Assessing modified activated carbons for the degradation and mineralization of Lamotrigine by catalytic ozonation

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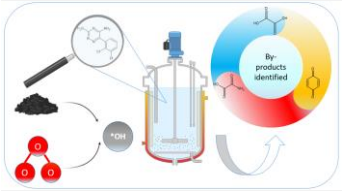

Lamotrigine (LTG) is one of the most commonly detected anti-epileptic drugs in rivers and lakes worldwide. Catalytic ozonation appears as an excellent technology capable of removing this pollutant from waters, due to the capacity of the catalyst to convert O_3 into hydroxyl radicals, and thus degrade even the more persistent by-products. Among the catalysts used in this kind of reaction, activated carbon receives special attention due to its characteristics, which can be improved by some surface treatments. In this study, the catalytic activity of HNO_3 - modified activated carbon in the degradation and mineralization of LTG was evaluated in two conditions: LTG alone and in a mixture of pharmaceuticals, including carbamazepine (CBZ), and Ibuprofen (IBF). The results show that the modified activated carbon acts as an efficient catalyst in the mineralization of LTG, obtaining a TOC reduction of 57% for the LTG solution and 69% for the pollutant mixture.

Introduction

LTG is an antiepileptic drug that is commonly prescribed for patients with epilepsy. In recent years, it has also been used for other indications such as migraine, chronic neuropathic pain and mood disorders [1]. Only a fraction of this drug is metabolized by the human body, and the remaining fraction is excreted, ending up in the sewage system and contaminating water bodies. This fact makes it one of the most widely detected antiepileptic drugs in rivers and lakes around the world, along with other antiepileptics such as carbamazepine, gabapentin and primidone [2].

Catalytic ozonation emerges as an alternative for the degradation and mineralization of organic compounds such as LTG, as it generates hydroxyl radicals through the decomposition of O_3. Among the catalysts employed in this king of reaction, activated carbon receives special attention, because it has unique characteristics in its pore structure (pore shape, pore volume, average pore size and pore size distribution) and surface (surface morphology and functional groups) [3], besides its characteristics being easily tunable to favor the catalytic activity. For example, Cao et al. (2014), found an improvement in oxalic acid removal of 38.5% when an HNO_3-modified activated carbon was used in catalytic ozonation [4].

In this study, tests were carried out to evaluate the catalytic activity of HNO_3-modified activated carbon in the degradation and mineralization of LTG, both isolated or in a mixture with other pharmaceuticals, namely CBZ and IBF. Common ozonation by-products were also identified in this study.

Material and Methods

A commercial activated carbon (Degussa, Hydraffin as 12/450) was used, which was modified by oxidation with HNO_3 (6 M) followed by thermal treatment at 600 °C. This modified activated carbon was used as a catalyst in the ozonation of LTG. The catalytic ozonation tests were carried out with one solution of LTG (10 ppm) and another solution containing LTG, CBZ and IBF, each contaminant at a concentration of 10 ppm.

The experiments were conducted under controlled conditions in a stirred reactor. These conditions include stirring at 400 rpm, an ozone concentration of 50 mg/L, an ozone flow rate of 150 Ncm^3/min, a catalyst dose of 350 mg, a solution volume of 700 mL, and a reaction time of 180 min. Aliquots were taken at determined times along the reaction duration and analyzed by High-Performance Liquid Chromatography, coupled to a diode array detector (HPLC-DAD). Ozonation by-products, namely oxalic acid (OXL), oxamic acid (OXM) and benzoquinone (BZQ) were detected by HPLC-UV.

Results and Discussion

Figure 1 (a) shows the degradation of LTG with and without catalyst when isolated. The pollutant is degraded in less than 15 min in both cases. However, the TOC reduction for the test without catalyst was only 26%, while when modified activated carbon was used, it increased to 57%, indicating a more efficient mineralization of the LTG.

When evaluating the catalytic activity of the modified activated carbon in the degradation and mineralization of LTG in a mixture of pharmaceuticals, it is observed that LTG degradation is slightly affected when the other contaminants are present in the solution, with LTG being the most persistent contaminant compared to CBZ and IBF (Figure 1 b). Fitting to a first-order kinetic model, the

degradation rate constant for the LTG when isolated was 0.419 s^{-1}, while in the pollutant mixture was 0.087 s^{-1}. A TOC reduction of 69% was obtained for the pollutants' mixture after 180 min of reaction.

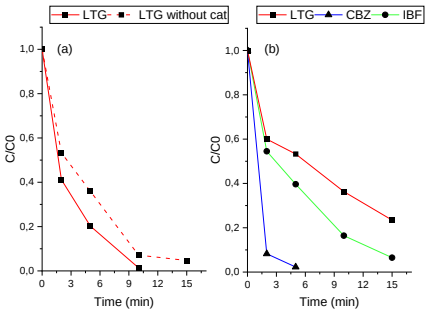

Figure 1. Degradation of the, (a) LTG and (b) pollutant mixture with LTG, CBZ and IBF.

In the catalytic ozonation reaction of the LTG solution, OXL and OXM were identified as by-products. In contrast, in the catalytic ozonation reaction of the pollutant mixture, BZQ, OXL and OXM were identified, see Figure 2. OXL is the main by-product generated in the LTG solution and pollutant mixture, which appears from 5 to 180 min. OXL contributes to 76% of the final TOC in the LTG solution and only represents 20% of the final TOC in the pollutant mixture, i.e. other by-products that have not been identified are generated.

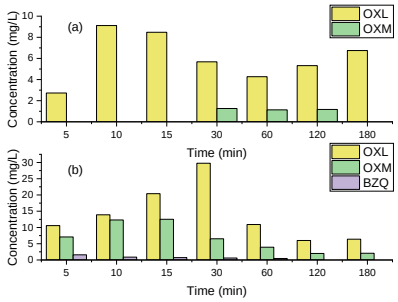

Figure 2. By- products identified in the catalytic ozonation of (a) LTG solution and (b) the pollutants mixture.

OXM appears from 30 to 120 min; at 180 min, it is no longer quantifiable for the LTG solution reaction. In the contaminant mixture reaction, it is identified from 5 to 180 min, with a more pronounced concentration than in the LTG solution, as expected.

Conclusions

The presence of modified activated carbon in the ozonation of the LTG solution did not significantly change the drug's degradation, but their presence improves the LTG's mineralization from 26% to 57%. OXL is the main degradation by-product contributing to the final TOC value. However, when LTG is in a mixture of pollutant, although the TOC reduction was quite expressive (69%), the identified by-products only justify 32.7% of the final TOC in the pollutant mixture, indicating that other by-products that have not been identified are generated. Nevertheless, the modified activated carbon is effective in promoting the mineralization of LTG, even in the presence of other pollutants.

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