Catalytic degradation of 4-chlorophenol with La/TiO$_2$ in dielectric barrier discharge system

1. Mass spectrum analysis

(a)

(b)

Fig. 1 Mass spectrums of 4-chlorophenol before treatment (a) and after treatment (b)
The pathways for the degradation of 4-CP have been suggested based on MS identification of some intermediates of reaction, known intermediates of degradation as reported [1, 2, 3, 4, 5] and possible products of degradation. The mass spectrums of initial 4-CP sample and degradation are shown in the first and second figures. The major intermediates detected in this case were: benzoquinone (m/z 107.99), hydroquinone (m/z 110.03), maleic acid (m/z112.89). Degradation is an oxidative process, and given a facile oxidation of hydroquinone to benzoquinone [6, 7]. Then the rings are broken to generate the corresponding carboxylic acid. Gradually, the carboxylic acids are mineralized to carbon dioxide and water.

References

2. Reactive species analysis

Fig. 2 HO• (a) and O₃ concentration of optimum La doping, synthetized TiO₂ and blank (b)
HO• was determined through chemical method using salicylic acid as the probe [1]. And ozone was measured by UV absorption at 254 nm using UV-vis spectrophotometer (TU-1810). In our DBD system, HO• can be formed when water is ionized by electric current and irradiated with high energy ultraviolet light. As Fig. 2a shown, catalyst can promote the production of HO•. And catalyst with doping La can strengthen this process. The formation HO• as follow [2-6]:

\[
\begin{align*}
H_2O & \rightarrow H^+ + HO^- & (1) \\
O_2 & \rightarrow O + O^+ & (2) \\
H^+ + O^+ & \rightarrow HO^* & (3) \\
TiO_2 + h\nu & \rightarrow TiO_2(h^+ + e^-) & (4) \\
OH^- + h^+ & \rightarrow HO^* & (5) \\
OH^- + h\nu & \rightarrow HO^* + e^-_{aq} & (6)
\end{align*}
\]

The concentration of ozone with catalyst is always higher than that without catalyst as shown in Fig. 2b. This result might be attributed to highly energized electrons \((e^-)\), holes \((h^+_{vb})\) in the valence band and electrons \((e^-_{cb})\) in the conductance band on the surface of catalyst, oxygen in gas or aqueous phase may be converted to more active species (i.e. \(O^•_{(aq.)}, O^•_2(aq.)\)) [7]. The reaction equation \([8, 9]\):

\[
\begin{align*}
O_{2(gas)} & \rightarrow O_{2(aq.)} & (7) \\
O_{2(aq.)} + e^-_{cb} & \rightarrow 2O_2^•_{(aq.)} & (8) \\
O_{2(gas)} + e^-_{(gas)} & \rightarrow 2O_2^•_{(gas)} \rightarrow 2O^•_{(aq.)} & (9) \\
O_{2(aq.)} + e^-_{(aq.)} & \rightarrow O_2^•_{(aq.)} & (10) \\
O_{2(aq.)}^• + h^+_{vb} & \rightarrow O_{2(aq.)} & (11) \\
O^•_{(aq.)} + h^+_{vb} & \rightarrow O_{(aq.)} & (12) \\
O_{(aq.)} + O_{2(aq.)} & \rightarrow O_3(aq) & (13)
\end{align*}
\]
And direct electron transfer and adsorption reactions are induced on the surface of TiO$_2$ under ultraviolet light and visible light [10, 11].

**References**


