Deep learning study for the photodegradation of a binary mixture in a heterogeneous catalyst of copper oxide nanoparticles supported onto nanozeolite

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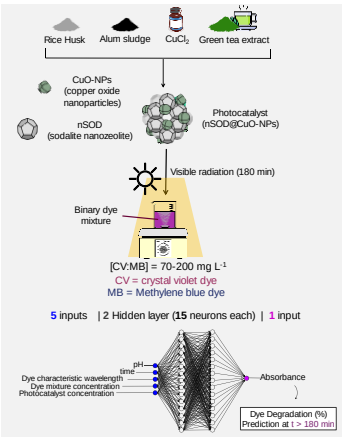


The present work aims to synthesize and characterize an eco-friendly supported nanocatalyst (nSOD@CuO-NPs) for application in the photodegradation of a dye binary mixture of crystal violet (CV) and methylene blue (MB) and to perform deep learning predictions. nSOD@CuO-NPs showed a mesoporous strucuture with analcime, sodalite, cuprite, and tenorite crystalline phases, ZP = -18.5 ± 4.30 mV, E_g = 1.67 eV, S_{BET} = 15 m^2 g^{-1}. 78.8% degradation (k = 0.0011 min^{-1}) for CV and 80.9% (k = 0.0013 min^{-1}) for MB were achieved under pH 6.71, T = 25 ± 2 °C, [nSOD@CuO-NPs] = 1.0 g L^{-1}, and [Dye mix.] = 135 mg L^{-1} after 180 min. The deep learning model showed high performance and reported that dye wavelength, dye mix. and catalyst concentration, time, and pH strongly affected the neural network's prediction ability. Therefore, the nanocatalyst shows promising photocatalytic activity, whereas the deep learning demonstrated to be a suitable tool for performing predictions about the progress of chemical reactions associated with AOPs.

Introduction

Annually, around 50.000 tons of synthetic organic dyes are produced and discharged in wastewater [1]. These organic dyes are hydrophilic, chemically and thermally stable, resistant to physio-chemical and biological wastewater treatment and a pose serious threat to aquatic animals and the environment. Heterogeneous photocatalysis using supported nanocatalysts (e.g. copper oxide nanoparticles supported onto nanozeolites, such as nSOD@CuO-NPs) has attracted many researchers due to the efficiency in degradation of organic dyes, with the generation of highly reactive oxygen species (i.e., $HO^{\bullet}$ e and $O_2^{-\bullet}$) which react non-selectively with the organic matter mineralizing them [2]. Copper oxide nanoparticles (CuO-NPs) show low toxicity, band gap energy (E_g) ranging from 1.2 - 1.7 eV, and can be produced from green synthesis [3]. However, the experimental runs can be time and cost-consuming, requiring computational tools such as deep learning to perform predictions about the process and to address the main important variables of the wastewater treatment. Thus, the present work aims to verify the suitability of deep learning using a multilayer perceptron artificial neural network (MLP-ANN) in the prediction of the degradation reaction progress in and beyond the experimental range to get insight into the catalytic activity.

Material and Methods

1. Synthesis of the heterogeneous supported catalyst: Nanozeolite sodalite (nSOD) was synthesized by hydrothermal method (180 ± 2 °C / 6 hours / 5 C° min^{-1}) from rice husk and aluminum waste as raw material [4]. CuO-NPs were synthesized by biosynthesis, followed by calcination (450 ± 2 °C / 6 hours) [5]. nSOD@CuO-NPs was prepared by impregnation method [6], where the catalytic support (nSOD) was mixed with 2.5 wt.% of the photoactive phase (CuO-NPs) under magnetic stirring (100 rpm / 90 min). After, the sample was dried (80 ± 2 °C) for 3 hours and calcined (450 ± 2 °C for 4 hours).

2. Characterization: The samples were analized 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}), Difuse Reflectance Spectroscopy (DRS) and Energy Dispersive X-ray Analysis (EDX).

