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 peroxyl radical and singlet oxygen from oxidants such as oxygen, hydrogen peroxide and ozone. The presence in watewaters of bicarbonate anion (HCO_3^-) can significantly reduce the concentration of •OH due to scavenging processes that lead to H_2O and to a much less reactive oxygen species, the carbonate radical $•CO_3^-$, 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.

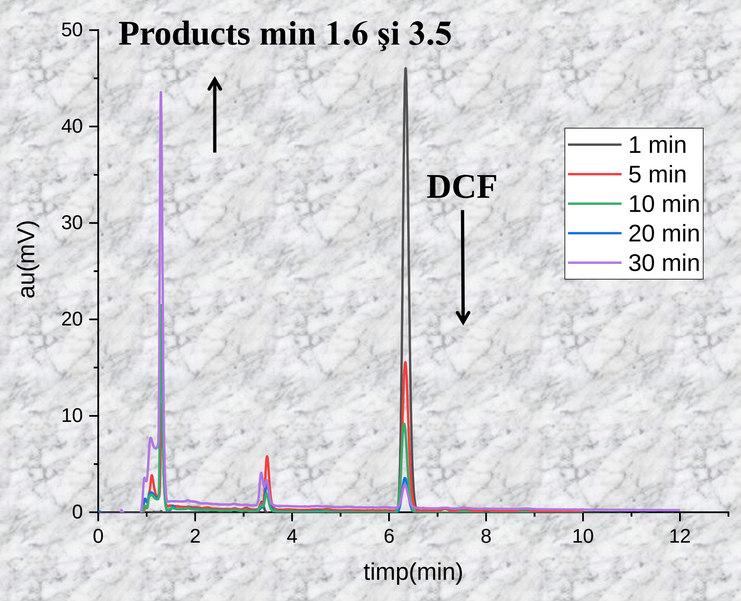
Chemical oxidation with hydrogen peroxide and sodium bicarbonate is an efficient method for degradation of non-steroidal anti-inflammatory drugs, such as diclofenac. The activity of certain microcomponents have also been studied to see if they have an influence on the degradation reaction. The following microcomponents 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.

Experimental

The diclofenac (0.3mM) oxidation was performed with a system consisting of hydrogen peroxide 0.05M and sodium bicarbonate 0.05M and CoSO4 4µM or $NaNO_2$ 50µM (as activators) in a small batch reactor (5mL). Samples of 20 µL were taken over time and analyzed by HPLC (C8 colum, 15 x 0.46 cm, 5µm, elution system acetonitril: 0.1% phosphoric acid in water 50:50 in isocratic mode, 1ml/min flow rate) using a uv-viz detector at λ=278 nm.In these conditions diclofenac has a retention time at 6.3 min.

