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Research Article

Novel Fe(II) phthalocyanine complexes for TiO_2 sensitization

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Photocatalytic degradation, 4-chlorophenol, iron phthalocyanine, phthalocyanine/TiO_2 composite, H_2O_2.

ABSTRACT

A group of novel azo-bridged phenolic iron(II) phtalocyanine (Fe(II)Pcs) derivatives which have peripheral or non-peripheral substitution on macrocyclic ring were produced and characterized employing various spectroscopic methods. Peripheral or nonperipheral substituted Fe(II)Pc molecules (defined as Fe(II)Pc-1, Fe(II)Pc-2, Fe(II)Pc-3, Fe(II)Pc-4) were used for sensitization of TiO_2 nanopowder to prepare photoactive composite catalysts (Fe(II)Pc/TiO_2, 1% of the mass of TiO_2) using wet deposition method. The as-obtained composite materials were characterized by SEM, EDX, UV-Vis DRS and XRD. The results revealed that the Fe(II)Pc derivatives were successfully immobilized on TiO_2 and the anatase crystalline phase have absorption in the visible light region. Fe(II)Pc sensitized catalysts were tested for the photocatalytic removal of 4-chlorophenol (4-CP) in the presence of H_2O_2. Photocatalytic experiments showed that the H_2O_2 assisted Fe(II)Pc/TiO_2 composites achieved high degradation of 4-chlorophenol except for Fe(II)Pc-4/TiO_2. The photocatalytic efficiencies of the catalysts follow the order: Fe(II)Pc-3/TiO_2 (93.21%) > Fe(II)Pc-1/TiO_2 (87.61%) > Fe(II)Pc-2/TiO_2 (83.86%) > TiO_2 (67.74%) > Fe(II)Pc-4/TiO_2 (64.71%).

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TiO_2 duyarlaştırılması için yeni Fe(II) ftalosiyanin kompleksleri

Anahtar Kelimeler:
Fotokatalitik uzaklaştırma, 4-klorofenol, demir ftalosiyanin, ftalosiyanin/TiO_2 kompozit, H_2O_2.

ÖZET

Yeni bir grup makrosiklik halkaya periferal veya periferal olmayan substitusyon içeren azo-köprülü fenolik demir (II) ftalosiyanin türevleri sentezlendi ve çeşitli spektroskopik yöntemler kullanılarak karakterizasyon çalışmaları yapıldı. Islak biriktirme yöntemi kullanılarak fotoaktif komposit katalizörler (Fe(II)Pc/TiO_2, TiO_2'in kütlece % 1) hazırlamak için TiO_2 nanotozunun duyarlaştırılmasında periferal veya periferal olmayan substitue Fe(II)Pc molekülleri (Fe(II)Pc-1, Fe(II)Pc-2, Fe(II)Pc-3, Fe(II)Pc-4 olarak tanımlandı) kullanıldı. Elde edilen kompozit materyallerin SEM, EDX, UV-Vis DRS ve XRD teknikleri ile karakterizyon çalışmaları yapıldı. Sonuçlara göre Fe(II)Pc türevleri TiO_2 yüzeyine başarılı bir şekilde yüklendiği ve anataz kristal faz görünür bölge ışınlarında absorpsiyon yaptığı görüldü. Fe(II)Pc ile duyarlaştırılmış katalizörler H_2O_2'nin varlığında 4-klorofenolün fotokatalitik uzaklaştırılması test edildi. Fotokatalitik çalışmalara göre H_2O_2 varlığında Fe(II)Pc-4/TiO_2 kompozit materyalinin dışında diğer Fe(II)Pc/TiO_2 kompositlerle, yüksek bir verim elde edidiği görülmüştür. Katalizörlerin fotokatalitik verimleri sıralaması Fe(II)Pc-3/TiO_2 (% 93,21) > Fe(II)Pc-1/TiO_2 (% 87,61) > Fe(II)Pc-2/TiO_2 (% 83,86) > TiO_2 (% 67,74) > Fe(II)Pc-4/TiO_2 (% 64,71) şeklindedir.

1. Introduction

In general, chlorinated phenolic compounds (CPs) are considered to be common priority recalcitrant organic pollutants in wastewater due to their non-biodegradable character and toxic (even at low concentrations) impacts on human health and the ecosystem [1]. These pollutant compounds are generated from waste solutions in chemical industry processes and agricultural productions [2]. 4-chlorophenol, in particular, has been recognized as a representative model of priority toxic compound in water due to its high solubility and ability to bioaccumulate in organisms [3]. Many different biological and chemical wastewater treatment methods have been used to remove chlorophenols. Recently, advanced oxidation processes (AOPs) are one of the most effective chemical methods for decomposing 4-CP pollutants from wastewater [4]. The AOPs can be categorized depending on usage of photocatalyst as homogeneous or heterogeneous process. The homogeneous process is commonly known as photo-Fenton, which requires interaction between iron ions and hydrogen peroxide (H_2O_2) under irradiation [5]. However, due to the complicated separation of iron ions from the reaction medium, its practical and economical application appears to be difficult so far. Consequently, there has been increased interest in immobilization of iron ions on a surface or another compound.

