

Phenol removal from a heterogeneous Fenton process under optimized conditions using iron supported on perlite

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Abstract

This work aimed to evaluate an iron ion impregnation technique on perlite mineral and assess its performance in a heterogeneous Fenton-like reaction at ambient temperature, under acidic and alkaline conditions, for phenol removal. The catalyst preparation involved a suspension of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) followed by thermal treatment (calcination). Different dosages of 35% (m/m) H_2O_2 and catalyst were applied, with interactions obtained from an experimental design developed through a Central Composite Rotatable Design (CCRD). Phenol removals at pH 4 achieved desired results (phenol concentration ≤ 5 ppm), with phenol degradation $\geq 98.33\%$ within 15 minutes of reaction. At pH 6, phenol removal varied at different times, depending on the applied catalyst and H_2O_2 concentrations. The catalyst exhibited good activity in alkaline media, reaching phenol removals ≤ 5 ppm at pH 8 and 9, in 15 and 60 minutes of reaction, respectively. The three variables (pH, catalyst concentration, and H_2O_2) individually showed significant effects (p-value less than 0.05) on the final phenol concentration. A significant effect was also observed in the interaction between pH and catalyst.

Keywords: Heterogeneous Fenton; Phenol; Perlite; Experimental Design.

1. Introduction

Recently, there has been a surge in water body pollution, driven by the advancement of various activities linked to global population growth. The availability of potable water and sustainable proposals regarding effluent treatment are issues addressed in the Sustainable Development Goals (SDGs) [1]. Phenol and its derivatives are widely found in water, posing a significant danger due to their difficult degradation, leading to a decrease in oxygen availability in aquatic ecosystems. Phenols are easily absorbed through the skin, acting as potent endocrine disruptors and causing damage to the spleen, heart, lungs, and other organs. Therefore, the efficient removal of these phenolic organic pollutants from water has become one of the primary goals in water purification and wastewater treatment [2]. Advanced oxidation processes, such as the classic Fenton reaction, are widely considered a useful method for producing highly active hydroxyl radicals ($\bullet\text{OH}$). Toxic organic pollutants can be

decomposed into mineralized salts, water, and carbon dioxide through the action of highly reactive hydroxyl radicals [3]. However, the traditional Fenton system (homogeneous Fenton) requires an extremely low pH value (< 4). Moreover, the process generates a significant amount of iron sludge, resulting in secondary contamination. To overcome these challenges, within the scope of AOPs, heterogeneous Fenton reactions have been proposed as an alternative, employing various iron-containing materials as heterogeneous catalysts [4]. Experimental design based on statistical principles is a valuable tool for optimizing processes and evaluating the effects and impacts of factors on the desired responses. In this context, fractional factorial designs are effective for evaluating variables and selecting those that should be considered until reaching the Central Composite Rotatable Design (CCRD). The sequential design strategy of factorial designs is the best choice when many variables are involved. The factorial design methodology, coupled with response surface analysis, is a tool based on statistical theory that

offers reliable information about the process, reducing the empiricism associated with trial-and-error techniques [5].

2. Experimental

Materials preparation

The catalyst was prepared using 4 g of perlite. Perlite was previously washed with deionized water and dried in an oven at 105 °C for 24 hours. The perlite was then added to a suspension containing 8 grams of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 400 mL of deionized water. The suspension was kept under magnetic stirring and heating until saturation. After saturation, the perlite was filtered and dried again in an oven at 105 °C for 60 minutes. Subsequently, it was calcined in a muffle furnace for 180 minutes at 540 °C (in the presence of air). To remove the unimpregnated catalyst on the perlite, the material was washed with deionized water in several steps and subsequently dried in an oven for 24 hours [6].

Catalyst characterization

The crystallinity of the catalyst was analyzed by powder X-ray diffraction (XRD) model STADI-P (Stoe®, Darmstadt, Alemanha) The chemical bonds were detected by Fourier transform infrared spectroscopy (FTIR), model Cary 630 FTIR Spectrometer with ATR sampling module. The morphology and composition of the catalyst were investigated by scanning electron microscopy (SEM-EDS) model JMS-6701F, JEOL.

Experimental factorial design for phenol removal

The objective was to determine the best parameters related to the amount of heterogeneous catalyst and hydrogen peroxide concentration in a wide pH range for phenol decomposition. The experimental trial conditions were determined from an experimental design, developed by a Central Composite Rotational Design (CCRD). At room temperature, the effects of three variables were determined: the influence of pH (X1), varying from 3 to 9; the influence of catalyst concentration (X2), varying from 0.34 g to 0.75 g; and the influence of 35% m/m hydrogen peroxide (X3), varying from 0.30 g to 0.90 g. The experiments were carried out in a beaker, starting from 50 mL of phenol solution at a concentration of 300 ppm. The reaction medium was kept under magnetic stirring. In the first half hour of reaction, two samples were collected at

intervals of 15 minutes for phenol determination by chromatography in a Perkin Elmer Clarus 690 gas chromatograph. After this period, the samples were collected every 30 minutes.

