Photocatalytic Oxidation of Pharmaceuticals Mixtures in Water

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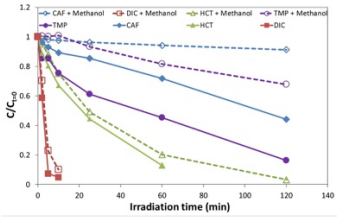

The photocatalytic degradation of aqueous multicomponent mixtures of common pharmaceuticals, caffeine (CAF), diclofenac (DIC), hydrochlorothiazide (HCT) and trimethoprim (TMP) by TiO_2 photocatalysis was investigated. DIC exerted significant hydroxyl radical scavenging activity with UVA-TiO_2 photocatalysis and inhibited the degradation of the other 3 pharmaceuticals. Mechanistic studies performed over the most efficient process (UVC-TiO_2) with radical scavengers revealed that DIC and HCT degraded primarily by photolysis and also by direct hole oxidation for DIC, while CAF and TMP degradation proceeded by hydroxyl radical attack. In the absence of DIC, the degradation rate of the pharmaceuticals increased significantly, implying the controlling role exerted by DIC on the photocatalytic degradation of pharmaceuticals mixtures in contaminated waters.

Introduction

Over the past few years pharmaceuticals residues in water have received increasing attention due to their persistency, accumulation, and potential impact to the environment. Among the wide range of pharmaceuticals, four of the most common in each class include diclofenac (DIC), trimethoprim (TMP), hydrochlorothiazide (HCT) and caffeine (CAF). The degradation of pharmaceuticals by heterogeneous photocatalysis is an attractive process since has the potential of exploiting solar light as the energy source for the activation of a semiconductor photocatalyst. However, pharmaceuticals photocatalytic degradation often reveals complex kinetics due to the formation of a wide range of transformation by-products which can display synergistic or antagonistic effects on the oxidation of the parent compound.

In this study, the kinetics of degradation of single and multicomponent mixtures of DIC, TMP, HCT and CAF by UVA and UVC photolysis and photocatalysis in slurry suspensions of TiO_2 was investigated. An appraisal of the oxidation mechanism, determined with the use of radical scavenger species explained the observed degradation kinetics of the pharmaceutical with the different processes, and the suppressing impact of DIC over the other pharmaceuticals was revealed.

Material and Methods

The degradation of pharmaceuticals was carried out in a photocatalytic reactor system with annular geometry (0.134 L, 7 mm path length) which was operated in continuous flow with total recirculation of the liquid between the photocatalytic reactor and a well-mixed vessel, saturated with oxygen by bubbling. The photoreactor was irradiated by a Philips 8W lamp, (either UVA or a UVC light bulb with identical dimension). The monochromatic photon flux measured at the wall of the UVC lamp was 260 W m^{-2}. The spectral averaged photon flux at the wall of the UVA lamp below 384 nm anatase TiO_2 absorption edge, was 154 W m^{-2}.

2 L of diluted aqueous solutions of pharmaceuticals (15.7 μM for each species) were loaded into the vessel. TiO_2 (P25) when used was added 0.4 (kg m^{-3}), which was optimal for achieving the maximum rate of photon absorption (optical thicknesses 3.24 (UVA lamp) and 3.37 (UVC lamp)). The adsorption of CAF, HCT, TMP and DIC on the TiO_2 catalyst at equilibrium was of 3, 5, 6 and 10%, respectively. The natural pH of the pharmaceutical's aqueous solution 7.0 ± 0.2, and 5.5 ± 0.2 in the presence of TiO_2, remained practically invariant during the degradation experiments. The temperature was 22-24°C during the experiments. ROS scavengers when used were added at these concentrations: methanol (10 mM), KI (1 mM) and NaN_3 (5 mM). The concentration of pharmaceuticals was determined by HPLC (Agilent 1100 series with DAD) and a Gemini C18 (250 × 4.6 mm, 5 μm) column (Phenomenex) after sample filtration (0.22 μm, 33 mm Sterile Millex ® Syringe Driven Filters Millipore).

Results and Discussion

Although photolysis of a near equimolar aqueous solution of CAF, HCT, TMP and DIC with UVA irradiation (Fig. 1) resulted in insignificant degradation of CAF, HCT and TMP, and 18% of DIC degradation, greater removal rates were obtained with the UVA-TiO_2 process (Fig. 2). DIC was removed at significantly faster rate than with UVA photolysis, while the degradation of HCT, TMP and CAF was greatly inhibited by the presence of DIC. Since the effect of direct photolysis of the pharmaceuticals within the UVA-TiO_2 process was insignificant the degradation of the pharmaceuticals was exclusively ascribed to the reaction with the radical oxygen species (ROS) formed as result of the photocatalytic process on the surface of TiO_2. However, the strong scavenging effect of DIC for ROS inhibited the removal of the other three pharmaceuticals from the mixture. This aspect was further elucidated with ROS scavenging experiments (results not shown).

