Biosynthesis and characterization of a novel supported nanocatalyst for the methylene blue dye photodegradation: Machine learning modeling and photocatalytic activity

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Abstract/Resumo

ABSTRACT – The present work aims to evaluate the photocatalytic activity of an alternative supported nanocatalyst (CuO-NPs@nANA) and to carry out a Machine Learning (ML) study to propose a reaction pathway for the MB dye degradation under visible light. Two machine learning algorithms (RF and XGB) were used in the regression model development from scientific papers concerning MB degradation (by GC-MS) to identify the degradation products of the reaction. XGB algorithm resulted in the best predictive model (R² equals 0.91 and 0.97 for training and testing, RMSE < 5.0), confirming the obtention of carbon dioxide (m/z =44), water (m/z = 18) and low-molar mass compounds at the final of MB degradation reaction. Moreover, 76.93% MB removal was reported at pH 10, [MB] = 200 mg L-1 and [CuO-NPs@nANA] = 0.5 g L-1 after 180 min under visible light, with *k* = 0.0088 min-1. Feature importance study revealed that the response m/w was strongly dependent on pH and reaction time. Therefore, this work confirms the potentiality of machine learning algorithms to develop predictive models for the elucidation of the degradation reaction pathway of organic dyes through heterogeneous photocatalysis.

*Keywords: nanozeolite, copper oxide nanoparticles, Methylene Blue, Machine Learning, heterogeneous photocatalysis.*

RESUMO - O presente trabalho visa avaliar a atividade fotocatalítica de um nanocatalisador suportado alternativo (CuO-NPs@nANA) e realizar um estudo de Aprendizado de Máquina (AM) para propor uma rota de reação para a degradação do corante MB sob luz visível. Dois algoritmos de aprendizado de máquina (RF e XGB) foram utilizados no desenvolvimento do modelo de regressão a partir de artigos científicos sobre degradação de MB (por GC-MS) para identificar os produtos de degradação da reação. O algoritmo XGB resultou no melhor modelo de predição (R² igual a 0,91 e 0,97 para dados de treino e teste, RMSE < 5,0), confirmando a obtenção de dióxido de carbono (m/z =44), água (m/z = 18) e compostos de baixa massa molar ao final da reação de degradação do MB. Além disso, 76,93% de remoção de MB foi relatada em pH 10, [MB] = 200 mg L-1 e [CuO-NPs@nANA] = 0,5 g L-1 após 180 min sob luz visível, com *k* = 0,0088 min-1. O estudo de importância característica revelou que a resposta m/w foi fortemente dependente do pH e do tempo de reação. Portanto, este trabalho confirma a potencialidade de algoritmos de aprendizado de máquina para desenvolver modelos preditivos para a elucidação do mecanismo de reação de degradação de corantes orgânicos por fotocatálise heterogênea.

*Palavras-chave: nanopartículas de óxido de cobre nanozeólita, azul de metileno, aprendizado de máquina, fotocatálise heterogênea.*

## Introduction

Worldwide, the textile industry is considered one of the major pollution sources of wastewater, once large amounts of water and synthetic organic dyes are used in dyeing and finishing processes (1). Annually, about 50,000 tons of the synthetic organic dyes produced are found in wastewater, being responsible for deleterious effects to biota and aquatic life (2). Organic dyes are toxic, chemically stable and resistant to conventional physio-chemical/biological wastewater treatments due to the low biodegradability of these contaminants (3). For example, Methylene Blue (MB) dye is thiazine cationic extensively used in textile industries as a colorant, being toxic to aquatic animals and extremely resistant to photo and biodegradation (4-5).

