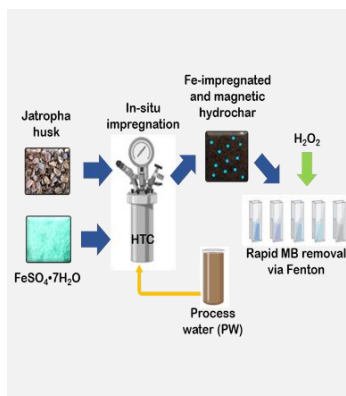


Sustainable in-situ preparation of magnetic hydrochar for rapid methylene blue removal via Fenton reaction

ORAL
Ph.D. Student: N
Journal: NONE

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Developing heterogeneous catalysts must include sustainable routes of synthesis. Hydrothermal carbonization (HTC) is a less energy-consuming process, which allows obtaining hydrochar, a promising material showing catalytic activity. Since HTC is conducted with water at subcritical conditions, process water (PW) is released after treatment. PW contains organic compounds that serve as reducing agents for the preparation of a metal loaded-hydrochar. This work proposes recirculating PW for an in-situ synthesis of magnetic hydrochar using Jatropha husk as raw biomass and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to obtain a Fe-modified hydrochar. Interestingly, the in-situ prepared hydrochar showed magnetic properties, useful for easy catalyst recovery after treatment. Remarkably, this material exhibited a rapid removal of methylene blue when underwent a Fenton reaction, reaching >99% removal after fifteen minutes.

Introduction

Hydrothermal carbonization (HTC) has emerged as a promising alternative for the preparation of green heterogeneous catalysts from waste biomass. It entails decomposing biomass in subcritical water resulting in a carbonaceous material (i.e., hydrochar) showing enhanced surface area and surface functionalization. The HTC process requires less energy consumption compared to other biomass-derived materials like pyrolysis since the reaction temperature range is lower (180-250°C) [1]. Further improvement of catalytic activity can be attained by supporting modifying the hydrochar surface [2]. In previous studies, plant extracts were used as reducing and stabilizing agents for in-situ loading of metals on hydrochar during the HTC process [3]. In this sense, the process water (PW) released after the hydrothermal treatment contain some molecules that may exhibit antioxidant activity [4]. In case PW is recirculated to subsequent HTC experiments, the organic compounds present in PW (e.g., phenolic compounds) may also serve as reducing and stabilizing agents for sustainable nanoparticle synthesis.

In this work, it is intended to prepare a Fe-modified hydrochar by taking advantage of the antioxidant activity of PW. It will be proved this functionalized hydrochar in presence of PW allows keeping the Fe^{2+} and Fe^{3+} species balanced for a heterogeneous Fenton reaction using methylene blue (MB) as target pollutant. Additionally, the resulting hydrochar showed magnetic properties, which favors the catalyst recovery after treatment.

Material and Methods

Herein, an in-situ hydrochar synthesis from Jatropha husk and Fe-functionalization was proposed. To this end, a typical HTC experiment is carried out in high-pressure reactor with the following operating conditions: reaction temperature=250°C, reaction time=180 min, biomass-to-water ratio=1/10, aqueous media= $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (0.5 M) according to a previous work [5]. In the PW-assisted experiment, a PW sample of a previous treatment was loaded into the reactor instead of water.

A brief PW characterization was conducted by analyzing the antioxidant activity was determined via Trolox equivalent antioxidant activity (TEAC), and total phenolic content with the Folin-Ciocalteu method according to the guidelines provided by Cartuche et al. [6].

The catalytic activity of the obtained hydrochars was tested by the MB removal in a batch study: 50 mL MB solution (initial concentration=0.2 mM), under magnetic stirring of 1000 rpm at room temperature (~20°C). To study the MB concentration profile over time, aliquots were taken and filtered with PES syringe filters (0.22 μm). MB concentrations were determined by a Hach DR/890 colorimeter. First, a one hour-treatment without H_2O_2 addition was performed to rule out the effect of a possible adsorption. Then, 70 μL of the H_2O_2 solution was added, and the effect of the Fenton reaction was registered over time.

