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Original Research article

Synthesis and Characterization of Novel Composite-Based Phthalocyanine Used as Efficient Photocatalyst for the Degradation of Methyl Orange

Hossein Salavati[a] *, Abbas Teimouri[a] *, Shahnaz Kazemi[b]

[a] Chemistry Department, Payame Noor University, 19395-3697, Tehran, I. R. of Iran
[b] Department of Chemistry, Birjand University, 97179-414, Birjand, Iran

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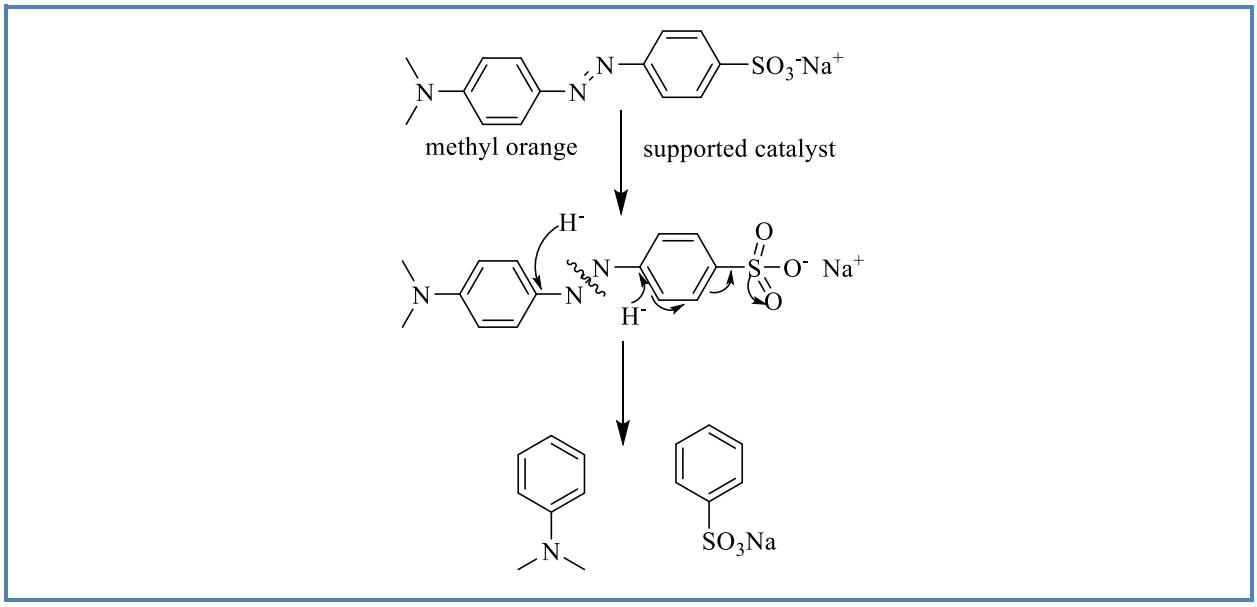
ABSTRACT

In this study, Copper-tetraaminophthalocyanine (CuTAP) was supported on polyvinylcholoride by reflux condition to produce heterogeneous recovarable catalyst. This catalyst was characterized using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-vis spectroscopy. The results showed that the photocatalytic degradation of methyl orange was performed in mild conditions at ambient pressure and temperature under visible light. The synthesized catalyst could be readily separated from the catalytic system by centrifuging and loss of activity was negligible when the catalyst was recovered in four consecutive cycles. The effects of operational various factors such as catalyst amount, initial dye concentration and contact time on degradation of methyl orange were investigated. Optimization results showed that maximum degradation of methyl orange efficiency 98.6 % was achieved at the optimum conditions.

Graphical Abstract



Introduction

Recently, polymer/inorganic composite performances have been reported in various fields such as chemistry, physics, electronics and optics because of their synergetic effects and potential applications in various sciences. The increasing efforts have been employed to the synthesis of multifunctional catalysts. Apparently, this interest has been discussed by the fact that multifunctionality is one of the most important characteristics of enzymes, the catalysts in biological systems. Synthetic model systems are investigated to elucidate the factors governing the efficient cooperation between various catalytic groups in catalysis. Polymers may advantageously use for the development of model systems for enzymes and of new multifunctional catalysts for catalytic reactions. The physical and chemical properties of polymers may be varied to a large extent and, therefore, tailormade polymers may be designed to hold a desired combination of catalytic active sites and for joined different structures [1, 2]. Phthalocyanines are conjugated macrocycles with good chemical and thermal stability, properties that allow them to be used in many various applications. Phthalocyanines are of interest not only as model materials for the biologically important porphyrins but also because the intensely colored metal complexes are of commercial applications as pigments and dyes. The copper derivatives being an important blue pigment [3-5]. Today literally thousands of various phthalocyanines have been studied in the chemical literatures. Typically, high temperatures and reaction times of hours are needed. In the early 1930s, a rich and varied chemistry and technology has improved around these interesting materials. There are literally thousands of publications and patents subjected to phthalocyanine

