

Synthesis, characterization and photocatalytic studies of some metal phthalocyanines

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Metal phthalocyanines (MPc) (M = Cu, Ni, Co and Fe) have been synthesized and characterized by XRD, IR, ESR and thermal technique. The solid state studies such as magnetic susceptibility, electrical resistivity and electron spin resonance have been carried out. Solar induced degradation of a textile dye Naphthol Blue Black (NBB) has been studied employing metal phthalocyanines.

Keywords: Photocatalysis, Metal phthalocyanines, Naphthol Blue Black, Solid state studies, Semiconductors

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Phthalocyanines are important class of organic semiconductors as they act as photosensitizer and behave as good catalysts under certain circumstances¹. Metallophthalocyanines (MPcs) are particularly attractive as potential catalysts for organic reactions such as oxidation because of their rather inexpensive and simple preparation on a large-scale, ability to absorb oxygen and chemical as well as thermal stability². In recent years, advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. Photodegradation of pollutants using semiconductor photocatalyst with solar light can make it an economically viable process since solar energy is an abundant and inexpensive natural energy source³. The main advantage of the photocatalytic degradation process is its mild operation conditions.

It is possible to excite phthalocyanine particles on irradiation with visible light⁴. The metal free phthalocyanine, cobalt phthalocyanine and copper phthalocyanine anchored on TiO₂ or WO₃ are much more effective catalysts for the oxidation of Na₂S and Na₂S₂O₃ upon irradiation with visible light⁵. The use of metallophthalocyanine complexes such as iron tetrasulphophthalocyanine as a catalyst has recently been found effective in the oxidative degradation of persistent pollutants with H₂O₂⁶. The degradation of textile diazo dye Naphthol Blue Black (NBB) with

TiO₂ has been studied by Vinodgopal *et al.*^{7,8}. It was observed that NBB degrades to a colourless solution leading to complete mineralization. In the present investigation, the synthesis, characterization and photocatalytic degradation of textile diazo dye Naphthol Blue Black over metal phthalocyanines has been studied and attempts have been made to correlate with solid state studies.

Experimental Procedure

Metal phthalocyanines (MPc) (where M = Cu, Ni, Co and Fe) were prepared by method described elsewhere⁹. Required amount of phthalic anhydride, urea, metal salt and ammonium molybdate were suspended in nitrobenzene and heated at 190°C. After 4-5 h the mixture was filtered hot and then washed with nitrobenzene, followed by methanol. The crude product was boiled for 2 h, first with 1 N HCl and then with 1 N NaOH, filtered and washed with water each time until the filtrate was neutral. The solid material was then stirred in methanol, suction filtered, and dried at 60°C.

The phthalocyanines were characterized by recording X-ray diffractograms (PHILIPS XRD PW3710) and FTIR analysis (SHIMADZU model 4101). Thermal analysis was carried out by employing NETZSCH Geratebau GmbH Thermal Analyzer (STA 409PC) to find out the thermal

stability of phthalocyanines. The magnetic susceptibility in air was determined by Guoy method at room temperature, with a field of the order of 8000 gauss using $\{\text{Hg}[\text{Co}(\text{SCN})_4]\}$ as a standard material. The electrical resistivities of the phthalocyanines were measured by two probe method during cooling cycles from 150°C to room temperature. The Electron Spin Resonance spectra were recorded at room temperature using a Varian E-112, X-band spectrometer to get an insight of the paramagnetic species. TCNE was used as a reference standard for *g*-factor measurements. UV-Visible absorption spectra of the phthalocyanines were recorded in the UV-Visible region using pyridine as a solvent and Diffuse Reflectance Spectroscopy was used to find out the band gap energy of the samples.

Samples prepared were tested for photodegradation of textile diazo dye Naphthol Blue Black using oxygen and sunlight. The progress of the photocatalytic degradation was monitored by UV-Visible spectrophotometer by measuring the absorbance of the dye solution at λ_{max} .