The studied samples are labeled as follows: Only hydrochar of Jatropha husk=H_JH; Fe-modified-hydrochar: Fe_H_JH; and, Fe-modified-hydrochar with PW recirculation: Fe_H_JH_PW.

Results and Discussion

After antioxidant activity evaluation, the TEAC value for the PW obtained during the HTC processing of JH was $\sim 1597 \mu\text{M g}^{-1}$, and phenolic content of $\sim 64 \text{ mg GAE L}^{-1}$. These results proved the potential of PW from HTC to be used as a reducing agent for a subsequent Fe-modification of the hydrochar surface.

For the Fe-impregnated hydrochar, the XRD analysis depicted in Figure 1, provided some insights about the support of Fe_3O_4 on the hydrochar surface since peaks observed in the Fe_J_H_PW catalyst at $2\theta\text{-}30.2^\circ$, 35.6° , 43.2° , 57.2° , and 62.5° . Based on Huang et al. [7], these values are line with the (220), (311), (400), (511), and (440) crystal faces of magnetic Fe_3O_4 . Thus, evidencing the Fe-modification of the hydrochar surface compared to pristine hydrochar (H_JH), where those peaks were not observed.

Results shown in Figure 2 demonstrated the possibility of employing the Fe-impregnated hydrochar as heterogeneous catalyst for a Fenton reaction. For instance, the pristine hydrochar did not show any catalytic activity, while the Fe-impregnated materials exhibited remarkably results, especially the Fe_J_H_PW catalyst. This latter reached a $>99\%$ removal after fifteen minutes, with a rapid decrease of the MB concentration even at the first minute of treatment ($>80\%$ of removal).

Therefore, it is confirmed that the way Fe is supported on hydrochar surface when using PW as the reaction medium during the HTC process, makes the catalyst more effective in generating the $\cdot\text{OH}$ radicals.

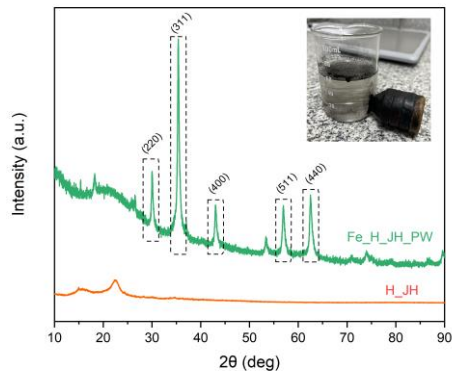


Figure 1. XRD patterns of H_JH and Fe_H_JH_PW samples.

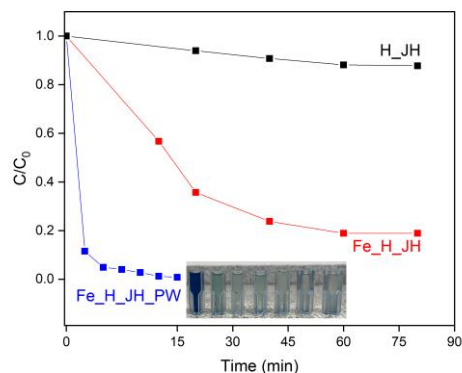


Figure 2. MB removal during Fenton reaction with the H_JH, Fe_H_JH, and Fe_H_JH_PW catalysts.

Conclusions

The antioxidant activity of the obtained PW during the hydrothermal treatment of Jatropha husk can contribute as reducing and stabilizing agent for the in-situ impregnation of Fe over the hydrochar surface. Probably, phenolic compounds are related to an enhanced support of Fe. From the XRD analysis, the obtained peaks are associated with crystal faces of magnetic Fe_3O_4 , making the heterogeneous catalyst recovery easier after treatment. Finally, this Fe-functionalized catalyst performed successfully for the MB removal during a Fenton reaction, with fast removal rates. This novel approach of in-situ preparation of Fe-based catalyst promoted the formation of $\cdot\text{OH}$ radicals for an improved pollutant degradation.

Acknowledgments

Universidad San Francisco de Quito USFQ for the Collaboration Grants and Poligrant projects.

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