and its analogs. Phthalocyanine complexes of transition metals are attractive as potential catalysts because of their rather cheap and easy preparation in a large scale and their thermal and chemical stability. Their macro cyclic skeleton resembles that of porphyries complexes widely used by nature in the active sites of materials. Phthalocyanines constitute a remarkably versatile class of compound with different technological applications. It was reported that the metallophthalocyanine end-capped poly (aryl ether sulfone) were synthesized from the ortho phthalonitrile endcapped polymers. These polymers had high Tg and were soluble in common organic solvents [6-11]. Copper and iron were used as the metals in the above preparation. Synthesize amorphous polymers could be advantageous due to having high glass transition temperatures and excellent oxidation and thermal stability, as they are soluble in common organic solvents, and allow for easy solution processing and chemical modification. Application of supported phthalocyanine in degradation of dyes as pollutants was investigated in recent years [12-14]. Biologically active molecules, such as drugs, hormones and drugs have been attached to polymers for a number of uses [15, 16, and 1]. Particularly interesting is the homogeneous catalysis by metal ions and metal complexes which are attached to macromolecules. In this case the polymer does not serve solely as an inert carrier but the polymer chain influences the behaviour of the catalytic sites. Various applications of polymers in catalysis are solid polymeric support, weakly crosslinked polymer, non-crosslinked polymer, and noncrosslinked polymer fixed on a solid support [17-20]. Many investigation have been reported that phthalocyanines was used as catalyst in degradation of dyes [21]. More interesting from a mechanistic point of view is the application of soluble (non-cross-linked) polymers in catalysis. In this study, we describe the synthesis and characterization of metalophthalocyanine immobilized on polyvinylcholoride. The polyvinylchloride we used in this work is in the class of non-crosslinked polymer, in addition the polymeric structures may function both as carrier of the catalytic sites and as supplier of chlor as leaving groups for linkage of phthalocyanine.

Experimental

Materials and Methods

All reagents were purchased commercially and used without further purification. Elemental analysis was carried out a Perkin-Elmer 2400 instrument. UV–Vis spectra were recorded on a 160 Shimadzu spectrophotometer. Scanning electron micrographs (SEM) of the polymer and supported phthalocyanine were performed on SEM Philips XL 30 instrument. The FT-IR spectra were obtained by a Fourier transform Infrared Spectroscopy (JASCO FT/IR-4200, Japan), the X-ray diffraction

measurement was obtained using an X-ray diffract meter Bruker, D8ADVANCE [(Germany) using Cu Kα radition (λ=0.1540 nm)].

Synthesis of copper tetranitrophthalocyanine (denoted as CuTNPc)

To praper CuTNPc, 12.0 g copper sulfate pentahydrate, 37.0 g 4-nitrophthalic acid, 4.5 g ammonium chloride, 0.5 g ammonium molybdate and urea (60 g) were finely ground and transferred to a 500 cm^3 three-nacked flask containing 25 cm^3 of nitrobenzene. The temperature of the stirred reaction mixture was slowly heatead at 185°C and maintained at 185-190 ^{o}C for 4.5 h. The solid product was finely ground and washed with alcohol until excess of nitrobenzene was removed. The product was added to 500 mL 1.0 N sodium hydroxide containing 200 g sodium chloride and heated at 90°C until the the evolution of ammonia ceased. The solid product was filtered and then was treated with 1N hydrochloric acid and separated by centrifugation. Alternate treatment with hydrochloric acid and sodium hydroxide was repeated twice. The copper 4, 9, 16, 23-tetranitrophthalocyanine was washed with water until the excess chloride was removed [22]. The blue complex was dried at 125° C. Anal. for copper(II) tetraamino phthalocyanine, $C_{32}H_{12}N_{12}O_8Cu$: Calc. C, 50.83; H, 1.59; N, 22.33; Cu,8.40. Found: C, 51.38; H, 1.73; N, 22.80 [22, 23].

Synthesis of copper tetraaminophthalocyanine (denoted as CuTAPc)

Synthesis of copper 4, 9, 16, 23-tetraaminophthalocyanine 2 hydrate was according to the previous report [22, 23]. In briefly; About 10 g of finely ground copper 4, 9, 16, 23- tetranitrophthalocyanine powder was placed in 250 cm^3 water, after that 50 g of sodium sulfide nonahydrate was added subsequently and stirred at 50 ^{o} C for 5h. The solid product was separated by centrifuging the reaction mixture and treated with 750 mL of 1 N hydrochloric acid. The blue solid of copper tetraaminophthalocyanine hydrochloride was separated by centrifugation, after that 500 mL of sodium hydroxide (1 N) was added, stirred for 1h and centrifuged to separate the dark green solid compound. The product was washed with water, stirred and centrifuged for the removal of excess sodium hydroxide and sodium chloride. The obtained dark green CuTNPc was dried in vacuo over P_2O_5. Anal. For copper(II) tetraamino phthalocyanine, $C_{32}H_{18}N_{16}O_8Cu$: Calc. C, 57.5; H, 3.6; N, 24.9; Cu,9.80. Found: C, 57.18; H, 3.63; N, 25.03; Cu, 9.63.

Synthesis of supported catalyst (denoted as CuTAP @polyvinylchloride)

Praparation of CuTAP immobilized on polyvinylchloride was performed under reflux condition. Polyvinylchloride (1 g) was dispersed in 20 ml DMSO by ultrasonic irradiation for 30 min. A solution of Tetraamino-copper-phthalocyanine (0.1 g, in 10 ml DMSO) was dispersed in DMSO and

was added dropwise to the above solution. Then, the mixture was heated at 60°C for 12 h. The mixture was dried under vaccum at 100°c, then the obtained solid was washed with water.

