

## Photo-oxidation of Chlorophenols and Methyl Orange with Visible Light in the Presence of Copper Phthalocyaninesulfonate

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Copper phthalocyaninesulfonate was investigated as a photo-sensitizer for the elimination of recalcitrant organic pollutants, such as 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and methyl orange, in an aerated aqueous solution under visible light ( $\lambda > 450$  nm) irradiation. The photosensitizer was effective and highly stable, and could be used repeatedly.

The use of advanced oxidation process to eliminate organic pollutants in water has been actively studied in recent years.<sup>1,2</sup> Among those using electromagnetic radiation, the TiO<sub>2</sub> photocatalysis appears to be the most efficient one, by which a variety of organic contaminants could be mineralized into carbon dioxide in aqueous solution of wide pH. However, obvious disadvantages of this system are the expense of UV light and low quantum yield of reactive species formed on the irradiated semiconductor. Some progresses have been made using coupled, doped, and pigment-anchored semiconductor to extend the light absorption in the visible region and to improve charge carrier transfer into the reactive sites.<sup>2</sup> For economic and green treatment of organic pollutants in water, the development of a photocatalytic system that can operate with solar light and molecular oxygen remains still in great challenge.

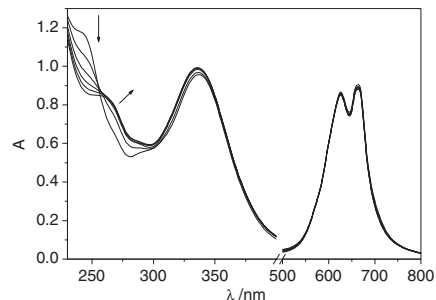
Metallophthalocyanines are a class of compounds that have intensive absorption in the visible region. Some of the complexes containing non-transition metal have proved to be efficient photosensitizers for photodynamic therapy and recently for the oxidation of chlorophenols and sulfur-containing compounds under visible light irradiation.<sup>3-7</sup> The singlet oxygen is involved in these processes, that is generated from the excited photosensitizer to the molecular oxygen via energy transfer. The ring-cleavage products of carbon dioxide and maleic/fumaric acids are identified in phenol oxidation,<sup>4,7a</sup> sensitized by aluminum phthalocyanine sulfonate (AlPcS), whereas only benzoquinone derivatives are found in chlorophenol oxidation.<sup>5</sup> Unfortunately, the MPcS photosensitizers (M=Al, Zn, Si, Sn) examined so far are not stable during the photosensitized reactions,<sup>4,5</sup> and they undergo different degree of self-photobleaching.

We have found recently that copper phthalocyanine sulfonate (CuPcS) is an effective photosensitizer with high stability for the elimination of recalcitrant pollutants such as 4-chlorophenol (CP), 2,4-chlorophenol (DCP), 2,4,6-trichlorophenol (TCP)<sup>8</sup> and methyl orange in water under visible light irradiation.

CuPcS was made simply by sulfonation of CuPc (copper phthalocyanine), a widely used dyestuff and pigment, with fumed sulfuric acid, followed by transformation into the sodium salt.<sup>9</sup> The photochemical reaction was carried out in an open

thermo-static vessel, irradiated by a Halogen lamp (500 W, Shanghai Yamin) through a solution filter of dichromate ( $\lambda > 450$  nm). The reaction was monitored by absorption spectrum on an Agilent 8453 spectrophotometer. Carbon dioxide and chlorine ions were analyzed respectively using BaCO<sub>3</sub> method,<sup>4,7a</sup> and a PCI-1 selective electrode on a pHS-3C meter (Shanghai Kangning) in the reference to the blank sample, for which analysis the irradiated sample was acidified by dilute sulfuric acid to pH1, followed immediately by bubbling N<sub>2</sub> and going finally through Ba(OH)<sub>2</sub> trap. The COD (chemical oxygen demand) was determined by a standard method of dichromate. All the solution after prepared was stored overnight in the dark for complex equilibrium.

Figure 1 gives the spectral changes recorded during CP oxidation, in an aerated aqueous solution of CuPcS at pH 12 under visible light irradiation. While the characteristic peaks of CuPcS remained almost unchanged, the peak at 244 nm due to CP was decreased gradually with time. Control experiments in the dark, or in deaerated solution, and/or under visible light irradiation without CuPcS showed no CP degradation.



**Figure 1.** Photosensitized oxidation of CP ( $3.8 \times 10^{-5}$  M) in water at pH 12 in the presence of CuPcS ( $1.8 \times 10^{-5}$  M) under visible light irradiation. The absorption spectrum was recorded at each 20 min.

