

HETEROGENEOUS PHOTOCATALYSIS OF COUMARIN AND 3-CARBOXYCOUMARINIC ACID EFFECT OF NaF AND METHANOL ON THE TRANSFORMATION RATE AND FORMATION RATE OF HYDROXYLATED PRODUCTS

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Abstract

Using heterogeneous photocatalysis, it is complicated to determine the formation rate of hydroxyl radical (HO•) and its relative contribution to the transformation of various target substances. In this work we compared the transformation rate of coumarin and 3-carboxycoumarinic acid (3CCA), and the formation rate of their fluorescent hydroxylated intermediates under various experimental conditions. The fluorescent spectroscopic methods were optimized. The effect of NaF and methanol as a radical scavenger were also investigated. Coumarin poorly adsorbs on the surface of TiO₂; addition of NaF has no effect on the adsorption capacity, while NaF significantly hinder the adsorption of 3CCA. NaF increases the transformation rate of both model compounds, while slightly decreases the formation of their hydroxylated intermediates. Methanol decreases the transformation rates, and this effect is less pronounced in the case of 3CCA, probably because of its favored adsorption on the TiO₂ surface.

Introduction

Heterogeneous photocatalysis is a widely researched process, due to its great potential to remove recalcitrant organic pollutants from various type waters, including drinking water. The most widely used commercial photocatalyst is TiO₂, due to its great activity under UV irradiation, good stability and low price. However several publication focuses on the preparation of new, highly reactive photocatalysts. The effectiveness of photocatalysts are often described by their ability to produce hydroxyl radicals (HO•), and the optimization of methods are usually include their improved HO•-production. However the determination of the formation rate of HO• is complicated. The detection of HO• by ESR or pulse-radiolysis are complicated processes, and usually very expensive. A more simple and available method is based on the detection of fluorescence intermediates forming during the reaction of aromatic compounds with HO•. This method is generally based on the formation of the hydroxylated intermediate of coumarin, which is the umbelliferone. Another, less investigated compound is 3-carboxycoumarinic acid (3CCA), and its hydroxylated intermediate, 7-OH-3-carboxycoumarinic acid (7OH-3CCA) (Fig.1.).

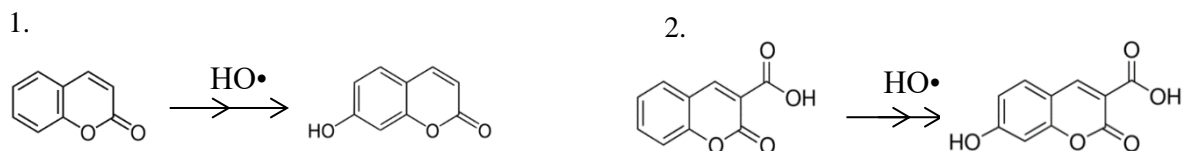


Figure 1. Coumarin and its fluorescent intermediate, umbelliferone (1.), and 3CCA and its fluorescent intermediate, 7OH-3CCA (2.) [1, 2]

Coumarin is also reported to react well with electrons ($k = 1,6 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [3]), therefore it may act as an electron scavenger. Transformation via direct charge transfer may be even more important using 3CCA, because of the affinity of carboxyl groups for metal oxide surfaces. The surface properties, especially the surface charge are highly important due to their influence on radical generation rate and adsorption of organic compounds. The $-\text{OH}$ groups of TiO_2 surface can be replaced by $-\text{F}$ groups via addition of NaF to the suspension. This is able to result in significant changes surface properties of the catalyst. [4]

The goal of our research is the determination and comparison of the transformation rates of two model compounds (coumarin and 3CCA), and the generation rates of formed hydroxylated intermediates. We have investigated the effect of methanol as a non-adsorbing $\text{HO}\cdot$ radical scavenger, and NaF, the surface changing agent on the transformation rate of both non-adsorbed coumarin and well adsorbed 3CCA and the formation rate of their hydroxylated intermediates.

Experimental

250 cm^3 aqueous solutions of coumarin and 3CCA ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) were irradiated in a reactor with a fluorescent mercury-vapor lamp emitting UV-light between 300 and 400 nm wavelengths. The TiO_2 containing suspension was circulated using a peristaltic pump with 330 $\text{cm}^3 \text{ min}^{-1}$ flow rate, thermostated at $25 \pm 1^\circ\text{C}$ and saturated with air. The TiO_2 photocatalyst (Aeroxide P25[®]) was added in 1.0 g dm^{-3} concentration, and dispersed by sonication. NaOH and HCl solutions were used to set the pH (measured with InoLab pH 730p) when needed. Methanol or NaF was added to the solutions in $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ concentration. The samples were centrifuged and filtered using 0.22 μm syringe filters to remove the TiO_2 before analysis.

