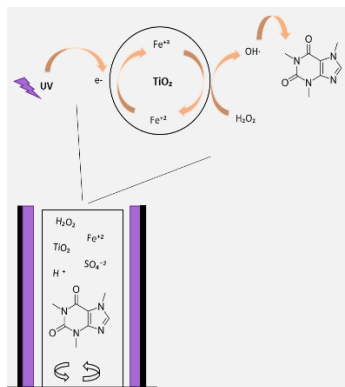


Heterogeneous photo-Fenton for caffeine degradation: comparison between kaolin waste and commercial anatase

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Ph.D. Student: Y
Journal: CEJ

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Caffeine is an excellent indicator of water contamination related to human activity. Among advanced treatments, Advanced Oxidative Processes (AOPs) have been an important option to achieve high levels of degradation and mineralization. This study investigates a heterogeneous UV-photo-Fenton treatment with TiO₂ from commercial anatase and from kaolin waste. The variables studied were anatase/kaolin waste concentration, UV radiation and reaction time. According to the response surfaces, catalyst concentration, ultraviolet radiation, and time contribute positively for caffeine degradation, achieving percentages from 90% to 100%. However, ANOVA demonstrates that only UV radiation and reaction time are statistically significant. Degradation reached the range of 90–100%, both for anatase and kaolin waste. For mineralization, the best result was obtained at the central point, which was 33.1% for anatase and 17.4% for kaolin waste.

Introduction

Aquatic contamination is a problem that increases with society's industrialization. Caffeine (CAF) is an alkaloid used in food and pharmaceutical products, and it is an excellent indicator of water contamination related to human activity [1].

In order to achieve effective removal, several techniques have been studied, including Advanced Oxidative Processes (AOPs), in which highly reactive hydroxyl radicals are generated. One of the AOPs with great potential is the Fenton, where the generation of OH• occurs through the decomposition of hydrogen peroxide catalyzed by Fe²⁺ ions [2].

To optimize the Fenton process, other homogeneous and heterogeneous catalysts can be used to increase the generation of OH• [3]. The main issue involving heterogeneous catalysts lies in the separation processes after the reaction and the final disposal of the solid. Thus, it is relevant to investigate the reuse of waste with catalytic potential.

The present work aims to investigate a heterogeneous photo-Fenton process with kaolin waste as catalyst for CAF degradation and mineralization and the impact of operational parameters such as catalyst concentration, UV radiation and reaction time.

Material and Methods

Caffeine (>96%, Sigma-Aldrich) stock solution was prepared with distilled water and diluted for the experiments. Hydrogen peroxide (35%, Neon) and ferrous sulfate heptahydrate (99%, Neon) were applied as Fenton reagents. Titanium (IV) oxide anatase (>99%, Sigma-Aldrich), with a particle size smaller than 0.044mm, surface area of 8.943 m² g⁻¹ and porous volume of 0.015 cm³ g⁻¹, and kaolin waste with a particle size smaller than 0,044mm, surface area of 11.742 m² g⁻¹, and porous volume of 0.037 cm³ g⁻¹) were used as catalysts. According the

company that provided kaolin waste, it contains 4% anatase mass percentage. H₂SO₄ (98%, Anidrol) and NaOH (98%, Synth) 1 M solutions were used for pH adjustment.

A Central Composite Design (CCD) was used to obtain response surfaces as to evaluate the degradation and mineralization of CAF. To gauge the accuracy of the model, analysis of variance (ANOVA) was performed. The variables studied were anatase/kaolin waste concentration ([TiO₂]=8, 16, 20, 24, 32 mg L⁻¹), UV radiation (0, 1340.3, 2010.4, 2680.5, 4020.8 W m⁻²) and reaction time (5, 15, 30, 45, 60 min). CAF concentration, volume, pH and Fenton reagents concentration were fixed in 10 mg L⁻¹, 250 mL, pH 3 and [H₂O₂]= 88μL L⁻¹; [Fe²⁺]=0,8 mg L⁻¹, respectively.

The CAF stock solution was diluted to 10 mg L⁻¹ for a volume of 250 mL. In acid pH, ferrous sulfate solution and anatase or kaolin waste were added, according to the conditions of each experiment. The reactor was transferred to an UV chamber, in which the lamps had been previously turned on to homogenize the system. H₂O₂ was added in order to start the reaction time. As the reaction time ended, the pH was adjusted to 11 to stop the Fenton process.

CAF concentration was assessed by high-performance liquid chromatography (HPLC) and mineralization was analyzed by total organic carbon (TOC) concentration.