In the present investigations, Naphthol Blue Black as received was used without further purification. The photodegradation of the dye was observed taking 100 mL of the 10^{-5} M dye solution and 200 mg of the prepared photocatalyst. The dye solution was first aerated by bubbling oxygen for 5-10 min before adding the catalyst. The irradiation was carried out keeping the reaction mixture under sunlight during fixed time period of 11:00 to 16:00 h. The desired pH of the solution was adjusted by the addition of previously standardized HCl and NaOH solution. The filtration was performed by using Whatmann 41 filter paper to obtain the desired accuracy in the measurement of absorbance (O.D.) of the dye solution. A UV-Visible spectrophotometer was used for measuring absorbance at different time intervals. The λ_{max} for the dye was determined by scanning the dye solution in the visible region from 400-700 nm range with the help of an UV-Visible spectrophotometer.

Results and Discussion

The metal phthalocyanines were characterized by recording the X-ray diffractograms. The d_{hkl} and 2θ values obtained were compared with the values reported in the literature (ICDD-PDF Files) and found to be in good agreement¹⁰. Metal phthalocyanines are found to be in stable β form with planar symmetry. Fig. 1 shows XRD pattern of Cu and Ni

phthalocyanine. Further metal phthalocyanines were characterized by UV-Visible spectroscopy and the observed data matches with the data reported in the literature (Table 1).

Phthalocyanines were also characterized by IR spectroscopy^{10,11}. IR spectra of phthalocyanines show following absorption peaks. The peaks around 1121-1123, 1090-1092, 1067-1070, 947-949, 872-885 and 754 cm^{-1} are due to phthalocyanine skeletal vibrations. The peaks observed at 1420-1423, 1335 cm^{-1} are due to aromatic phenyl ring. The peaks around 1286, 1226, 1202-1210 cm^{-1} are due to C-N stretch. The peaks observed at 1165-67, 1001-1005 cm^{-1} are assigned to C-H in plane bending vibration and peaks due to C-N bending are

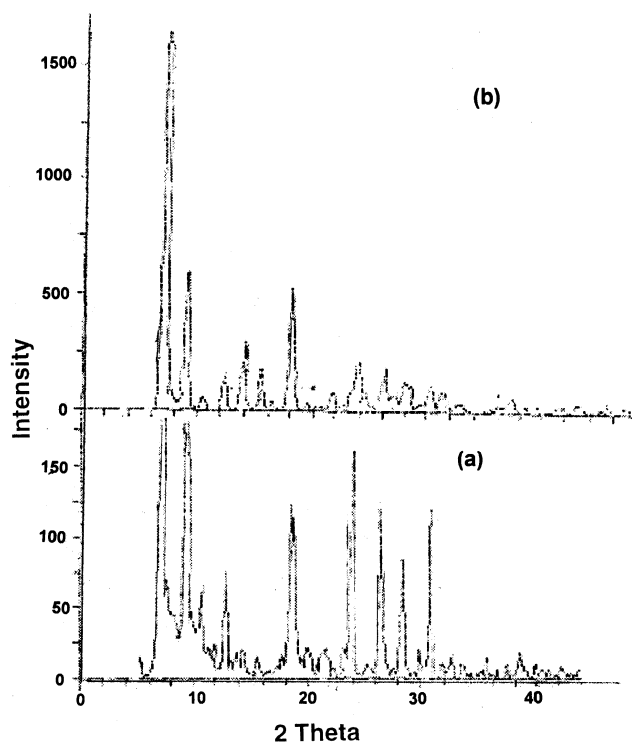


Fig. 1 — Powder XRD pattern of (a) CuPc and (b) NiPc

Table 1 — UV- Visible data of metal phthalocyanines

Sr No	Sample	Wavelength λ_{max} (nm)
1	Copper phthalocyanine	673
2	Cobalt phthalocyanine	658
3	Iron phthalocyanine	655
4	Nickel phthalocyanine	667

identified at 901 and 799-802 cm^{-1} , respectively. The peaks at 770-773 cm^{-1} are due to C-H out-of-plane bending. The sharp peaks observed at 1610-1616 cm^{-1} were attributed to C = C, C = N and ring stretching (skeletal band).

