# Aluminium(III) adsorption: a soft and simple method to prevent $TiO_2$ deactivation during salicylic acid photodegradation†

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**Deposition of poisoning species on $TiO_2$ during salicylic acid photodegradation can be halted when Al(III) has been previously adsorbed on the catalyst surface; this widens the application of photocatalysis to more concentrated solutions.**

Semiconductor heterogeneous photocatalysis has attracted considerable attention owing to its high capability to eliminate biorecalcitrant contaminants by means of $OH^{\bullet}$ radicals generated in mild conditions.[1] To promote applications on a large scale, the efficiency of this technique must be improved.[2] In this sense, catalyst deactivation is one of the major drawbacks of heterogeneous photocatalysis. The prevention of catalyst deactivation would lead to lower economic costs and higher organic matter mineralization efficiency with no need for catalyst regeneration steps. We have previously reported that Al(III) adsorption enhances the photocatalytic activity of $TiO_2$ for maleic acid mineralization.[3] Here, it is shown that for salicylic acid (SA), a model aromatic compound, this simple modification of $TiO_2$ not only noticeably enhances the rate of SA photodegradation but also prevents the formation of poisoning species.

$TiO_2$ deactivation is often observed in gas–solid photocatalytic processes, due to the accumulation of strongly adsorbed degradation by-products.[4] In exchange, $TiO_2$ poisoning in water suspensions is rarely reported. Both the competitive adsorption of the solvent and its ability to solve mineralization intermediates help to keep the surface of the catalyst clean.[5] The low organic concentration usually employed allows the catalyst to be reused.[6] Furthermore, the photocatalytic efficiency decay could be too slow to be noticed on a single catalyst use and, in general, this is the experimental procedure used. On the other hand, the studies that report $TiO_2$ deactivation during the photocatalytic degradation of organic compounds in the aqueous phase[7] pay little attention to the nature of the poisoning species. In other studies, ageing or deactivation in aqueous suspensions has been related to the accumulation of inorganic byproducts,[8] but the formation of organic poisoning adsorbates should not be excluded.

SA photodegradation and adsorption has been subject of numerous studies.[9–11] Only in a few of these reports has catalyst deactivation been observed. Simultaneous photoredution of Cr(VI) and photoxidation of SA lead to significant $TiO_2$ deactivation. The poisoning substance has been tentatively proposed to be some Cr–$L_n$ complex where L is a SA mineralization intermediate.[12] SA photodegradation on biased $TiO_2$ electrodes has also been observed to lead to surface deactivation that, in this case, has been ascribed to the formation of (non-characterized) insulating polymers.[13]

The effect of SA concentration on photodegradation rate under our experimental conditions was studied.‡ The high radiation flux used ($8.31 \times 10^{-6}$ einstein $L^{-1}$ $s^{-1}$, uranil actinometer) is expected to favour efficiency decay when strongly adsorbed organics are present.[14] Increasing SA concentration has a negative effect on the observed degradation rate (Table 1). A possible explanation is surface displacement of species like water or hydroxide by salicylate complexes, which would cause lower yields of hydroxyl radical formation.[14,15] Besides, the amount of surface hydroxides is directly related to the ability of the $TiO_2$ surface to adsorb oxygen molecules.[16] When electron scavengers are scarce, the adsorbate promoted electron–hole recombination becomes favoured.[14,17]

SA photodegradation is greatly enhanced by adsorbed Al(III) (Fig. 1). Catalyst modification is simply done by mixing the $TiO_2$ powder with an $Al(NO_3)_3$ solution.§ The Al(III) concentration used is enough to saturate the $TiO_2$ surface, which corresponds to a surface concentration about 0.22 Al(III) atom per $nm^2$. The lack of SA degradation due to the presence of Al(III) in the aqueous phase was proved by carrying out experiments in the absence of $TiO_2$. This means that a surface phenomenon must promote the observed improvement in catalyst photoactivity.