3. Results and Discussion

The results show that the characterization techniques used in this study, FTIR, XRD, SEM-EDS, proved that in the synthesized catalyst there was the incorporation of Fe (~20%) on the raw perlite, which is mainly formed by Al and Si oxides, but which also presents Fe in its composition, in a low percentage (~2%). The analyses confirmed the incorporation of Fe and its stability on the support even after reactions in acidic and alkaline conditions. For the experimental design conducted, with an initial phenol concentration of 300 ppm, Table 1 shows the 17 experiments with the values of the independent variables (pH, catalyst, and hydrogen peroxide). The values of the dependent variables (responses), in phenol degradation and removal percentage, were discussed, aiming to obtain a concentration ≤ 5 ppm and a removal percentage $\geq 98.33\%$, respectively. The assays were analyzed at three different times, 15, 30, and 60 minutes.

Table 1. Assays and their variables of the heterogeneous Fenton process with the final concentration of phenol and its respective removal percentage at 15, 30, and 60 minutes.

Experiments	pH	Catalyst (g)	H ₂ O ₂ (g)
1	4	0,42	0,42
2	8	0,42	0,42
3	4	0,67	0,42
4	8	0,67	0,42
5	4	0,42	0,78
6	8	0,42	0,78
7	4	0,67	0,78
8	8	0,67	0,78
9	3	0,55	0,60
10	9	0,55	0,60
11	6	0,34	0,60
12	6	0,75	0,60
13	6	0,55	0,30
14	6	0,55	0,90
15	6	0,55	0,60
16	6	0,55	0,60
17	6	0,55	0,60

In experiments 1, 3, 5, 7, and 9, the desired results were obtained (phenol concentration ≤ 5

ppm), with phenol degradation $\geq 98.33\%$ in 15 minutes of reaction. These results were expected for the experiments with pH 4 (experiments 1, 3, 5 and 7), and the trial with pH 3 (trial 9); since acidic pH provides the best results in phenol degradation in the presence of iron and hydrogen peroxide. For the experiments with pH 6, close to neutrality, trial 14 with the use of 0.90 g of H_2O_2 , 5 ppm of phenol was obtained in the first 15 minutes. This did not occur in the other experiments (11, 12, 13, 15, 16, and 17). For experiments 11 and 13, the specification of 5 ppm occurred within 60 minutes of reaction time, which shows the influence of the concentration of the reagents, since for trial 11 the minimum amount of catalyst was used (0.34 g), and for trial 13 the minimum amount of H_2O_2 was dosed (0.30 g). For experiments 12, 15, 16, and 17, the expected was reached in 30 minutes of reaction, having in common the pH 6 and the amount of 0.60 g of H_2O_2 , varying only the catalyst in trial 12 (0.75 g). Among the experiments at alkaline pH, trial 8 (pH=8), 0.67 g of catalyst and 0.78 g of H_2O_2 stands out, obtaining a concentration of 4 ppm (1.33%) of phenol in 15 minutes and after 60 minutes of reaction it was verified that all the phenol was degraded. Trial 4 (pH = 8) reached 5 ppm of phenol after 60 minutes of reaction. The other experiments with pH 8, experiments 2 and 6, did not have a satisfactory response after 60 minutes, as they presented 88 and 55 ppm of phenol respectively. Common to these two experiments is the low amount of catalyst (0.42 g). Trial 10, with pH = 9, had an excellent response with 60 minutes of reaction, where 5 ppm of phenol was obtained.

Regression data was tabulated for 60 minutes with calculations of the effects of variables X_1 , X_2 , and X_3 for pH, catalyst, and H_2O_2 respectively, with their interactions where the p-value less than 0.05 indicates which variables and/or their interactions are significant at the 95% confidence level. All three variables individually presented significant effects (p-value less than 0.05) on the final phenol concentration. A significant effect can also be observed in the interaction between pH and catalyst. The Analysis of Variance (ANOVA)

of the model for the final phenol concentration after 60 minutes was performed, demonstrating that the model is statistically significant: $R^2 = 94.70\%$. These significant effects can be visualized in the Pareto chart, Fig. 2. In Figures 3 (a) and (b), the response surface between the interaction of pH with the catalyst is presented. It is verified in (a) that pH 3.88 and 0.67 g of catalyst, after 60 minutes of reaction, the final phenol concentration is 0.01 ppm, which was expected for an acidic pH. In (b), with pH 9 and a catalyst concentration of 0.74 g, the final phenol concentration is 2.97 ppm. It is not expected phenol decomposition at alkaline pH, which initially demonstrates excellent catalytic activity in the system. This behavior may be related to specific characteristics of the catalyst where the iron cations are under the influence of a strong electrostatic field in the perlite structure which can prevent or delay the formation of iron hydroxides as the pH increases. The improvement observed may be attributed to the combination of adsorption and catalytic oxidation processes [6].

