

Copperphthalocyanine immobilized Zn/Al LDH as photocatalyst under solar radiation for decolorization of methylene blue

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Abstract

Zn/Al hydrotalcite-like compounds (HTLcs) with Zn/Al molar ratios of 2:1, 3:1, 4:1 were synthesized by co-precipitation method and were used as supports for the immobilization of Cu(II) tetrasulphonated phthalocyanine (CuPcTs). XRD and UV–vis DRS were used to characterize the solids after adsorption of CuPcTs on HTLcs. The photocatalytic decolorization of methylene blue (MB) was studied under solar radiation over Zn/Al (2:1)–(CuPcTs) and the corresponding dark control was also carried out for comparison purposes. The effect of time, pH, adsorbate concentration, catalyst dosage, H₂O₂, potassium persulphate and sodium chloride amount was studied as a function of the percentage of decolorization. The percentage of decolorization increases with the increase in pH of solution. A maximum of 75% decolorization of methylene blue was achieved at 4 h solar irradiation as against 33% in dark control. The process obeys pseudo-first order kinetics.
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1. Introduction

In recent years phthalocyanines and porphyrins themselves or their supramolecular arrangements have been used not only in the sensor field for technological application [1,2] but also as homogeneous or heterogenised homogeneous catalysts in a variety of oxidation reactions through a biomimetic approach [3]. It has been established that metal-free phthalocyanine complexes and those containing a central metal ion with filled up electron shells or d-orbitals exhibit a high photocatalytic activity in the complete oxidation of sulphur containing compounds [4–7]. Upon irradiation with visible light the phthalocyanine complexes with long lived excited triplet state exhibit catalytic activities in the complete oxidation of sulphur containing compounds [8,9]. During the interaction between dioxygen and the long-lived triplet state of these complexes, a chemically more reactive ¹O₂ is being formed, which further interacts with compounds containing sulphur of various oxidation states. The layered double hydroxides (LDHs) having the general formula [M(II)_{1-x}M(III)_x(OH)₂]^{x+} [A_{x/n}mH₂O]^{x-}, consist of positively

charged metal hydroxide sheets composed of edge shared octahedral network. The positive charge on the metal hydroxide sheets are neutralized by exchangeable charge balancing anions present in the interlamellar space besides water molecules. These are one of the promising host materials for the intercalation of anionic metal complexes [10]. Many researches on HT derivatives have been devoted to the development of new catalytic material [11]. Several studies about the synthesis, characterization and catalytic applications of HTs containing anionic metal complexes have been reported [12]. Particularly interesting is the immobilization of macrocyclic ligands containing complexes as metallophthalocyanines in HTs. The immobilization of macrocyclic complexes on a readily recyclable solid support such as an LDH would greatly enhance the usefulness of such complexes for environmental pollution control. There are some reports on synthesis, characterization and catalytic activity of cobalt(II) phthalocyanine tetrasulphonate, copperphthalocyanine tertasulphonate and iron phthalocyanine intercalation into Mg/Al layered double hydroxide [13–16]. So far, very scant literature is available on the photocatalytic studies of copperphthalocyanine supported LDHs.

Furthermore, the photocatalytic process has attracted considerable attention by the scientific community as well as the environmentalists due to the following reasons:

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- (i) To use solar light, which is free and inexhaustible.
- (ii) The process is simple and degrades the pollutants to their non-toxic forms.
- (iii) Do not need secondary treatment.

In this paper, we have synthesized the Cu(II) phthalocyanine supported Zn/Al HTLcs with molar ratios 2.0, 3.0 and 4.0 and these are characterized by XRD, UV–vis DRS. The activity of the materials has been evaluated by studying the photocatalytic decolorization of methylene blue (MB), a sulphur containing cationic dyestuff, which is predominant in textile effluents and is mostly difficult to be degraded solely under solar radiation. The effect of time, pH, methylene blue concentration, catalyst dose, concentration of H₂O₂, potassium persulphate and sodium chloride was studied as a function of percentage of decolorization under solar radiation and the corresponding dark controls were also carried out for comparison.

2. Materials and methods

2.1. Materials

Zn/Al LDH with Zn(II):Al(III) molar ratios of 2.0, 3.0 and 4.0 were prepared by co-precipitation (at constant pH) method [10]. Copper phthalocyanine tetrasulphonic acid tetrasodium salt (CuPcTs, Acros Organics) was used as received. CuPcTs was supported by suspending 1 g of the HTlc in 50 mL of 0.6 mM CuPcTs aqueous solution [15,17]. The suspension was maintained under stirring at room temperature for 1 day. Blue solids were isolated by centrifuging and washing with deionised water until a colorless supernatant was observed. The solid samples were dried in a desiccator under vacuum by using silica gel as drying agent. The CuPcTs supported LDHs with Zn/Al molar ratios 2.0, 3.0 and 4.0 were abbreviated as Zn₂Al–CuPc, Zn₃Al–CuPc and Zn₄Al–CuPc, respectively.