Heterogeneous photocatalytic degradation process using TiO_2 as photocatalyst has been stated as an effective method due to the advantages over other AOPs, such as rapid degradation of organic pollutants to form CO_2, water and mineral acids without generating harmful by-products and operation under ambient temperature/ pressure [6,7]. Photocatalytic degradation involves the irradiation of TiO_2 particles with appropriate energy that is equal to or greater than its band gap, and results in the formation of electrons in the conduction band (e^-_{CB}) and positive holes in the valence band (h^+_{VB}), as well as the formation of ·OH radicals. These charge carriers react with the adsorbed substrates (H_2O/OH^- and O_2) and generate highly reactive hydroxy radical (·OH) and superoxide radical ($O_2^{\cdot -}$) [8]. These highly reactive species (h^+, ·OH and $O_2^{\cdot -}$) oxidize organic pollutants on the TiO_2 surface, and eventually decompose them to CO_2, H_2O and inorganic ions [9,10].

Titanium dioxide has been widely studied as a photocatalyst because of its non-toxic, green, low cost nature. However, the photocatalytic activity of TiO_2 for pollutant degradation is usually

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very low due to the high recombination rate of electron-hole pairs and low absorption in visible region [11-13]. Up to now, many methods have been developed to overcome these drawbacks, such as doping ions, coupling of TiO_2 with other semiconductor particles and dye sensitization of TiO_2 [14-17]. Among these strategies, using a dye photosensitizer can both enhance the separation efficiency of electron-hole pairs and increase the photocatalytic activity [18]. Another effective approach for inhibiting the recombination of photogenerated charge carriers and enhancing the photocatalytic degradation of the organic pollutants that are resistant to degradation is the usage of strong chemical oxidants such as $S_2O_8^{2-}$ and H_2O_2 [19]. The addition of H_2O_2 to the photocatalytic degradation process plays an important role in accelerating the oxidative degradation of phenolic compounds in water by effectively forming hydroxyl radicals that are critical oxidants for the destruction of organic pollutants during the photochemical reactions [20].

It is known that phthalocyanines (Pc) are good sensitizers. Phthalocyanines (Pcs) and their metal derivatives (MPcs) are a kind of organic semiconductors that possess strong absorption in visible region as well as excellent photochemical and thermal stability. Pcs have attracted significant attention in different scientific and technological areas including catalysis, chemical sensors, solar energy conversions and photosensitizers [21-23]. Many reports have been published related to the photocatalytic performance of TiO_2 enhanced by organic-inorganic hybrid composites employing Pcs [18, 24,25]. Combination of Pc sensitized TiO_2 nanocomposite and H_2O_2 is a new approach and only a few studies have been concerned with H_2O_2 assisted Pcs sensitized TiO_2 for photocataytic degradation of organic pollutants. This approach combines both features of photo-Fenton (as Fe(II)/H_2O_2/UV) and dye sensitized TiO_2 (as Pc/TiO_2/UV). Ranjit et al. [26] reported that Fe(III) phthalocyanine modified TiO_2 (prepared by a sol-gel method) had enhanced activity for the degradation of organic pollutants (*p*-aminobenzoic acid, *p*-nitrobenzoic acid, *p*-chlorophenoxyacetic acid, salicylic acid and aniline) as compared to bare TiO_2. The hybrid composite of Fe(II)Pc and TiO_2 nanostructure has been intensively investigated, in particular, for the cooperative functions of the two components of the photocatalyst, Fe(II)Pc and TiO_2 in the generation of ·OH radicals. In this case a Fe(II)Pc derivative has been used for the sensitization.

As it is well known, phthalocyanine derivatives are not easily dissolved in water due to their nonpolar character. A typical Pc molecule contains peripheral, nonperipheral and axial positions. New Pc derivatives can be synthesized containing polar functional groups such as carboxyl, sulfoxyl and nitro on those positions. As a result of this substitution, polar character of Pc derivative is increased leading to better attachment of dye on TiO_2 surface. A good example of this improvement has been reported recently. Guo et al. [27] reported the improvement of methyl orange photodegradation under visible light radiation using H_2O_2 assisted Pc sensitized TiO_2. They have used a one-dimensional 2,9,16,23-tetranitrophthalocyanine iron(III) derivative for immobilization on TiO_2 nanofiber heterostructures.

In this paper, we have synthesized a group of Fe(II)phthalocyanine derivatives containing azobridged phenolic functional groups on non-peripheral and peripheral positions. These substitutions were first time synthesized by our group and specially designed to increase the polarity of the dye for better attachment on TiO_2. Non-peripheral positioned Fe(II) phthalocyanines were defined as Fe(II)Pc-1 and Fe(II)Pc-2 and peripheral positioned ones were Fe(II)Pc-3 and Fe(II)-Pc-4 (Scheme).