Thermal studies have indicated the thermal stability of metal phthalocyanines and decomposition behaviour at different temperatures. Phthalocyanines do not have sharp melting point. They decompose at elevated temperature. It is observed that cobalt phthalocyanine is stable upto 410°C and starts decomposing at around 425°C and shows weight loss till 700°C. It was assumed that the decomposition products might be hydrocarbon, ammonia and metal oxide and different thermal events were observed on TG/DSC thermogram¹². FePc, NiPc and CuPc show similar thermal pattern with slightly lower decomposition temperature for FePc and NiPc.

Electrical resistivity of the phthalocyanines was measured by two probe method during cooling cycles from 150°C to room temperature. Variation of electrical resistivity with temperature for phthalocyanines is shown in Fig. 2. Phthalocyanines are a class of organic semiconductors, whose electrical properties have considerable importance owing to their potential application in electronic devices and sensor systems¹³. Shihub and Gould¹⁴ have calculated the activation energy of CoPc films as 0.54 eV. It was suggested that freshly prepared samples may contain different kinds of defects such as vacancies, grain boundaries and dislocations, which may be partially annealed out by heat treatment resulting in a decrease in the density of defects and in local structural rearrangements. Desorption of the oxygen which is a major source of intrinsic conductivity leads to an increase in the resistance of the material, thus proving the sensitivity of the electronic conduction of phthalocyanine to the presence of oxygen. The annealing temperature of 170°C is sufficient to desorb oxygen without causing structural changes in the material. Semiconducting property of the CuPc polymorphs can be accounted for the differences in the interaction of the highly conjugated π -electrons between the molecules and inter-molecular spacing. It crystallizes into β -form, which is the most stable form¹¹. A Pc molecule is a good electron donor. The ring of N atoms around the central metal atom forms a potential well that is responsible for the semiconducting properties¹⁵. All the metal phthalocyanines under investigation show

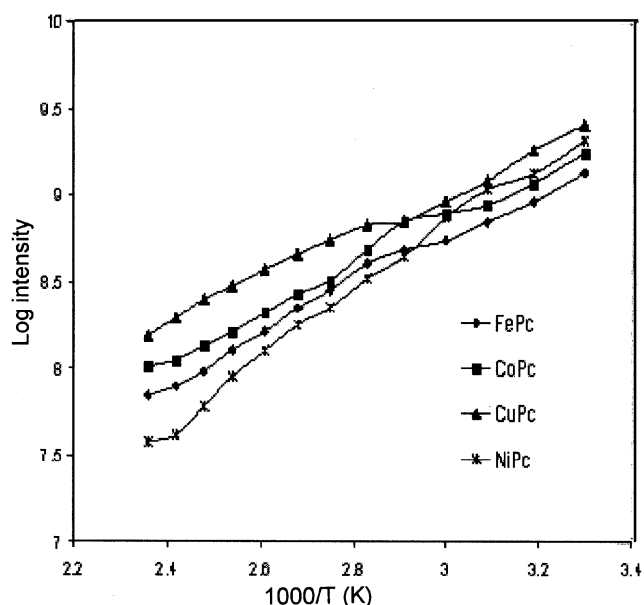


Fig. 2 — Variation of electrical resistivity with temperature of metal phthalocyanines

semiconductor behaviour. They show decrease in electrical resistivity with increase in temperature.

The magnetic susceptibility of samples was determined by Guoy method at room temperature. Copper phthalocyanine and cobalt phthalocyanine are paramagnetic whereas nickel phthalocyanine is diamagnetic and iron phthalocyanine is ferromagnetic. Higher or lower values of μ_{eff} indicate the contribution of direct or super exchange intermolecular interaction to spin only value. Differences in magnetic moment values and their variations may be due to the difference in intermolecular interactions, spacing and inclination of the molecules in the crystal lattice. The observed magnetic susceptibility values are represented in Table 2.