2.2. Physico-chemical characterization

The powder XRD patterns of the samples were recorded on a Philips (Model-1710, Holland) semiautomatic X-ray diffractometer with an auto divergent slit fitted with a graphite monochromator using Cu K α radiation at a scanning speed of 2° min⁻¹, operated at 40 kV and 20 mA.

The UV–vis DRS spectra of the samples were recorded in a UV–vis spectrophotometer (Varian, Cary 1E, Australia). Pellets of 2 mm thickness were prepared taking 0.05 g of sample along with boric acid and boric acid was also used as reference material. The spectra were recorded in the range of 800–200 nm.

Specific surface area (BET) was determined by the N₂ adsorption–desorption method at liquid nitrogen temperature (–196 °C) using Quantasorb (Quantachrome, USA). Prior to adsorption measurements, the samples were degassed at 110 °C in vacuum (1 × 10⁻⁴ Torr).

2.3. Photocatalytic decolorization and adsorption

The photocatalytic decolorization of methylene blue was performed by taking 20 mL of 100 ppm (MB) solution in 100 mL

Pyrex flask containing 1 g L⁻¹ of catalyst. The solutions were exposed to sunlight (the average solar intensity = 0.80 kW m⁻²) at room temperature (33 ± 2 °C) and agitated with magnetic stirrer so that no appreciable amount of catalyst remained at the bottom of the reaction vessel. All the experiments were performed in duplicate during the first half of April 2005 (sunny days), from 10:00 a.m. to 14:00 p.m. The decolorization of methylene blue due to adsorption was measured by carrying out similar experiments in dark. After irradiation, the suspension was centrifuged and the methylene blue content was analysed quantitatively by measuring the absorption band at 660 nm using UV–vis spectrophotometer (Cary 1E, Varian, Australia). The filtrate was scanned in the range 200–800 nm to know if at all copper phthalocyanine is leached out from the hydrotalcite support during the photocatalytic experiment.

3. Results and discussion

3.1. Physico-chemical characterization

X-ray diffraction patterns of the HTlc prepared by co-precipitation correspond to the layered structure of hydrotalcite-like materials. As shown in Fig. 1, the XRD pattern of the CuPcTs supported LDHs is similar to that of the neat precursor considering that only CO₃²⁻ ions occupy the interlamellar space. This is evidencing the fact that metallophthalocyanines are not

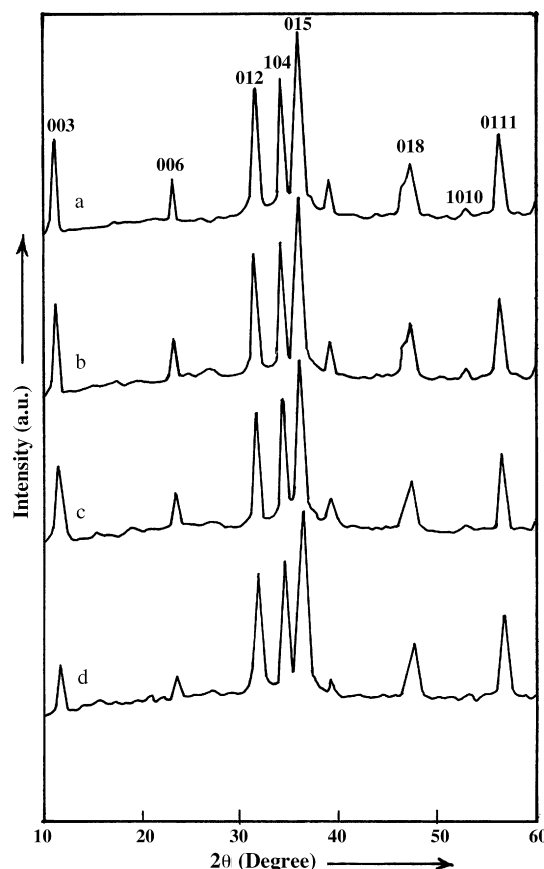


Fig. 1. XRD pattern of copperphthalocyanine immobilized Zn/Al LDH: (a) Zn₂Al; (b) Zn₂Al–CuPc; (c) Zn₃Al–CuPc; (d) Zn₄Al–CuPc.