Fig. 2. Pareto chart for the significant effects of the variables pH (X_1), catalyst (X_2), and hydrogen peroxide (X_3).

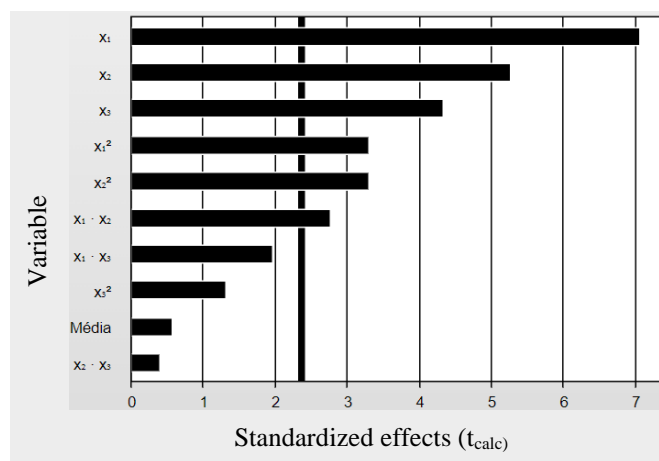
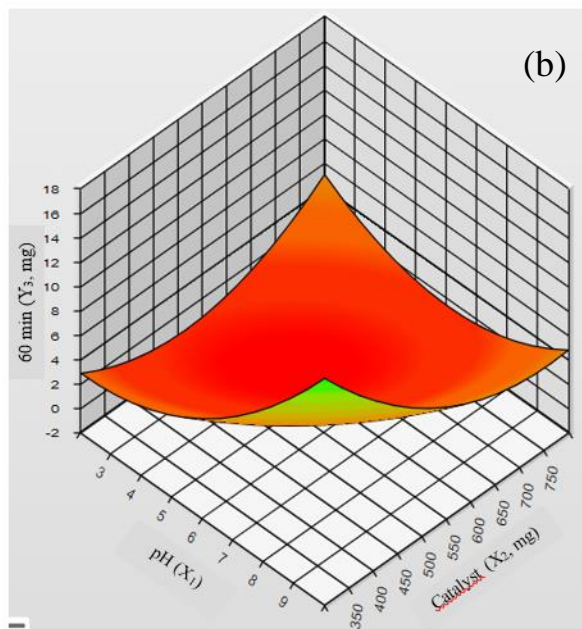
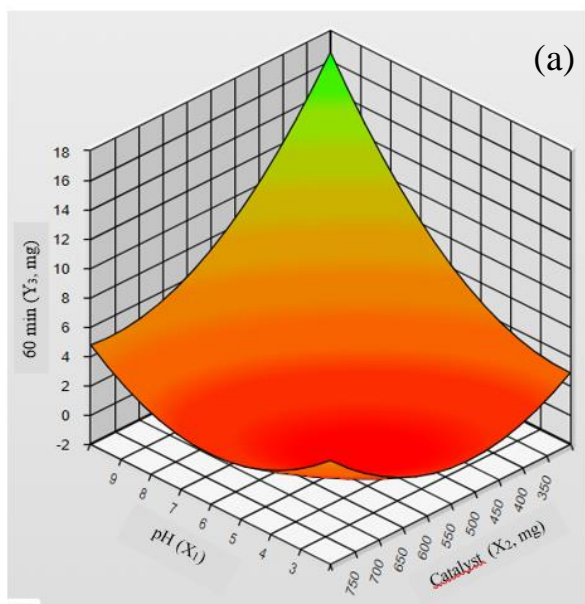


Fig. 3. Response surface for the interaction between the variables pH (X_1) and catalyst (X_2), in relation to phenol concentration after 60 minutes. In (a) pH 3.88 and 0.67 g of catalyst and (b) pH 9.0 and 0.74 g of catalyst.



as presented in the characterizations. The synthesized catalyst exhibited satisfactory performance under both acidic and alkaline conditions. The operating conditions determined by the applied experimental design optimized the responses obtained in phenol removal percentage, identifying significant variables and their respective interactions, minimizing the use of reagents in quantities exceeding those necessary. It was determined that for pH 3.88 and 9, the ideal amount of catalyst is 0.67 and 0.74 g, respectively, for a fixed peroxide mass (0.6 g). The reaction method shows promise for applications in large-scale systems for the treatment of phenolic effluents.

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Conclusion

The results showed that the iron impregnation method on the perlite mineral was satisfactory,