Simultaneous removal of Bisphenol S, Carbamazepine and Clonazepam from water and wastewater using Ti-biomass based composites

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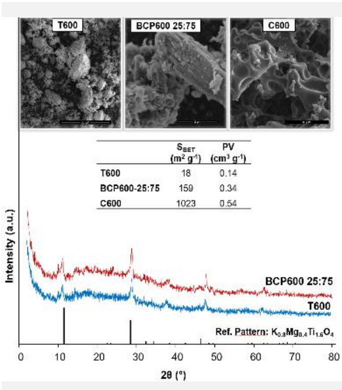

The combined effects of Ti-biomass based composites (BCPs) for enhanced removal of mixed Bisphenol S (BPS), Carbamazepine (CBZ) and Clonazepam (CZP) in water and wastewater have been explored. Three massic ratios of Ti to biomass (25:75, 50:50 and 75:25) and two calcination temperatures (400 and 600 °C) were evaluated. The adsorptive and photocatalytic capability of the composites were studied. In the presence of sunlight simulation, the BCP600-25:75 (composite formed by 25%:75% Ti:coconut biomass) exhibited the best removal performance (95.0%, 91.7% and 96.7%) of BPS, CBZ and CZP, respectively, surpassing the commercial TiO_2-P25 (13.5%, 20.0% and 97.1% for BPS, CBZ and CZP, respectively). The applicability of the BCP600-25:75 on real wastewater was also investigated. BCP sintethized produced with coconut shell biomass showed great potential for removal of these three contaminants from water.

Introduction

Contaminants of emerging concern (CECs) are mostly recalcitrant substances that enter the aquatic environment, and their continuous increase negatively impacts the ecosystems [1]. Low concentrations of some of these CECs in aqueous matrices have been reported to cause reproductive and endocrinal disabilities on human and wildlife system but also the increase on antibiotic resistant bacteria [1]. Although there are extensive studies on the generation, fate, potential impact, and ecological risks associated to CECs in the aquatic environment, investigations on how to effectively remove Bisphenol S (BPS), Carbamazepine (CBZ) and Clonazepam (CZP) is still lacking [2].
The sinthesis of composites by doping TiO_2 with carbonaceous biomass can significantly improve the surface functionalities, adsorption performance, and expand the number of potential applications [3]. Coconut shell biomass is considered as a potential precursor for composites with sorptive and photocatalytic properties because it exhibits chemical stability, high mechanical force, and porous structure heterogeneity [4].
The improved efficiency of Ti-biomass composite photocatalysts (BCPs) on the removal of CECs has been confirmed in multiple studies [5]. However, most studies to date have investigated the removal of dyes and/or a single contaminant. Choosing BPS, CBZ and CZP as target contaminants, both adsorption and photocatalytic capacities of BCPs were explored. In addition, the removal of BPS, CBZ and CZP by BCPs was analyzed on real wastewater.

Material and Methods

Coconut shell biomass (BC) was prepared according to Oliveira et al. (2012) [4]. BCP composites (25:75, 50:50, 75:25 weight ratios) were synthesized using a sol-gel method adapted from Silvestri et al. (2019) [5]. Titanium isopropoxide (TTiP), BC, and KOH (30%) in isopropyl alcohol (250 mL) were mixed, dried, and pyrolyzed at 400 or 600 °C for 2h. After neutralization with 1 M HCl and ultrapure water wash, composites labeled as BCPX-Y were obtained, where X is the calcination temperature (400 and 600) and Y is the Ti:BC weight ratio (25:75, 50:50, and 75:25).
Control samples (C400, C600, T400, T600) were prepared in the same condition of the composite.
The removal of mixed BPS, CBZ and CZP solution (0.4 mg L^{-1}) by composites and controls (100 mg L^{-1}) were tested towards adsorption (without light) and photocatalytic tests under sunlight simulation spectrum lamp (adjusted for ~15 W/m^2 of UV-A irradiance) without pH adjustment (pH ≈ 6.0).
The BPS, CBZ and CZP levels before and after treatment were determined by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) Waters Xevo-TQD. The chacterization of BCP600-25:75, T600 and C600 were performed by Fourier-transform infrared spectroscopy (FTIR), surface area BET (Brunauer, Eminett e Teller), Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).