The concentration of intermediates in solution is also affected by the presence of Al(III).‡ The direct oxidation pathway of SA through catechol formation is favoured over the degradation route through dihydroxybenzoic intermediates. The effect of Al(III) is visible to the naked eye. While bare $TiO_2$ turns a yellowish-brown colour, the Al(III) modified catalyst remains nearly uncoloured. Hence, the most remarkable effect due to the presence of Al(III) is related to the intermediates accumulated on the catalyst surface. Adsorbed intermediates were extracted by alkaline aqueous solutions and analyzed by $^{1}H$ and $^{13}C$-NMR and ESI-MS.‡ In the case of bare $TiO_2$, the extracted substance corresponds to 678 a.m.u. oligomer (3 repeated units of 226 a.m.u.). The NMR spectra indicate that the oligomer contains monomeric units whose

**Table 1** Kinetic constant and initial rate for different $[SA]_0$

| $[SA]_0$/mM[a] | 0.05 | 0.10 | 0.25 | 0.50 | 1.00 |
|---|---|---|---|---|---|
| $r_0/10^6$ M $min^{-1}$ | 1.7 | 1.5 | 1.2 | 1.0 | 0.17 |

[a] $[SA]_0$ were calculated without considering adsorption.

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† Electronic supplementary information (ESI) available: experimental procedure for the extraction of the poisoning substances and additional figures. Fig. S1: SA and intermediates evolution during the photodegradation processes. Fig. S2: detail of $^{1}H$-NMR spectrum of deactivating species. Fig. S3: detail of $^{13}C$-NMR and DEPT-135 spectra of deactivating species. Fig. S4: ESI-MS spectrum of deactivating species. Fig. S5: ATR-FTIR spectrum of SA adsorbed on bare and Al(III) modified $TiO_2$. See http://www.rsc.org/suppdata/cc/b4/b416598e/

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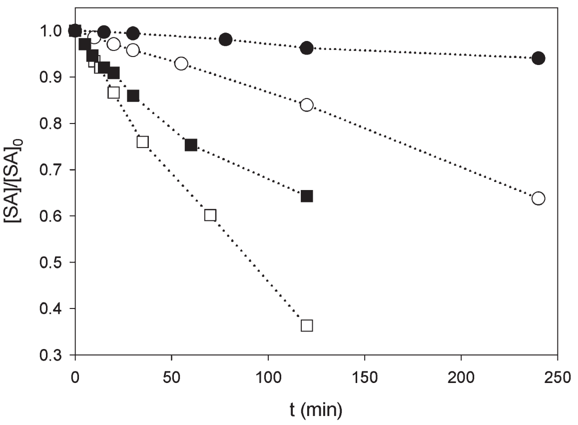

**Fig. 1** Effect of adsorbed Al(III) on $TiO_2$ (1.5 g $L^{-1}$) on the evolution of remaining SA with irradiation time. $pH_0 = 3.0$; $T = 25.0$ °C. $[SA]_0$ is the value without considering adsorption. Square symbols, 0.25 mM; round symbols, 1.00 mM. Black symbols, bare $TiO_2$ catalyst; empty symbols, Al(III) modified $TiO_2$ catalyst.

structure is related to 1,3-dioxanol rings. This substance is chemically far from SA. Dioxolane-type intermediates have been found after photodegradation of salicylate modified $TiO_2$ nanoparticles.[18] When Al(III) is adsorbed over the titania surface, no substances different from those observed in the aqueous phase are detected by the alkaline extraction treatment. Hence, the oligomer species must be connected with the poisoning phenomenon. $TiO_2$ deactivation has been associated to the deposition of polymers.[19] However, polymeric nature is not a reason to be a poisoning species. To block the $TiO_2$ photocatalytic activity, the adsorbate must be chemically inert or able to act as a recombination centre.[20] To get a deeper insight into the ability of Al(III) to prevent catalyst deactivation, an experiment where the same amount of SA was periodically added to the reactor was performed (Fig. 2).