Substituted Fe(II) phthalocyanines were incorporated to TiO_2 using wet deposition method to produce dye sensitized photocatalysts (Fe(II)Pc-1/TiO_2, Fe(II)Pc-2/TiO_2, Fe(II)Pc-3/TiO_2 and Fe(II)Pc-4/TiO_2). The main target of this study is to produce effective hybrid catalysts that have both features of photo-Fenton and dye sensitization of TiO_2. Photo-Fenton character of the catalyst was provided by hydrogen peroxide and Fe(II) ions located in phthalocyanine complex. On the other hand Fe(II)Pc was expected to enhance the photocatalytic action of the catalyst. Photocatalytic ability of produced catalysts were measured for the degradation of 4-chlorophenol as model pollutant.

2. Experimental

2.1. Materials and reagents

All chemical reactions were performed under oxygen-free, dry nitrogen medium. 1,8-Diazabycyclo[5.4.0]undec-7-ene (DBU), 4- and 3-nitrophthalonitrile were bought from Sigma-Aldrich. All solvents were dried and purified according to Perrin and Armarego's methods [28]. Experimental details of starting compounds, substituted phthalonitriles **(1-4)** [29], Fe(II)Pc-1 and Fe(II)Pc-2 have been described previously [30]. Production and structural evaluation of peripheral positioned Fe(II)Pc-3 and Fe(II)Pc-4 derivatives were performed in this study. All of the reagents were analytical grade and used without further purification. TiO_2 nanopowder (anatase) with average particle size about 44 nm was purchased from Sigma-Aldrich (Darmstadt, Germany). 4-Chlorophenol and H_2O_2 were also obtained from Sigma-Aldrich, and all solutions were prepared with deionized and ultrapure water.

2.2. Equipments

Mass spectral analyses were performed with a Micromass Quattro LC/ULTIMA LC-MS/MS spectrometer in positive ion mode using chloforom–methanol as solvent system. FTIR spectra were recorded on a Perkin–Elmer Spectrum One FTIR spectrometer. Melting points were measured on an electrothermal apparatus and are uncorrected. UV-Vis spectra were recorded with a Shimadzu 2101 UV-Vis spectrophotometer.

The morphology analyses of prepared samples were performed on a ZEISS EVO LS-10 scanning electron microscope (SEM). Energy dispersive X-ray (EDX) analysis was done with the same instrument to determine the composition of the composites. The UV-Vis diffuse reflectance spectroscopy (DRS) of the samples was recorded on Shimadzu UV-3600 UV-vis NIR spectrophotometer. X-ray diffraction (XRD) measurement was carried out using A Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=0.1541 nm) over the range 2θ=20-60°) at room temperature. 4-CP and its intermediates were identified and quantified by HPLC (HITACHI, Japan).

2.3. Synthesis and characterization of Fe(II)Pc derivatives

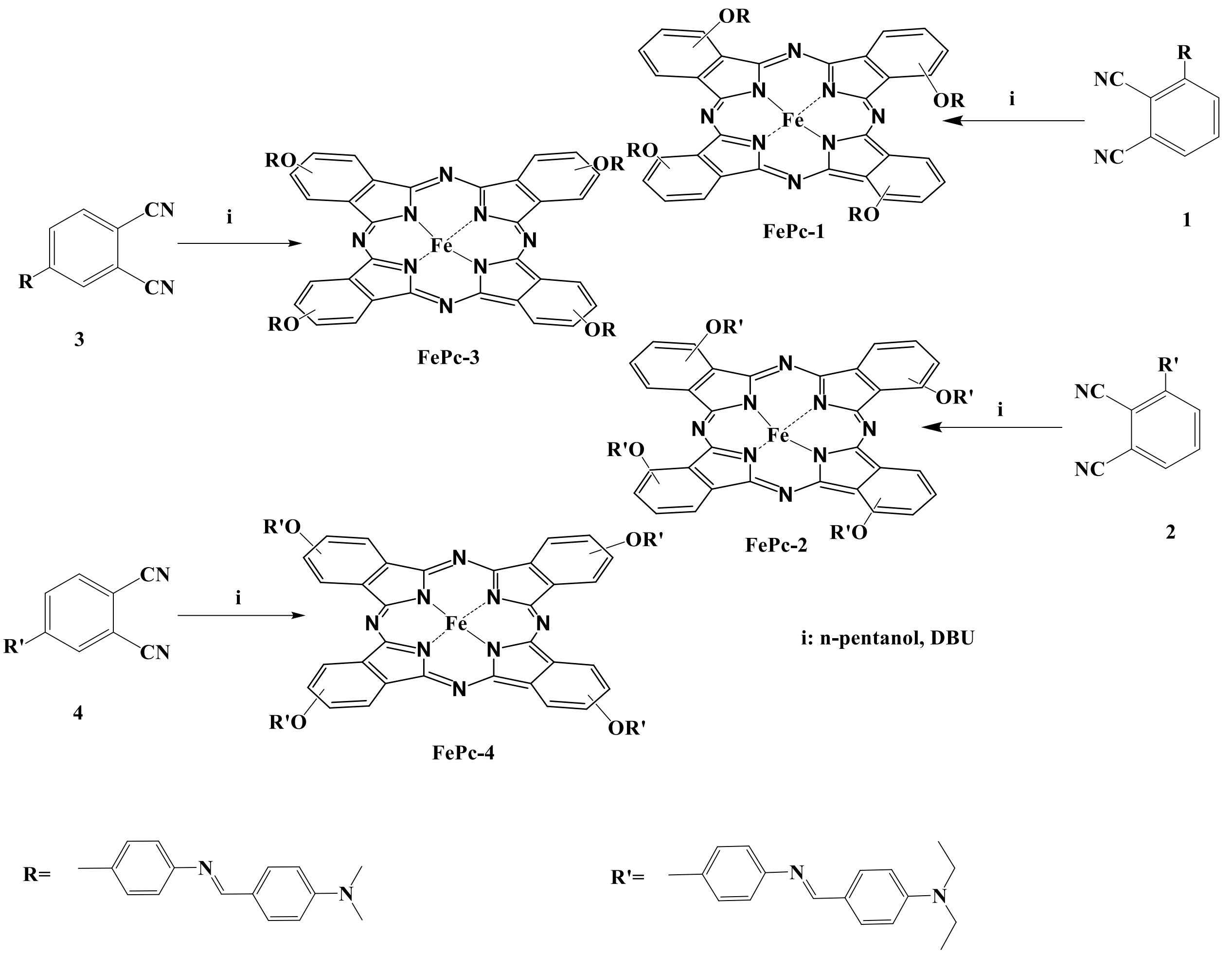
The synthesis of starting materials and target iron(II) phthalocyanines were carried out by a few reaction steps. Scheme shows the main reactions used for the synthesis. In general, synthesis contains three main steps. At the first step, (E)-4-(4-(dimethylamino) benzilideneamino) phenol and (E)-4-(4-(diethylamino) benzilidenamino) phenol were prepared according to literature procedure [31], and 4- and 3-nitrophthalonitriles were purchased from Sigma-Aldrich. Then, substituted phthalonitriles were synthesized, and data of the compounds are given elsewhere [29]. Finally new Fe(II)Pcs were synthesized, and the procedure and spectral data are given below.

