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DETERMINATION OF HYDROXYL RADICALS USING COUMARIN AND COUMARIN-3-CARBOXYLIC ACID DURING GAMMA RADIOLYSIS AND HETEROGENEOUS PHOTOCATALYSIS

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Abstract

Coumarin and 3-carboxycoumarinic acid, two fluorescent probes commonly used for HO• detection has been used during gamma radiolysis and heterogeneous photocatalysis. The O_2 dependency and the radiation yield of their hydroxylated flurescent products (7-hydroxy-coumarin and 7-hydroxy-3-carboxycoumarinic acid) has been investigated during gamma radiolysis. The radiation yields were found to be 1.2(±0.2) % in O_2-free solutions, while it was 2.9 (±0.06) % in the presence of O_2, proving the importance of peroxyl radicals in the formation of these products. The results obtained from radiolysis experiments, were employed during heterogeneous photocatalysis performed with commercial TiO_2 catalyst. The effect of dissolved O_2 was also investigated, as its electron scavanging role during photocatalyis is also important. The formation rate of HO• during photocatalysis was calculated from the formation rate of the fluorescent products, and were found to be 1.8×10^{-7} mol dm^{-3} s^{-1}, while the quantum efficiency for its formation is 0.0038.

Introduction

Advanced oxidation processes (AOPs) have been investigated in the last few decades for their possible use as an additional wastewater purification method. During AOPs different reactive species form, the most important one is the hydroxyl radical (HO•), due to its high reaction rate with most organic pollutants. However several methods can be employed, like time-resolved spectroscopy, ESR, the determination of HO• formation rates is a complicated task. Fluorescent probes, like terephtalic acid or coumarines, have also been applied during heterogeneous photocatalyis to evaluate the formation rate of HO•. [1-5]

In this study coumarin (COU) and coumarin-3-carboxylic acid (3-CCA) have been used as a fluroescent probe for determination of the HO• formation rate. They are reported to form highly fluorescent hydroxylated prodcts in their reaction with HO•, 7-hydroxy-coumarin (7-HO-COU) and 7-hydroxy-3-carboxycoumarinic acid (7-HO-3-CCA), respectively. The formation rate of both hydroxylated products are reported to be dependant on dissolved O_2. In the presence of O_2 they form via peroxyl type radicals, while in the abscence of O_2 they form via dismutation, significantly reducing their formation rate. [1-3]

The application of COU and 3-CCA for HO• detection was investigated during two, different AOPs. In the case of gamma radiolysis the formation rate of all reactive species (HO•, e_{aq}^{-}, H•) is well determined, since the values of their radiation yields (G value) are well known. Heterogeneous photocatalysis is also a highly researched field of AOPs, but the reacton mechanisms are often not clear. The transformation of organic compounds is mostly related to the reactions with HO•. In addition, the reactions initiated directly by the photogenerated charges (h_{vb}^{+} and e_{cb}^{-}) has to be taken into consideration too. The reactions take place on the surface or close to the surface of photocatalyst, and consequently the interactions between the photocatalyst and substrate may have an important role.

The aim of this study is to determine the radiation yields of 7-HO-COU and 7HO-3-CCA, and investigate the effect of dissolved O_2 during gamma radiolysis. Based on these result, the formation rate of HO• and the quantum yield of the HO• formation ($\Phi_{HO•}$) may be determined during the heterogeneous photocatalysis. By comparing the transformation of the non-adsorbed COU, and the well adsorbed 3-CCA, we may investigate the importance of adsorption on the reactions of these substrates with HO•.

Experimental

In the gamma-radiolysis experiments a ^{60}Co gamma source was used in a panoramic type irradiator, the dose rate was 1.48 Gy min^{-1}. The solutions of COU and 3-CCA were irradiated in sealed ampulles, which were saturated with either O_2, N_2O or N_2. All experiments were performed in 10^{-4} mol dm^{-3} solutions of COU and 3-CCA in pH = 7.0 (in 0.01 mol dm^{3} phosphate buffer).

Photocatalysis experiments were performed in a glass reactor. 1.0 g dm^{-3} TiO_2 Aeroxide P25 (Acros Organics) was added to the 250 cm^{3} solutions, and irradiated using a fluorescent UV light source (GCL303T5/UVA, Lighttech) emitting in the 300-400 nm range. The photon flux of the lamp was 1.20×10^{-5} mol$_{photon}$ min^{-1}, determied by ferrioxalate actinometry. Since 3-CCA adsorbed on the photocatalyst surface (≈30 % adsorbed on TiO_2), NaF was added to the samples, for the desorption of the analytes. All samples were centrifuged at 15000 RPM, and filtered using 0.22 µm syringe filters (FilterBio PVDF-L).