The transformation of coumarin ($\lambda_{\text{max}}=277 \text{ nm}$) and 3CCA ($\lambda_{\text{max}}=291 \text{ nm}$) were followed using spectrophotometry (Agilent 8453). Fluorescence spectroscopy (Hitachi F4500) was applied to determine the concentration of formed hydroxylated intermediates. The determination of formed umbelliferon concentration was based on the intensity of the emitted fluorescence light at 455 nm. The wavelength of excitation was 455 nm. The determination of 7OH-3CCA concentration was based on the intensity of the emitted fluorescence light at 447 nm at pH = 9.0. The wavelength of excitation was 387 nm.

Results and discussion

At first, the adsorbed amount of coumarin and 3CCA on TiO_2 surface was determined. While coumarin does not show significant affinity for the TiO_2 surface, 3CCA adsorbed well. Addition of NaF to the suspension hindered completely the adsorption of 3CCA on the TiO_2 surface, due to the changing the surface $-\text{OH}$ groups with $-\text{F}$ groups. Adsorption capacity of poorly adsorbed coumarin was not changed by this way. Desorption of 3CCA and 7OH-3CCA is necessary before the determination of their concentration, therefore we added 0.125 mol dm^{-3} NaF to each sample (recovery $\approx 98\text{-}100\%$) before analysis. Addition of NaF to the TiO_2 suspension changed the pH from 3.8 to 7.0, which effect is caused by the replacement of OH^- ions.

Due to the significant overlapping the absorption spectra of coumain and umbelliferon, 345 nm was choose as excitation wavelength, thus coumarin absorption does not disturb significantly the excitation of umbelliferon. We also investigated the pH-dependence of the fluorescence light intensity of umbelliferone, and finally set pH = 5.5 for each measurement. The concentration of coumarine was determined by spectrophotometric way (due to the absorption at 277 nm). The determination of formed umbelliferon concentration was based on the intensity of the emitted fluorescence light at 455 nm. The wavelength of excitation was

455 nm. Similar investigations were done for 3CCA, when pH was proved to be much more important factor. Deprotonated form of 3CCA emits intensive fluorescence light. Consequently pH has to be set 9.0, to avoid the emission and disturbing effect of this fluorescent light. 7OH-3CCA has an even stronger fluorescence, and its emission spectrum just slightly overlaps with its absorption spectrum and no overlapping with absorption spectrum of 3CCA. (Fig.2.) Thus the concentration of 3CCA was determined by spectrophotometric way (due to the absorption at 291 nm, pH = 3.8) The determination of formed 7OH-3CCA concentration was based on the intensity of the emitted fluorescence light at 447 nm at pH = 9.0. The wavelength of excitation was 387 nm.