Result and discussion

Characterization

The synthesized catalyst was finaly ground to powder and was characterized using the FT-IR, XRD, and SEM. IR spectra of tetranitrophthalocyanine and tetraaminophthalocyanine following same vibrational peaks for basic skeleton of phthalocyanines [22]. Fig.1 shows absorption bands around 1121-1123, 1090-1092, 1067-1070, 947-949, and 872-885 and 754 cm^{-1} are subjected to skeletal vibrational modes of phthalocyanines compounds. The bands at 1420-1424, 1335 cm^{-1} showed phenyl rings. The bands at 1286, 1226, 1202-1210 cm^{-1} are related to C-N band. The supported catalyst showed absorption bands at 1165-67, 1001-1005 cm^{-1}, the peaks could be attributed to C-H in plane bending vibration. The peaks subjected to C-N bending are observed at 901 and 799-802 cm^{-1}, respectively. The peaks observed at 770-773 cm^{-1} regions are related to C-H out of plane bending. The intense peaks observed at 1610-1616 were related to C=C, C=N and ring stretching. The peak at 1525 related to nitro group in tetranitrophthalocyanine. The bands around 1097 and 1133cm^{-1} are related to Cu-N bands.The peaks at 3182-3485 cm^{-1} in CuTAP spectrum related to amino groups,in addition the sharp absorption bands are appeared at around 1608 cm^{-1} due to the $-NH_2$ in plane bending vibrations modes. So it confirms the formation of CuTAP [22, 23]. The peak for amino groups of CuTAP shifted to lower wavenumber at 3396 cm^{-1} due to linked amino groups in phthalocyanine to polymer and confirmed that the tetraamino phthalocyanine supported on polymer, in addition the peaks discussed above related to skeleton of phthalocyanines are observed after supporting and confirmed the stability of catalyst structure.

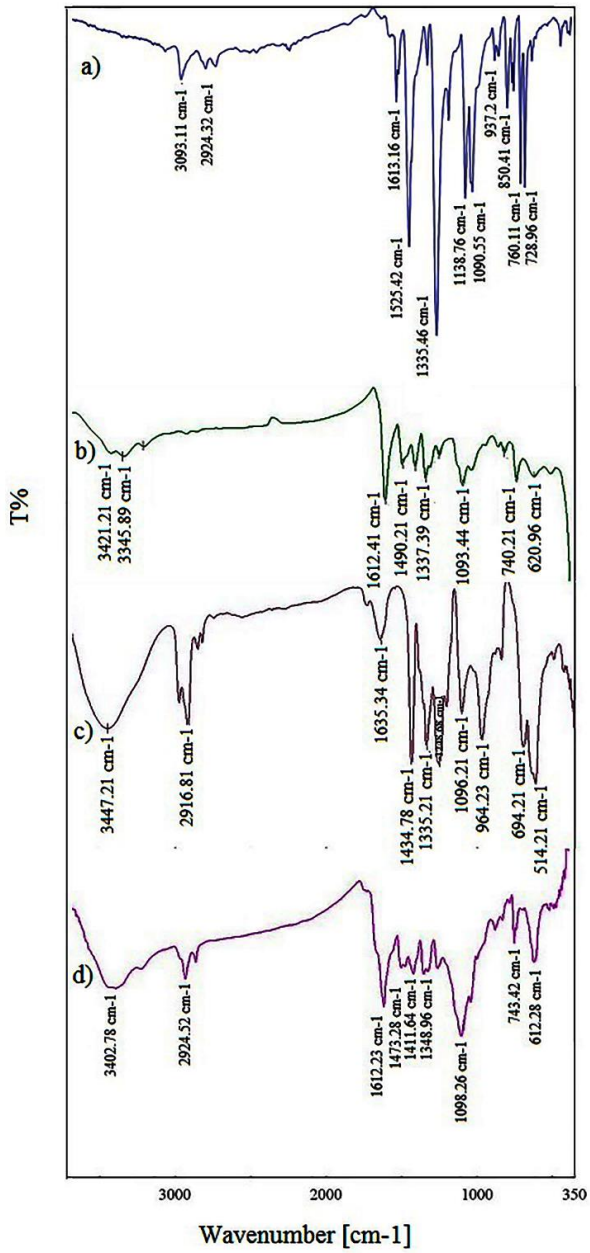
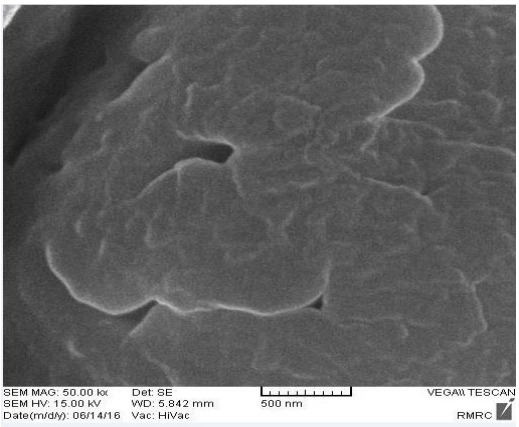
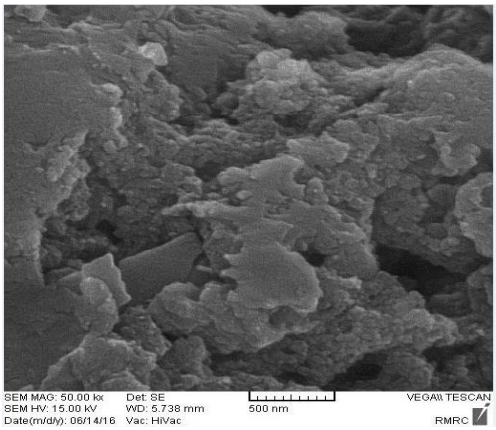


Figure 1. FT IR spectrum of a)CuTNP, b) CuTAP, c) polyvinylcholoride, d) polyvinyl choloride joined phthalocyanin

The morphology of polymer-phthalocyanine composite is shown in Fig. 2. An obvious change in the morphology of polyvinylchloride confirmed that the phthalocyanine has been supported on polyvinyl chloride. The supporting procedure led to the disappear smoother and compressed surface than that of intact polymer. For the supported catalyst the average diameter of particles

was estimated to be 52.4 nm by averaging its diameters measured in several directions in the SEM images.





a) **b)**

Figure 2. SEM spectra of a) polyvinylchloride and b) polyvinyl chloride joined phthalocyanine.