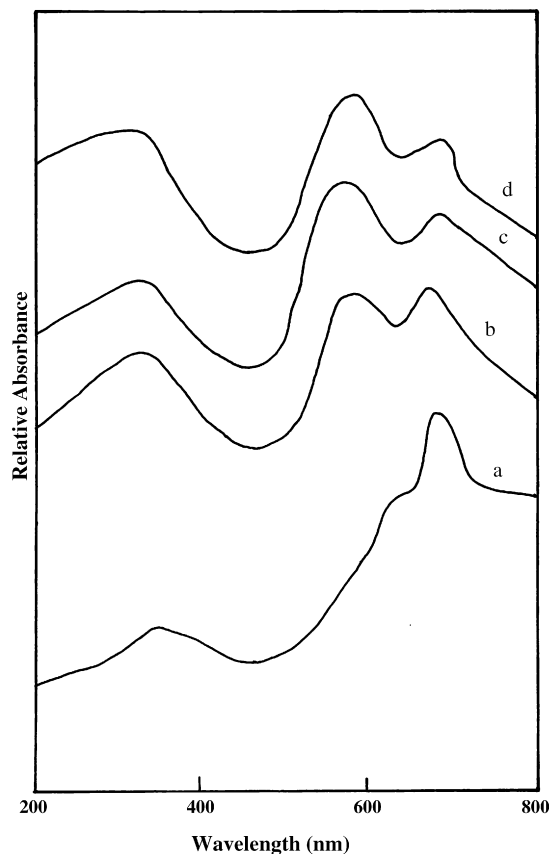


Fig. 2. UV-vis DRS of (a) CuPcTs; (b) Zn₂Al-CuPcTs; (c) Zn₃Al-CuPcTs; (d) Zn₄Al-CuPcTs.

present between the hydroxide layers but probably on the basal surface and edges. Similar observations have also been made by others [13]. The BET surface area of 110 °C dried neat and CuPcTs supported Zn/Al HTLcs was found to be 32 and 23 m²/g, respectively.

Fig. 2 shows the diffuse reflectance spectra (DRS) of CuPcTs supported on the Zn₂Al, Zn₃Al, and Zn₄Al matrices. For comparison purpose, the spectrum of CuPcTs in the solid state is also included. The spectra show two characteristics phthalocyanine absorption bands: B band at about 350 nm and the Q band at 670–680 nm (both are attributed to π - π^* macrocycle ring transitions) [18]. In case of supported materials, the phthalocyanine electronic spectrum shows an overall broadening and a blue shift of the Q band as a consequence of dimerisation and higher aggregates formation. The strong absorption at 620–630 nm is related to the formation of dimeric species and a shoulder on the red side of the Q band is attributed to the aggregates.

3.2. Photocatalytic decolorization of methylene blue

3.2.1. Effect of reaction time

To study the photocatalytic activity of the prepared samples, a series of experiments were carried out with varying different parameters. Fig. 3 shows the effect of irradiation time on the photocatalytic decolorization of MB. From the figure it was observed that with the increase in irradiation time, there is an increase in the photodecolorization process and reaches maxi-

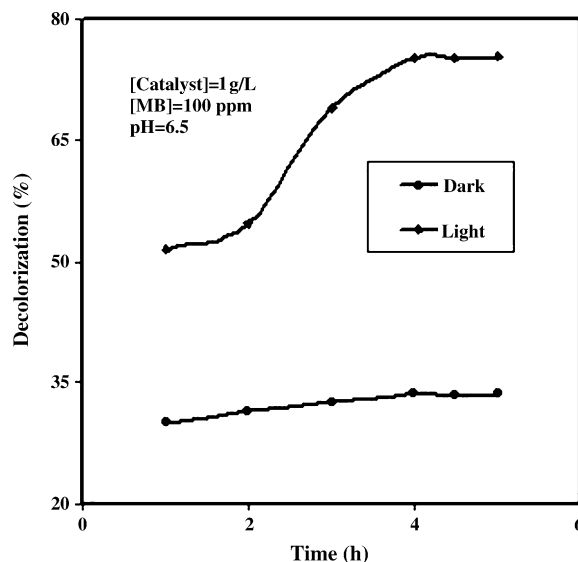


Fig. 3. Effect of time on photocatalytic decolorization of methylene blue. Temperature 30 °C; [MB] = 100 mg L⁻¹; catalyst = 1 g L⁻¹; pH 6.5.

