Comparison between the photocatalytic degradation of drug and dye molecules under visible radiation: thermodynamic studies

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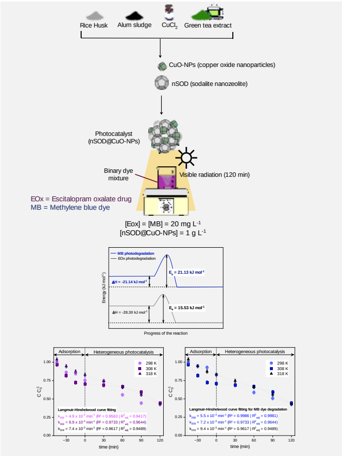


The present work aims to carry out a thermodynamic study for the degradation of the pollutants methylene blue dye (MB) and escitalopram oxalate drug (EOx) using an eco-friendly copper oxide supported onto sodalite nanozeolite nanocatalyst (nSOD@CuO-NPs). The nanocatalyst showed a porous structure with analcime, sodalite, cuprite, and tenorite crystalline phases, S_{BET} = 15 m^2 g^{-1}, pH_{ZCP} 8.30, ZP = -18.5 ± 4.30 mV, and E_g = 1.38 eV. The degradation reaction for both pollutants was characterized as a spontaneous ($\Delta G < 0$), favorable ($\Delta S > 0$), and exothermic ($\Delta H < 0$) process. Photodegradation of MB requires higher activation energy (E_a ~ 21 kJ mol^{-1}) than those for EOx (E_a ~ 15 kJ mol^{-1}). The apparent pseudo first-order rate constant and organic pollutants removal increased as temperature increase. Therefore, thermodynamic studies can be successfully used to get information about the catalyst activity and for the evaluation of the energetic reliability of the process.

Introduction

The widespread use and demand of psychiatric drugs have resulted in environmental concerns, since the disposal of these drugs (approximately 50%) are partially metabolized, being removed from human urine and feces, and disposed of in large amounts in surface waters [1,2]. These two types of contaminants are toxic, chemically/thermally stable, with low biodegradability, and highly water-soluble, making it difficult to remove them from conventional biological and physio-chemical wastewater treatment processes. Moreover, Advanced Oxidation Processes (AOPs) have been efficient for the removal of drugs and organic dyes from wastewater. Heterogeneous photocatalysis, which is based on the photoactivation of semiconductors followed by high reactive oxygen species (hydroxyl and superoxide radicals, $HO^{\bullet}$ and $O_2^{\bullet-}$) able to mineralize the organic matter to CO_2 and H_2O [3]. Nanocatalysts based on copper oxide nanoparticles supported onto nanozeolites showed promising results for the degradation of synthetic organic dyes and drugs under visible light, resulting in degradation up to 90% [4,5]. The present work aims to carry out a thermodynamic study for the degradation of the pollutants methylene blue and escitalopram oxalate using an eco-friendly copper oxide supported onto sodalite nanozeolite nanocatalyst (nSOD@CuO-NPs).

Material and Methods

1. Synthesis of the heterogeneous supported catalyst: The heterogeneous supported nanocatalyst (nSOD@CuO-NPs) was synthesized by the impregnation method, where nSOD (catalytic support) being hydrothermally synthesized and CuO-NPs (active phase) obtained by biogenic synthesis, using green tea as reducing agent. More information can be found in the literature [6].

2. Characterization: The samples were analyzed by X-ray diffraction (XRD); Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy; N_2 porosimetry; Zeta Potential (ZP); Zero-Charge Point (pH_{ZCP}), and Difuse Reflectance Spectroscopy (DRS).

3. Photocatalytic Activity and Kinetic Study: The photocatalytic activity tests were performed in a batch system using escitalopram oxalate drug – EOx ($C_{20}H_{21}FN_2O$, MW = 324.39 g mol^{-1}) and methylene blue dye – MB ($C_{16}H_{18}N_3SCl$, MW = 319.85 g mol^{-1}) as a target pollutants and the catalyst in suspension (1 $g.L^{-1}$) in a slurry reactor under visible irradiation (Bulb LED Lamp with 600 W m^{-2}) in two steps: (a) in dark condition: adsorption of the dyes mixture molecules onto the catalytic surface without irradiation (60 min), and (b) photocatalytic degradation of the target pollutants individually under visible radiation: aliquots (~3 mL) were collected at time 0, 15, 30, 45, 60, 75, 90, 105, and 120 min, being centrifuged (4000 rpm / 10 min) and diluted (1:10 v v^{-1}). The absorbance measurements were carried out in a UV-Vis spectrophotometer (λ = 238 nm for the EOx, and λ = 663 nm for the MB). The experiment data were fitted to the Langmuir-Hinshelwood model (for apparent rate constant evaluation), according to Eq. (1) [7].