Unlike metal, reduction of the phthalocyanine ring manifests with the formation of new bands between 500 and 600 nm and absorption of the original bands, characteristic for MPc^{2-}, are significantly weaker. The phthalocyanine unit is able to gain up to four electrons and hence formation of MPc^{6-} takes place. Oxidation occurs through removal of one or two electrons from the HOMO. Intensity is lost and a new broad band formation between 700 and 800 nm and another at 500 nm is observed. By making use of spectroelectrochemistry it can be judge whether redox process occurs on the metal or on the Pc unit. Fig 3a shows that the formation of CuTNP and CuTAP were confirmed with UV–vis in H_2SO_4 (15 M), that band with highest intensity in range of 500-800 nm related to Q band, which intense color of phthalocyanine subjected to this band, and with lowest intensity due to B band. For tetraaminophthalocyanine the soret band (B band) shifted to longer wavelength due to reduction of nitro groups to amino groups. In addition UV–vis has been also applied for characterize the optical properties of the Pc –Polymer composite. Preparation of supported catalyst was confirmed using UV–vis in DMF. Fig 3b shows electronic spectrum of composite with a broad and intense absorptive band in the range from 500 to 800 nm with splitting in the observed band due to non semitrical positions of amino groups on phenyl rings in supported phthalocyanine. As shown in Fig 3b after formation of the Pc-Polymer composite the Q band due to $\pi \ldots \pi^*$ transitions present in the uv spectrum of composite in DMF with red shift due to immobilization of phthalocyanine on the surface of polymer. The outstanding photocatalytic activity of this composite related to the existence of this broad band.

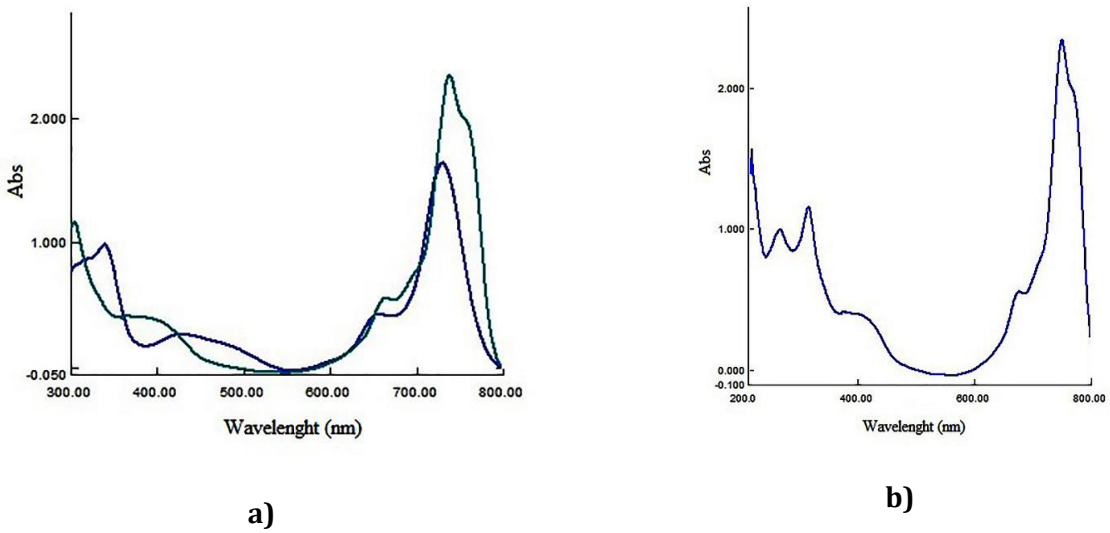


Figure 3. Uv-vis spectra of CuTNP (blue line) and CuTAP (green line), b) Pc –Polymer

Figure 4 shows that XRD patterns of the polyvinylcholoride and CuTAPc powders are essentially the same but differ slightly from that of the synthesized CuTAPc@PVC. Immobilization of phthalocyanine on the surface of polyvinylcholoride led to change in the powder XRD pattern when campared with that for polyvinyl choloride. The XRD patterns of the PVC and CuTAPc powders are essentially the same but differ slightly from that of the synthesized catalyst. Confirmed that the formation of a new material and a possible change in crystallinity and interplanar space. The average particle size of supported catalyst powder was calculated from XRD line broadening, using the Debye–Scherer equation, $D= (0.89\lambda)/(\beta_{1/2}\cos\Theta)$, where λ is the wavelength of Cu λ^{a} radiation, $\beta_{1/2}$ is the full width at half maximum (FWHM) and Θ is the Bragg angle. The average particle size calculated was about 52 nm, which was in accordance with the SEM observations.

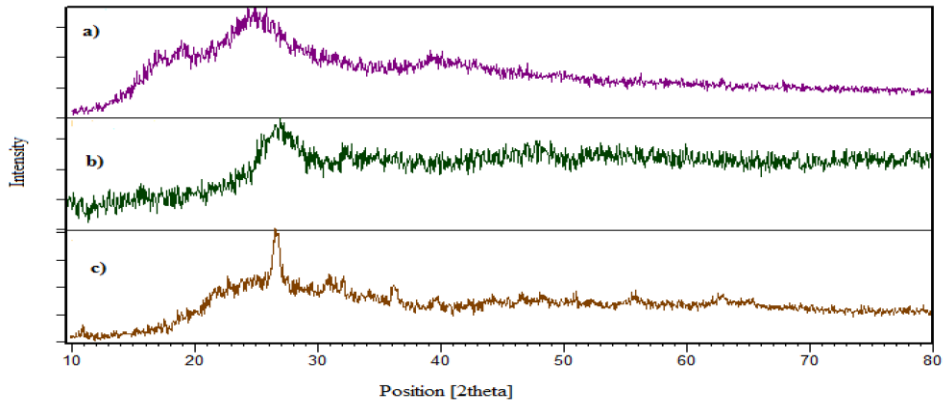


Figure 4. XRD patterns of a) polyvinylcholoride b) CuTAPc c) CuTAPc supported polyvinylcholoride.

