Utilization of Cliff Sediment as a Catalyst for Phenol Degradation in Photo-Fenton Reactions

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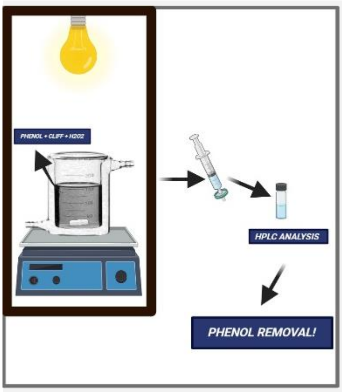

The objective of this study was to evaluate the degradation of phenol in the Photo-Fenton reaction using sediment iron sourced from cliffs obtained at Ponta Negra Beach, RN. The methodology involved transforming the cliff into powder, which was analyzed by XRF, and in experimental phenol degradation assays. The assays varied in terms of the initial contaminant concentration (10, 30, and 50 $mg.L^{-1}$) while the other parameters remained constant: catalyst concentration (2 $g.L_{-1}$), hydrogen peroxide concentration (6 mM), pH 3.0, and temperature (20°C). The phenol concentration in the samples was measured by HPLC. Ultimately, it was obtained that the elaborated cliff powder contains 47.21% iron (III) oxide, followed by 27.08% aluminum oxide, and 24.19% silicon dioxide. Among the studied phenol concentrations, the solution with 10 $mg.L^{-1}$ showed the best degradation result (93.54%) under the studied reaction conditions.

Introduction

Current industrial development is accountable for the generation of large volumes of wastewater containing harmful organic pollutants to human health and the environment. Phenol and its derivatives are commonly found in industrial wastewater, exhibiting high toxicity, recalcitrance, and bioaccumulative properties [1]. Consequently, effluents containing this pollutant require treatments aiming to remove or minimize them. Advanced oxidative processes (AOPs) can be considered efficient techniques for treating highly contaminated wastewater. The Photo-Fenton process stands out as a highly efficient AOP that utilizes hydrogen peroxide, Fe^{2+} or Fe^{3+} ions, and UV radiation under acidic conditions to generate hydroxyl radicals with the purpose of degrading present contaminants [2]. Due to the presence of iron oxide in the composition of cliffs [3], it is believed that their utilization as a heterogeneous catalyst in the Photo-Fenton process could be viable.

Therefore, this study aimed to evaluate the degradation of phenol in aqueous solution through the Photo-Fenton reaction, using sediment iron from cliffs at Ponta Negra Beach, RN, as a source of iron.

Material and Methods

The cliff sediments used were collected at Ponta Negra Beach, RN. The samples were manually fragmented using a hammer, and subsequently macerated with the assistance of a mortar and pestle. Finally, the cliff sediments were sieved through a 150 mesh (0.106 mm) sieve, and the passing particles were used as Photo-Fenton catalysts. The obtained cliff powder was analyzed using Energy Dispersive X-ray Fluorescence Spectrophotometry (XRF) with a model EDX-720 (Shimadzu). The concentration of phenol in the samples was measured using ultra-high-performance liquid chromatography (UPLC, Prominence UFLC-XR, Shimadzu).

Concerning the experimental procedure, the phenol solution was adjusted to pH 3.0 with a 0.5 M H_2SO_4 solution. Three ranges of initial phenol concentration were studied, namely 10, 30, and 50 $mg.L^{-1}$, maintaining the cliff concentration at 2.0 $g.L^{-1}$ and the oxidant hydrogen peroxide (H_2O_2) concentration at 6 mM for each concentration studied. The experimental setup consisted of a 250 mL jacketed reactor connected to a thermostatic bath at 20°C for temperature control, under a metal vapor lamp (Ourolux, 150 W). Thus, 100 mL of the phenol solution was added to the reactor, along with the catalyst mass and hydrogen peroxide volume. The mixture was kept under mechanical agitation, and the reaction time was 120 min. At each experimental point, the samples were filtered using a PTFE syringe filter (0.45 µm), transferring 0.9 mL of each sample to vials containing 0.1 mL of methanol, and finally sent for analysis in the UPLC.

Results and Discussion

Through the XRF analysis conducted on the processed cliff particles, as shown in Table 1, it was observed that their chemical composition comprises 47.21% iron oxide (III), followed by 27.08% aluminum oxide and 24.19% silicon dioxide.

As demonstrated in other works in the literature [4,5], the amount of iron present in the material signifies a positive indication of its utilization as a catalyst for the Photo-Fenton reaction for phenol degradation.

Table 1. Chemical composition of cliff particles by XRF.

Composition	Mass Fraction
Fe_2O_3	47.21
Al_2O_3	27.08
SiO_2	24.19
Others	1.52

For the phenol degradation assays, the experimental results obtained are observed in Figure 1. Promising results were obtained in the assays with initial phenol concentrations of 10 and 30 mg.L^{-1}, representing degradation rates of 93.54% and 87.37%, respectively, within 120 minutes of reaction. However, when the initial phenol concentration was set to 50 mg.L^{-1}, the results obtained were not equally favorable compared to the other conditions studied, with only 26.61% degradation observed at the time.

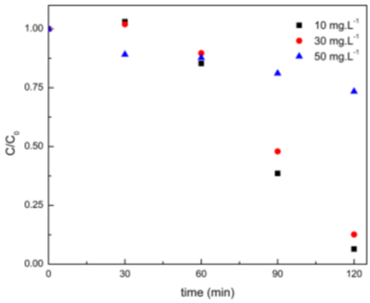

Figure 1. Phenol degradation over time at different initial concentrations. [Catalyst] = 2 g.L^{-1}, [H_2O_2] = 6 mM, pH = 3.0.

Thus, it is possible to observe a decrease in phenol degradation efficiency as the initial concentration of the contaminant increases, for the aforementioned experimental conditions. This behavior can be explained by a deficiency in the reactive sites on the surface of the catalyst, which in this case was the cliff powder [6]. Alternatively, it may indicate that the quantity of iron present in the catalyst was insufficient to promote the generation of hydroxyl radicals and consequently degrade a larger amount of phenol.

Although not being a commercially used catalyst, the powder made from cliff particles showed satisfactory performance in phenol removal from water. Similarly to the cliff, other low-cost materials, natural or sometimes byproducts of industrial processes, are being experimentally employed as alternative catalysts for Photo-Fenton reactions, as shown in Table 2.

Conclusions

The processed cliff powder presented 47.21% of iron (III) oxide in its composition and acted satisfactorily as a catalyst in the Photo-Fenton reaction. Among the studied initial concentrations, the initial concentration of 10 mg.L^{-1} yielded the best degradation result (93.54%) under the analyzed experimental conditions.

Table 2. Contaminant removal using alternative catalysts in Photo-Fenton reactions.

Catalyst	Pollutant	Conditinons	Efficiency(%)	Reference
Cliff	Phenol	[Catalyst] = 2 g/L [H_2O_2] = 6 mM; pH = 3	10 mg.L^{-1}: 93.54% (120 min)	This work
Ametyst mining reject	Phenol	[Catalyst] = 0.75 g/L [H_2O_2] = 7.5 mM;pH = 3	50 mg.L^{-1}: 96.5% (180 min)	[4]
Basalt	Methylene blue	[Catalyst] = 1 g/L [H_2O_2] = 5 mM; pH = 2	70 mg.L^{-1}: 100% (60 min)	[7]
Fly ash	Procion Red HE7B	[Catalyst] = 0.6 g/L [H_2O_2] = 4 mM; pH = 3	50 mg.L^{-1}: 93.6% (60 min)	[8]

Acknowledgments

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