2.3.1. General procedure

Under N_2 atmosphere, 1 mmol of the substituted phthalonitrile compounds (**1-4**) and anhydrous $FeCl_2$ (0.031 g, 0.25 mmol) were dissolved in 4 mL of n-pentanol in glass sealed tubes. 3 drops of DBU were added to the medium of each solution, and the temperatures were increased to 160 °C. Purifications of the Pc compounds were carried out by column chromatography using silica gel as stationary phase.

2.4. Preparation of Fe(II)Pc/TiO_2 Catalysts

All Fe(II)Pc/TiO_2 composite samples were prepared by following a similar procedure as described by Sun and co-worker [33]. In a typical preparation, a certain amount of each Fe(II)Pc (the mass ratio of Fe(II)Pc to TiO_2 nanopowder was around 1% w/w) derivative was dissolved in 1 mL dimethyl formamide (DMF). Afterward, the solution of Fe(II)Pc in DMF was added slowly into TiO_2 suspension (1.25 g/L). The mixture was stirred for 24 h at ambient temperature to attain the absorption/desorption equilibrium. Then, the blue-green precipitates were collected through a membrane (pore size, 0.45 μm), washed several times with distilled water and dried in a vacuum oven at 80 °C for 6 h. Finally, the Fe(II)Pc/TiO_2 nanocomposite was completely grounded in an agate-mortar, and stored in the dark



Scheme. Synthetic route used for the production of Fe(II)Pc derivatives.

until usage. The amount of the adsorbed Fe(II)Pc on TiO_2 was calculated by the concentration of remaining Fe(II)Pc in aqueous solution after wet deposition.

2.5. Photocatalytic experiments

The photocatalytic activity measurements of all composites (Fe(II)Pc-1/TiO_2, Fe(II)Pc-2/TiO_2, Fe(II)Pc-3/TiO_2, Fe(II)Pc-4/TiO_2) for the photocatalytic degradation of 4-CP solution were carried out in a quartz cell at atmospheric pressure and room temperature. The quartz cell was filled with 5 mL of 4-CP solution (10 mg/L), and 10 mg catalyst was used for photocatalytic experiments. H_2O_2 concentration was 43.1 mM. A 365 nm near visible UV lamp (ENF-260/C/FE, 6W) was placed in front of the quartz cell. The distance between the lamp and the quartz cell was 10 cm. The reaction mixture was kept uniform through agitation with a magnetic stirrer in the presence of the light. Experiments were conducted for 150 min and the liquid samples (1 mL) were collected at preset time intervals. The samples were filtered by 0.45 μm membrane filters (Millipore) to remove fine particles from the liquid phase before HPLC analysis of 4-CP.