Thus, advanced wastewater treatments, such as Advanced Oxidation Processes (AOPs) are required to mitigate the environmental problems. Among AOPs, heterogeneous photocatalysis has been attractive for organic pollutant degradation, mainly due to the simple operation, versatility and high efficiency in the removal of organic dyes from aqueous solutions (6). Heterogeneous photocatalysis involves the reaction between the organic pollutant (e.g., MB dye) and reactive species of oxygen (ROS) generated in the process, mainly the hydroxyl radical (●OH), in the presence of a catalyst under UV or visible radiation (7). Alternative nanocatalysts have been encouraging new research on the photocatalytic degradation of dyes, especially due to their special properties (e.g., high surface area and porosity) and relatively low-cost of production (8). For example, copper oxide nanoparticles (CuO-NPs) supported onto low-silica nanozeolites have been used for the cationic dye photodegradation (9). Studies reported CuO-NPs as a p-type semiconductor with narrow band gap energy (Eg ~ 1.2-1.7 eV), low toxicity and cost-effective when obtained by biogenic synthesis (10-11). Moreover, about 94% of MB removal was reported in the literature, in which CuO-NPs supported onto nanozeolite X was used as a photocatalyst (12). Other studies confirmed that CuO-NPs supported onto nanozeolite X was able to retain 95% of the initial photocatalytic activity after 4 cycles of heterogenous photocatalysis under solar radiation for the removal of MB in the presence of another cationic dye, rhodamine B (RhB) (13).

Despite the high efficiency informed in the mentioned works, few studies involving an eco-friendly CuO-NPs@nanozeolite nanocatalyst were found in the literature. Also, the elucidation of the degradation mechanism of MB dye in heterogenous photocatalysis is required before scale-up. However experimental procedures to define a generic reaction pathway can be time and cost-consuming, requiring the use of alternative tools, such as computational tools based on decision trees (e.g., Xtreme Gradient Boosting – XGB, and Random Forest – RF algorithms) (14-15).

In this context, the present work aims to verify the photocatalytic activity of a novel and eco-friendly CuO-NPs@nanozeolite photocatalyst and to propose a reaction pathway of MB degradation through a generalized predictive model obtained from machine learning algorithms.

## Experimental section

*Synthesis and characterization of the nanocatalyst*

The supported heterogeneous nanocatalyst (CuO-NPs@nANA) was synthesized by the impregnation method, according to the literature (16), where the CuO-NPs were used as nanocharges and analcime nanozeolite (nANA) as the matrix or catalytic support.

CuONPs were obtained by biogenic synthesis using *Camelia sinensis* extract was used as a reducing/stabilizing agent of copper(II) chloride dihydrate (CuCl2∙2H2O, ACS reagent, ≥99.0%, Sigma-Aldrich®) in an aqueous solution (1 mol L-1) (17). The metallic precursor solution and the extract (1:1 w/w) were placed under magnetic stirring (150 rpm / 90 min) at 50-70 °C for 1.5 h (pH ≈ 6). The precipitation product formed was centrifuged at 4500 rpm for 15 minutes, with the settled material being dried in an oven operating at 80 °C for 12 h.

nANA was synthesized by hydrothermal method, according to the literature (18). After, the nANA was filtered (ϕ = 0.45 µm) and washed with distilled water and ethanol 70% (pH ≈ 7). The nANA was dried in an oven at 80°C for 12 h.

Then, the CuO-NPs@nANA nanocatalyst was prepared by mixing CuO-NPs and @nANA in beaker containing 100 mL of distilled water and calcinated (450 °C for 4 h with 10 ºC min-1).

*Characterization*

X-ray diffraction (XRD) analysis was performed in a Bruker diffractometer, model D2 Advanced with copper tube (λCu-α = 1.5418 Ǻ) ranging from 10º to 70º. ASAP 2020 equipment (USA) by Micromeritics® was used to determine the surface area (SBET) and porosity (Dp and Vp) by N2 porosimetry using the BET/BJH method. The band gap energy (Eg) was determined by UV-Vis Diffuse Reflectance Spectroscopy (DRS) using JASCOV-670 equipment, with wavelength ranging from 200 to 800 nm. Zero Charge Point (pHZCP) was evaluated by 11-point assays, using NaOH 0.1 mol L-1 and HCl 0.1 mol L-1 for pH adjustments (19). Then, a plot of initial pH *versus* final pH was performed to find the region in which no significant changes in pH were observed. The surface charge was obtained by zeta potential (ZP) in an Electrophoretic Light Scattering method (PALS) (NANOBROOK OMNI) using an electrode (BI-SREL or BI-ZEL) under a scattering angle of 15° at room temperature (293.15 K).