ESR spectra of Cu and Co phthalocyanine are shown in Fig. 3. The data are in agreement with the magnetic susceptibility results, regarding the paramagnetic nature of the compounds. The ESR signal observed is due to $-1/2g\beta H$ to $+1/2g\beta H$ transition, where β is the electron Bohr magneton, g is the Lande, or spectroscopic splitting factor and H is the applied magnetic field. FePc is ferromagnetic and NiPc is diamagnetic. Therefore, ESR spectra of these were not recorded. ESR data of these samples are represented in Table 2. The UV-Visible spectrum observed for phthalocyanines originates from

Table 2 — Magnetic susceptibility and ESR data of representative samples

Sample	Magnetic susceptibility (χ_g cgs units)	μ_{eff} (B M)	ESR g value	Line width (gauss)
Copper phthalocyanine	27.9×10^{-6}	2.61	2.00277	500
Cobalt phthalocyanine	1.8×10^{-6}	1.58	2.5962	1912
Iron phthalocyanine	Ferromagnetic	-	-	-
Nickel phthalocyanine	Diamagnetic	-	-	-

molecular orbitals within the aromatic 18π electron system and from overlapping orbitals on the central metal¹⁶.

The photocatalytic reaction was studied with different experimental conditions like using different amount of the catalyst, without aeration, without catalyst, without irradiation and changing the pH conditions from acidic to basic. The degradation products were analyzed by HPLC analyzer for qualitative analysis of the dye sample for the representative sample. The UV-Visible spectrum of naphthol blue black dye is shown in Fig. 4. The NBB dye has absorption in visible region at λ_{max} 618 nm in water.

The optimum amount of catalyst for solar induced photocatalytic degradation of naphthol blue black was found to be around 200 mg of the catalyst for 100 mL of the dye solution as shown in Fig. 5. The rate of dye degradation increases with the amount of photocatalyst that may be attributed to the increase in the exposed surface area of the semiconductor. But after a certain limit (200 mg), if the amount of photocatalyst is increased further, there will be a saturation point. According to Kartal *et al.*¹⁷, the amount of photocatalyst affects both the number of active sites on photocatalyst and the penetration of light through the suspension. It has been also reported by Sakthivel *et al.*¹⁸ that increase in the loading of photocatalyst increase the rate of deactivation of activated molecules by collision with ground state photocatalyst.

Oxygen is an electron scavenger and it traps the photogenerated electrons from the conduction band forming O_2^- ions and thus preventing the electron-hole recombination¹⁹. In absence of oxygen, electron-hole recombination occurs, thus, decreasing the rate of degradation. Similar results were observed by Zhang³ and reported that dissolved O_2 in the reaction plays an important role by trapping the conduction band electrons forming super oxide ions (O_2^-) and thus

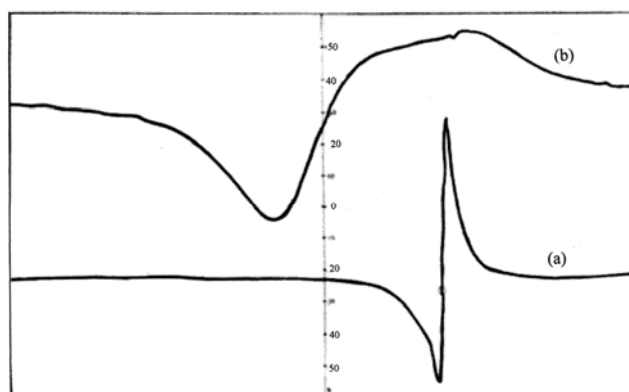


Fig. 3 — ESR spectra of (a) CuPc and (b) CoPc at room temperature

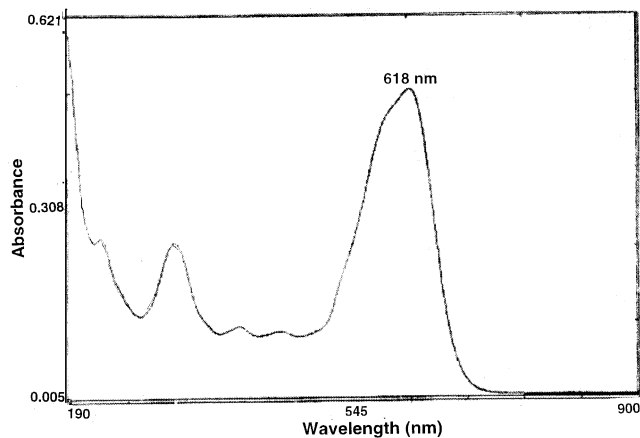


Fig. 4 — UV-Visible spectra of naphthol blue black dye

delays the electron-hole recombination ($O_2 + e^- \rightarrow O_2^-$) and at the same time H_2O_2 is formed from O_2 .