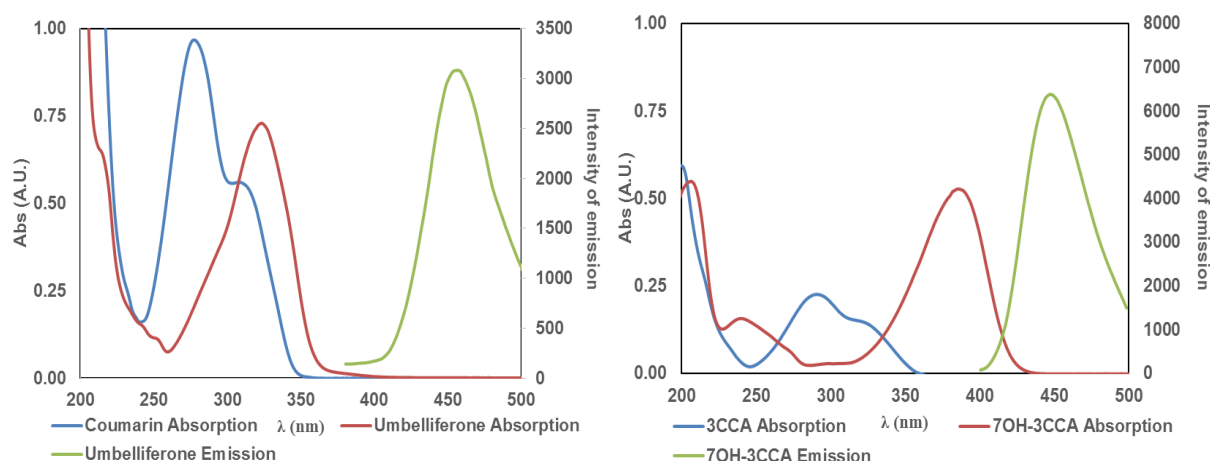


Figure 2. Absorption and emission spectra of coumain (pH = 5.5), 3CCA (pH = 9.0) and their hydroxylated intermediates

Addition of NaF significantly increased the transformation rate of coumarin, and slightly changed the formation rate of umbelliferone. However the maximum value of the concentration of formed umbelliferone and probably the transformation rate of this hydroxylated intermediate is significantly increased by NaF. Addition of methanol, as HO• scavenger reduced both the transformation rate of coumarin and formation rate of umbelliferone.

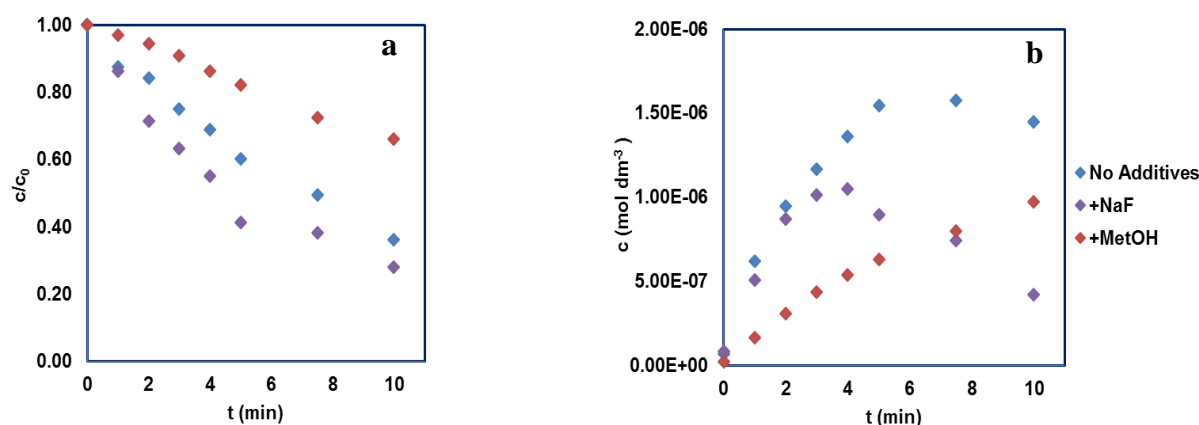


Figure 3. The relative concentration of coumarin (a), and the concentration of umbelliferone (b) as a function of time

Addition of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ NaF completely hinders the adsorption of 3CCA and 7OH-3CCA. Using 3CCA, which is well adsorbed on the surface of TiO_2 , experiments were done

with and without addition of NaF before filtration of treated samples. Addition of NaF is aimed to enhance the desorption of the 3CCA and 7OH-3CCA from the surface of the TiO₂ before determination of their concentration.

Addition of NaF increased the transformation rate of 3CCA in TiO₂ suspension under UV radiation, despite of that, the amount of adsorbed 3CCA was strongly decreased. At the same time the formation rate of 7OH-3CCA did not change. Methanol decreased both the transformation rate of 3CCA and formation rate of 7OH-CCA by scavenging HO•. We have to mention that, the effect of MeOH is much more pronounced in the case of coumarin than in the case of 3CCA most likely because of the different adsorption properties.

