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BICARBONATE ACTIVATED HYDROGEN PEROXIDE OXIDATION OF DICLOFENAC IN AQUEOUS SOLUTION

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Introduction

Diclofenac is a non-steroidal anti-inflammatory drug used in the form of oral tablets or in the form of gel and it is one of the most spread organic pollutant, together with its metabolites.

There are many ways to eliminate the organic pollutants, like diclofenac, from waters; among them, advanced oxidation processes (AOPs) are widely used, since they are able to produce oxidizing radicals like hydroxyl, superoxide radical, hydroxy peroxy radical and singlet oxygen from oxidants such as oxygen, hydrogen peroxide and ozone. The presence of bicarbonate anion (HCO_3^-) in wastewater can significantly reduce the concentration of $\bullet\text{OH}$ due to scavenging processes that lead to H_2O and to a much less reactive oxygen species, the carbonate radical $\bullet\text{CO}_3^-$, but also it was proved that the bicarbonate anion is as activator for hydrogen peroxide in sulfide oxidation reactions, epoxidation of alkenes and degradation of several dyes through generation of carbonate and superoxide radicals.

Chemical oxidation with hydrogen peroxide and sodium bicarbonate is an efficient method for degradation of non-steroidal anti-inflammatory drugs, such as diclofenac. The activity of certain micro components have also been studied to see if they have an influence on the degradation reaction. The following micro components were used for this experiment: CoSO_4 and NaNO_2 . It has been observed that the presence of nitrites has an inhibitory effect on the degradation reaction, while the presence of cobalt ions in very low concentrations has an activating effect.

Materials and methods

The diclofenac (0.3mM) oxidation was performed with a system consisting of hydrogen peroxide 0.05M and sodium bicarbonate 0.05M and CoSO_4 4 μM or NaNO_2 50 μM (as activators) in a small batch reactor (5mL). Samples of 20 μL were taken over time and analyzed by HPLC (C8 column, 15 x 0.46 cm, 5 μm , elution system acetonitrile: 0.1% phosphoric acid in water 50:50 in isocratic mode, 1ml/min flow rate) using a UV-VIS detector at $\lambda=278$ nm. In these conditions, diclofenac has a retention time at 6.3 min.

Results and conclusions

From the chromatograms recorded in time, it was observed that there is a visible decrease of the peak corresponding to diclofenac; also, we observed the appearance of other peaks at retention times of 1.6 min and 3.5 min, proving that the oxidation of

diclofenac leads to the formation of several organic products. From the areas of peaks associated with diclofenac, we calculated the unreacted diclofenac concentration and estimated the rate constant according to a pseudo first order kinetics:

$$[DF] = [DF]_0 e^{-k_f t}$$

The reaction obey a pseudo first order kinetics, as it can be seen in figure 1. The presence of small amounts of Co^{2+} leads to an important increase of the kinetic constant, while the presence of NO_2^- ions leads to a slightly decrease of the kinetic constant.

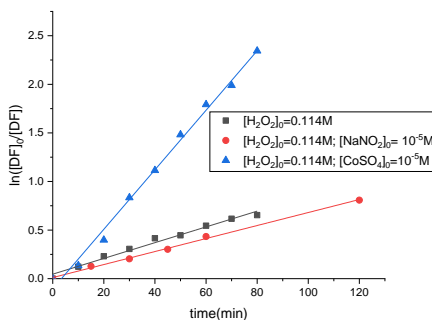


Figure 1. Kinetic curves for diclofenac oxidation in the presence of Co^{2+} and NO_2^- ($[DF]_0=0.05\text{mM}$, $[\text{NaHCO}_3]_0=3\text{mM}$)

The other organic products obtained in the reaction were quantified via HPLC-MS; the results showed a complex mechanism for diclofenac oxidation, with a mineralization degree of 85%.

The results showed that the bicarbonate activated hydrogen peroxide is a very good method for diclofenac degradation in the presence of cobalt ions, the results being very promising for diclofenac remediation.