Degradation of methyl orange

Methyl orange

Methyl orange was selected as model dye for consideration of photocatalytic degradation of dyes as pollutants. Methyl orange is a pH indicator frequently used in titrations due to its distinct and clear color changes. Because it changes color at the pH of a midstrength acid, it is usually used in titrations for acids. Unlike a universal indicator, methyl orange does not have a full spectrum of colour change, but has a sharper end point. Methyl orange shows red colour in acidic medium and yellow colour in basic medium. The structure of methyl orange and the related UV-vis spectrum of methyl orange was shown in Fig. 5. The characteristic peak for methyl orange observed at 464 nm.

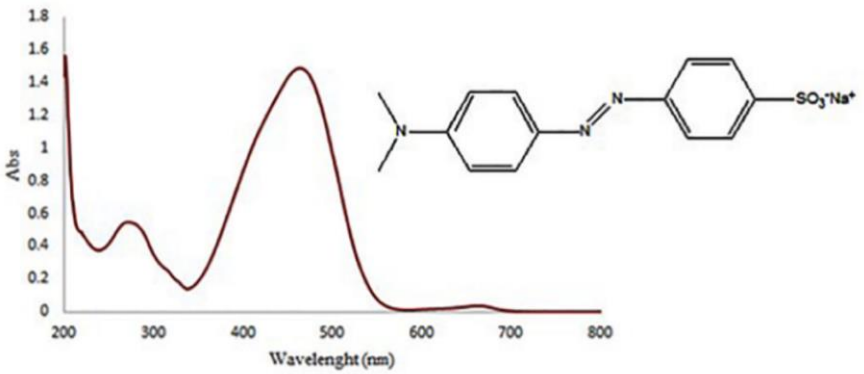


Figure 5.UV-vis spectrum of methyl orange (MO).

The photocatalytic reaction was carried out under different experimental conditions, using different amounts of catalyst. Photodegradation of methyl orange was done under visible light.. Accordingly, dye degradation was studied at various pHs as one of the important factors. It was revealed that the degradation of methyl orange was 95.50% at pH=5.34. For considering the effects of phthalocyanine in promote the photo catalytic activity of polyvinylchloride, all reactions were repeated under the same reaction conditions using polyvinylchloride as photo catalyst. For investigation of phthalocyanine effect on the photocatalytic reaction the experiment was performed with polyvinylcholoride as catalyst. The result showed that even up to 150 min the degradation was negligible in the presence of polyvinylcholoride as catalyst and confirmed that the photo catalytic activity of PVC has increased by supporting of phthalocyanine (Figure 6).

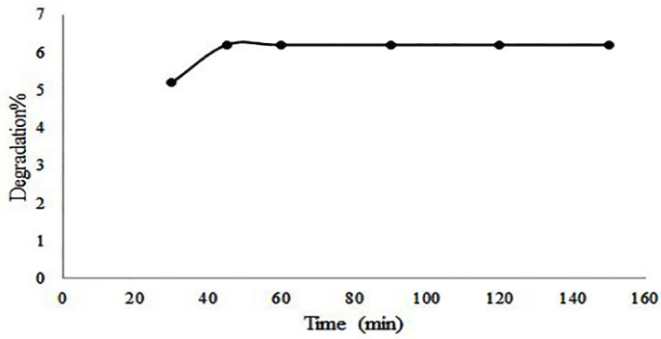


Figure 6. Degradation of a) aqueous solution of MO by visible light with polyvinylcholoride as catalyst under visible light after 150 min.

Effect of various factors on the photocatalytic degradation of methyl orange

The photocatalytic reaction was performed under different experimental conditions, using different amounts of catalyst, various pH, different intensity of ultrasonic irradiation and different initial concentration of methyl orange for investigation of photocatalytic reactions; this were done without irradiation, and the pH conditions were changed from acidic to basic. Methyl orange as selected dye had absorption in the visible region at 464 nm in water, so the spectrum changes was investigated at maximum wavelength at 464 nm. In addition Blank reactions: a) with visible light but without catalyst; b) with catalyst but without light were performed for the conditions was studied. Conversion values obtained in the blank reactions were in the range of 5 - 11%.

Effect of pH on photocatalytic degradation of methyl orange

Dye degradation was studied at different pHs as one of the main factors in photocatalytic procedures. The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles. First, is related to the ionization state of the surface according to the following reactions, as well as to that of reactant dyes and products such as acids and amines. The pH conditions were changed from acidic to basic. pH changes can be thus influence the adsorption of dye molecules onto the modified polymer surfaces, an important step for the photocatalytic oxidation to take place. The wastewater from 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 hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dyes. In this study the pH based on experiments was changed at 2.3 to 10.7 and optimized pH was obtained at 5.1 (Fig. 7). These results might be due to the fact that it was much easier for copper phthalocyanine to lose electrons under acidic media, and thus its photocatalytic performences would improve.