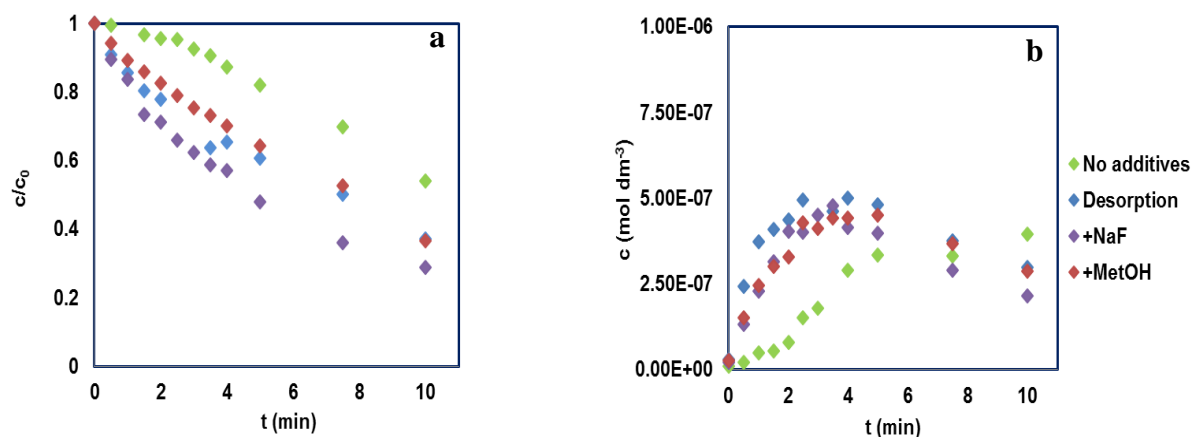


Figure 4. The relative concentration of 3CCA (a), and the concentration of 7OH-3CCA (b) as a function of time

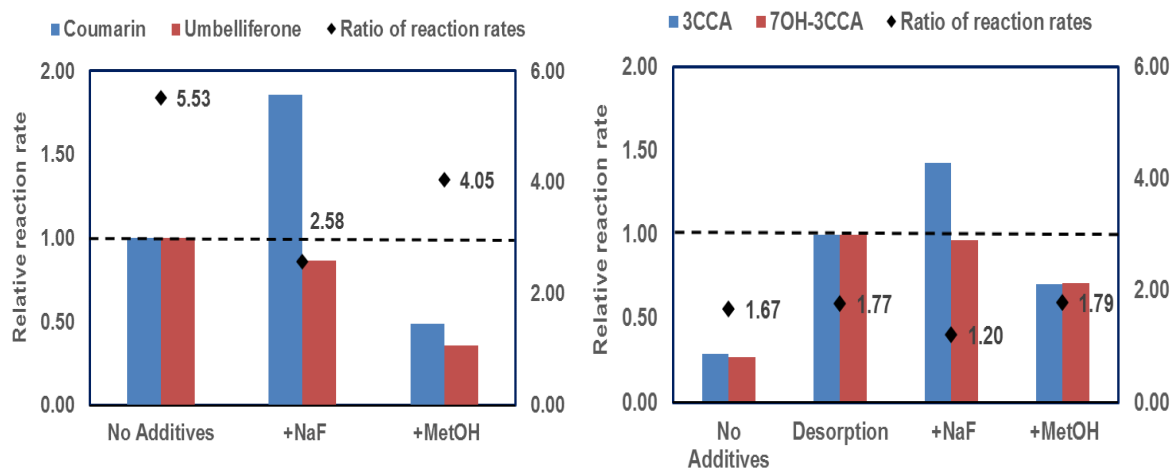


Figure 5. The relative reaction rates of the transformation of coumarin and 3CCA and formation of their hydroxylated intermediates, and the ratio of these values

The importance of HO• was proved by comparing the ratio of the transformation rate of the model compound and formation rate of the hydroxylated intermediate. In the case of coumarin, NaF significantly reduced this value (5.53→2.58), which probably indicates a change in the reaction mechanism. In the case of 3CCA this value changes to a lesser extent (1.77→1.20), which may indicate, that the influence of NaF via changing the adsorption properties is more important in this case. Addition of methanol slightly decreases these values (5.53→4.05 and 1.77→1.79). NaF is probably able to affect the transformation rate by two

different ways: changing the surface properties of TiO₂ the relative contribution of the direct charge transfer and HO• based reaction can change too. The most important effect of methanol is the decrease of the relative contribution of the HO• based reaction to the transformation of parent compounds (coumarin and 3CCA).

Conclusion

- Heterogeneous photocatalysis of coumarin and 3-Hydroxycoumarinic acid (3CCA) were investigate and compared in the presence of NaF and methanol.
- NaF strongly prevents the adsorption of 3CCA, while it has no effect on the adsorption of coumarin.
- NaF increases transformation rates for both model compounds, while reducing the formation of hydroxylated intermediates, possibly due to changes in their access to photogenerated charges and HO•.
- Methanol reduces the transformation rate of coumarin and 3CCA together with the formation rate of their hydroxylated intermediates by scavenging the HO•.

References

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