Application of MOF Based on Iron and Terephthalic Acid to Drug Removal in Aqueous Effluents

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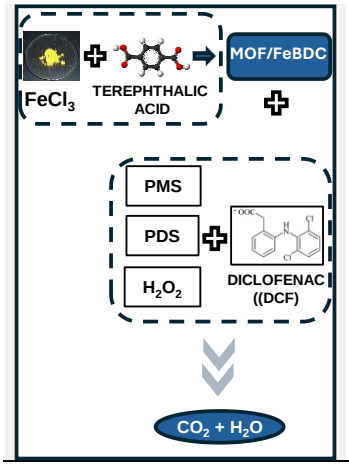

Human activities have increased the amount of organic substances, called emerging contaminants, in water bodies. Among these contaminants, diclofenac must be highlighted since it is one of the most pharmaceutical contaminants detected in water in the world. In this context, advanced oxidative processes using a metal-organic framework (MOF) as a catalyst come up as promising solution for the removal and degradation of drugs in water. In this work, MOF based on iron and terephthalic acid (MOF/FeBDC) was synthesized and applied to degrade diclofenac (DCF). Oxidation tests showed MOF/FeBDC activated oxidant potassium peroxymonosulfate (PMS), promoting higher drug degradation (91% of DCF) and faster reaction. Reuse tests indicated that MOF/FeBDC is not degraded for PMS and is stable after five cycles. Germination tests on lettuce seeds suggested the products formed after DCF oxidation did not present environmental toxicity.

Introduction

The growing demand for fresh water and the low efficiency in the removal of emerging contaminants by conventional water treatment have motivated several research studies, leading to the development of more sustainable material. Among more than 10,000 human and veterinary drugs produced by the pharmaceutical industry, that contaminate the environment, two are widely detected in water bodies in various parts of the world: amoxicillin and diclofenac [1]. At the same time, a new class of highly porous crystalline materials, metal-organic frameworks (MOFs), comes up as a promising alternative for the removal and degradation of drugs, since some advanced oxidative processes require materials that have high porosity and surface area, stable structure, and good dispersion in water [2]. In this work, MOF based on terephthalic acid and iron (MOF/FeBDC) is synthesized, characterized and applied as catalyst in advanced oxidative processes (AOPs) for effective removal and degradation of diclofenac in water bodies.

Material and Methods

An aqueous solution of iron (III) chloride, $FeCl_3$ (0.01 mol) had the pH adjusted to approximately 1, adding sulfuric acid. In another pot, sodium hydroxide and terephthalic acid (0.02 mol) were added to distilled water to produce a terephthalate (BDC) solution. The iron solution was heated to boiling, and then the sodium terephthalate solution was slowly added. The resulting mixture was kept under heating at reflux for 24 h. At the end of this period, the synthesized material, MOF/FeBDC, was washed with distilled water and dried at 100 ºC. The material was characterized using various techniques, including powder X-ray diffraction (XRD), thermogravimetric analysis, Fourier transform infrared spectroscopy (FTIR), adsorption-desorption isotherms of N_2, and scanning electron microscopy (SEM)—the last two presented in this work.

Oxidation tests were carried out using 0,5 mL of 0.02 mol L^{-1} solutions of oxidants potassium peroxymonosulfate (PMS), potassium peroxydisulfate (PDS), or hydrogen peroxide (H_2O_2), 20 mL of 100 ppm DCF solution and 5 mg of MOF/FeBDC. The oxidation kinetics was carried out by removing aliquots at times 10, 20, 40, 60, 90, 120 and 180 min, analyzed in a Shimadzu HPLC equipment (LC-20A) with UV-RID detectors at a wavelength of 250 nm. At the end of the reactions, aliquots were sent for oxidation product analysis by electrospray ionization analysis in negative mode, coupled to a mass detector (ESI(-)-MS) (Thermo Scientific model Ion-Trap LCQ Fleet equipment).

Oxidation tests varying essential parameters in this process were carried out in the following conditions: absence of MOF/FeBDC, PMS concentration improving from 0.01 to 0.03 mol L^{-1}, drug concentration increasing from 25 ppm to 75 ppm and MOF/FeBDC mass changing from 3.0 to 7.0 mg. The best condition from each test was applied to the next to obtain the optimal oxidation parameters.

