Does UV really accelerate the degradation of pollutants by Fe(VI), or is there another reason?

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Considering the remarkable oxidation capacity of hypervalent iron (Fe(IV)) and Fe(V)) species, the exploration of pathways for the activation or catalysis of Fe(VI) has been further advanced. This is achieved through the utilization of external energy such as ultraviolet(UV). In recent studies, we have found that some scholars believe that UV can accelerate the degradation of pollutants by promoting the self-decay of Fe(VI) to generate hypervalent iron and hydroxyl radicals . This mainstream view has persisted until now. Although recent studies have shown that UV can effectively promote the generation of hypervalent iron, the UV system has ignored the characteristic that hypervalent iron is extremely unstable under UV irradiation.

Herein, we investigated the stability of Fe(VI) after light exposure through DFT and UV-Vis spectroscopy experiments, and the results showed that Fe(VI) is more prone to decay upon light irradiation. Using methyl phenyl sulfoxide (PMSO) as a probe, we cleverly designed experiments on PMSO degradation and (methyl phenyl sulfone) $PMSO_2$ generation under UV irradiation and non-UV irradiation conditions. It was found that in 1.0 M borate buffer (pH = 9.2), more PMSO was degraded under the combined conditions of UV and Fe(VI) than with Fe(VI) alone (4.58~22.09%), depending on the molar ratio of PMSO to Fe(VI). However, the production of $PMSO_2$ after 10 minutes was less than that in the Fe(VI) alone group, and this gap became more obvious at the end of the 30-minute reaction (about 5.5 μM less $PMSO_2$). What promoted the degradation of PMSO? The study revealed that 50 μM PMSO can be effectively oxidized by ·OH under the condition of 1 mM H_2O_2 with UV (100% oxidation) and can also be efficiently oxidized by ~90.92% in the 200 μM Fe^{3+} with UV system. In the UV and Fe(VI) system, PMSO is degraded with extremely high efficiency by ·OH rather than by Fe(VI) itself. If that is the case, why not use the photo-Fenton system instead of consuming a lot of energy in the Fe(VI) and UV system? Because in terms of effect, there is not much difference between the two, but the cost of the photo-Fenton system is lower.