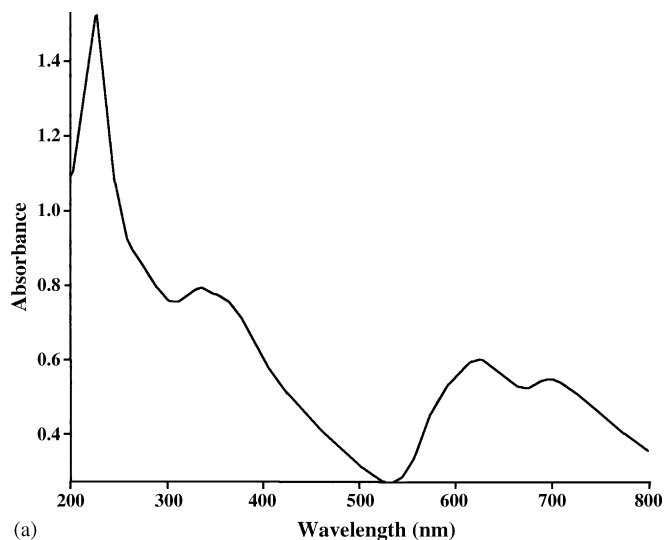
mum (75%) at 4 h. Thereafter the value remains almost constant. This could possibly be due to the fact that with increase in the time of irradiation there is an increase in the number of photons, which in turn increases the photodegradation process. But the percentage of adsorption in dark controls is 33% only and under UV radiation with 125 W medium pressure Hg vapour lamp (365–366 nm) the decolorization of MB is 47%.

From the electronic spectra of filtrates (Fig. 4) after photodecolorization process, no peak (λ_{\max}) corresponding to CuPcTs complex was observed and therefore copper from the complex supported on the LDHs is not leached out during the decolorization process.

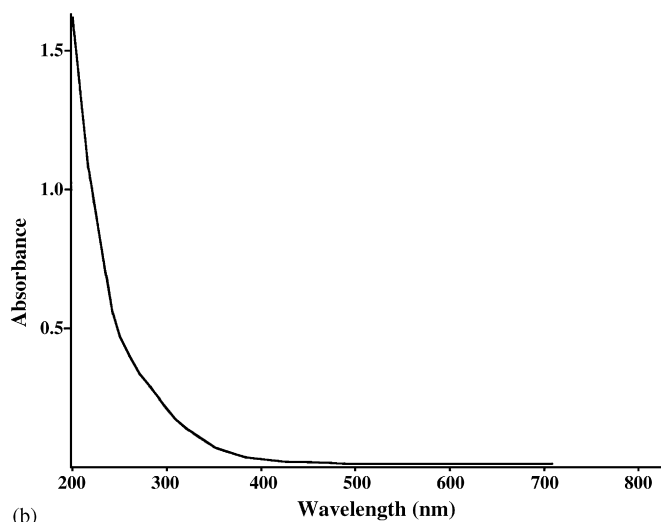
3.2.2. Effect of initial concentration of methylene blue

As the initial pollutant concentration is an important parameter so far as the decolorization of MB is concerned, the MB decolorization was studied over the concentration range 40–100 ppm with other parameters such as pH, catalyst concentration remaining constant (Fig. 5). The decolorization is highest (88.7%) at 40 ppm and thereafter decreases. This could possibly be due to the fact that with increase in the concentration of MB, the light absorbed by the substrate is more as compared to the catalyst, which is not effective in bringing about the photodecolorization process. So, at higher concentration the photodecolorization decreases. Besides, almost no decolorization of MB (<1%) is found to take place when the same is kept under solar light.

In order to study the kinetics of the photocatalytic decolorization of MB, a graph was plotted taking $\ln C_0/C$ versus time, where C_0 is the initial concentration of MB and C is the concentration at any time t . The graph follows straight line trend (Fig. 6) which indicates that the decolorization process follows first order kinetics. The calculated data for first order rate constants (k) at 50 and 100 ppm MB concentrations were found to be 0.355 and 0.235 h⁻¹, respectively, which show a decreasing trend with increase in MB concentration.



(a)



(b)

Fig. 4. Electronic spectra of (a) CuPcTs and (b) filtrate after photodecolorization of MB.

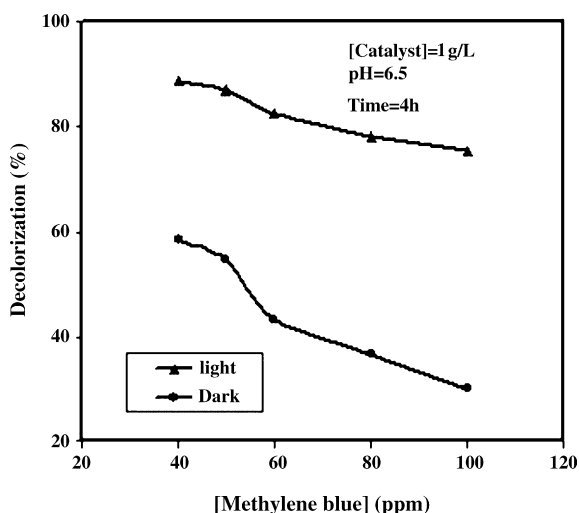


Fig. 5. Effect of initial concentration on photocatalytic decolorization of methylene blue. Temperature 30 °C; catalyst = 1 g L⁻¹; time = 4 h; pH 6.5.