2.6. Analytical methods

4-CP and its intermediates were identified and quantified by HPLC equipped with a C18 reverse phase column (250 cm x 4.6 mm x 5 μm) at 25 °C. A mixture of methanol:water (60:40, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. Injection volume for all samples was a 20 μL. Detection was performed at 280 nm with a UV/Vis detector. The photocatalytic degradation percentage of 4-CP was determined from HPLC peak area data and calculated using the equation given below:

$$\text{Photocatalytic degradation (\%)} = \frac{[4-CP]_o - [4-CP]t}{[4-CP]_o} \times 100$$

where $[4\text{-CP}]_o$ is the initial 4-CP aqueous solution concentration and $[4\text{-CP}]_t$ is the residual 4-CP concentration after the treatments.

3. Results and discussion

3.1. Synthesis and characterization

The schematic representation of the synthesis reactions of the Fe(II)Pcs was shown in Scheme. The purification was performed by column chromatograph over silica gel. The organo-solubility of all phthalocyanines is good in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, DMSO and DMF. The chemical characterizations were succeeded by FTIR, NMR, UV-Vis spectroscopy and mass spectral data and given below. Structural evaluation of non-peripheral positioned Fe(II) phthalocyanines namely Fe(II)Pc-1 and Fe(II)Pc-2 have already been published in our previous publication [30]. Therefore, spectral data related to Fe(II)Pc-3 and Fe(II)Pc-4 are given here.

3.1.1. Fe(II)Pc-3: Reaction time: 8 h. Solvent system for column chromatography: chloroform:methanol (100:21). Yield: 0.098 g, (25.79%). ^{1}HNMR (DMSO-d_6), (δ:ppm): 8.42 (s, 4H, HC=N), 7.60-7.49 (m, 20H, ArH), 7.29-7.19 (m, 8H, ArH), 6.70-6.65 (m, 16H, ArH), 3.08 (s, 24H, CH_3). IR ν_{max}/cm^{-1}: 3031 (Ar-H), 2918-2850 (Aliph. C-H), 1591, 1497, 1467, 1224, 1174, 1093, 943, 816. UV-Vis [(chloroform) [(log ε)]: 685 (5.01), 620 (4.35), 359 (4.88). MS; m/z: 1539.92 $[M+H]^+$.

3.1.2. Fe(II)Pc-4: Reaction time: 12 h. Solvent system for column chromatography: chloroform:methanol (100:20). Yield: 0.116 g, (28.40%). ^{1}HNMR (DMSO-d$_6$), (δ:ppm): 8.45 (s, 4H, HC=N), 7.71-7.52 (m, 10H, ArH), 7.48-7.33 (bm, 6H, ArH), 7.25-7.16 (m, 6H, ArH), 7.3-6.96 (m, 6H, ArH), 6.72-6.54 (m, 16H, ArH), 3.44-3.36 (q, 16H, CH_2), 1.15-1.08 (t, 24H, CH_3). IR ν_{max}/cm^{-1}: 3040 (Ar-H), 2959-2849 (Aliph. C-H), 1583, 1497, 1465, 1227, 1164, 1051, 954, 814. UV-Vis [(chloroform) [(log ε)]: 683 (5.07), 620 (4.56), 358 (5.09). MS; m/z: 1615.23 [M-CH_3]$^+$.

The ^{1}H-NMR spectra of the Fe(II)Pc complexes were very similar to that of their corresponding starting compounds except the broadness of the signals. In the IR spectra of the corresponding Fe(II)Pc the proof of the cyclotetramerizations was the absence of C≡N vibrations of the substituted phthalonitrile derivatives **(1-4)** at around 2232 cm^{-1} [29]. In the mass spectra of the substituted Fe(II)Pc-3 and Fe(II)Pc-4 parent molecular ion peaks at m/z=1539.92 [M+H]$^+$ and 1615.23 [M-CH_3]$^+$, respectively, proved the proposed structures.

Pcs have two strong absorption regions in their electronic spectra. One is called as Q-band (at 600-750 nm) and the other one is called as B or Soret band (at 300-500 nm). The Q-bands of the phthalocyanine metal complexes are observed as singlet due to their degenerate D_{4h} symmetry [33]. The absorption spectra of Fe(II)Pcs in chloroform at 1x10^{-5} M concentration are shown in Fig. 1. Q-bands arising from $\pi \rightarrow \pi^*$ transitions were observed at 685 nm for Fe(II)Pc-2 and 683 nm for Fe(II)Pc-4 as singlet with shoulders at 620 nm. Furthermore, the B bands caused by deeper π levels to LUMO transitions were observed at 359 nm for Fe(II)Pc-3 and 358 nm for Fe(II)Pc-4. Actually these shiftings compared to unsubstituted Fe(II)Pc (λ_{max}=657 nm) are important for the sensitization studies [34]. If the Pc derivative itself absorbs long wave radiation, the sensitized TiO_2 product is able to work under visible light. Therefore, all Fe(II)Pc derivatives exhibit high absorption behavior due to substituted groups on macrocyclic ring. It should be kept in mind that these substitutions also provide good attachment of Fe(II)Pc molecules on TiO_2 surface leading to production of more oxidant species like hydroxyl or peroxide radicals.

