

### §30. Study of Microwave Effect on Photocatalytic Surface by Using In-Situ Observation Techniques

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The microwave specific effect(s) that can impact a microwave-assisted and photo-assisted reaction occurring on the surface of ZnO particles was examined by comparing the process occurring under rich magnetic field conditions and under magnetic/electric field conditions. The features of the photoassisted process in the presence of microwaves rich in a magnetic field (*H*) and an electric field (*E*) are described on the basis of (i) the degradation dynamics of 4-chlorophenol (4-CP) at ambient temperatures, (ii) the number of •OH radicals produced.

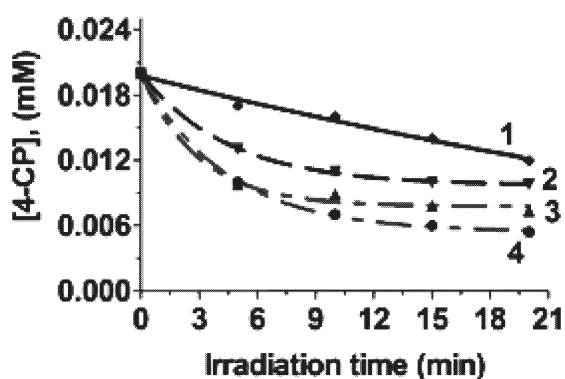


Fig. 1. Temporal decrease of 4-CP concentration by using the UV/MW-EH (curves 2), UV/MW-H (curves 4), UV/CH (curves 1) and UV (curves 3) methods with ZnO

The temporal course of the degradation of 4-CP in aqueous ZnO and TiO<sub>2</sub> dispersions with the UV/MW-*EH*, UV/MW-*H*, UV/CH and UV methods was monitored at 279 nm using HPLC techniques. Results are illustrated in **Fig. 1**.

In ZnO dispersions, the rates of degradation of 4-CP by the UV/MW-*EH* method ( $k_{\text{obs}} = 0.22 \text{ min}^{-1}$ ) and UV/MW-*H* method ( $k_{\text{obs}} = 0.23 \text{ min}^{-1}$ ) were somewhat slower relative to the UV method ( $k_{\text{obs}} = 0.34 \text{ min}^{-1}$ ) – see **Fig. 1**. It is

significant to note that the UV/CH method led to an even slower degradation of the toxin by a factor of ca. 20 ( $k_{\text{obs}} = 0.017 \text{ min}^{-1}$ ) compared to the UV method alone. Evidently, conventional heating caused a decrease in the photoactivity of ZnO. Even more important are the tenfold slower degradation kinetics for the UV/CH method ( $k_{\text{obs}} = 0.017 \text{ min}^{-1}$ ) relative to the UV/MW-*EH* method ( $k_{\text{obs}} = 0.22 \text{ min}^{-1}$ ) despite the process occurring under otherwise identical temperature conditions of the bulk solution. The faster degradation of 4-CP was observed whenever the microwaves were rich in magnetic field as compared to the UV and other methods. These results are consistent if the *heat*, whether from conventional or dielectric sources, caused the decrease of the photoactivity of the metal oxide. We also deduce that the UV/MW-*EH* method was superior to the UV/CH procedure because of the presence of a magnetic field in the former. Thus, the decrease of photoactivity can be controlled by the magnetic field effect, although for ZnO the photoactivity was somehow decreased by the thermal effect of the microwave radiation. A final point is worth noting for the UV/MW-*EH* and the UV/MW-*H* methods regarding the 4-CP/ZnO dispersions. Although the dynamics are identical in both cases, the extent of degradation of the 4-CP was only 50% for the former method and 75% for the UV/MW-*H* method, both reaching a plateau after 20 min of irradiation. We infer that the microwaves *EH versus H* fields may additionally cause the nature of intermediates formed to be different. That is, the fields no doubt also impact on the nature of such intermediates and the degradation pathways of the toxin. At the stage of our current studies, the latter were not the objectives of the present study and are discussed no further, although they certainly raise a few questions.

In the case of ZnO, the photoactivity was enhanced by the microwave specific (non-caloric) effect originating in large part from the microwaves' magnetic field *H*.

- 1) Horikoshi, S. et. al.: J. Phys. Chem. C, **113** (2009) 5649.
- 2) Horikoshi, S. et. al.: Appl. Cat. B, in press.