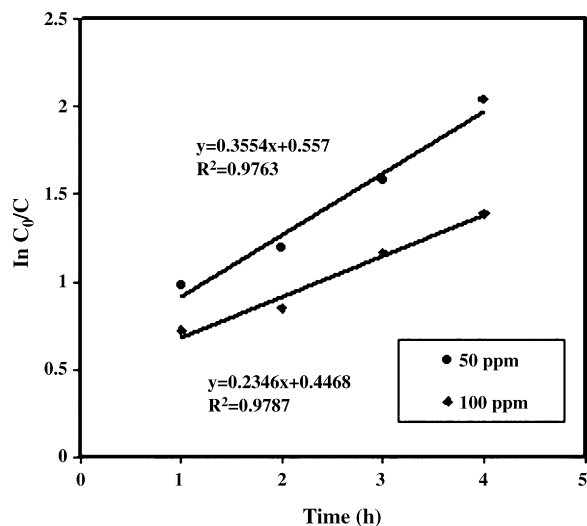


Fig. 6. Plot of $\ln(C_0/C)$ vs. time (h). Temperature 30 °C; [MB] = 100 mg L⁻¹; time = 4 h; catalyst = 1 g L⁻¹.

3.2.3. Effect of catalyst concentration

A series of experiments was carried out to assess the optimum catalyst loading by varying the amount of catalyst from 0.5 to 2.5 g L⁻¹ with methylene blue concentration (100 ppm) and at pH 6.5. It was observed that with increase in the catalyst concentration, the percentage of decolorization increases from 70.2 to 98.2% (Fig. 7). An enhanced adsorption of photons was observed with increasing catalyst concentration, thereby generating more singlet oxygen and consequently the decolorization percentage [19].

3.2.4. Effect of pH

The wastewater from the textile industries usually has a wide range of pH values. Generally pH plays an important role both in the characteristics of textile wastes and generation of active sites. Hence an attempt has been made to study the influence of pH on the photodecolorization of MB in the pH range 4–8.

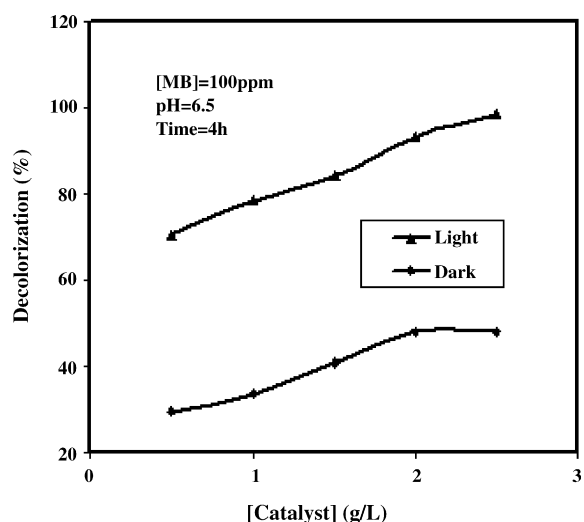


Fig. 7. Effect of catalyst dose on photocatalytic decolorization of methylene blue. Temperature 30 °C; [MB] = 100 mg L⁻¹; time = 4 h; pH 6.5.

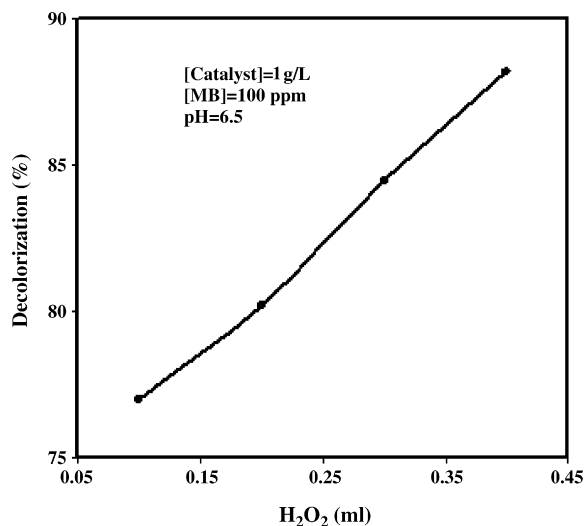


Fig. 8. Effect of hydrogen peroxide on photocatalytic decolorization of methylene blue. Temperature 30 °C; [MB] = 100 mg L⁻¹; time = 4 h; catalyst = 1 g L⁻¹; pH 6.5.

With increase in the pH, the percentage of decolorization of MB increases from 58 to 81%. This is mainly due to the following facts:

- The acidic products produced by the degradation reaction are neutralized by OH⁻ ions in alkaline medium [19]. But in acidic medium it is retarded by the high concentration of protons.
- CuPcTs complex is stable in alkaline medium and therefore its presence on the Zn/Al HTLcs surface enhances the photo decolorization of MB.

However, we have carried out all the experiments in natural pH (6.5) conditions.

