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The Effect of the Simultaneous Presence of Four Non-Steroidal Anti-Inflammatory Drugs During the Vacuum Ultraviolet Photolysis

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Abstract

Non-steroidal anti-inflammatory drugs (NSAIDs) are somewhat recently recognized pollutants, which are widely used by the society. Their sources in natural waters are the domestic and industrial effluents. Moreover, their possible interference with the water cycle and concurrent effects on the human health system has been implicated.

Advanced oxidation processes (AOPs) could help to solve this problem as alternative methods, which are based on the generation of reactive radicals to induce the transformation of organic contaminants beside biological methods, which are often ineffective for this purpose. Vacuum ultraviolet (VUV) photolysis is a suitable method among AOPs to study the effects of different parameters on the radical set and on the degradation of organic contaminants, since the generated radical set is well-known.

In this study, we aimed to investigate the simultaneous determination of pharmaceuticals (four non-steroidal anti-inflammatory drugs), namely ibuprofen, ketoprofen, naproxen and diclofenac. In this work we examined the degradation of compounds simultaneously, as wastewaters generally are multi-component solutions, where the components can effect the rate of decomposition of each other due to the competition for the reactive radicals. The pairing of the binary compounds in solution were ibuprofen+naproxen and ketoprofen+diclofenac, in order to be able to separate them by liquid chromatography. The results show that under the applied conditions (photon flux and initial concentration) the rates of the simultaneous degradation were slightly lower than in cases of one-component solutions because of the competition of the pharmaceuticals for the reactive species as we expected, however the influence of the competition was minor.

Introduction

Chemicals, such as pesticides, pharmaceutical products are continually being released into the environment in increasing amounts causing concerns as they are non-biodegradable and also being hazardous to living organisms, including humans. Traditional treatment processes are not designed to remove these compounds [1]. Consequently, the development of efficient processes is needed in order to remove them from wastewaters and drinking water.

During this work the simultaneous VUV photolytic degradation of NSAIDs were examined. These compounds are non-sterane arylcarboxylic acids containing phenyl groups.

Ibuprofen ((*RS*)-2-(4-(2-methylpropyl)phenyl)propanoic acid), ketoprofen ((*RS*)-2-(3-benzoylphenyl) propanoic acid), naproxen ((*RS*)-2-(6-methoxynaphthalen-2-yl)acetic acid) and diclofenac (2-(2-(2,6-dichlorophenylamino)phenyl) acetic acid) (*Fig. 1*) are pharmaceuticals with analgesic, anti-pyretic and anti-inflammatory properties. Their annual

production surpasses several kilotonnes, which has led to environmental concentrations from ppt to ppb levels to be found [2, 3].

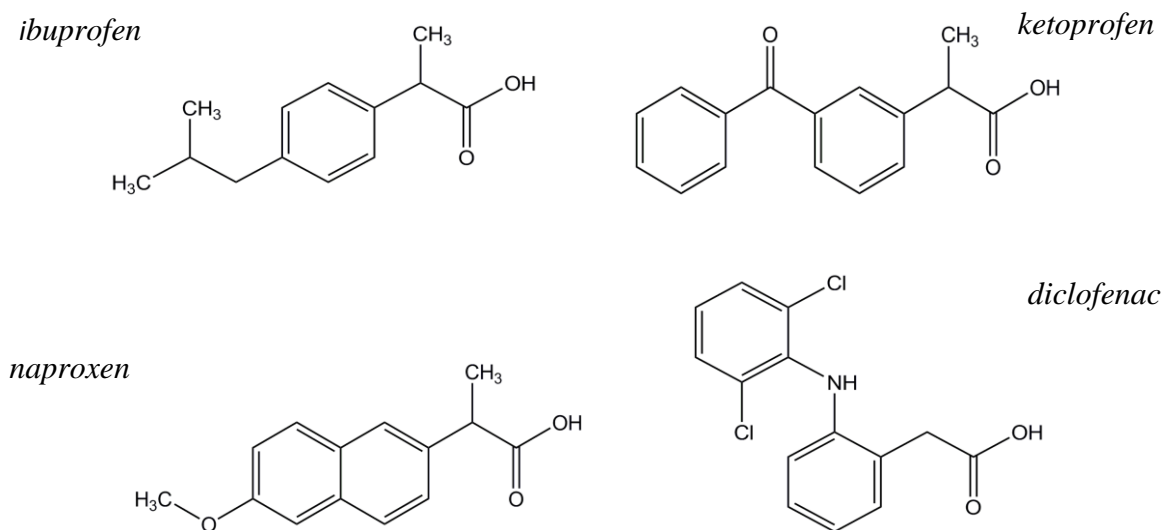
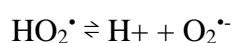
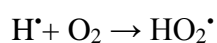


Fig. 1: The chemical structure of NSAIDs examined

During VUV photolysis, the homolysis of H₂O molecule takes place initiated by high-energy VUV photons generated by xenon excimer lamps emitting radiation at wavelengths shorter than 200 nm [4]. The primary radicals generated are mainly hydroxyl radicals ([•]OH) and hydrogen radicals (H[•]). In O₂-saturated solutions the radical set contains [•]OH in elevated concentration and hydroperoxyl radicals/superoxide radical anions (HO₂[•]/O₂^{•-}) because H[•] is trapped by molecular oxygen.



$$\Phi_{\cdot\text{OH}}^{172\text{ nm}} = 0.42 \text{ [5]}$$

$$k = 2.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \text{ [6]}$$

$$\text{p}K_a = 4.8 \text{ [7]}$$

The aim of this study was to compare the simultaneous degradation of NSAIDs with the case when only one compound is present in the system.