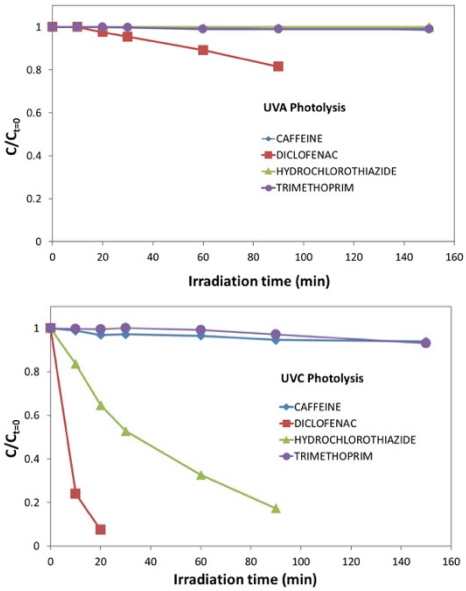

Fig. 1. Photolysis of equimolar solutions of DIC, TMP, HCT and CAF in ultrapure water at pH 7 under UVA and UVC irradiation. C_0 = 15.7 μM for each pharmaceutical.

With the UVC-TiO_2 process (Fig. 2) the synergy between photolysis and photocatalysis resulted in faster pharmaceuticals removals in comparison to the UVA-TiO_2 and UVC photolysis processes (Fig. 1). The rate increases more significantly for DIC and HCT due to the fast UVC photolysis observed for these two compounds, while a more moderate increase was observed for CAF and TMP. As previously shown, the presence of DIC in the mixture may exert an inhibitory action on the other pharmaceuticals, scavenging the photocatalytically produced ROS, although such effect is mitigated by the rate of direct UVC photolysis (Fig. 1) of the pharmaceuticals previously observed.

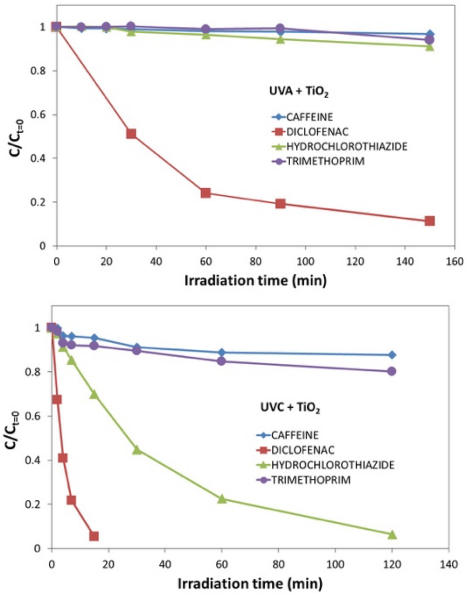

Fig. 2. Photocatalytic degradation of equimolar solutions of DIC, TMP, HCT and CAF in ultrapure water under (a) UVA-TiO2 and (b) UVC-TiO_2 at pH 5.5. C_0 = 15.7 μM for each pharmaceutical.

ROS scavenging experiments revealed that the degradation of the pharmaceuticals with the UVA-TiO_2 process was controlled by hydroxyl radicals and by the photocatalytic process, with negligible contribution from photolysis, and DIC exhibited a strong inhibitory effect on the other pharmaceuticals due to its fast hydroxyl radical scavenging properties. Further mechanistic details will be presented at the meeting.

Conclusions

This study demonstrated a strong inhibitory effect of DIC over the photocatalytic degradation of other pharmaceuticals. In consequence, the detection and removal of DIC in pharmaceuticals water and wastewater should be targeted to tailor an efficient treatment process by UV-TiO_2 photocatalysis. The UVC-TiO_2 process yields a more efficient treatment process due to the combined effect of photolysis and photocatalysis. With this process the removal of DIC and HCT primarily occurred by photolysis and also by direct hole oxidation of DIC, with a much smaller contribution from photocatalytically generated ROS, while the removal of CAF and TMP primarily proceeded by hydroxyl radical attack. The results collectively show that the photocatalytic oxidation of pharmaceuticals mixtures should be carefully examined to determine the impact of inhibitory species on the photocatalytic treatment process of contaminated water and wastewater.