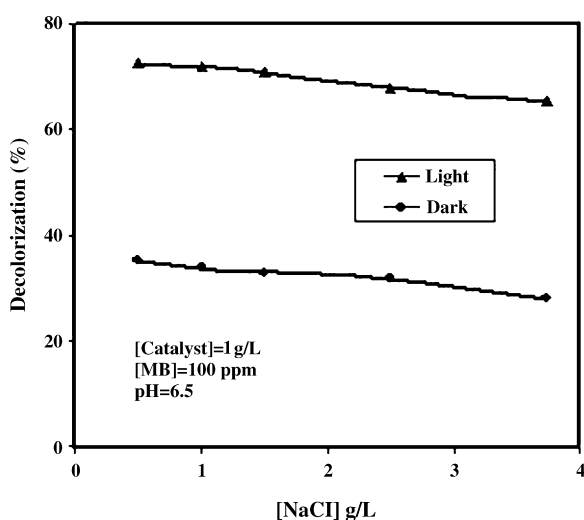


Fig. 9. Effect of sodium chloride concentration on photocatalytic decolorization of methylene blue. Temperature 30 °C; [MB] = 100 mg L⁻¹; time = 4 h; catalyst = 1 g L⁻¹; pH 6.5.

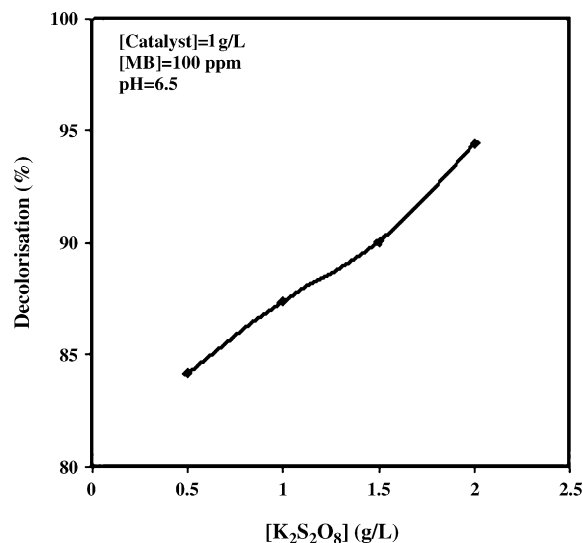


Fig. 10. Effect of potassium persulphate concentration on photocatalytic decolorization of methylene blue. Temperature 30 °C; [MB] = 100 mg L⁻¹; time = 4 h; catalyst = 1 g L⁻¹; pH 6.5.

3.2.5. Effect of hydrogen peroxide

From the investigation of the effect of H₂O₂ on the MB decolorization process, significantly improved photodecolorization was observed (Fig. 8) due to generation of reactive singlet oxygen ¹O₂^{*} by breakdown of H₂O₂ (Eq. (2)). On varying the amount of H₂O₂ from 0.1 to 0.4 mL, the percentage of decolorization increases from 77 to 88% [20]:



3.2.6. Effect of inorganic salts

Sodium chloride usually comes out in the effluent along with the wastes of textile mill. In order to see the effect of NaCl on the photocatalytic decolorization of MB, experiments were performed by varying the NaCl concentration while keeping all other conditions constant (Fig. 9). With increasing the Cl⁻ concentration from 0.5 to 3.75 g L⁻¹ there is a decrease in the decolorization percentage from 72 to 65%. This may be due to the fact that Cl⁻ ion reacts with Cl radical formed at the long lived excited triplet state of the complex to form Cl²⁻ as a result of which the formation of singlet oxygen is hindered and therefore, the decolorization of MB is decreased [21].

The effect of potassium persulphate on the photocatalytic degradation of methylene blue was investigated by varying its

Table 1
Effect of Zn/Al molar ratio on MB decolorization

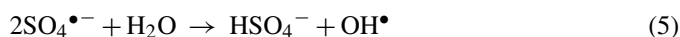
Zn/Al molar ratio	Photodecolorization (%)
2:1	75
3:1	75.5
4:1	75.8

Table 2

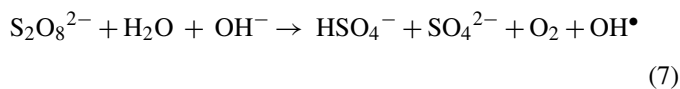
Comparison of MB decolorization of the present work with that of the report published in the literature