Results and Discussion

The material, an orange powder, was obtained and characterized. From the N_2 adsorption and desorption isotherm, it was observed that the material presents a type IV isotherm (Figure 1(a)), characteristic of mesoporous materials, with

hysteresis in the range of p/p_0 = 0.7 to 0.9. The point p/p_0 = 0.1 indicated point B, where monolayer coverage is complete. The specific surface area, calculated by the BET method, equals 130.54 $m^2 g^{-1}$. This area is much smaller than that found for some Fe/BDC MOFs, probably due to water being used and not DMF. Despite a relatively low surface area for MOF, this is close to or greater than the specific surface area of other materials based on metal-organic networks containing iron reported in the literature.

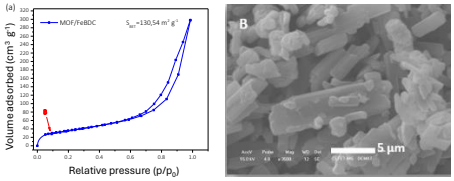

Figure 1. (a) Adsorption-desorption isotherms of N_2, and (b) SEM images for MOF/FeBDC.

The images obtained for the MOF (Figure 1(b) show a material with a heterogeneous, regular surface, with particles of different sizes but with the same needle shape.

The influence of MOF/FeBDC in oxidation medium was comproved in Figure 2(a), since this catalyst activated PMS oxidant, promoting higher drug degradation and faster reaction. Considering different oxidants, it was possible to see that potassium peroxymonosulfate (PMS) exhibited the best activity, promoting the oxidation of 91% of DCF, against 39% for potassium peroxydisulfate (PDS) and 23% for H_2O_2.

After that, the material was tested in different reaction conditions to evaluate the best oxidation parameters. PMS was used since it was the best oxidizing agent. The effect of PMS and drug concentrations and catalyst mass was evaluated.

About the effect of oxidant concentration, it was possible to note (Figure 2b) that an increase of PMS concentration from 0.01 to 0.03 mol L^{-1} raised the content of diclofenac degradation from 85 to 91%, respectively.

Diclofenac content seems unimportant in the oxidation process since its degradation percentage was very close when the concentration of the drug was increased from 25 ppm to 75 ppm (Figure 2c).

The catalyst mass was investigated, combining better drug and oxidant concentrations. The results suggested the increase of MOF/FeBDC content from 3.0 to 7.0 mg improved the reaction speed and the percentage of drug degradation (from 88.6 to 91.4%) since there were more sites for PMS activation with more catalyst quantity (Figure 2d).

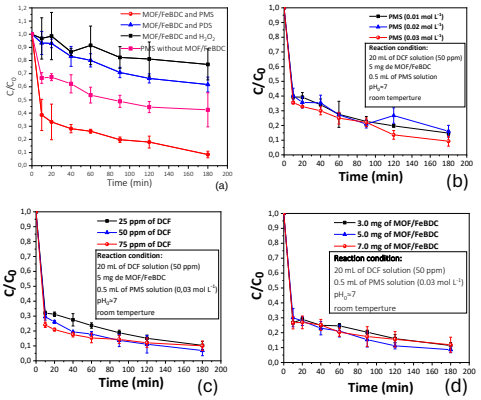

Figure 2. (a) DCF oxidation kinetics, at room temperature and pH ≈ 7, from using different oxidants. Analysis of the effect of (b) PMS concentration, (c) DCF concentration, and (d) MOF mass on oxidation.

After the DCF degradation reactions, the resultant solutions were analyzed by electrospray ionization mass spectroscopy in negative mode, coupled to a mass detector (ESI(-)-MS) and the results suggested complete drug mineralization.

Material reuse tests carried out on the best oxidation conditions showed MOF/FeBDC is not degraded for PMS, indicating it is stable and possible to be reused several times.

The products formed in the DCF oxidation process were evaluated for toxicity, and germination tests were carried out on Lactuca Sativa (lettuce) seeds. After five days (120 h), the length of the germinated seed roots was measured, and the results suggested that the products formed after DCF oxidation did not present toxicity to the environment.

Conclusions

MOF/FeBDC showed a high capacity to act as a catalyst in PMS activation, leading to the complete mineralization of 91% of DCF, as suggested in ESI(-)-MS results. Furthermore, the MOF/FeBDC could be reused for five times, indicating good stability of this material. The solution formed after the oxidation process does not present toxicity, as can be proved by lettuce seed tests.

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References

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