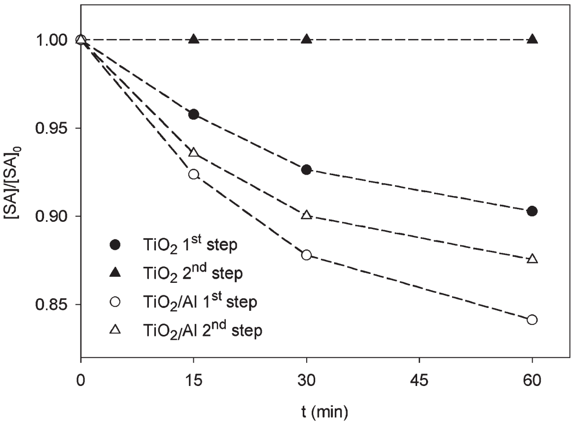

**Fig. 2** Effect of adsorbed Al(III) on $TiO_2$ (1.5 g $L^{-1}$) on the evolution of remaining SA with irradiation time at $pH_0 = 3.0$; $T = 25.0$ °C. The initial [SA] was 5.0 $10^{-4}$ M. The solution was irradiated for one hour. Four samples of 5 mL each were removed from the reactor at fixed times. After one hour, the UV lamp was switched off and 20 mL of 2.0 $10^{-3}$ M SA was added. Next, the suspension was allowed to equilibrate in the dark for 30 minutes before irradiating for one more hour.

While almost complete deactivation is observed on bare $TiO_2$ after the first run, the Al(III) modified catalyst performs higher degradation yields than bare $TiO_2$ and maintains the photocatalytic activity. The same SA addition was repeated twice. At the end of the third and fourth one hour irradiation steps (not shown) SA elimination (7% and 5% respectively) is only observed when Al(III) is present. The decreasing percentage of eliminated SA can be related to the catalyst dilution and the increase of intermediates that might compete for the catalyst surface.

Under the experimental conditions of the assay described above, the SA concentration was lowered 20% due to adsorption on bare $TiO_2$ whereas it was reduced only 12% in the presence of Al(III). This suggests that Al(III) is blocking some of the SA adsorption sites. Degradation rate enhancement is not, therefore, due to increased SA concentration on or near the catalyst surface, as it has been observed in lantanide-doped titania materials.[21] Furthermore, the ATR-FTIR spectra (measured *ex situ*; Tensor Bruker, equipped with MKII Golden Gate) of SA adsorbed onto $TiO_2$ does not show significant changes due to the presence of Al(III).‡ As a tentative explanation for the reported results, it seems that adsorbed Al(III) avoids surface blocking by strong adsorbates, favouring oxygen scavenging of photogenerated $e^{-}_{cb}$. This decreases electron–hole recombination and probably prevents the evolution of organic species through reductive pathways. Also, the results above show that the presence of Al(III) leads to lower amounts of adsorbed SA in the dark. In this sense, the positive effect of Al(III) could involve, to some extent, a lower adsorption of the photogenerated intermediates.

The addition of a soluble Al(III) salt is a straightforward way to improve the photocatalytic activity of $TiO_2$. The easy and mild procedure reported here is an interesting alternative to the literature methods (doped materials preparation or composite materials preparation) which require thermal treatments.

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## Notes and references

‡ $TiO_2$ Degussa P-25 (0.600 g) was added to a SA aqueous solution at different concentrations (0.400 L). The pH was adjusted to 3.0, with diluted $HClO_4$ or NaOH, and the suspension was sonicated for 10 minutes, and then magnetically stirred in the dark for 30 minutes. After this, irradiation with a 125 W medium pressure Hg-lamp was carried out under air bubbling. A water-cooled Pyrex glass jacket filtered UV ($\lambda < 290$ nm) and IR radiations. Under these experimental conditions, neither air stripping nor direct photolysis contribute significantly to SA elimination. The photocatalytic process was stopped by filtration. The concentration of SA and intermediates was measured by HPLC with a UV–Visible diode array absorbance detector; stationary phase: Hypersyl ODS column 5 μm 25 × 0.46 cm; mobile phase: acetonitrile–water (40 : 60) mixture at pH 3 (phosphate buffer) at isocratic flow rate (0.75 mL $min^{-1}$).

§ In the experiments to study the Al(III) effect, the $TiO_2$ (0.600 g) was suspended into 2.0 × $10^{-4}$ M $Al(NO_3)_3$ aqueous solution (0.20 L). After adjusting the pH value to 3.0, the suspension was sonicated for 10 minutes and stirred for 30 minutes in the dark. Next, 0.200 L of SA solution at different initial concentrations (twice the concentration used in the corresponding bare $TiO_2$ assay) were added, and the pH readjusted to 3.0 if necessary.

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