3. Photocatalytic Activity and Kinetic Study: The photocatalytic activity tests were carried out in batch system using CV with MB dyes (135 $mg.L^{-1}$, pH 6.71) (as a target molecules) 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 CV:MB: under visible radiation, aliquots (~2 mL) were collected at time 0, 15, 30, 45, 60, 75, 90, 105, 120, 150 and 180 min, centrifuged (3500 rpm / 5 min) and diluted (1:10 v v^{-1}). The absorbance was determined by UV-Vis spectrophotometer (λ = 590 nm for the CV, and λ = 663 nm for the MB). The kinetic rate constant was

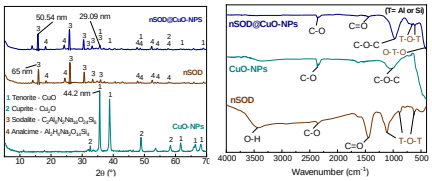
determined using the Langmuir-Hinshelwood model, according to Eq. (1) [7].

$$C_i = C_{i0} * e^{-k*t} \quad (1)$$

4. Deep Learning Study: To evaluate the progress of the photodegradation reaction and to predict the degradation percentage (%R) at times higher than the experimental set (t > 180 min, e.g., 200 - 300 min) a multilayer perceptron regression artificial neural network (MPL–ANN) algorithm was used [8]. The permutation importance (PIMP) method was carried out to identify the variable that affects the degradation percentage (%R) and hence the model prediction ability.

Results and Discussion

Figures 1(a) - 1(b) show the XRD diffractograms and ATR-FTIR spectra, respectively, of the catalytic support, photoactive phase and supported catalyst



(a) (b)

Figure1. XRD diffractograms and ATR-FTIR spectra of nSOD, CuO-NPs, and nSOD@CuO- NPs.

The diffractograms showed that the nSOD@CuO-NPs showed the catalytic support crystallite phases (analcime and sodalite) and of the crystallite phases of photoactive phase (cuprite and tenorite), with crystallite size ranging from 29.09 to 50.54 nm. The ATR-FTIR spectra identified the stretching and bending vibrations characteristic of zeolite were in both nNSOD and SOD@CuO-NPs. N_2 porosimetry revealed that all samples were mesoporous ($2 < D_p < 50$ nm) with a pore diameter between 12.9 and 37.1 nm. nSOD, CuO-NPs and nSOD@CuO-NPs showed a surface area of the 2, 14 and 15 $m^2\ g^{-1}$, respectively, Thus, there was an increase of the surface area of the nSOD@CuO-NPs due to the incorporation of the photoactive phase (CuO-NPs) onto the catalytic support (nSOD). The pore volume reduced from 0.05 $cm^3\ g^{-1}$ to 0.004 $cm^3\ g^{-1}$. nSOD@CuO-NPs showed zero-charge point (pH_{PZC}) of 7.46 and ZP = –18.5 ± 4.3 mV. EDX analysis reported the following elemental composition for the nSOD@CuO-NPs: Cu (0.49 wt.%), Na (2.99 wt.%), Al (3.99 wt.%), Si (5.44 wty.%), and O (43.37 wt.%). DRS spectra informed the band gap energy of the 2.22 eV (CuO-NPs), 1.65 eV (nSOD), and 1.67 eV (nSOD@CuO-NPs). The apparent rate of the pseudo first-order reaction from the ideal condition by CCRD 2^3 , 0.0011 min^{-1} (CV dye), and 0.0013 min^{-1} (MB dye), whereas the %R was 78.8% for CV, and 80.9% for MB, after 180 min (pH 6.71, T = 25 ± 2 °C, [nSOD@CuO-NPs] = 1.0 g L^{-1}, and [Dye mix.] = 135 mg L^{-1}). Table 1 shows the prediction carried out using MLP-ANN algorithm in the deep learning study.

Table 1. Predictions[a] carried out with MLP-ANN algorithm.[b]

Time (min)	Y_{pred}	Y_{obs}	Error
180	0.168	0.139	3%
240	0.127	0.115	1%
300	0.089	0.035	5%

[a] Predictions performed for MB dye degradation.

[b] Activation function: ReLU | weight uptdating function: AdamW | initial learning rate of 0.1% | neural network: 5:15:15:1 (5 inputs, 2 hidden layers with 15 neurons each, and 1 response). | R^2 of 0.87 and RMSE of 0.067.

Thus, PIMP score reveleaded that that characteristics of wavelength, dye mixture concentration, catalyst concentration, time, and pH affect the neural networks' prediction ability and hence, the degradation percentage (%R).

Conclusions

nSOD@CuO-NPs showed good photocatalytic activity (~80 % dye degradation) with suitable application in the degradation of persistent organic pollutants under visible light. The deep learning algorithm showed to be a promising and suitable tool for performing predictions about the progress of chemical reactions associated to advanced wastewater treatments, and for identifying the variables that affect the most the degradation reaction. The artificial neural networks (e.g., multilayer percepetron regressors) can be sucessfuly used to predict the progress of chemical reactions involved in photocatalytic degradation processes and for optimization purposes, being characterized as a good starting point for scale-up studies perfoming.

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