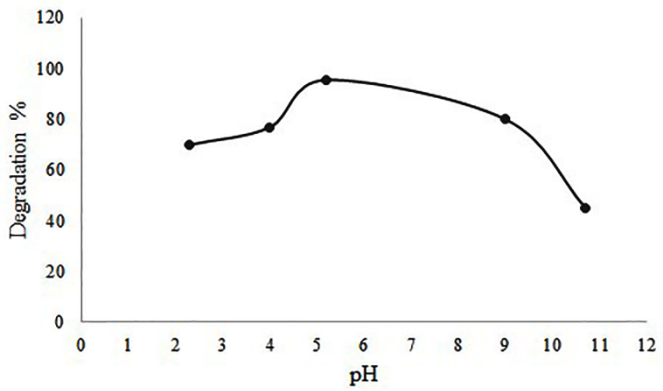


Figure 7. Effect of pH on photocatalytic degradation of methyl orange, C_o=60 ppm, Time=90 min.

Effect of catalyst amount on photocatalytic degradation of methyl orange

It was found that the Optimum amount of the catalyst for visible induced photocatalytic degradation of methyl orange was around 11 mg of the synthesized catalyst which was made for 30 mL of the methyl orange solution and initial concentration C_0=60 ppm. The rate of dye degradation was increased with enhancing the amount of catalyst. This could be due to the increase in the exposed surface area of the catalyst. However, it must be noted that after a certain limit (11 mg), if the amount of catalyst had been increased further, there would have been a saturation point. Both the number of active sites on photocatalyst and the penetration of light through the suspension are affected by the amount of photocatalyst. The increase in the loading of photocatalyst can increase the rate of the deactivation of activated molecules by collision with the ground state photocatalyst (Figure 8).

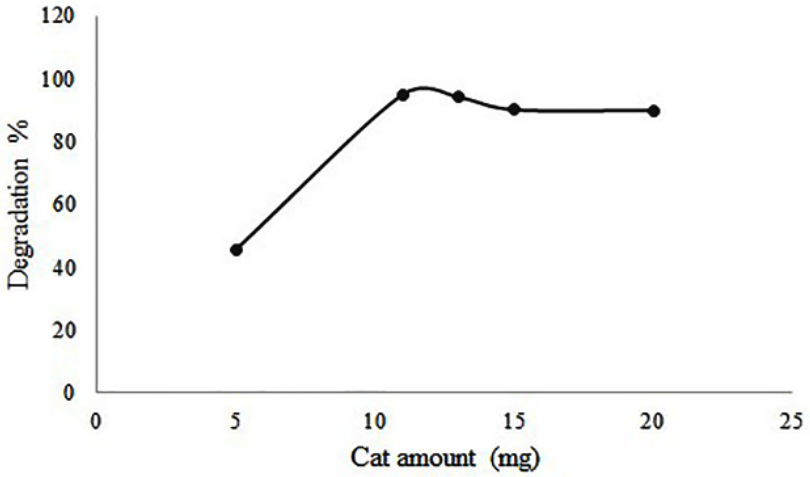


Figure 8. Effect of catalyst amount on photocatalytic degradation of methyl orange, pH=5.1

Effect of time on photocatalytic degradation of methyl orange

In addition the influence of time on the degradation of methyl orange was examined for 10 min up to 45 min based on experiments and the results showed that with increasing the time the degradation was increased but after 90 min the degradation was nearly constant, so the optimized time was 90 min (Fig. 9). It should be noted after 90 min no clear change in degradation was observed, so the optimized time was 90 min.

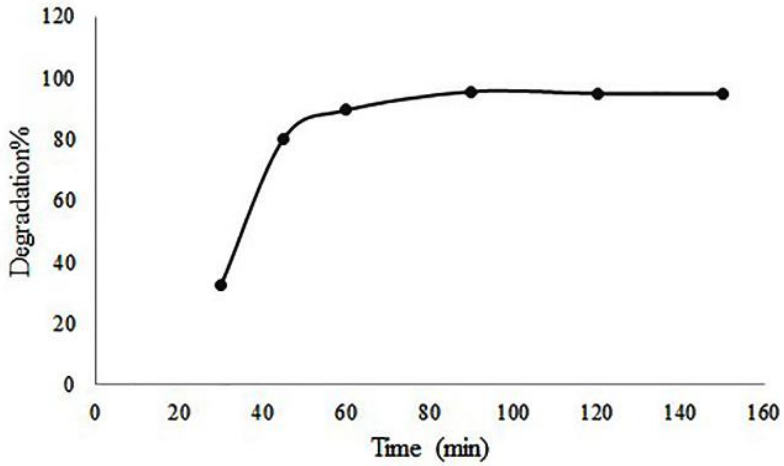


Figure 9. Effect of time on photocatalytic degradation of methyl orange, C_o=60 ppm, Time= x min, pH=5.1.

Effect of light irradiation on photocatalytic degradation of methyl orange

For investigation of light irradiation effect on the photocatalytic reaction the experiment was performed with catalyst but without irradiation of light. The result showed that even up to 120 min the degradation was negligible in dark condition (Figure 10).

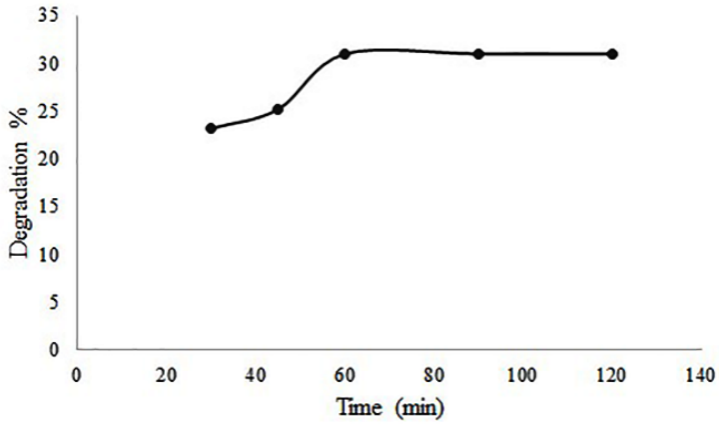


Figure 10. Degradation of methyl orange with supported catalyst in dark condition, C_o=60 ppm, pH=5.1.

