

PHOTOCATALYTIC ACTIVITY INDUCED BY ZINC PHTHALOCYANINE SYNTHESIZED BY MICROWAVE IRRADIATION

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Abstract

Zinc phthalocyanine, synthesized under microwave irradiation proved to be an interesting photocatalyst. The degradation of Rose Bengal, as model organic dye, under visible light irradiation was used to study the adsorption/photocatalytic activity. The huge potential of the synthesized molecule for the removal of organic pollutants was demonstrated by its absorption capacity, which was far larger than that of dye degradation.

Introduction

Many manufacturing industries across the world directly discharge their wastes into freshwater bodies utilized for drinking and agricultural purposes. The most common contaminants that could be found are synthetic colors, and dye chemicals used to color various substances and materials. These are persistent and stable environmental pollutants waiting for unconventional wastewater treatment methods. To immediately address these challenges, the development of more efficient and low-cost protocols and photocatalysts is required.

Photocatalysis is an effective technique for the degradation and mineralization of hazardous pollutants from the environment. In that context, a variety of photocatalysts have been studied. Zinc phthalocyanine (ZnPc), a symmetrical 18π -electron aromatic macrocycle has won considerable research interest and enjoys applications in fields of non-linear optics, chemical sensors, semiconductors, and catalysts¹. However, there hasn't been as much focus on developing advanced synthetic techniques and photocatalytic testing for this kind of molecule. In this work, we present a detailed study of the photocatalytic activity of ZnPc synthesized under microwave irradiation. The macrocyclic compound was obtained in high yield and purity after only a few minutes of heating.

Experimental

All chemicals: zinc (II) acetate dehydrate (>99%, Sigma-Aldrich), 1,2-dicyanobenzene ($\geq 98\%$, Sigma-Aldrich), *N, N*-dimethylformamide (>99%, Alfa Aesar), dimethyl sulfoxide (>99%, Fisher Chemicals), and methanol ($\geq 99\%$, Sigma Aldrich) were of the highest purity commercially available and were used without further purification. Mili-Q deionized water (electrical resistivity = $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used.

ZnPc was synthesized in a microwave reactor (noted as ZnPc_{MW}) as described in our previous work². The starting compounds 1,2-dicyanobenzene (2.5 mmol, 0.320 g), zinc (II) acetate dihydrate (0.63 mmol, 0.138 g), and 1 mL of DMF were heated at 250 °C for 5 minutes in microwave reactor. After cooling to room temperature precipitate was filtered off and washed with 3% HCl, water, methanol, and dried. The resulting deep purple crystals remain after the processing of the reaction mixture. The yield of ZnPc_{MW} is 68 %.

Photocatalytic testing was performed in the presence of a ZnPc_{MW} photocatalyst in concentration of 0.5 mg/ml and RB organic dye (0.03 mM). The reaction was performed in the

cylindrically shaped closed homemade photoreactor with six LEDs operating at 370 nm. For the experiments of photolysis and photocatalysis, samples were kept in dark conditions for 60 minutes in order to establish the adsorption/desorption equilibrium followed by irradiation for 240 minutes.

Microwave-assisted synthesis was performed in a mono-mode microwave reactor Anton Paar Monowave 300. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed in 400–4000 cm^{-1} range with a spectral resolution of 4 cm^{-1} at room temperature by Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with built-in all reflective ATR diamond. The ultraviolet-visible (UV/Vis) absorption spectra were recorded on Shimadzu 1800 UV-Vis spectrophotometer equipped with a temperature controller in the range of 200–800 nm.

Results and discussion

The development of robust and cheap photocatalysts for visible-light-induced organic substrate transformations is a significant uprising research topic at the crossroads of green chemistry and modern synthetic methodology. A microwave-enhanced synthetic route has been evaluated as a fast and efficient method for obtaining ZnPc_{MW} after only five minutes of heating, at 250 $^{\circ}\text{C}$, compare to six hours for traditional methods² (Figure 1a).

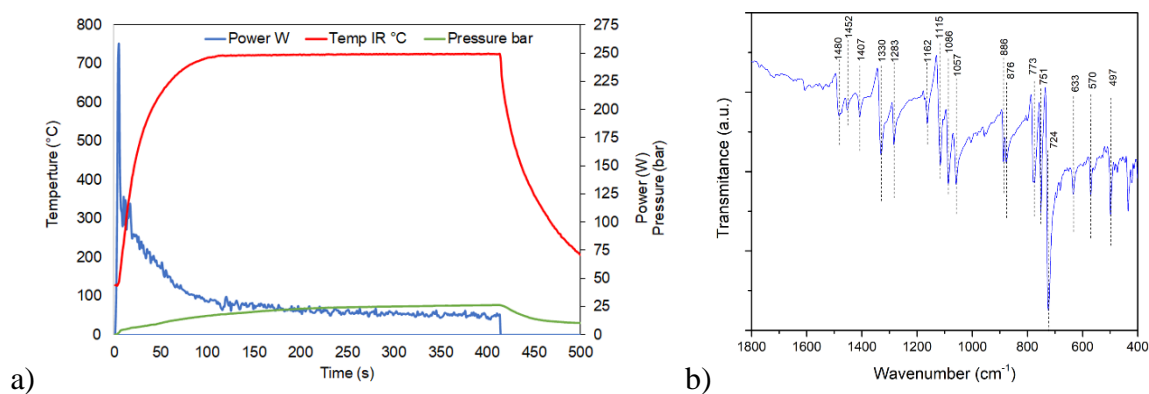


Figure 1. Microwave heating profile for ZnPc_{MW} synthesis, and FTIR spectra of synthesized crystals.