Catalyst	Light source	Concentration of MB (ppm)	Amount of catalyst	Time	References
TiO ₂ and TiO ₂ support	Photoreactor of Platform de Almeria (Spain)	30	0.5	2 h	[23]
P25 TiO ₂	480 W xenon	10	0.1 wt.% of suspension	–	[24]
TiO ₂ mounted pumice	UV light of intensity 1.6 MW cm ⁻²	3	1.6 g (0.1 g of TiO ₂)	48 h	[25]
TiO ₂ loaded on activated carbon	UV radiation from black light (10 W)	20	–	30 h	[26]
TiO ₂ thin film	12.8 W UVA black light	3	–	10 min	[27]
(Sr _{1-x} La _x) TiO _{3+δ} -TiO ₂ composite	500 Xe	6	0.20	6 h	[28]
	20 W blue florescent light	90	0.52 g L ⁻¹	4 h	[29]
Carbon coated TiO ₂ combustion	125 W medium pressure mercury lamp	200	0.5 kg m ⁻³	2.6 h	[30]
Synthesized TiO ₂	Solar radiation	100	1 kg cm ⁻³	3.6 h	[30]
P25	High pressure 125 W mercury lamp	30	0.5 kg cm ⁻³	2 h	[31]
TiO ₂	125W Philips	26	2.5 g L ⁻¹	2 h	[32]
ZrO ₂ /TiO ₂	UV light	9	1 g L ⁻¹	–	[33]
SO ₄ ²⁻ /TiO ₂	Solar radiation	100	1.6 g L ⁻¹	4 h	[34]
TiO ₂ /ZrP 2 wt.% and TiO ₂ /TiP 4 wt.%	Solar radiation	20	1 g L ⁻¹	4 h	[35]
Zn ₂ Al-CuPcTs	Solar radiation	100	1.0 g L ⁻¹	4 h	This work

concentration from 0.5 to 2.0 g L⁻¹ and the data is presented in Fig. 10. The percentage degradation of MB dye increases with increasing the concentration of K₂S₂O₈ and reaches an optimum value, 94% in 4 h time at 2.0 g L⁻¹ K₂S₂O₈ concentration. The enhanced degradation in the presence of S₂O₈²⁻ ion may be due to the generation of useful oxidant, sulphate anion radical [22]:



The net reaction can be written as



3.2.7. Effect of Zn/Al molar ratio

CuPcT is a sensitizer for the decolorization of MB, but itself is soluble in water and therefore it needs a support for the decolorization process. For this Zn/Al HTLcs were chosen as the supporting material. However, Zn/Al molar ratio has almost no effect on the photo decolorization of MB. The percentage decolorization of MB by using different Zn/Al molar ratio but with same CuPcTs amount was given in Table 1.

4. Possible mechanism of MB decolorization

It has been established that upon irradiation with visible light the phthalocyanine complexes with long living excited triplet state exhibit high catalytic activity in the complete oxidation of organic pollutants containing sulphur. During interaction between oxygen molecule and long living excited triplet state of these complexes chemically more reactive singlet oxygen is formed, which further interacts with organic pollutant (methylene blue) for its oxidation. The photocatalytic process

is dependent on the electronic structure of the complex and the central metal atom. The immobilized copperphthalocyanine complex can reversibly co-ordinate and activate molecular oxygen:



The resultant oxidized products of MB under solar radiation by Zn/Al CuPc may be H₂O, NO₃⁻, SO₄²⁻ and NH₄⁺. To the best of our knowledge there is no report found on the decolorization of MB using Zn₂Al-CuPcTs. The present results can be directly compared with other catalysts published earlier (Table 2). While optimizing the photocatalytic reaction conditions we found that 75% of 100 ppm of MB can be decolorized by 1 g L⁻¹ of Zn₂Al-CuPcTs in 4 h time under solar radiation. These results were found be comparable or even better than those reported earlier with respect to the concentration of MB, amount of catalyst, time and solar radiation, etc.

5. Conclusions

- (1) PXRD patterns of the samples show that CuPcTs are adsorbed on Zn/Al HTLcs rather than intercalation in the interlamellar region.
- (2) Zn₂Al-CuPcTs was proved to be efficient sensitizer for methylene blue decolorization under solar light than the dark controls. A maximum of 75 and 33% of decolorization of methylene blue was achieved at 4 h time and catalyst dose 1 g L⁻¹ under solar radiation and dark control, respectively.
- (3) The presence of CuPcTs on LDH is responsible for the formation of singlet oxygen which helps in decomposition of methylene blue.
- (4) H₂O₂ significantly increases the photodecolorization of MB due to formation of more amount of singlet oxygen.

- (5) The presence of $K_2S_2O_8$ was found to have enhancing effect on photodecolorization of MB whereas NaCl showed a retarding effect.