Results and Discussion

Through ANOVA it was possible to evaluate which parameters influence CAF degradation. The model was a good fit to the experimental data, which can be demonstrated by R²= 0.932 for anatase and R²= 0.936 for kaolin waste. According to Pareto charts (Fig. 1), UV radiation and reaction time, as well as their interaction, are positively significant factors.

However, the catalyst dosage under the studied conditions did not demonstrate a significant effect on CAF degradation.

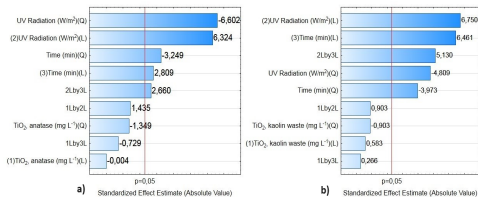


Figure 1. Pareto chart of main and interaction effects from the experimental design for anatase a) and kaolin waste b).

Interaction between dependent and significant independent variables was evaluated by the following quadratic equations (Eqs. 1-2).

Interaction between UV radiation ($x=[W\ m^{-2}]$) and reaction time ($y=[min]$) for CAF degradation ($R=[\%]$) with anatase:

$$R = 0,000351x + 0,015846y - 0,000248y^2 + 0,000003xy \quad (1)$$

Interaction between UV radiation ($x=[W\ m^{-2}]$) and reaction time ($y=[min]$) for CAF degradation ($R=[\%]$) with kaolin waste:

$$R = 0,000209x + 0,015599y - 0,000305y^2 + 0,000006xy \quad (2)$$

The response surfaces (Fig. 2-4) demonstrate that the increase of catalyst concentration, UV radiation, and time results on the increase of CAF degradation, achieving percentages in the range of 90–100%, both for anatase and kaolin waste. The results are coherent, once AOPs allow a fast degradation of organic compounds through low selectivity of OH⁻ [3]. Both 5-minute-long experiments or those without radiation have obtained degradation percentages of up to 72% for anatase and 43% for kaolin waste. Therefore, the use of radiation and catalysts in AOPs not only guarantees the degradation of the pollutant but also acts on its mineralization, as it promotes greater generation of hydroxyl radicals [4].

Conclusions

In brief, kaolin waste has obtained a similar performance as anatase for the degradation of CAF. However, the applicability of kaolin waste would be possible through the study of modifications to its characteristics, improving mineralization results when compared to commercial anatase.

Acknowledgments

Acknowledgements to the REJEMEA project financed by FINEP, the Coordination for the Improvement of Higher Education Personnel (CAPES), the Laboratory of Separation and Unitary Operations (LASOP) and Postgraduate Program in Chemical Engineering (PPGEQ) at the Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil.

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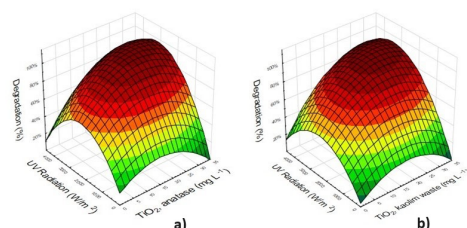


Figure 2. Degradation of CAF as function of TiO₂ dosage and UV radiation for anatase a) and kaolin waste b).

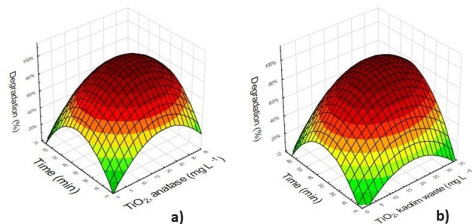


Figure 3. Degradation of CAF as function of TiO₂ dosage and reaction time for anatase a) and kaolin waste b).

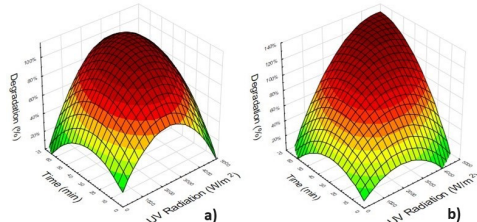


Figure 4. Degradation of CAF as function of reaction time and UV radiation for anatase a) and kaolin waste b).

When it comes to mineralization, anatase showed better results. At the central point, where the highest percentage was obtained, mineralization reached 33.1%, while for the kaolin waste this result was 17.4%. This can be explained by the high amount of kaolin waste, due to the 4% TiO₂ percentage, which could have reduced the absorption of UV radiation, causing a light scattering effect [5,6].