Catalytic behavior, separation, and recyclability

The stability of the supported catalyst was monitored using multiple sequential degradation of dyes with synthesized catalyst under visible light. For each of the repeated reactions, the catalyst was reused, washed four times with water and dried before being used with fresh methylene blue solution. Figure 11 shows that the catalysts were consecutively reused five cycles. The catalyst was reused for five runs and loss of activity was negligible. For investigation of the catalyst was intact after photo catalytic reaction the FT-IR spectrum of catalyst after reused was taken and the result showed the peaks at 1081 cm $^{-1}$, 1344 cm $^{-1}$, 1470 cm $^{-1}$, 2912 cm $^{-1}$, 3375 cm $^{-1}$ and 1610 cm $^{-1}$ corresponding to the supported catalyst was remained after reused with shift due to adsorption procedure (Figure 12).

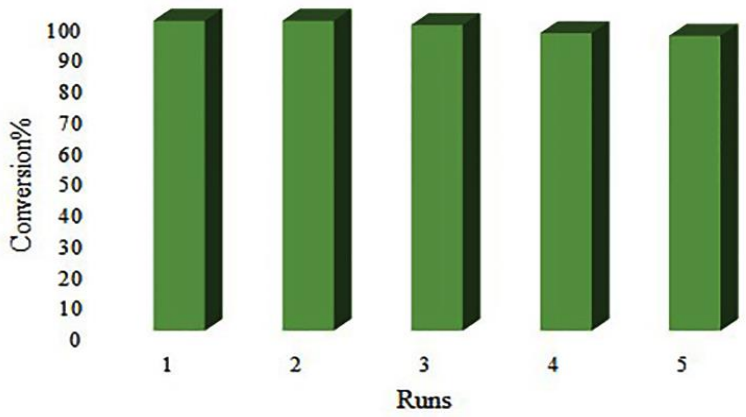


Figure 11. Reusability of catalyst in degradation of MO with synthesized catalyst

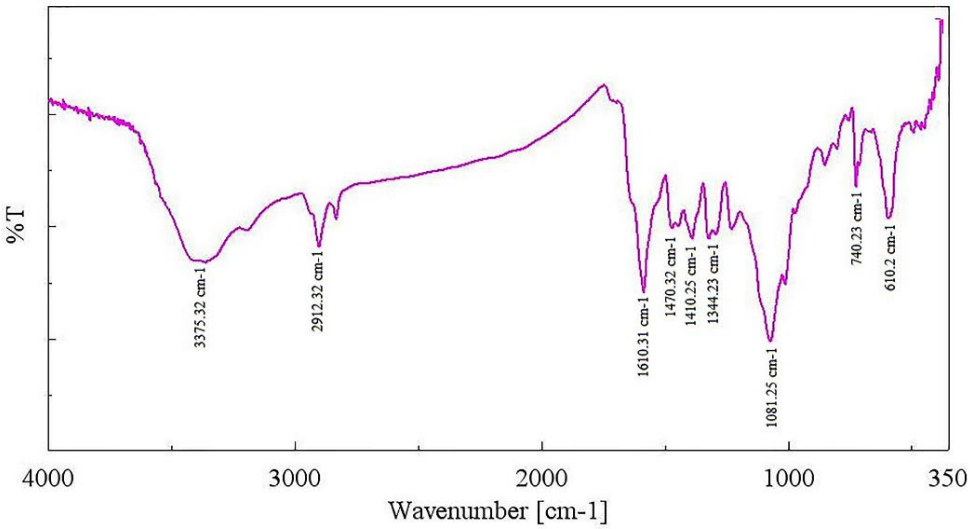


Figure 12. FT-IR spectrum of reused catalyst after degradation of MO

Proposed mechanism for degradation of methyl orange under visible light

Many researchers have proposed different mechanisms for the degradation of dyes as pollutants. To exposure to visible light irradiation, the supported catalyst contain metal ions probably excited by light to give exited electron. This excited state will provide an electron in the conduction band leaving a hole in the valance band. This electron is finally trapped by molecular O_2 forming O_2^- ions. The valance band hole creats hydroxyl radical from hydroxyl ions which can attack the adsorbed dye easily, so leading to their complete mineralization finally. Scheme 4 suggests the photocatalytic degradation pathways. In addition proposed mechanism for excitation of electron in degradation of MO by supported catalyst was shown in Figure 13 and Figure 14.