*Photocatalytic test and kinetic of degradation*

The photocatalytic degradation of MB was carried out in a slurry reactor at 25 ± 2 °C under visible light (202 W m-2). The volume used was 100 mL in all experimental were carried out in duplicate with the following conditions: [MB] = 200 mg L-1, [CuO-NPs@nANA] and pH 10.

The experimental data of MB photocatalytic degradation were adjusted to the Langmuir-Hinshelwood model (L-H), according to the Eq. (1) (20):

|  |  |
| --- | --- |
|  | (1) |

Where *Ci0* and *Ci* are the initial concentration and concentration at time t, in mg L-1; *k* is the apparent rate of the pseudo first-order reaction (min-1); and *t* is reaction time (min).

*Degradation reaction pathway*

To investigate a possible reaction pathway for the MB degradation, a ML algorithm was used to propose a generalist equation for the reaction pathway taking place in 180 min under visible light. Thus, two decision tree-based models (XGB and RF algorithm) were used to predict the products and byproducts which appear with high frequency during and after the process. 7-fold cross validation (cv = 7) was used for all algorithms. The input variables (pH, nanocatalyst and dye concentration) and the response (mass-charge ratio) of the ML algorithm were data reported by GC-MS of scientific works that used heterogeneous photocatalysis in the MB degradation under visible light, using metallic heterogeneous supported nanocatalysts. Table 1 shows the configurations of each ML algorithm used in this work.

**Table 1.** Machine learning model configurations.

|  |  |  |
| --- | --- | --- |
| **Model** | **Configuration** | **Ref.** |
| RF | Maximum depth trees: 1, 2, 3, 5, 7, 10, 15 mNumber of decision trees: 25, 50, 75, 100, 150 | (21) |
| XGB | Maximum depth of the trees: 10, 20, 30, 50, 100, 200 mSampling: bootstrapping | (22) |

According to Table 1, RF was investigated in terms of number of decision trees and their maximum depth. Regarding XGB, the maximum depth of the trees of the model was varied to find the increase in the computational and learning power of the regression model. The criteria adopted for the selection of the model used to propose the reaction pathway of the MB degradation were the algorithm with the highest determination coefficient (R² - Eq. 2) and the root mean squared error (RMSE – Eq. 3) for training and testing dataset.

|  |  |
| --- | --- |
|  | (2) |

|  |  |
| --- | --- |
|  | (3) |

Where: *yi,exp* and *ŷi,pred*are the actual and the predicted value of the response and *N* is the data size.

*Feature importance*

To evaluate the contribution of each parameter of the dataset used in the ML study, a feature importance study was carried out. The influence of each variable (input data) was measured by permutation score value was carried out (23). All permutation score above 0.50 was considered to significantly influence the response of the machine learning predictive model, m/z ratio, and then, the products and byproducts generated during the photocatalytic degradation of MB.

## Results and Discussion

*Machine learning model selection*

Figure 1 shows the XRD diffractograms of the CuO-NPs, nANA and CuO-NPs@nANA, where CuO-NPs@nANA showed the phases analcime associated with nanozeolite (COD 9008387) and tenorite (COD 1011148), associated to copper oxide, which confirms the impregnation of copper oxide in the nanozeolite during the synthesis. Moreover, the average crystallite diameter of CuO-NPs@nANA was lesser than analcime and tenorite (50.54 nm and 29.09 nm) indicating that good electrostatic interaction between the nanocatalyst and the catalytic support, resulting in high values of SBET.