Dye degradation was studied at different pH conditions which is one of the important factors. It has been observed that degradation of dye is faster in alkaline pH i.e. at pH 10. In alkaline medium, there is a greater probability for the formation of hydroxyl

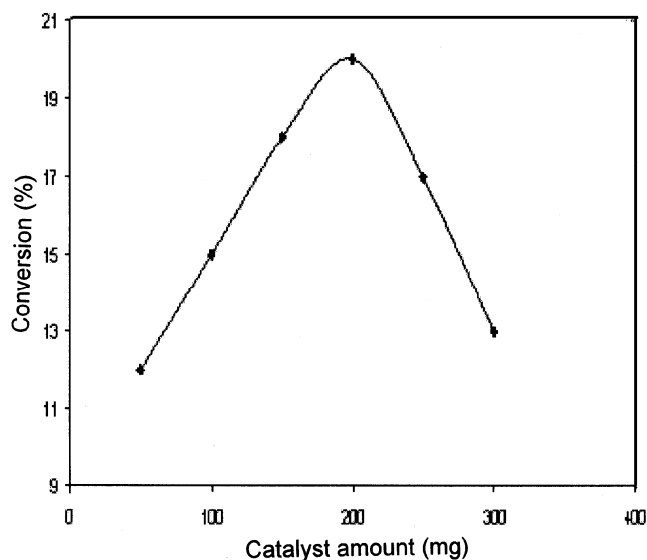


Fig. 5 — Optimization of catalyst amount for the degradation of NBB dye

radical (OH^\cdot), which can act as an oxidant, thus increasing the rate of photodegradation of the dye²⁰. Increasing of the $p\text{H}$ of the dye solution from 4 to 10 increases the photocatalytic reaction after 240 min irradiation time. The photocatalytic degradation was faster in alkaline $p\text{H}$ than in acidic $p\text{H}$ range. At alkaline $p\text{H}$, the negative surface of the semiconductor with OH^- ions act as an efficient trap for the photo-generated holes and produce hydroxyl radicals. At higher $p\text{H}$, the hydroxyl radical and O_2^- radical can easily diffuse from the negative surface of semiconductor into the bulk of the reaction solution. Hence, hydroxyl radical is responsible for dye degradation.

Metal phthalocyanines showed a good photocatalytic activity for the degradation of NBB dye when irradiated under solar light. Band gap energies for these phthalocyanines are shown in Table 3. Iron phthalocyanine has larger band gap than copper, cobalt and nickel phthalocyanine. It is tempting to say that for higher the band gap higher is the activity which may not be true always and also depends on many other factors. FePc is ferromagnetic and NiPc is diamagnetic, whereas CuPc and CoPc are paramagnetic but showed marginally low photocatalytic activity than FePc and NiPc. CuPc shows lowest conversion. So magnetic and ESR data may not have much influence on photocatalytic activity. Absorption spectra obtained after completion of the NBB dye degradation indicate that the

Table 3 — Band gap energy of metal phthalocyanines

Sr No	Sample	Band gap energy (eV)
1	Copper phthalocyanine	2.87
2	Cobalt phthalocyanine	4.71
3	Iron phthalocyanine	5.67
4	Nickel phthalocyanine	3.81