Results and Discussion

Table 1 shows the removal (in %) of BPS, CBZ and CZP by the blank control (i.e. without composite) was negligible, indicating that these compounds are stable under dark conditions [2] . In the absence of light (adsorption), commercial activated carbon (A.C.), C600 (coconut biomass calcined at 600 °C) and the BCP600 25:75 composite obtained the highest removal responses.

In the presence of sunlight simulation, the best responses were obtained by the BCP600 25:75 (95.0%, 91.7% and 96.7% removal of BPS, CBZ and CZP, respectively) followed by TiO_2-P25 (13.5%, 20.0% and 97.1% of BPS, CBZ and CZP, respectively) (Table 1). C600 presents removal close to 100% for all pollutants even before exposure to light.

The BCP600 25:75 composite was selected for its dual sorptive and photocatalytic capabilities, efficiently eliminating BPS, CBZ, and CZP from water. Coconut biomass provides adsorption sites for the contaminants, enhancing their proximity to TiO_2 sites via surface diffusion. This proximity fosters degradation through the generation of reactive oxidative species (ROS) on the TiO_2 surface, stimulated by simulated sunlight [3,5].

The characterization of the materials showed that BCP600-25:75 has a hybrid morphology between the coconut biomass and Ti with rougher vessel structures, provided by the SEM images (**Fig.1**). The specific surface area of the BCP600 25:75 composite was found to be greater than that of the T600 control, attributed to the presence of coconut biomass. The specific surface area obtained for the C600 is of significant interest due to the observed value been close to 1000 $m^2 g^{-1}$. The BCP600-25:75 was indexed with the $K_{0.8}Mg_{0.4}Ti_{1.6}O_4$ phase (JCPDS 01-073-0671 - Potassium Magnesium Titanium Oxide) (**Fig.1**). Therefore, the formation of a TiOx compound, partially substituted by K and Mg, with an oxygen stoichiometry of O = 1.6 was observed, closely approaching the expected O_2 stoichiometry of TiO_2.

BCP600-25:75 was evaluated for treating real wastewater spiked with the contaminants. The initial concentration of BPS, CBZ and CZP in the aqueous matrix (250 µg L^{-1} each) reduced to 26, 78 and 110 µg L^{-1} of BPS, CBZ and CZP, respectively, when the wastewater was treated with BCP600-25:75 (Table 1). The observed reductions in contaminant concentrations are in line with findings from previous studies by Alfred et al. (2020) [3]. These reductions may be attributed to the presence of other organic substrates in the real wastewater, which could potentially compete for active sites on the composites or interact with reactive species in the reaction medium.

Conclusions

The post-annealing treatment temperature of 600 °C of the Ti:coconut composite with biomass ratio of 25:75 (BCP600 25:75) presented the best performance regarding three contaminants removal. The removal of CBZ and CZP by BCP600 25:75 is mainly through adsorption. However, the photocatalytic hability of the composites also plays an important role in removing these CECs from water. The competition among diverse organic substances for adsorption sites emphasizes the intricacy of real wastewater matrices, underscoring the need to consider these complexities in designing and evaluating composite materials for water treatment.

Table 1. Removal of Bisphenol S, carbamazepine and clonazepam in ultrapure water and wastewater* by synthesized composites and controls.[a]

	BPS		**CBZ**		**CZP**	
	ADS (%)	**ADS+PHOTO (%)**	**ADS (%)**	**ADS+PHOTO (%)**	**ADS (%)**	**ADS+PHOTO (%)**
Adsorption control (dark)	0	n.a.	6	n.a.	6	n.a.
Photolysis	n.a.	0	n.a.	0	n.a.	21
Activated Carbon	100	100	100	100	100	100
TiO2-P25	n.a.	13	n.a.	20	n.a.	97
BCP600-25:75	**8**	**95**	**89**	**92**	**95**	**97**
BCP600-50:50	0	36	20	24	37	40
BCP600-75:25	0	22	8	15	32	31
BCP400-25:75	0	0	0	10	15	19
BCP400-50:50	0	0	0	8	7	12
BCP400-75:25	0	11	0	9	9	12
Controls						
C400	16	16	22	0	33	31
C600	100	100	100	100	100	100
T400	0	52	0	7	13	28
BCP600-25:75 (EF)*	**n.a.**	**89**	**n.a.**	**68**	**n.a.**	**57**

[*] In bold, composite with best removal performance. Legend: n.a.: not applied; E.F.: effluent.

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