**Figure 1.** XRD diffractograms of the CuO-NPs, nANA and CuO-NPs@nANA.

Table 2 shows the textural properties of the nanocatalyst (CuONPs-@nANA) and its counterparts (CuO-NPs and nANA). CuO-NPs, nANA and CuO-NPs@nANA were characterized as mesoporous nanomaterials, once Dp ranged from 2 to 50 nm (24). It was noticeable that nANA showed a higher surface area than CuO-NPs due to defects (e.g., vacancy) of the chemical structure of the nanozeolite analcime, which contains atoms (Al, Si, O) with different sizes in its composition (25). The surface area of CuO-NPs@nANA slightly reduced compared to nANA (from ~18 to ~14 m2 g-1). It was due to the incorporation of the CuO-NPs in the nanozeolite structure, reducing the vacant sites and interstices of the mesoporous nANA, which agreed with the behavior found for nanocomposites (26). However, CuO-NPs@nANA showed higher pore volume than its counterparts, which is positive for photocatalytic activity. Thus, high pore volumes and surface area tend to increase the photocatalytic activity of nanocomposites, hence increasing the MB dye degradation (27).

**Table 2.** Surface area (SBET), pore volume (Vp), pore diameter (Dp) and zeta potential (PZ) of the CuO-NPs, nANA and CuO-NPs@nANA.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Dp (nm)** | **SBET (m2 g-1)** | **Vp (cm3 g-1)** |
| CuO-NPs | 9.11 | 13.01 | 0.02800 |
| nANA | 12.07 | 18.48 | 0.03440 |
| CuO-NPs@nANA | 16.61 | 14.78 | 0.3750 |

The pHZCP for nANA, CuO-NPs and CuO-NPs@nANA were 8.18, 7.73, and 7.49, respectively. Moreover, DRS analysis revealed the Eg = 1,28 eV for CuO-NPs@nANA, which is comparable to values of other versatile and promising photocatalyst reported in the literature (28). The ZP of all samples ranged from -29.23 to -51.23 mV, suggesting physio-chemical stability due to electrostatic factors for the nanocatalyst and its counterparts (29).

*Photocatalytic degradation*

The heterogeneous photocatalysis parameters set to this work were [MB] = 200 mg L-1, [CuO-NPs@nANA] = 0.5 g L-1 and pH 5.9 carried out under magnetic stirring at 25°C, in which 74.91% dye removal from aqueous solution was achieved (Figure 2.



**Figure 2**. Kinetic curve of MB photocatalytic degradation.

According to Figure 2, the Langmuir-Hinshelwood fitted the experimental data, being confirmed from R2 and R2adj values, which are close to unity. Moreover, the accuracy of the linearized Langmuir-Hinshelwood model can be confirmed with the values of the error functions (SAE, SSE, ARE). Furthermore, a MB removal of about 75% was observed in Figure 2 (C C0-1 ~ 0.75) after 180 min of the photocatalytic degradation process under visible light. The apparent rate constant evaluated was 0.0088 min-1, suggesting that about 0.88% of the dye molecules in solution are degraded after each minute (30). Therefore, considering this pattern, it is expected 79.2% degradation of MB in the aqueous solution after 90 min. However, the actual observed value was 76.93%, which is slightly lower the predicted value due to side reactions such as the generation of intermediate products (parallel reactions) and the uncontrollable and undesirable recombination between the electron (e-) and hole (h+) pair and regeneration of H2O from H+(aq) and •OH(aq) (31). To further investigate the explain former assumption, a theoretical study obtained from supervised machine learning algorithm is described in the following section.

*Machine learning for MB degradation reaction pathway*

Two ML algorithm was used to propose a generic reaction pathway for MB degradation. Table 3 informs the performance of each machine learning algorithm tested.

