Performance analysis of pure MIL-53(Fe) MOF and immobilized on chitosan beads for catalytic ozonation of organic contaminants

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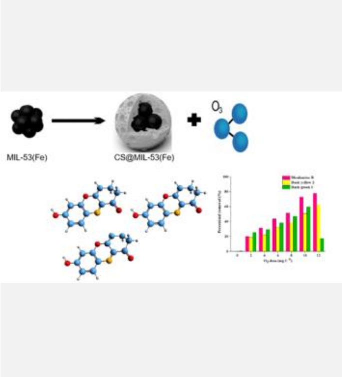

Catalytic ozonation is an efficient method for achieving the complete mineralisation of organic pollutants. Thus, in the present study, the MOF MIL-53(Fe) was synthesised and immobilised on chitosan spheres and applied to the removal of organic dyes and pharmaceuticals from water. The use of chitosan has been widely publicized, since it is a natural polymer, biocompatible, biodegradable, non-toxic and come from abundant materials.MIL-53(Fe)-catalysed ozonation was evaluated for the removal of emerging contaminants, including pharmaceuticals and dyes. Although there were challenges in identifying the crystal structure of MIL-53(Fe), SEM analysis revealed clustered formations with non-uniform octahedral properties.The results showed greater removal of naproxen, ketoprofen and dyes in the presence of the catalyst, with variations in removal efficiency observed under different conditions.

Introduction

Catalytic ozonation is an efficient method to achieve complete mineralization of organic pollutants. Metal-organic frameworks (MOFs) are solid materials composed of organic ligands and metal centers. MOFs have been reported as effective catalysts in the literature due to their stability, high porosity, and surface area.

However, some studies studies have reported that the structure of MOFs can be damaged during the ozonation process, hindering their practical application [1]. Furthermore, the application of heterogeneous catalytic systems has been a challenge due to the difficulty of separating the catalyst from the treated solution, which limits their recycling and large-scale use.

Beads are a viable option for wastewater treatment due to their ease of preparation and separation, and their ability to prevent secondary contamination because of their stable form. Chitosan is a natural, abundant, non-toxic, and biodegradable biopolymer, and is commonly used to prepare beads.

In this work, the synthesis and characterisation of the MOF MIL-53(Fe) was successfuly carried out. The effectiveness of a simple ozonation system and ozonation in the presence of the MIL-53(Fe) catalyst was evaluated for the removal of two classes of emerging contaminants: drugs (ketoprofen, naproxen, and ibuprofen) and dyes (rhodamine B, basic yellow 2, and basic green 1). The MIL-53(Fe) catalyst was immobilised on chitosan beads using a simple dripping method (CS@MIL-53(Fe)), and a comparison of contaminant removal performance s by MIL-53(Fe) and CS@MIL-53(Fe) catalysts was conducted.

Material and Methods

MIL-53(Fe) was synthesized using a solvothermal method based on the methodology of Rezvani et al [2], with some modifications. First, 4 mmol of $Fe(NO_3)_3.9H_20$ and 1,4-H_2BDC were dissolved in 30 mL of DMF and stirred for 2 h at room temperature. Then, the solution was transferred to a Teflon-coated stainless steel reactor and kept at 150 ºC for 15 h. Finally, the resulting product was washed with ethanol and ultrapure water and dried at 60 ºC for 24 h. The MIL-53(Fe) catalyst was immobilized on CS beads using the methodology proposed by Camparotto et al. [3]. First, a solution of CS and acetic acid (3% w/v) was stirred vigorously overnight. Next, MIL-53(Fe) was added to the solution in a 1:1 ratio and left to stir vigorously for 4 hours. The resulting solution of CS and MIL-53(Fe) was then dripped onto a solution of sodium tripolyphosphate crosslinking agent (5% w/v). The beads were washed with ultrapure water, frozen at -80 ºC, and freeze-dried. The ozonation experiments were performed in a cylindrical glass batch reactor with a capacity of 2 L connected to an ozone generator (Ozonar GT 8000, Brazil), which bubbled ozone through porous porcelain diffusers inside the reactor. The ozone dose applied was 12 mg L^{-1} and the feed gas flow rate was 0.5 L min^{-1}. The ozone dose was measured by iodometry. The dye solutions (50 mg L^{-1}) and the drugs solutions (10 mg L^{-1}) were subjected to single ozonation and to ozonation in the presence of MIL-53(Fe) MOF catalyst (25 mg L^{-1}). 2 mL samples were taken every minute for 10 min (0, 2, 4, 6, 8, 10, 12 mg L^{-1} of ozone dose). The solutions were ozonized at pH 5.5 (± 0.02).