3.2. Production of Fe(II)Pc Immobilized TiO_2 and Photocatalyst Characterization

The Fe(II)Pc organometallic dye easily adsorbed on TiO_2 photocatalyst from DMF solution and only a small amount of Fe(II)Pc remained in solution. The amount of Fe(II)Pc immobilized on TiO_2 photocatalyst was 0.95% (w/w) for all derivatives.

The UV-Vis diffuse reflectance spectra (DRS) of neat TiO_2 and Fe(II)Pc/TiO_2 catalysts are shown in Fig. 3. In the TiO_2 spectrum, there is no absorption in visible region, whereas the composite materials exhibitted the characteristic peaks of Fe(II)Pc molecule which means it was successfully modified with TiO_2 surface and increased the visible region light harvest of TiO_2.

X-ray diffraction was carried out to determine the crystal structure of TiO_2 samples and the effect of dye on the crystal structure of TiO_2. Fig. 2 is the XRD patterns of the bare TiO_2 (a), Fe(II)Pc-1/TiO_2 (b), Fe(II)Pc-2/TiO_2 (c), Fe(II)Pc-3/TiO_2 (d) and Fe(II)Pc-4/TiO_2 (e) composite particles. All samples showed anatase peaks and no difference was observed after Fe(II)Pc loading. The TiO_2 crystalline size calculated by Scherrer's equation using the line-width at half-maximum of the XRD peaks at 2θ=25.25 was around 40 nm for all samples.

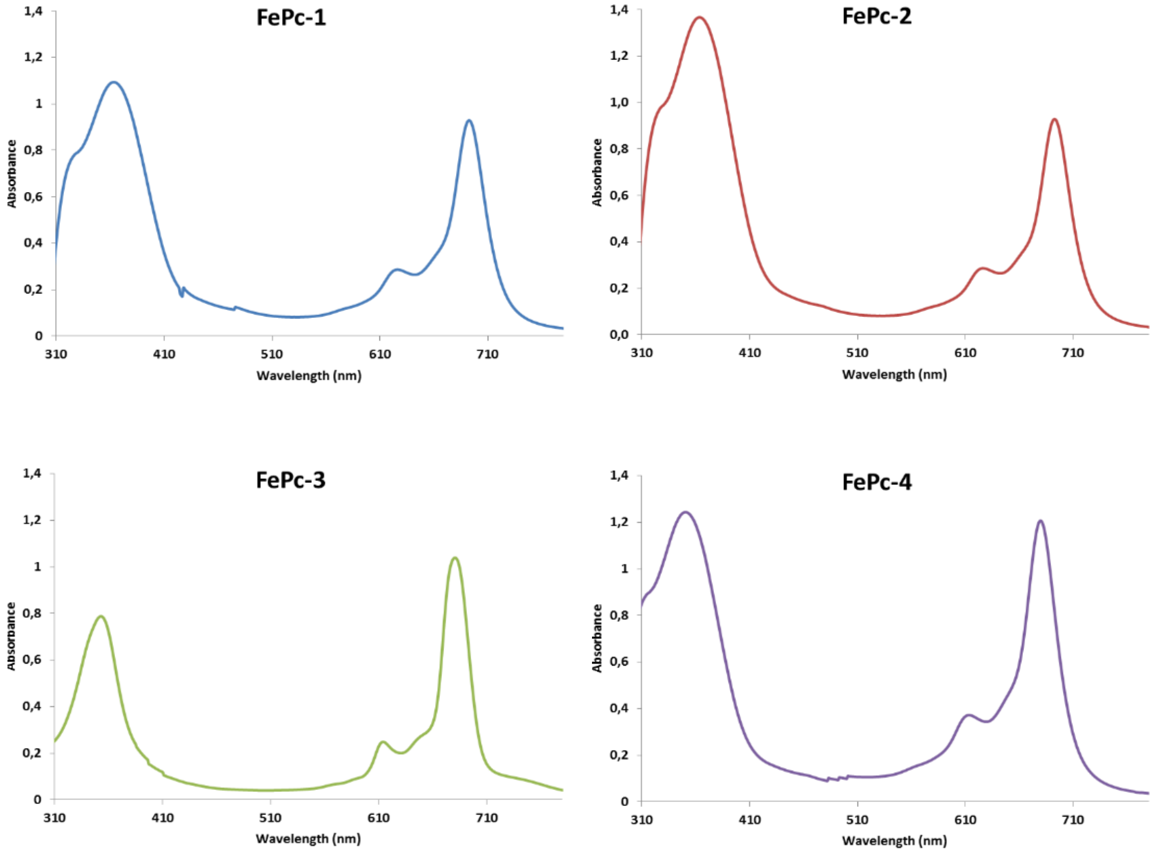


Fig. 1. Absorption spectra of Fe(II)Pcs in chloroform at 1x10^{-5} M concentration.