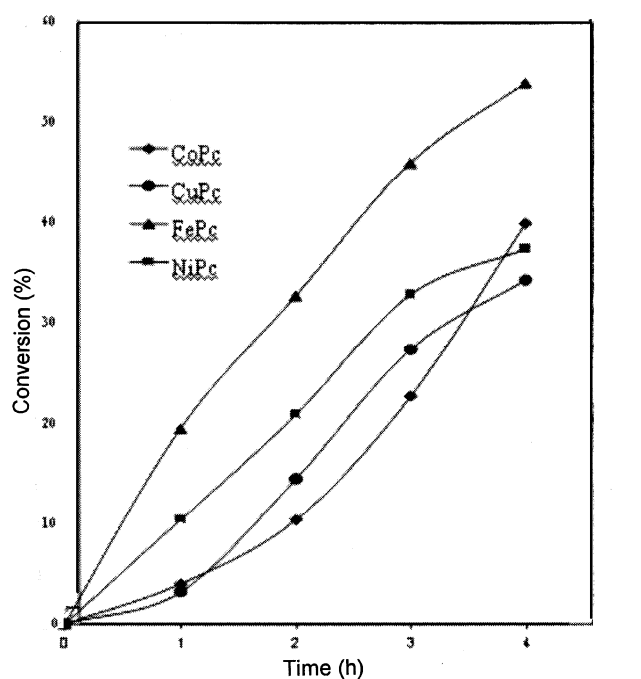


Fig. 6 — Percentage conversion of NBB dye at neutral $p\text{H}$

degradation products are colourless. Thus, the photocatalytic degradation provides an efficient way to mineralize this textile diazo dye. Figures 6 and 7 show the percentage conversion of NBB dye with time on MPC at neutral $p\text{H}$ and $p\text{H}$ 10, respectively.

Many investigators have suggested various mechanisms for the degradation of dye pollutants²⁰. On exposure to solar radiation, the metal phthalocyanine semiconductor (MPC) will be excited by light to give MPC^* . This excited state will provide an electron (e^-) in the conduction band leaving a hole in the valence band. This electron is then trapped by molecular O_2 forming O_2^- ions. The valence band hole generates hydroxyl radical (OH^\cdot) from hydroxyl ions,

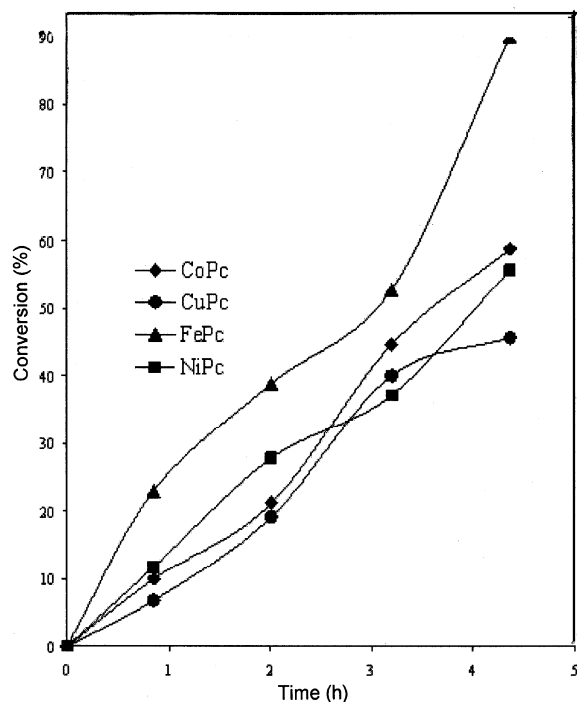
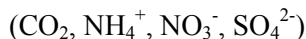
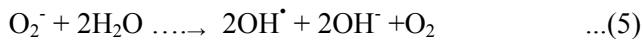
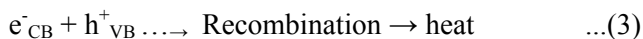
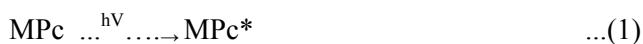


Fig. 7 — Percentage conversion of NBB dye at pH 10

which can easily attack the adsorbed dye, thus leading finally to their complete mineralization. Scheme I suggest the photocatalytic degradation pathways, which are in agreement with others²⁰.



Scheme I

Conclusion

The synthesized metal phthalocyanines have stable β form with planar symmetry. They have better thermal stability compared to other organic compounds and show semiconductor behaviour. CuPc and CoPc are paramagnetic, whereas NiPc is diamagnetic and FePc is ferromagnetic. The phthalocyanines, show good photocatalytic activity for the degradation of naphthol blue black. The textile diazo dye naphthol blue black is degraded totally and complete mineralization is observed.

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