$$\ln(C_{t0}/C_t) = k * t \qquad (1)$$

4. Thermodynamic studies: To evaluate the activation energy (E_a / kJ mol^{-1}) of the catalyst (Eq. 2) for EOx and MB degradation and the thermodynamic parameters of the photocatalytic process: Gibbs‘ energy (ΔG / kJ mol^{-1}), enthalpy (ΔH / kJ mol^{-1}), and entropy (ΔS / kJ mol^{-1}) of the reaction, according to Eq. (3-5):

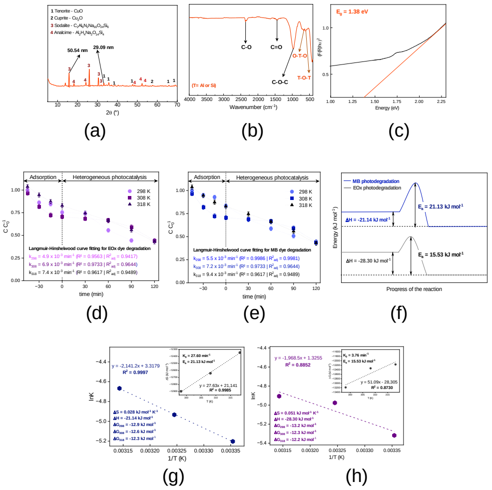
$$\ln(k) = k_0 - E_a/RT \qquad (2)$$

$$\Delta G = -RT * \ln(k) \qquad (3)$$

$$\Delta G = \Delta H - T * \Delta S \qquad (4)$$

Results and Discussion

Figures 1(a) – 1(c) show the XRD diffractograms and ATR-FTIR spectra, DRS results (Tauc plot by Kubelka-Munk function) of the supported nanocatalyst. Figures 1(d) – (f) report the degradation curve of MB and EOX and the results of the curve fitting of the Langmuir-Hinshelwood model, whereas 1(f) – (h) inform the thermodynamics properties (Gibbs‘ energy, enthalpy, and entropy changes) and for activation energy for the catalyst (E_g) and its associated pre-exponential factor (k_0).



(a) (b) (c)

(d) (e) (f)

(g) (h)

Figure1. (a) XRD diffractogram, (b) ATR-FTIR spectrum, (c) Tauc Plot for the nSOD@CuO-NPs nanocatalyst; (d) degradation curve of EOx drug and (e) MB dye under visible light ([Eox] = [MB] = 20 mg L^{-1} | pH ~ 7 | T = 298, 308, 318 K | 120 min), (f) energy diagram for the degradation reactions and nanocatalyst; (g) thermodynamic properties for the EOx and MB photodegradation obtained from linear regression (Arrhenius and Erying Plots).

The diffractograms identified analcime and sodalite crystallite phases associated with the catalytic support (nANA), and tenorite and cuprite phases for the active phase (CuO-NPs). Crystallite size ranged from 29.09 to 50.54 nm. The ATR-FTIR spectra identified the stretching and bending vibrations characteristic of zeolitic materials. N_2 porosimetry reported pore diameters (D_p) ranging from 2 to 50 nm with a pore volume equal to 0.004 cm^3 g^{-1}. Moreover, the synthesized nanocatalyst showed zero-charge point (pH_{PZC}) 7.48, ZP = –18.5 ± 4.3 mV, and E_g = 1.38 eV. Regarding thermodynamic studies, it was observed that the degradation reaction for both pollutants was characterized as a spontaneous ($\Delta G < 0$), favorable ($\Delta S > 0$), and exothermic ($\Delta H < 0$) process. Moreover, the EOx degradation reaction is more exothermic (ΔH = -28.30 kJ mol^{-1}) than the MB degradation reaction (ΔH = -21.14 kJ mol^{-1}), indicating that the EOx degradation is more favorable in terms of energy, as it produces more heat. However, the degradation of the MB dye requires a higher activation energy (Ea ~ 21 kJ mol^{-1}) than that of the EOx drug degradation (Ea ~ 15 kJ mol^{-1}) to initiate the degradation reaction. Moreover, the kinetic rate constant and the removal percentage increased as temperature increased, in the following order: 60.1 % (298 K | k = 5.5 min^{-1}), 81.2 % (308 K | k = 7.2 min^{-1}), and 87.3 % (318 K | k = 9.4 min^{-1}) for MB; and 56 % (298 K | k = 4.9 min^{-1}), 61.8 % (308 K | k = 6.9 min^{-1}), and 74.7 % (318 K | k = 7.4 min^{-1}) for EOx. This is due to the increase of the kinetic energy of molecules, the frequency, and the collisions between reacting molecules and the catalyst, resulting in a faster reaction rate.

Conclusions

The thermodynamic study reveals that both the MB and EOx degradation reactions are spontaneous, and exothermic, with the EOX reaction being more energetically favorable. However, higher activation energy is required for the MB dye degradation. Furthermore, the thermodynamic study can be a suitable tool to get information about the catalyst activity and the energetic reliability of the process.

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