MOFs for The Removal of Emerging Pollutants by Catalytic Ozonation
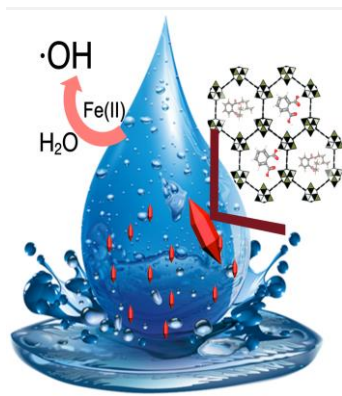
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The present work deals with the study of the degradation of a model mixture (dimethyl phthalate (DMP) and dioctyl phthaltate (DOP)) in an aqueous system with ozone. An ozone-oxygen flow rate and concentration at 2 L min^{-1} and 3.8 mg L^{-1} respectively. The MOF (MIL 88-A) were synthesized by hydrothermal treatment. The ozonation results showed that DMP and DOP in aqueous solution decomposes, obtaining a higher removal in catalytic ozonation. However, the presence of the catalyst improves the degree of mineralisation (63%) in 120 min of treatment due to the generation of reactive species . Moreover, this MOFs shows a stability in this process since after 120 min of treatment there is no leaching of the material.

Introduction

In recent decades, water pollution has become a major concern worldwide, and despite the installation of wastewater treatment plants, water pollution continues to increase dramatically year after year [1]. As new chemicals are produced and applied in different sectors, emerging organic pollutants are newly developed compounds with potential negative effects on the environment and human health. Among these emerging pollutants are phthalates which account for 93% of the products that are used as plasticizers, mainly found in PVC, emulsion paint, children's toys, and so on [2]. In recent years, Advanced Oxidation Processes (AOPs) have emerged as a new alternative for the treatment of wastewater-containing compounds that are difficult to biodegrade [3]. One of the most promising AOPs is catalytic ozonation, where the catalyst promotes the decomposition of ozone to favour the formation of highly reactive radicals, where a wide range of catalysts have been employed for the removal of various toxic organic compounds [4]. Based on the widespread detection of phthalates in the environment, it is necessary their elimination. To our knowledge, this is the first investigation which use MIL 88-A as a catalyst to model mixture of dimethyl phthalate (DMP) and dioctyl phthalate (DOP) by catalytic ozonation.

In this study will sistematicaly explain the influence of MIL 88-A on model mixture removal using ozone as oxidant agent. We expect this work can provide a new vision for the application of MIL 88-A in catalytic ozonation and promote the technology due to its excellent stability.

Material and Methods

The synthesis of MIL 88-A was performed with 3.96 g of FeCl$_3$·6H$_2$O and 1.74 g of C$_3$H$_3$O$_4$ in 75 mL of deionised water. After stirring for 30 min, the solution was transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was kept at 85°C for 12 hours and then cooled to room temperature. The precipitates were filtered and washed with deionised water and ethanol, followed by drying at 60 °C for 24 hours.The catalysts were evaluated by conventional (O$_3$) and catalytic (O$_{3\ cat}$) ozonation; this was carried out in a glass reactor (capacity approximately 950 mL). The reactor is charged with 600 mL of a model mixture (DMP and DOP) solution at a concentration of 20 mg L^{-1} each and a catalyst concentration of 0.1 mg L^{-1}. Ozone was produced from extra dry oxygen at a flow rate of 0.2 L min^{-1} using a corona discharge type generator to obtain an ozone concentration of 3.8 mg L^{-1}, taking samples at the following times; 5,10,15,30,60,90 and 120 min.The degradation of the pollutant and some by-products formed during treatment was monitored by high performance liquid chromatography (HPLC) using a YMC ODS column, using a mobile phase of ACN:H₂O (70:30) at a flow rate of 1 mL min^{-1} and at a wavelength of 210 nm. An atomic absorption (AA) Fe study was developed by using a Perkin Elmer AAnalyst 100 atomic absorption spectrometer with an iron lamp and a flow rate of 0.3 L min^{-1} of acetylene: oxygen.