The FT-IR spectral measurement is carried out to ascertain the functional group structures for ZnPc_{MW} . The absorption peaks at 480 cm^{-1} , 1452 cm^{-1} , 1330 cm^{-1} , 1162 cm^{-1} , 1115 cm^{-1} , and 886 cm^{-1} were assigned to Pc skeletal vibration (Figure 1b). The peaks located at 1407 and 1283 cm^{-1} are assigned to the stretching vibration of the aromatic phenyl ring and C–N= covalent bond, respectively. Absorption peaks observed around 1086 cm^{-1} and 1057 cm^{-1} were assigned to C–H in-plane bending vibrations. The peaks observed at 773 cm^{-1} and 724 cm^{-1} were assigned to C–H out-of-plane bending vibrations. The bands at 751 cm^{-1} , 633 cm^{-1} , 570 cm^{-1} , and 497 cm^{-1} also belong to in-plane skeletal deformation vibrations of the isoindole fragments. The absence of metal-free Pcs characteristic absorption peak around 1000 cm^{-1} confirmed the reaction selectivity and purity of the synthesized compound.

The photocatalytic reaction of Rose Bengal (0.03 mM) removal in water media under UV (370 nm) light was performed in the presence of ZnPc_{MW} as photocatalyst. Reaction was carried out at pH5 (Figure 2). After 60 min of adsorption/desorption the ZnPc_{MW} showed strong adsorption capacity towards RB dye with 96% of the dye adsorbed after 60 min in dark.

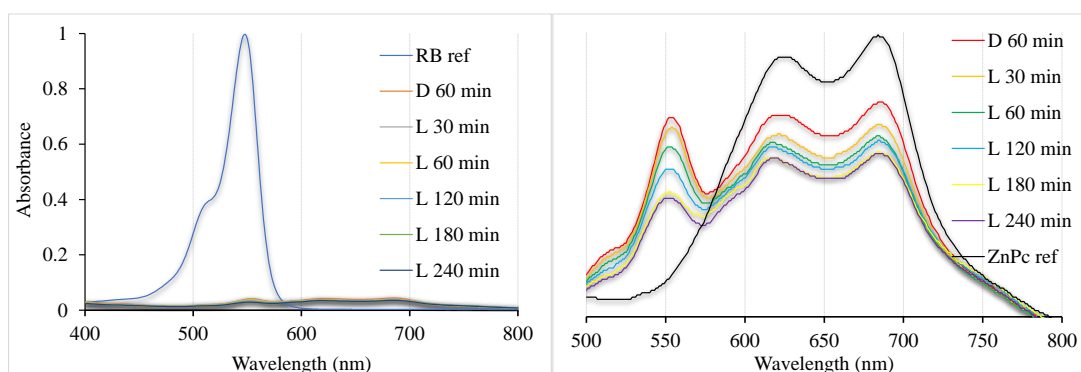


Figure 2. a) The absorbance spectra of RB degradation in the presence of ZnPc photocatalyst, and b) RB absorbance and ZnPc peak in time under UV light irradiation.

In terms of the photocatalyst removal efficiency towards RB organic dye, under 240 min of exposure to the UV light, 97% of the RB dye was successfully removed from water media (Figure 3). Obtained results suggested strong capacity of ZnPc as adsorbents for toxic organic dyes.

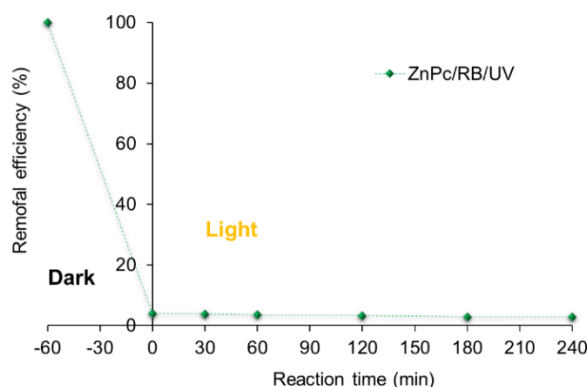


Figure 3. RB removal efficiency in the presence of ZnPc_{MW}.

Conclusion

Significant rate enhancements, purity and stability of macrocyclic compound of ZnPc_{MW} lead to valuable and efficient photocatalyst. Photocatalytic testing revealed a strong potential for the ZnPc photocatalyst application as an adsorbent for RB in a water medium. Dye removal is followed by its high percent of final degradation.

Acknowledgements

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References

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