The transformation of COU and 3-CCA (λ^{COU}_{max} = 277 nm, $\lambda^{3\text{-}CCA}_{max}$ = 291 nm, ε^{COU}=10300 dm^{3} mol^{-1} cm^{-1}, $\varepsilon^{3\text{-}CCA}$=12170 dm^{3} mol^{-1} cm^{-1}) has been followed using UV-Vis spectrophotometry (Agilent 8453). The formation of 7-HO-COU and 7-HO-3-CCA were followed using fluorescence spectroscopy (Hitachi F4500) at 455 and 447 nm, respectively. The initial transformation rates of COU and 3-CCA were determined from linear regression fits to the actual concentration versus the duration of irradiation, up to 15 % conversion. The initial formation rates of 7-HO-COU and 7-HO-3-CCA were obtained from the linear regression fits to the actual concentration versus the duration of irradiation.

Results and discussion

First the effect of O_2 on the formation of 7-HO-COU and 7-HO-3-CCA was investigated. In the case of radiolysis mainly HO• and e_{aq}^{-} forms from water. In the presence of O_2 e_{aq}^{-} transforms into $O_2^{•-}$. Since both $O_2^{•-}$ and its protonated form, $HO_2^{•}$ have a low reactivity towards organic compounds, mainly HO• is responsible for the transformation of COU in this case. Moreover, from carbon centered radicals peroxyl radicals form immediately. The formation of peroxly radicals opens a new pathway for the formation of hydroxilated products via unimolecular $HO_2^{•}$ elimination. In O_2-free solutions both the HO• and the e_{aq}^{-} are able to initiate the transformation of COU. Without O_2, the formation of 7-HO-COU happens via bimolecilar dismutation. The formation rate of HO• in the presence of O_2, air or N_2 can be calculated ($r_0^{HO•}$ = 6.91×10^{-9} mol dm^{-3} s^{-1}). In N_2O saturated solutions e_{aq}^{-} transforms into HO•, and doubling the HO• yield ($r_0^{HO•}$ = 1.33×10^{-8} mol dm^{-3} s^{-1}).

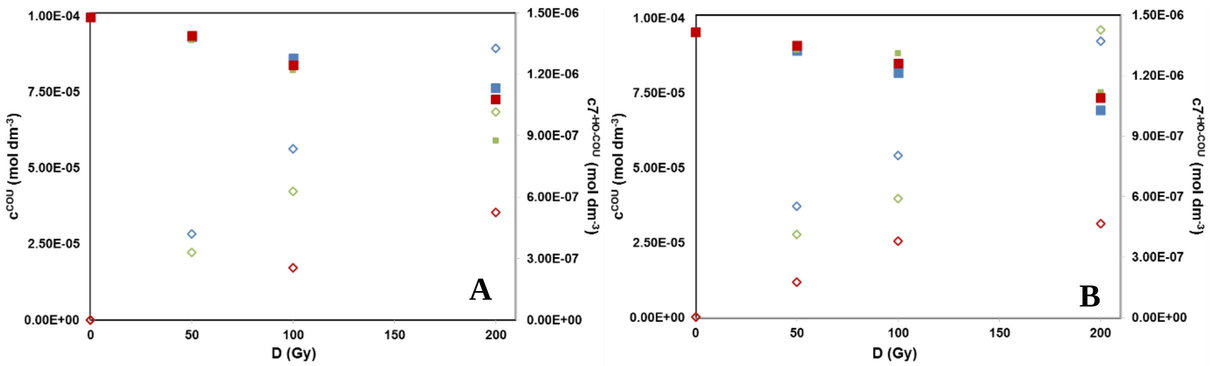

Figure 1. Concentration of COU (A) and 3-CCA (B) as a function of dose in O_2 (■), N_2O (■)) and N_2 (■) saturated solutions, and the formation of 7-HO-COU during gamma radiolysis in O_2 (◊), N_2O (◊) and N_2 (◊) saturated solutions.

The effect of the different gases on the transformation rate of COU and 3-CCA were negligible. Despite the similar transformation rates, the formation rate of the hydroxylated products show significant differences. The lowest formation rate can be observed in O_2-free solution, due to the lack of the possibility of peroxyl radical formation, and probably because of the significant contribution of e_{aq}^- to the transformation of COU/3-CCA, which do not result in hydroxilated products. The formation rates in N_2O saturated solutions are greatly increased, due to the increased HO• formation rate. The formation rates are even higher in the presence of O_2, despite the lower HO• formation, proving the importance of peroxyl radicals in the formation of the hydroxylated products. (Figure 1. and Table 1)

From the formation rates of the hydroxylated products and the formation rate of HO•, the radiation yield for both fluorescent product can be calculated. In N_2 saturated solutions 0.94 and 1.35 %, in N_2O saturated solutions 1.16 and 1.29 %, while in O_2 saturated solutions 2.99 and 2.86% of HO• produces 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA, respectively.