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References

- [1] C.G. Claessens, W.J. Blau, M. Cook, M. Hanack, R.J.M. Nolte, T. Torres, D. Wohrle, *Monatshfte für Chemie* 132 (2001) 3.
- [2] G. Stasi, L. Valli, G. Mele, G. Vasapollo, G. Rosso, R. Rella, Proceedings of the 5th Italian Conference (Extended to Mediterranean Countries) on Sensors and Microsystems, World Scientific Publishers, Singapore, 2000, p. 87.
- [3] M. Chibwe, L. Ukrainczyk, S.A. Boyd, T.J. Pinnavaia, *J. Mol. Catal. A: Chem.* 113 (1996) 249.
- [4] V. Ilieva, A. Iliev, L. Bilyarska, *J. Mol. Catal. A: Chem.* 126 (1997) 99.
- [5] V. Iliev, V. Alexiev, L. Bilyarska, *J. Mol. Catal. A: Chem.* 137 (1999) 15.
- [6] V. Iliev, A. Ilieva, *J. Mol. Catal. A: Chem.* 103 (1995) 147.
- [7] V. Iliev, L. Prahov, L. Bilyarska, H. Fisher, G. Schulz-Ekloff, D. Wohrle, L. Petrov, *J. Mol. Catal. A: Chem.* 151 (2000) 161.
- [8] M.E. Perez-Bernal, R. Ruano-Casero, T.J. Pinnavaia, *Catal. Lett.* 11 (1991) 55.
- [9] E.W. Abel, J.M. Pratt, R. Whelan, *J. Chem. Soc. Dalton Trans.* 6 (1976) 509.
- [10] F. Cavani, F. Trifiro, A. Vaccari, *Catalysis Today* 11 (1991) 173.
- [11] B.F. Sels, D.E. De Vos, P.A. Jacobs, *Catal. Rev.* 43 (2001) 443.
- [12] V. Rives, M.A. Ulibarri, *Coord. Chem. Rev.* 181 (1999) 61.
- [13] C.A.S. Barbosa, A.M.D.C. Ferrira, V.R.L. Constantino, A.C.V. Coelho, *J. Incl. Phenom. Macro. Chem.* 42 (2002) 15.
- [14] C.A.S. Barbosa, A.M.D.C. Ferrira, V.R.L. Constantino, *Eur. J. Inorg. Chem.* (2005) 1577.
- [15] C.A.S. Barbosa, P.M. Dias, A.M.C. Ferrira, V.R.L. Constantino, *Appl. Clay. Sci.* 28 (2005) 147.
- [16] S. Kanan, S.V. Awaste, M.S. Agashe, *Stud. Surf. Sci. Catal.* 113 (1998) 927.
- [17] K.A. Carrado, J.E. Forman, R.E. Botto, R.E. Winans, *Chem. Mater.* 5 (1993) 472.
- [18] M.J. Stillman, T. Nyonkong, in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, vol. 1, VCH publishers, New York, 1989, p. 133.
- [19] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere* 46 (2002) 1173.
- [20] Y. Ogata, K. Tomizawa, K. Furuta, in: S. patai (Ed.), *The Chemistry of Peroxide*, Wiley, Chichester, 1983, p. 720.
- [21] V. Nadtochenko, J. Kiwi, *Inorg. Chem.* 37 (1998) 5233.
- [22] J.K. Kochi (Ed.), *Free Radicals*, vol. II, John Wiley and Sons, New York, 1973, p. p672.
- [23] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.-M. Herrmann, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 27.
- [24] S.-K. Lee, P.K.J. Robertson, A. Mills, D. McStay, N. Elliott, D. McPhail, *Appl. Catal. B: Environ.* 44 (2003) 173.
- [25] X.-Y. Chuan, M. Hirano, M. Inagaki, *Appl. Catal. B: Environ.* 51 (2004) 255.
- [26] M. Toyoda, Y. Nanbu, T. Kito, M. Hirano, M. Inagaki, *Desalination* 159 (2003) 273.
- [27] R. Fretwell, P. Douglas, *J. Photochem. Photobiol. A: Chem.* 143 (2001) 229.
- [28] S. Otsuka-Yao-Matsuo, M.J. Ueda, *Photochem. Photobiol. A: Chem.* 168 (2004) 1.
- [29] B. Tryba, A.W. Morawski, T. Tsumura, M. Toyoda, M. Inagaki, *J. Photochem. Photobiol. A: Chem.* 167 (2004) 127.
- [30] G. Sivalingam, K. Nagaveni, M.S. Hegde, G. Madras, *Appl. Catal. B: Environ.* 45 (2003) 23.
- [31] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, *Appl. Catal. B: Environ.* 39 (2002) 75.
- [32] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, *Appl. Catal. B: Environ.* 31 (2001) 145.
- [33] M. Hirano, C. Nakahara, K. Ota, O. Tanaike, M. Inagaki, *J. Solid State Chem.* 170 (2003) 39.
- [34] P. Mohapatra, K.M. Parida, *J. Mol. Catal. A: Chem.* 258 (2006) 118.
- [35] D.P. Das, K.N. Baliarsingh, M. Parida, *J. Mol. Catal. A: Chem.* 261 (2006) 254.