Experimental

Reactor configurations

In this study, the experiments were performed in the apparatus containing a 20 W xenon excimer lamp (Radium XeradexTM) emitting at 172±14 nm of wavelength. 250 ml aqueous solutions were circulated by a peristaltic pump between the reactor and reservoir tanks (both thermostated at 25 ± 0.5 °C) at 375 ml min⁻¹ flow rate. To investigate the influence of oxygen, O₂ gas (99.995 % purity) was bubbled through the solutions starting 15 minutes before and until the end of the irradiation. The *c*₀ values of NSAIDs were 0.5×10⁻⁴ mol L⁻¹ in individually, thus the total initial concentration of NSAIDs in the combined solutions were 1.0×10⁻⁴ mol L⁻¹.

Analytical methods

Ibuprofen and naproxen were purchased from Fluka, ketoprofen and diclofenac were purchased from Sigma-Aldrich. The purity of acetylsalicylic acids was >98% in each case.

The samples were analyzed by an Agilent 1100 HPLC equipment (using an LiChroCART® C18 reverse-phase column) with a diode array detector. In our case acetonitrile and 1% aqueous acetic acid were used in 1:1 ratio as eluent at a flow rate of 0.8 ml min⁻¹. The wavelengths of quantification were 220 nm in the case of ibuprofen, 256 nm in the case of ketoprofen, 230 nm in the case of naproxen and 280 nm in the case of diclofenac.

Results and discussion

The results show that the rate of degradation of NSAIDs decreased when the compounds applied were present simultaneously compared with the one-component cases (*Fig. 2a and b*).

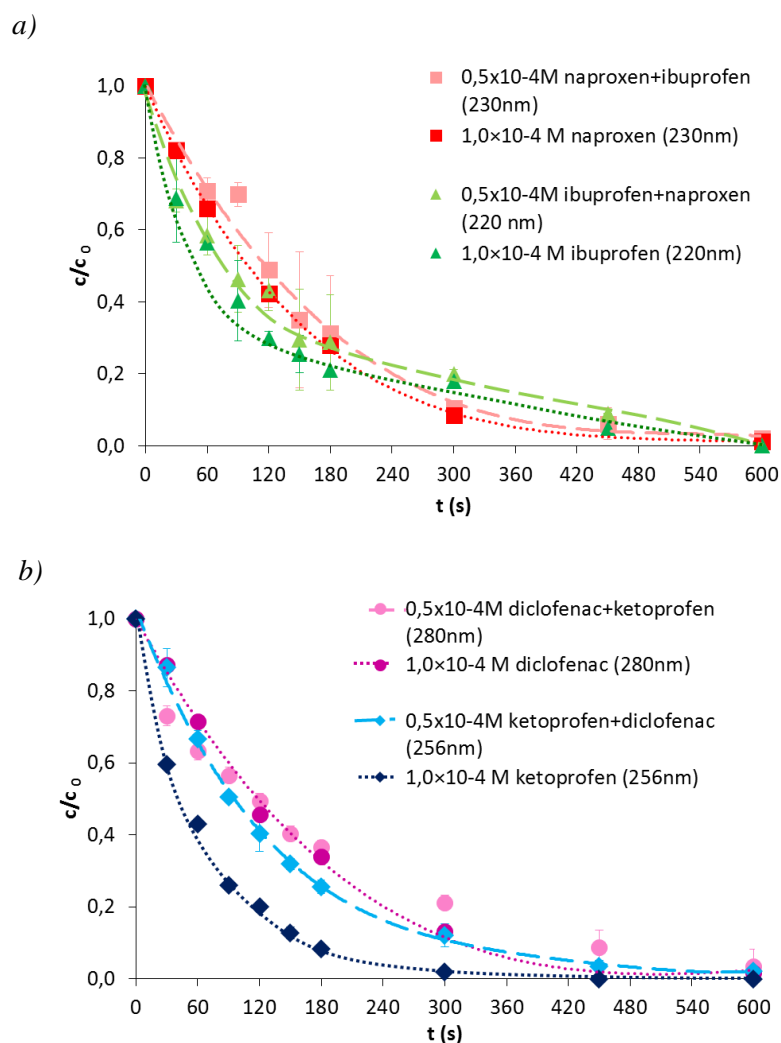


Fig. 2: The kinetic curves of NSAIDs in the presence of dissolved oxygen during vacuum ultraviolet photolysis

Table 1:Reaction rate constants of $\cdot\text{OH}$ radical with NSAIDs

	$k(\text{substance}+\cdot\text{OH})(\times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1})$
Ibuprofen	6.05
Naproxen	5.50
Ketoprofen	5.05
Diclofenac	8.85

This phenomena can be explained by the completion of NSAIDs mainly for the hydroxyl radical. Regarding the rate constants of reactions of NSAIDs with $\cdot\text{OH}$, in case of ibuprofen and naproxen this values are similar, thus the degrees of the reduction of degradation rates were similar also (*Fig. 2a*).

However, in cases of ketoprofen and diclofenac, the second one has one order of magnitude higher reaction rate constant with $\cdot\text{OH}$ (*Table 1*). This means that diclofenac competes with ketoprofen for the radicals successfully, which results that the ketoprofen decomposes with significantly lower rate in the presence of the second contaminant than in the absence of that (*Fig. 2b*).

Conclusion

- The effect of simultaneous presence of NSAIDs on their VUV photolysis was investigated.
- The rates of transformation of NSAIDs were lower in solutions that contained simultaneously two contaminants than in one-component solutions.
- Diclofenac reacts more effectively with $\cdot\text{OH}$ than ketoprofen, thus during their simultaneous VUV-irradiation the transformation rate of ketoprofen decreased significantly.

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