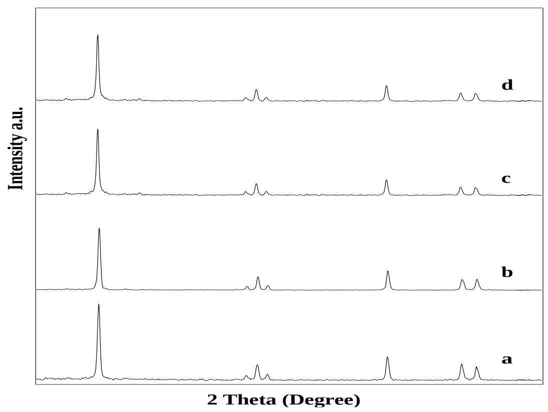


Fig. 2. XRD patterns for Fe(II)Pc-1/TiO_2 (a), Fe(II)Pc-2/TiO_2 (b), Fe(II)Pc-3/TiO_2 (c), and Fe(II)Pc-4/TiO_2 (d).

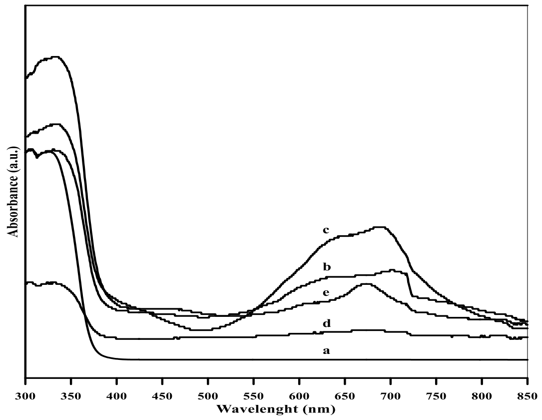


Fig. 3. UV-Vis diffuse reflectance spectra (DRS) of pure TiO_2 (a), Fe(II)Pc-1/TiO_2 (b), Fe(II)Pc-2/TiO_2 (c), Fe(II)Pc-3/TiO_2 (d), and Fe(II)Pc-4/TiO_2 (e).

The morphologies of the different composite samples were determined by SEM and shown in Fig. 4. It was found that the prepared samples are composed of spherical like structures. EDX spectrum of the Fe(II)Pc-1/TiO_2 is given in Fig. 5. The EDX spectra of the other prepared catalysts were similar. According to the EDX analysis, the spectrum peaks of Fe, Ti, O and N elements can be identified. Ti and O peaks were from TiO_2 catalyst, and N and Fe peaks come from the Fe(II)Pc, proving that the Fe(II)Pc sensitized TiO_2 was successfully prepared.

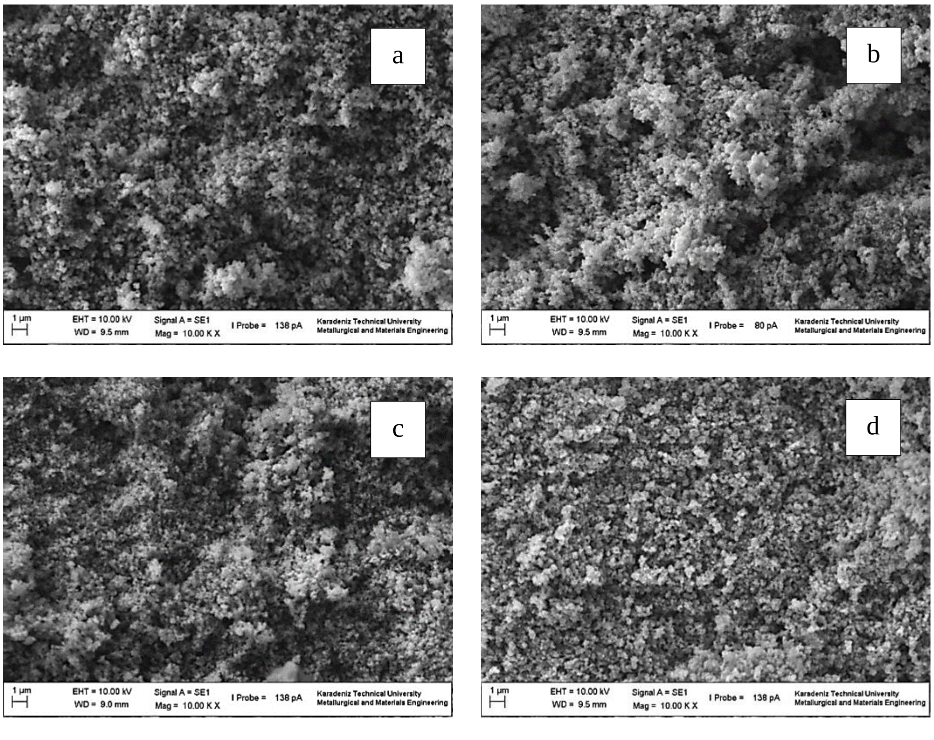


Fig. 4. SEM images of Fe(II)Pc-1/TiO_2 (a), Fe(II)Pc-2/TiO_2 (b), Fe(II)Pc-3/TiO_2 (c), and Fe(II)Pc-4/TiO_2 (d).

