Optimization of the photocatalytic degradation of clomazone using binary ZnO based nanomaterials in aquatic environment

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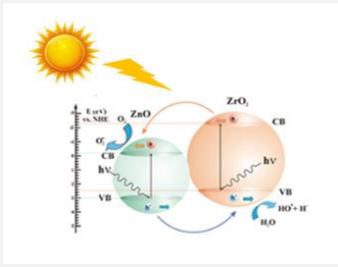

Herbicide clomazone, a widely used against both grass and broadleaf weeds, presents a significant environmental challenge due to its high water solubility. This characteristic increases the risk of contamination to surface and ground waters, demanding effective removal strategies. Heterogeneous photocatalysis, particularly utilizing ZnO-based nanomaterials, has been promising in degradation of various organic pollutants.This research aimed to investigate the removal efficiency of the herbicide clomazone with sustainable heterogeneous photocatalysis with newly synthesized binary coupled photocatalysts, i.e ZnO/MeOx nanopowders (ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2). Various experimental parameters, including catalyst loading and initial pH, were examined to determine optimal removal efficiency. Chemometrics was utilized to define the optimal photocatalytic conditions.

Introduction

Photocatalysis, as one of the advanced oxidation processes, is considered green method for pollutant removal, mainly due to the possibility of harnessing globally available natural sunlight, which is free and benign towards the environment [1]. In this process the light acts as an activator of the catalyst, accordingly named photocatalyst. Heterogeneous photocatalysis is a term used to describe a photocatalytic system in which the reactants are in different phases. This is a surface phenomenon where reactions occur within the active center on the photocatalyst (PHC) in the presence of light [2]. Accordingly, ZnO, MgO, CeO_2, and ZrO_2 are cost-effective semiconductors extensively utilized in catalysis, electronics, photodegradation, and for various other applications, due to their beneficial properties. These materials are favored for their affordability, non-toxic nature, and desirable optical characteristics within the UV/near-visible spectrum.

The focus of this research was to investigate the removal efficiency of the clomazone (CLO) using sustainable heterogeneous photocatalysis with ZnO/MgO, ZnO/CeO_2 and ZnO/ZrO_2 nanopowders as photocatalysts. Various factors (i.e. PHC type and loading and initial pH) were also examined. Finally, photocatalytic activities of the newly synthesized ZnO/ZrO_2 photocatalyst and pristine ZnO, MgO, CeO_2, and ZrO_2 photocatalysts were compared under optimal experimental conditions.

Material and Methods

The pesticide CLO (CAS No 81777-89-1, 98.8% purity, Sigma−Aldrich) was used in the experiments of photocatalytic degradation. The following chemicals were used as the components of the mobile phase for liquid chromatography: acetonitrile (ACN, 99.9%, Sigma−Aldrich) and orthophosphoric acid (85%, *pro analysis*, Sigma–Aldrich). The initial pH values were set using 0.1 mol/L $HClO_4$ (70% (*w*/*w*), > 99.99%, Sigma Aldrich) and 0.1 mol/L NaOH (*pro analysis*, MOSS & HeMOSS). In the photocatalytic degradation experiments, three different ZnO-based catalysts were tested, hereinafter marked as ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2. These new ZnO-based mixed powder photocatalysts were prepared by three-step mechanochemical-assisted calcination procedures. Photocatalytic experiments were performed as previously described by our group [3]. The examinations under simulated sunlight irradiation (SSI) were performed using 50 W halogen lamp (Philips). The experiments were carried out using 20 mL of 0.05 mmol/L solution of CLO with/without 10 mg (γ = 0.5 mg/mL), 20 mg (γ = 1.0 mg/mL) and 40 mg (γ = 2.0 mg/mL) of ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2 under different initial pH values (6−7; 8−9; 10−11) set by portable pH meter (WTW ProfiLine pH 3110). The samples were analyzed using a high-pressure liquid chromatograph with diode array detector (UFLC-DAD, Shimadzu Nexera, Tokyo, Japan). The chromatographic conditions for CLO, was the following: 60 : 40 (ACN : H_2O, v/v), flow rate 1.0 mL/min, injection volume 20 μL, column temperature 25 °C, absorption maximum with DAD detector at 210 nm. Descriptive statistics provided information about the dataset. Continuous variables were tested by multivariate analysis of variance (MANOVA). Pearson's linear correlation tested the relation

between the pairs of continuous variables. Linear regression was employed to build and compare mathematical models.

Results and Discussion

In order to evaluate the data of the photocatalytic efficiency of ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2 in the removal of CLO, multivariate analysis was employed. Experiments were designed as full factorial randomized experimental design. Dependent variables were percentages of degraded pollutant. Independent variables were: (1) type of photocatalyst (ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2); (2) catalyst loading (0.5, 1.0, and 2.0 mg/mL); and (3) initial pH of suspension. All samples were analyzed minimally as duplicates. Looking more into details (interactions), it could be noted that catalyst loading of 2.0 mg/mL for almost all photocatalysts yielded the best degradation for CLO. It is well-known that the photocatalytic degradation is dependent on the initial pH value. The pH value affects the charge properties of the photocatalyst's surface and investigated organic pollutant. In Table 1 there are shown the optimal parameters for CLO degradation. The greatest performance of ZnO/ZrO_2 can be explained by the lowest bandgap energy (3.241 eV), which indicates that this semiconductor can be efficiently activated under SSI.

The efficiencies of the newly synthesized binary photocatalyst ZnO/ZrO_2 and pristine ZnO, MgO, CeO_2, and ZrO_2 were compared, along with direct photolysis of CLO. This evaluation aimed to assess and potentially validate the enhanced photocatalytic activity facilitated by the eco-friendly synthesis approach. As depicted in Fig. 1, the ZnO/ZrO_2 photocatalyst emerged as the most proficient in CLO removal under optimized experimental conditions. This supports hypothesis that coupling of photocatalysts enhances efficiency, particularly in the visible region.

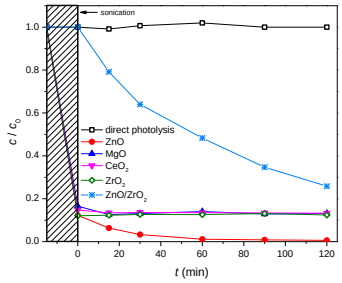

Figure 1. Photolytic and photocatalytic degradation of CLO (0.05 mmol/L) in the presence of different photocatalysts (2.0 mg/mL) using SSI.

Table 1. Optimal parameters for degradation of CLO.

Factor	Parameter
Removal efficiency (%)	77
PHC type	ZnO/ZrO_2
PHC loading (mg/mL)	2.0
Initial pH	~10

Conclusions

The ZnO/MgO, ZnO/CeO_2, and ZnO/ZrO_2 nanomaterials were successfully prepared by three-step mechanochemical-assisted calcination procedures, i.e. without harmful and expensive chemicals, accounting for the foundation of green chemistry. The highest degradation efficiency was achieved in the presence of ZnO/ZrO_2, when 77% of CLO was removed after 120 min of SSI under the optimal experimental conditions obtained using chemometrics. Namely, the optimal removal of CLO was achieved by the ZnO/ZrO_2 with concentration of 2.0 mg/mL and pH ~10.

Acknowledgments

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