Results and Discussion

The phase compositions of our synthesised Fe-based MIL-88A were verified by the X-ray diffraction patterns in Figure 1. where the structure type of MIL 88-A according to the literature is hexagonal a = 11.18 Å and c = 14.68 Å. It is shown that the synthesised MIL-88A has a high quality crystallinity and its particle size

distribution is very narrow. The diffraction peaks are mainly located around 2θ = 10.63° and 12.21°, which are respectively assigned to the (100) and (101) planes of MIL 88-A. The positions of the peaks are very consistent with the literature [5], indicating that MIL 88-A has been successfully prepared.
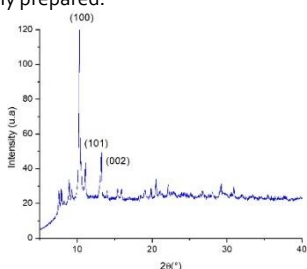

Figure 1. XRD pattern of MIL 88-A.

The FTIR (Figure 2) spectrum of the rod-like MIL 88-A catalyst shows two characteristic peaks at 1602 and 1398 cm^{-1} due to the stretching vibration of CO. Also, the peaks at 1203 cm^{-1} (C–C stretching), 976 cm^{-1} (C–H bending), and 554 cm^{-1} (Fe–O stretching) were indicated in FTIR of rod-like MIL 88-A . The spectrum also shows a broad band between the regions 3000 and 3600 cm^{-1} indicating the presence of water, which could help it to generate the oxygen vacancies favouring the formation of oxidative species.The dimensionless profile of model mixture (DMP and DOP) in aqueous solution for O_3 and O_{3cat} is showed in Figure 3 during 120 min. The presence of catalyst in the medium reaction favored the model mixture removal in comparison with conventional ozonatio. The model mixture removal was 70% while for O_{3cat} almost complete elimination was obtained in the same timeof reaction. The TOC analyses to obtain the global catalytic activity (Figure 4) shows the benefit of using a catalyst as it increased the degree of mineralization by approximately 20 percent (63.70%) over the conventional treatment (41.97%) during 120 min.The stability of catalyst is an important parameter to consider; with the purpose of knowing the stability of

the material, an AA study was carried out and the results showed that after 120 min there is no presence of the iron ions present in the sample.It is an excellent result because there are several reports which indicating the leaching of iron in acid conditions.
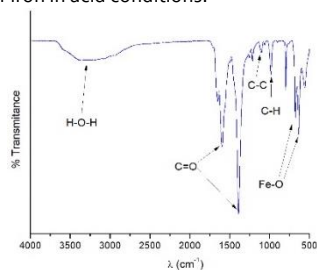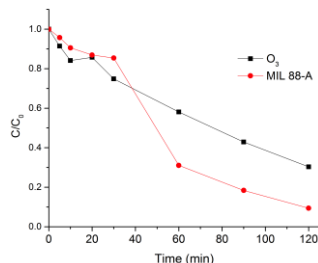

Figure 2. FTIR spectrum of MIL 88-A.

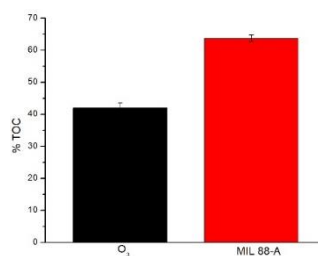**Figure 3.** DOP and DBP degration by convectional and catalytic ozonation.

Figure 4.TOC removal

Conclusions

Both conventional and catalytic ozonation almost completely degraded the model mixture, achieving a higher removal of contaminants using the catalyst after 120 min of treatment, a removal of 92% was obtained while ozonation has a removal of 70%. The benefit of the use of the catalyst was mainly reflected in the removal of total organic carbon reaching 63% while for the conventional treatment it was 41%, thus demonstrating that MIL 88-A is a viable catalyst.

References
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