Results

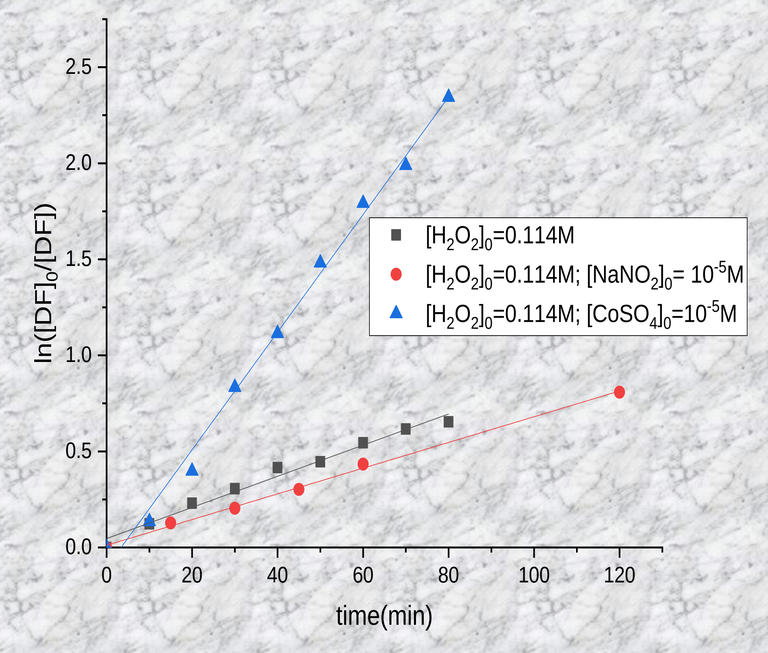
$$DF + H_2O_2 + NaHCO_3 + CoSO_4$$



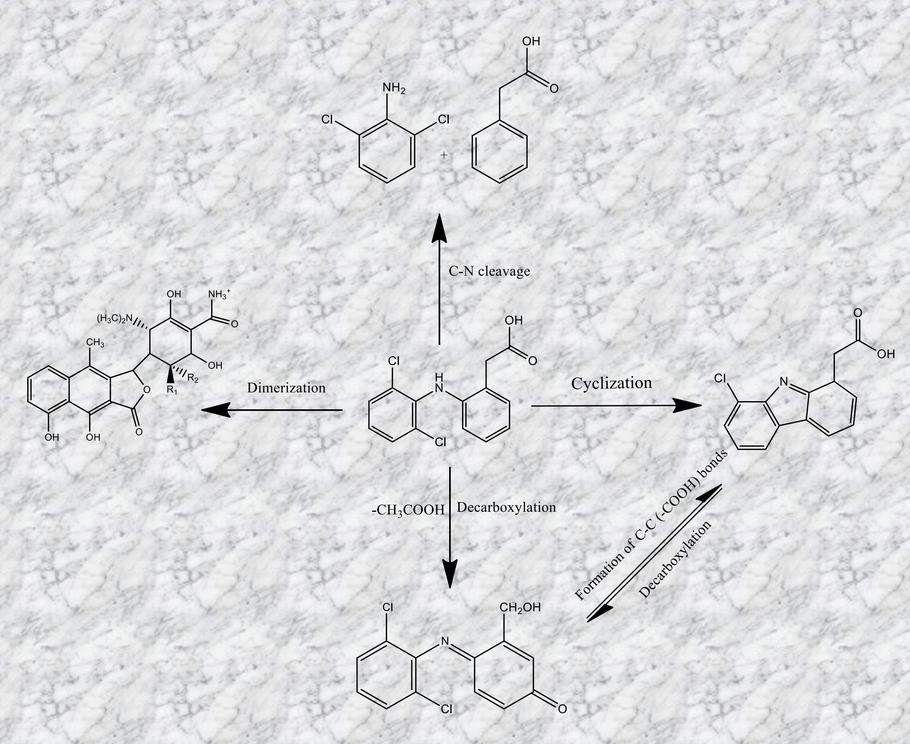
$$ln\left(\frac{[DF]_0}{[DF]}\right) = k_I t \longrightarrow \boldsymbol{k_I}$$

Initial concn.	$k_I(min^{-1})$	$t_{1/2}$(min)	r^2
$[H_2O_2]$=0.057M	(8.15±0.20) 10^{-3}	85	0.9917
$[H_2O_2]$=0.114M	(5.38±0.12) 10^{-3}	129	0.9956
$[H_2O_2]$=0.114M; $[NaNO_2]$= 10^{-6}M	(6.84±0.11) 10^{-3}	101	0.9984
$[H_2O_2]$=0.228M	(0.28±0.10) 10^{-3}	2435	0.9862
$H_2O_2]$=0.228M; $[CoSO_4]$= 10^{-6}M	(28.78±0.18) 10^{-3}	24	0.9956

Kinetic curves for diclofenac oxidation in the presence of Co^{2+} and NO_2^- ($[DF]_0$=0.05mM, $[NaHCO_3]_0$=3mM)



Degradation pathways for diclofenac oxidation



Conclusions

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