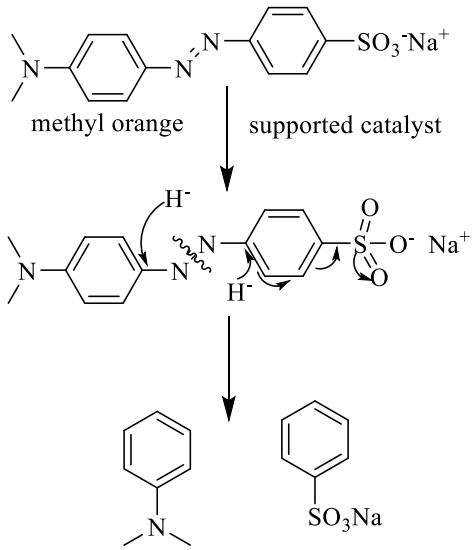


Figure 13. Proposed mechanism for degradation of MO by supported catalyst

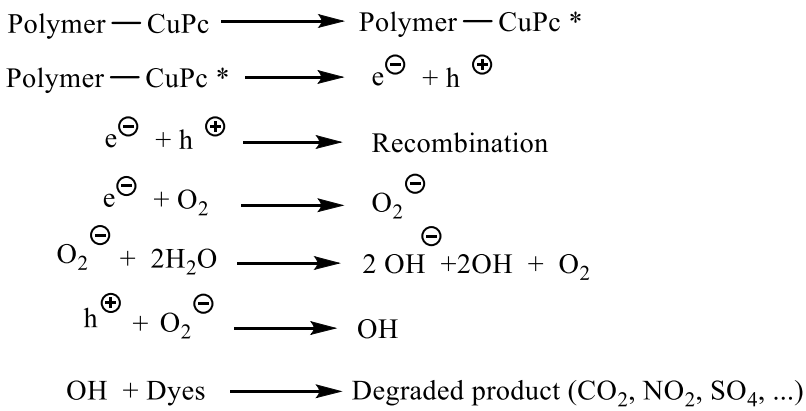


Figure 14. Proposed mechanism for excitation of electron in degradation of MO by supported catalyst

Table 1. Compares the photocatalytic activity of the supported catalyst with those of other reported catalysts for the degradation of dyes.

Table 1. Comparison of reaction data for the present method in degradation of dyes and other reported methods.

Catalyst	Degradation %	Ref
HPW@PPy	Methyl orange	This work
CoPc@Fiber	Acid Orange II	24
CoPc@Chitosan	Acid Red 73	25
Phthalocyanines	Naphthol blue black	26
Pc@Hydrotalcites	Rhodamine B	27

Conclusion

The catalyst was prapared by immobilization of tetraaminophthalocyanine on polyvinylcholoride. The catalyst was successfully used in the degradation of dyes as pollutants under visiblelight. This catalyst showed excellent photocatalytic activity and could, therefore, be reused at least four times, with only a slight decrease in catalytic activity. In addition, this catalyst could be easily separated at the end of the reaction by centrifuged.

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References

[1] Park J.H., Allen M.G., Prausnitz M.R. *J Controll. Rel.,* 2005, **104**:51

[2] Jawahar N., Meyyanathan S.N. *Int. J. Health. Allied. Sci*., 2012, **1**:217

[3] Hassani L., Hakimian F., Safaei E., Fazeli Z *J. Mol. Struc.,* 2013, **1052**:221

[4] Nackiewicz J., Kliber M. *Arkivoc.* 2015, **i**:269

[5] Colak S., Yildiz S.Z. *Turk. J. Chem*., 2014, **38**:1153

[6] Lukyanets E.A., Nemykin V.N. *J. Porphy. Phthalocy*., 2010, **14**:1

[7] Spikes J.D. Photochem. Photobiol*.,* 1986, **43**:691

[8] Danziger J., Dodelet J.P., Lee P., Nebesny K.W. *Chem. Mat*., 1991, **3**:821

[9] De Boni L., Piovesan E., Gaffo L., Mendonca C.R. *J. Phy. Chem*., 2008, **112**:6803

[10] Topal S.Z., Isci U., Kumru U., Atilla D., Gurek A.G, Hirel C., Durmu M., Tommasion J.B., Luneau D., Berber S., Dumoulin F., Ahsen V. *Dalton. Transac*., 2014, **43**:6897

[11] Wohrle D., Schlettwein D., Kirschenmann M., Kaneko M., Yamada A. *J. Macromol. Sci. Chem*., 1990, **27**:1239

[12] Wenxing C., Wangyang L., Yuyuan Y. *Environ. Sci. Technol.,* 2007, **41**:6240

[13] Esther F. *Environ. Int*., 2004, **30**:953

[14] Giuseppe M., Roberta D., Giuseppe V. *j. Catal*., 2003, **217**:334

[15] Liechty W.B., Kryscio D.R., Slaughter B.V., Peppas N.A., *Annual. Rev. Chem. Biomol. Engin.,* 2010*,* **1**:149

[16] Yang W., Pierstorff E. *J. Lab. Aut*., 2012, **17**:50

[17] Haibin J., Shuliang L., Xiaohong Z. *Mol.,* 2016, **21**:833

[18] Salvo A.M.P, Giacalone F., Gruttadauria M.. *Mol*., 2016, **21**:1288

[19] Leng Y., Zhao J., Jiang P., Wang. J. *ACS. Appl. Mat. Inter.,* 2014, **6**:5947

[20] Leng Y., Wu J., Jiang P., Wang J. *Catal. Sci. Technol.,* 2014, **4**:1293

[21] Juliana S., Souza Mauricio V.B. *J. Phys. Chem. C.,* 2016, **120:**11561

[22] Achar B.N., Lokesh K.S. *J. Solid. State. Chem*., 2004, **177**:1987

[23] Achar B.N., Lokesh K.S. *J. Org. Chem*., 2004, **689**:3357

[24] Wang T., Li Y., Qu G., Liang D., Hu Sh. *Water Air Soil Pollut.* 2016, **227**:464

[25] Shen Ch., Song Sh., Zang L., Kang X., Wen Y., Liu W., Fu L., *J. Hazard. Mat*., 2010, **177**:560

[26] Borker P., Salker V. *Ind. J. Chem. Technol*., 2006, **13**:341

[27] Xu M., Zhu M., *Key. Engin. Mat*., 2014, **515**:575

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