$\geq$0.988	$\geq$0.793
Temperature	$\geq$0.897	$\geq$0.992	$\geq$0.807
pH	$\geq$ 0.520	$\geq$0.965	$\geq$0.932

Figure Captions

Fig. 1. a) Influence of the initial concentration of tartrazine on degradation of tartrazine solution monitored at 426 nm. b) Pseudo-first order rate constant for the different initial concentration of tartrazine. (m_{cat} = 10.0 mg, V_0 = 0.200 dm^3, γ_{Ox} = 200 mg dm^{-3}, T = 303 K, and pH_i 3.7).

Fig. 2 a) Influence of the Oxone$^®$ concentration on degradation of tartrazine solution monitored at 426 nm, b) Pseudo-first order rate constant for the different Oxone$^®$ concentrations. (m_{cat} =10.0 mg, V_0 = 0.200 dm^{-3}, γ_{Tar} = 50.0 mg dm^{-3}; T = 303 K and pH_i 3.7).

Fig. 3 (a) Catalytic decolorization of tartrazine in the presence of Co/cCh-S catalyst monitored at 426 nm for temperature range from 298 K - 313 K; (b) Pseudo-first order rate constant for the different temperatures (m_{cat} =10.0 mg, V_0= 0,200 dm^{-3}, γ_{Tar} = 50.0 mg dm^{-3}; γ_{Ox} = 200 mg dm^{-3} and pH_i 3.7)

Fig. 4 Arrhenius plot of Oxone$^®$ activated catalytic oxidative tartrazine degradation in the presence of Co/cCh-S (m_{cat} =10.0 mg, V_0= 0.200 dm^3, γ_{Ox} = 200 mg dm^{-3}, γ_{Tar}= 50.0 mg dm^{-3} and pH_i 3.7).

Fig. 5 a) Influence of the pH_i on degradation of tartrazine b) Pseudo-first order rate constant for different pH_i (γ_{Tar} = 50.0 mg dm^{-3} ; V_0 = 0.200 dm^3; γ_{Ox} = 200 mg dm^{-3}; m_{cat} =10 mg; T = 303 K).