Ashes from Thermoelectric Plants Used as an Alternative Catalyst for Carbamazepine Degradation via Heterogeneous Fenton Reaction

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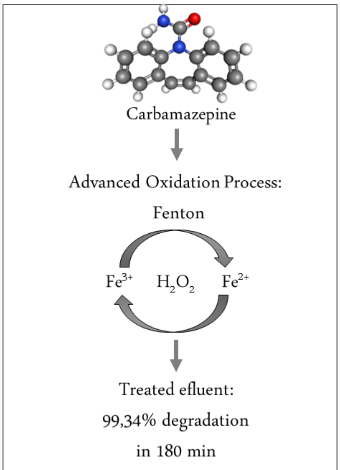

In this study, coal ash, derived from a thermal power plant, was utilized as a catalyst aiming to degrade carbamazepine in water via heterogeneous Fenton reaction. The ashes were characterized using SEM-EDS, FTIR, BET, and XRD techniques. The variables hydrogen peroxide concentration and catalyst dosage were evaluated through a 2^2 experimental design. Based on the characterization, the material exhibited a mesoporous structure and showed a 5.5% iron content as iron oxide, well-distributed on the material's surface. The optimal degradation rate of CBZ was achieved under conditions of [catalyst] = 1.4 g L^{-1}, [H_2O_2] = 4.0 mM, with pH fixed at 3.0, resulting in a degradation efficiency of 99.34% after 180 minutes of reaction. In light of the findings, it is evident that the ashes can be considered a promising catalyst for Fenton reactions aimed at degrading CBZ in wastewater.

Introduction

In recent years, water has been continuously contaminated with numerous artificial chemical pollutants, among which emerging contaminants (ECs) serve as prime examples, making water safety a global issue [1]. Among ECs, carbamazepine (CBZ) can be cited, which is a widely used antiepileptic medication detected in various aquatic environments. Due to its stability, bioaccumulation, and toxicity, CBZ has emerged as an EC requiring urgent treatment, as it has the potential to pose health risks to humans [2, 3]. An alternative for CBZ removal from contaminated waters is advanced oxidative processes (AOPs). Among the various AOPs, the Fenton process stands out, based on the decomposition, in acidic media, of hydrogen peroxide (H_2O_2) using iron salts to generate hydroxyl radicals (•OH) capable of degrading numerous pollutants. Enhancement of this AOP can be achieved through the incorporation of heterogeneous catalysts into Fenton, which would improve the system by facilitating catalyst recycling and reducing ferrous sludge [4, 5]. One option for a heterogeneous catalyst being studied for the Fenton process is heavy ash derived from coal combustion in thermal power plants, as it contains iron oxide in its composition [6, 7]. Thus, the present study aims to evaluate the degradation of carbamazepine in aqueous solution through the application of heterogeneous Fenton oxidation, using heavy ash as a catalyst for H_2O_2 activation.

Material and Methods

All experiments were conducted using a CBZ solution with an initial concentration of 20 mg.L^{-1}. The reaction pH was adjusted to 3.0 with sulfuric acid (0.5 M). The system was maintained under magnetic stirring throughout the 180-minute reaction period. The reaction volume was 50 mL of the initial solution. The degradation study of CBZ was conducted using a 2^2 + 3 central points experimental design, with the variables analyzed being the catalyst concentration (x_1) and the oxidant concentration (x_2). In addition to these assays, two more control points were performed using only the catalyst or only the oxidant with the CBZ solution. After the reaction period, 2 mL samples were collected and filtered with a 0.45 µm PTFE syringe filter to separate the ash particles and added to a vial with methanol (10% v/v) to halt the reaction. Monitoring of the phenol concentration from the experimental design was carried out by high-performance liquid chromatography (Shimadzu) with a Diode Array Detector (HPLC-DAD) at a wavelength of 270 nm.

Results and Discussion

The characterization of the ashes indicated that the material is primarily composed of silica (64%), alumina (18%), and iron (9.9%). XRD analysis demonstrated that the main phases obtained in the sample were quartz, mullite, and iron oxide. SEM images revealed that the ash particles have a heterogeneous morphology, with iron uniformly distributed on the material's surface. The FTIR analysis spectrum showed bands related to Si-O-Si stretching at 1060 cm^{-1} and 794 cm^{-1}, Al-O bonding at 690 cm^{-1}, and Fe-O stretching at 550 cm^{-1} and 445 cm^{-1}. BET analysis of the material's porosity indicated the predominance of mesopores on the surface, with a bimodal distribution of pore sizes, with peaks between 4 and 15 nm. The material's specific surface area was 2.0 m^2 g^{-1}.

The results of the experimental design are depicted in Figure 1. Upon analyzing the data, it is evident that the best CBZ degradation results were obtained in experiments 2 (+1 and -1) and 4 (+1 and +1), with degradation values of 99.34% and 99.33%, respectively, being nearly identical. In light of this, it is apparent that the concentration of H_2O_2 did not have significant influence on the final degradation, unlike the concentration of the ashes. Research conducted on CBZ degradation indicated that the Fenton process achieved maximum degradation of 42.6% under different conditions and using different Fe^{2+} sources [3], with removal in the range of 84-100% of the initial CBZ [8]. The central points (experiments 5 to 7) showed good reproducibility, with a standard deviation of 4.9%, indicating a linear behavior of the system. Another point to note was the control points. For the CBZ assay with only the ashes, a degradation of 25.91% was obtained, and for the CBZ with H_2O_2 point, 27.20%, indicating that individually, the ashes and the oxidant already have the capacity to degrade or remove CBZ through adsorption without the need to be associated. From these results, it can be inferred that the adsorption process of CBZ through the ashes occurred concomitantly with heterogeneous Fenton. ANOVA indicated that the system was not significant (Fcal/Ftab = 1.04), and only the variable x_1 was statistically significant.

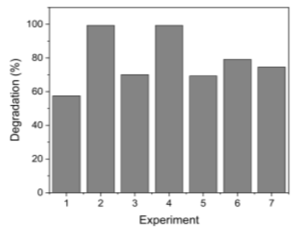

Figure 1. Degradation of CBZ (20 mg.L^{-1}) by heterogeneous Fenton process, pH = 3.0

Conclusions

The study served to indicate that the ashes were efficient sources of Fe for the Fenton reaction, and the proposed system achieved a maximum CBZ degradation of 99.34% under optimal conditions, triggering further research into other experimental design conditions, as well as the application of ashes for the adsorption process.

Acknowledgments

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