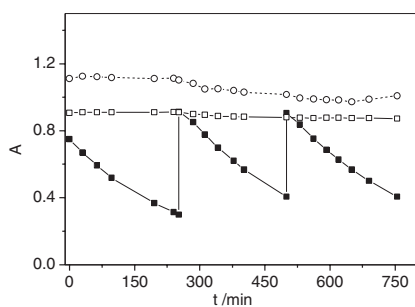
In difference spectrum, the intermediates appeared to display absorption at about 269 and 320 nm, the peaks not in agreement with any of *p*-benzoquinone (BQ), hydroquinone, phenol and fumaric acid possibly formed at pH 12. The BQ formation was confirmed in this study when the reaction was performed at pH 3 or at pH 7.<sup>5</sup> Effort to identify the intermediates by GC-MS technique was failed, probably due to the difficulty in detection of small molecule with either high or low boiling points (the sample was prepared by bubbling N<sub>2</sub> after CH<sub>2</sub>Cl<sub>2</sub> extraction). However, the degradability in situ of the unknown intermediates was confirmed by analysis of COD, CO<sub>2</sub> and chloride ions. After aqueous solution of CP ( $7.6 \times 10^{-5}$  M) at pH 12 was irra-

diated in the presence of CuPcS ( $1.8 \times 10^{-5}$  M) for 5 h, the COD was removed by 48%. Further irradiation for another 5 h led to  $\text{CO}_2$  of 38% and  $\text{Cl}^-$  of 96% formed, respectively, which indicates the mineralization.

CuPcS was also effective for the photosensitized oxidation of other organic pollutants in water such as DCP, TCP and methyl orange. Similar to Figure 1, the characteristic peaks of the model substrates became decreased with irradiation time. Unlike CP oxidation that was very slow at pH 7, however, these compounds in water could degrade efficiently at either pH 12 or pH 7. The COD removal yield was 33%, measured from TCP ( $5.0 \times 10^{-4}$  M) oxidation at pH 7 for 5 h. The result suggests that the photo-sensitized reaction is limited by the chemical reactivity of the target molecule. This was further supported by the reactions under the same conditions in which X3B and rhodamine B did not degrade at all.

The stability of the photosensitizer was excellent, as demonstrated by repeated experiments for methyl orange (MO) degradation in water at pH 7 (Figure 2). The characteristic absorption of MO at 463 nm was far away from either CuPcS or MO reaction intermediate located at 248 nm, making its analysis convenient. During 750 min of irradiation, almost the same rate of MO degradation was kept, while the photosensitizer did not change its absorbance significantly. For the first, second and third run, the degradation percentage of MO was 60, 55 and 50%, respectively. After three repeated experiments, the spectral band of CuPcS at 665 and 628 nm was decreased by 9.3% and 3.8%, respectively.

The synthesis method of CuPcS has great influence on the sensitizer photoactivity. The CuPcS-II, prepared by urea process using sodium 4-sulfophthalic acid (Aros) as starting ligand,<sup>9</sup> was much less efficient than CuPcS-I as described above using sulfonation method. For example, the initial rate of CP oxidation in water at pH 12, monitored by the spectral loss at 244 nm, was  $5.24 \times 10^{-3}$  and  $6.39 \times 10^{-4}$ /min in the presence of CuPcS-I and CuPcS-II, respectively. The former was noted



**Figure 2.** Absorbance change with irradiation time of MO ( $5.6 \times 10^{-5}$  mol/L) at 463 nm (■), CuPcS ( $1.8 \times 10^{-5}$  mol/L) at 628 (□) and 665 nm (○). The data was recorded during three repeated experiments in water at pH 7. After the first and second run, 2.5 and 2.0 mL of MO stock solution was added respectively.

less aggregated in water than the latter, evidenced by the dimer at 626 nm and the monomer at 665 nm (Ref. Figure 1). In addition, the average number of sulfonate groups substituted on the ring of CuPcS, measured by  $\text{BaCrO}_4$  method, was 1.3 and 4.0, respectively. In a mixed solvent of methanol/water (1:1, v/v) at pH 12, both the complexes were disassociated in different degree into the monomeric species, and in such a solvent CP oxidation became faster, with the rate of  $7.67 \times 10^{-3}$ /min for CuPcS-I and  $1.03 \times 10^{-3}$ /min for CuPcS-II. The evidence shows that CuPcS in the monomeric form is more photoreactive than the corresponding dimer, similar to those observed for other photosensitizers.<sup>4,5</sup> This is attributed to the dimerization that enhances nonradiative quenching of the excited state and thus reduces the reactivity. In the presence of singlet oxygen quencher, sodium azide (0.01 mol/L), on the other hand, the reaction were all depressed substantially, suggesting that singlet oxygen is involved as the main reactive species initiating the organic degradation.

In summary, CuPcS has been shown to be an effective and stable photosensitizer for organic degradation in water under visible light irradiation. It is noted that compared to other MPcS (M=Al, Zn, Sn), CuPcS is more photostable, but is less efficient for organic photooxidation. Although complete mineralization of organic pollutants takes some time of irradiation, the result might draw attention to take advantage of CuPc derivatives used widely nowadays as pigments and painting for air pollutant treatment under solar or home-lamp illumination.

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