Table 1. Initial transformation rates of COU and 3-CCA and initial formation rates of 7-HO-COU and 7-HO-3-CCA during gamma radiolysis

	r_0^{COU} (× 10^{-9}mol dm^{-3} s^{-1})	$r_0^{7\text{-}HO\text{-}COU}$ (× 10^{-10}mol dm^{-3} s^{-1})	$r_0^{3\text{-}CCA}$ (× 10^{-9}mol dm^{-3} s^{-1})	$r_0^{7\text{-}HO\text{-}3\text{-}CCA}$ (× 10^{-10}mol dm^{-3} s^{-1})
O_2	3.35	2.06	3.23	1.98
Air	4.33	1.55	2.40	1.71
N_2	3.38	0.64	2.73	0.93

During heterogeneous photocatalysis the main reactive species is the HO•. The photogenerated h_{vb}^+ and e_{cb}^- pair may also react with organic compounds, especially when there is special interaction between the substrate and the catalyst surface. COU and 3-CCA have different adsorption properties, as COU do not adsorb on the catalyst surface, as opposed to 3-CCA, due to the strong interaction between its carboxyl groups and Ti≡OH surface groups of phtocatalyst.

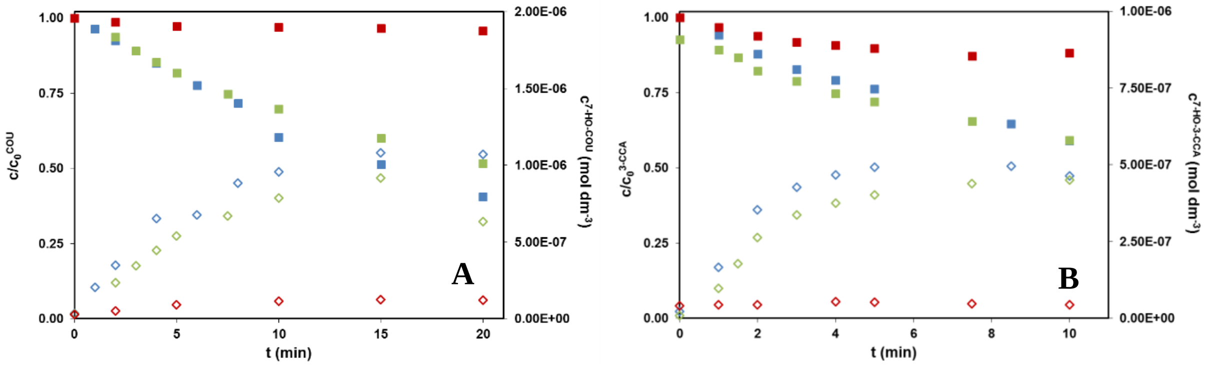

Figure 2. Transformation of COU (A) and 3-CCA (B) as a function of time, in O_2 (■), air (■) and N_2 (■) saturated suspensions, and the formation of 7-HO-COU during heterogeneus photocatalysis in O_2 (◊), air (◊) and N_2 (◊) saturated suspensions.

O_2 plays a crucial role as an electron scavenger, hindering charge recombination, and helping HO• formation via O_2•$^-$. In the case of COU there was no difference in the transformation rates determined in O_2 saturated and airated suspensions. At the same time, the formation rate of 7-HO-COU is nearly 1.5 times greater in the case of higher dissolved O_2 concentration. In the case of 3-CCA the transformation rate is also higher with 25% in the case of O_2 saturated suspension, while the formation rate of 7-HO-3-CCA increased with 33 %. In N_2 saturated suspensions the transformation of COU and the formation of 7-HO-COU is negligible. This suggests, that direct charge transfer reactions have a low probability, and HO• formation is negligible. The transformation rate of the well adsorbed 3-CCA is 47 % of the value measured in O_2 saturated suspension, and there is no 7-HO-3-CCA formation. This suggest that, 3-CCA transformation can happen via direct charge transfer, but this way does not results in hydroxilated products.

Table 2. Initial transformation rates of COU and 3-CCA and initial formation rates of 7-HO-COU and 7-HO-3-CCA during heterogeneous photocatalysis

	r_0^{COU} × 10^{-8} (mol dm^{-3} s^{-1})	**$r_0^{7-HO\ COU}$ × 10^{-9} (mol dm^{-3} s^{-1})**	**r_0^{3-CCA} × 10^{-8} (mol dm^{-3} s^{-1})**	**$r_0^{7-HO-3-CCA}$ × 10^{-9} (mol dm^{-3} s^{-1})**
O_2	6.15	2.55	8.98	2.77
Air	6.08	1.73	7.10	2.08
N_2	0.29	-	4.23	-

Using the results obtained from gamma radiolysis, the formation rate of HO• in the case of O_2 saturated TiO_2 suspension was found to be 1.78×10^{-7} and 1.86×10^{-7} mol dm^{-3} in the case of COU and 3-CCA respectively. Assuming that, TiO_2 absorbs completly the emitted photons from the light source, the quantum yield for the formation of HO• is 0.0037 and 0.0039, respectively.

Conclusion

- The formation of 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA requires HO•, while dissolved O2 highly enhances their formation rate.
- The radiation yield of 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA were determined in the case of gamma-radiolysis
- Based on radiation yields of the hydroxylated products, and the photon flux of the light source, the formation rate of HO• and its quantum efficiency has been determined during heterogeneous photocatalysis, using TiO_2 as photocatalyst

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