Results and Discussion

The MIL-53(Fe) XRD pattern (Figure 1) shows peaks at 33.18º and 35.71º, indicating the presence of hematite (Fe_2O_3). The crystal structure of MIL-53(Fe) could not be identified due to synthetic conditions that can affect significant changes in the XRD pattern. Previous studies have also reported difficulty in obtaining the crystal structure of this catalyst [4]. SEM analysis evaluated surface features and morphological alterations. The formations of MIL-53(Fe) clusters with non-uniform octahedral properties are depicted in Figure 2.

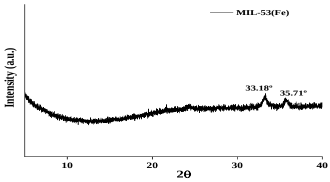

Figure 1. XRD of MIL-53(Fe).

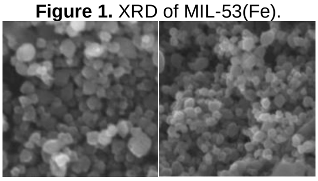

Figure 2. SEM images of MIL-53(Fe).

In the single ozonation of drugs (Figure 3), at doses of 8 mg O_3 L^{-1} and 12 mg O_3 L^{-1}, ibuprofen and naproxen achieved an ozonation rate greater than 50% removal, respectively. With the catalyst (Figure 4), naproxen removal increased to more than 90% at 12 mg O_3 L^{-1}, while ketoprofen removal increased from 10% to 30% at 10 mg O_3 L^{-1}. The catalyst resulted in higher removal rates for naproxen and ketoprofen, while ibuprofen showed an opposite trend, suggesting potential interference between ibuprofen and MIL-53(Fe).

For dyes, in single ozonation (Figure 5), the removal of Rhodamine B, Basic Yellow 2, and Basic Green 1 achieved ozonation rates of 53%, 50% and 46%, respectively, at 12 mg O_3 L^{-1}. The ozonation rate increased in the presence of the catalyst (Figure 6). For Rhodamine B and Basic Yellow 2, the maximum removal was greater than 80% and 60% at 12 mg O_3 L^{-1}, respectively, while for Basic Green 1, the removal was greater than 60% at 10 mg O_3 L^{-1}. The results suggest that the catalyst was effective in enhancing dye removal.

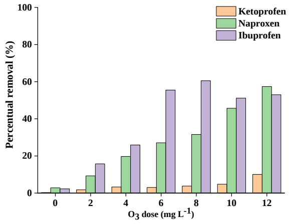

Figure 3. Drugs removal by single ozonation.

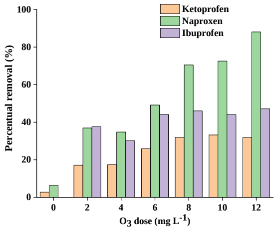

Figure 4. Drugs removal by ozonation catalytic.

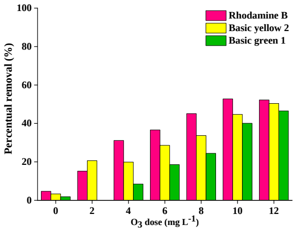

Figure 5. Dyes removal by single ozonation.

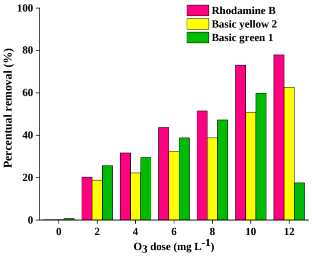

Figure 6. Dyes removal by ozonation catalytic.

Conclusions

The MIL-53(Fe) catalyst was effective in improving the removal of naproxen (<90%) and ketoprofen (<30%), and dyes Rhodamine B (80%), Basic Yellow 2 (60%), and Basic Green 1 (60%). Although catalytic ozonation with MIL-53(Fe) represents a promising route for the mineralization of organic pollutants, challenges such as potential structural damage during the process and the difficulty of catalyst separation prevent its practical application. The immobilization of MIL-53(Fe) on chitosan beads showed promise, allowing its viable application in contaminant removal processes.

Acknowledgments

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