**Table 3.** Performance of the machine learning algorithms tested.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Model** | **R2train** | **RMSEtrain** | **R2test** | **RMSEtest** |
| RF | 0.8532 | 4.6956 | 0.8030 | 5.2625 |
| XGB | 0.9125 | 3.830 | 0.9769 | 2.310 |

According to Table 3, the XGB model showed the best performance in the prediction of the intermediates and products of the MB dye degradation under visible light, once R2 for training and testing were greater than 0.90. Moreover, the RMSE for training and testing dataset were close (|RMSEtrain - RSMEtest| = 1.52), indicating low probability of overfitting (32). Furthermore, the value observed for R2test higher than R2train suggested that the XGB algorithm tested performed very well new data, being characterized as a suitable generalized model. The run time of the pattern recognition (machine learning processing time) was less than 5 seconds, requiring low computational power in this case.

*XGB model: feature importance evaluation*

Figure 3 shows the feature importance study, in which the permutation score for each input parameter used in the XGB model is informed. Thus, the reaction time and pH were significant to the XGB generalized model, once the permutation score was greater than 0.50. The greater the permutation scores greater the influence of the feature (input variable) on the response. Catalyst and dye concentration showed to not be important in the reaction pathway of the MB degradation. Thus, depending on the reaction time observed in the process, specific species are generated as intermediate or (by)products. According to experimental results, the higher the time higher the amount of low-mass chemical species observed (33). Moreover, Figure 3 also suggests that alterations in pH can significantly affect the intermediates and products formed during the degradation reaction, which was confirmed in experimental runs found in the literature (34).



**Figure 3.** Feature importance study generated from XGB model.

Figure 4 shows the generalized reaction pathway proposed for MB dye degradation observed for the experimental procedure of this work.



**Figure 4.** General reaction pathway for MB degradation under visible light.

According to Figure 4, the final products of the photocatalytic degradation of MB dye were carbon dioxide (CO2, m/z = 44), water (H2O, m/z = 18), aniline (C6H5NH2, m/z = 93), respectively. MB degradation achieved in the experimental run was 76.93%, suggesting that the remaining (23.07%) corresponded to unreacted MB. Also, the presence of aniline in the aqueous solution and trace amounts of chloride and sulfate ions should be analyzed to check the water quality. These ions are naturally found in surface water and wastewater composition, being not damaging to humans and aquatic life dependent on their concentration. Moreover, the proposed photocatalytic process was considered promising, once methylene blue is converted to low-mass and less toxic compounds and aniline, which can be easily removed from water by the next cycle of heterogeneous photocatalysis or other processes such as adsorption onto a low-cost nanoadsorbent (e.g., nanozeolites synthesized from agro-industrial waste).

Conclusions

The present study proposed the use of an alternative nanocatalyst for the photocatalytic degradation of MB dye in an aqueous solution under visible light. The obtention of CuO-NPs@nANA nanocatalyst with high purity, once analcime and tenorite phases are found in XRD for CuO-NPs and nANA, respectively. Additionally, the development of a generalist model obtained from a ML study was proposed to predict the intermediates and degradation products of heterogeneous photocatalysis. Thus, a reaction pathway for MB photocatalytic degradation was proposed, in which the XGB algorithm (max. tree depth: 50 m) generated a good predictive model. XGB showed a good accuracy (R2train = 0.9125 and R2test = 0.9769), with RMSE less than 4 g mol-1 for training and testing datasets, suggesting a low probability of overfitting. Moreover, after the final of the reaction (120-180 min), carbon dioxide (m/z = 44) and water (m/z = 18) were observed in GC-MS and in XGB prediction. Regarding the experimental run carried out in this work, 76.93% of MB degradation was achieved at [MB] = 200 mg L-1, [CuO-NPs@nANA] = 0.5 g L-1 and pH 10 after 180 minutes under visible light. Kinetic studies reported *k* = 0.0088 min-1. Therefore, this study confirms the potential use of ML algorithms as a suitable tool for making predictions of the degradation products and intermediate species generated during wastewater treatment. Owing to the good accuracy of the XGB prediction model, it can be considered a promising starting point for the scale-up of wastewater treatments with a focus on organic pollutants, as well as an alternative method to elucidate the degradation mechanism of these contaminants.

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