3.3. *Evaluation of photocatalytic experiments*

3.3.1. *Fe(II)Pc/TiO_2/UV and Fe(II)Pc/TiO_2/H_2O_2/UV hybrid process*

A solution of 4-CP (10 mg/L) was irradiated under three conditions: *i)* presence of H_2O_2/UV, *ii)* TiO_2/H_2O_2/UV and *iii)* Fe(II)Pc/TiO_2/H_2O_2/UV systems. In order to enhance the efficiency of the TiO_2/H_2O_2/UV process, non-peripheral (Fe(II)Pc-1, Fe(II)Pc-2) and peripheral (Fe(II)Pc-3, Fe(II)Pc-4) substituted phthalocyanines sensitized TiO_2 composite catalysts were used. 4-CP concentration was monitored right after the addition of catalyst (defined as 0 min) and after 150 min exposure. In general, the degradation percentage of 4-CP increased in the presence of all composite materials under near visible light irradiation (365 nm) (Fig. 6). Photocatalytic ability of the catalysts were in the order of Fe(II)Pc-3/TiO_2 > Fe(II)Pc-1/ TiO_2

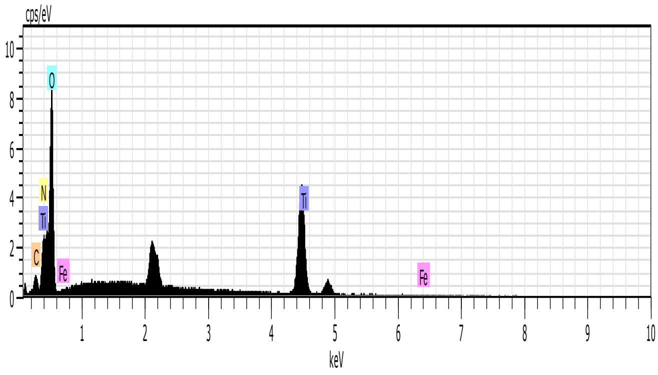


Fig. 5. EDX spectrum of Fe(II)Pc-1/TiO_2 composite catalyst

> Fe(II)Pc-2/TiO_2 > TiO_2 > Fe(II)Pc-4/TiO_2. 4-CP degradation was greatly enhanced with Fe(II)Pc-3 derivative reaching to 93.21% removal rate. Approximately 67.74% of 4-CP was degraded within 150 min with bare TiO_2.

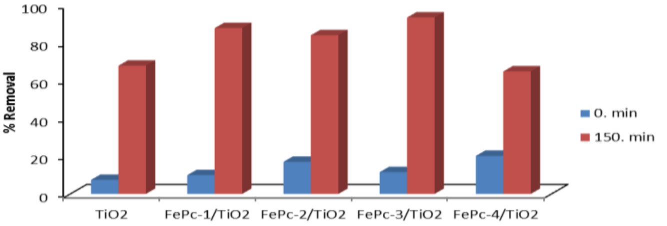


Fig. 6. The photocatalytic degradation of 4-CP in the presence of H_2O_2 with near visible light irradiat.

The presence of H_2O_2 can generate ·OH radicals, increasing the photocatalytic degradation of 4-CP. The photo-degradation in the presence of TiO_2/H_2O_2/UV catalyst system is consistent with an increase in hydroxyl free radical generation. In the presence of TiO_2/H_2O_2/UV system, hydroxyl and peroxyl radicals are formed by the following equations (Eqs. 1-5) [35]:

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$H_2O_{(ads)} + h^+ \rightarrow \cdot OH + H^+ \quad (2)$$

$$OH^-_{(surface)} + h^+ \rightarrow \cdot OH \quad (3)$$

$$H_2O_2 \xrightarrow{h\nu} 2\,\cdot OH \quad (4)$$

$$H_2O_2 \xrightarrow{h} HO_2\cdot^- + H^+ \quad (5)$$

Nguyen et al. [20] suggested that the optimum H_2O_2 to 4-CP ratio should be kept around 1:10. They have reported that the further increase in H_2O_2 concentration would decrease the degradation rate since H_2O_2 acts as an inhibitor consuming the hydroxyl radicals responsible for photocatalytic degradation of the 4-CP (Eq. 6):

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2\cdot \quad (6)$$

where $HO_2\cdot$ is a free radical, but it is less dominant in affecting the degradation as compared with ·OH radicals. Also, H_2O_2 is a better electron acceptor than oxygen leading to a significant decrease at e^-/h^+ recombination.

The experimental results indicate that the sensitization with Fe(II)Pc derivatives plays an important role in photocatalytic reaction resulting in the decomposition of organic pollutants. When Fe(II)Pc/TiO_2 composite is irradiated by near visible light, Fe(II)Pc molecule immobilized on TiO_2 nanopowder is excited and generated the singlet oxygen ($^1O_2$) via energy transfer. Fe(II)Pc molecule has a large heterocyclic structure, and π bonding, free electrons and metal ion at the center provide active sites for electron transfer (Fig. 7).

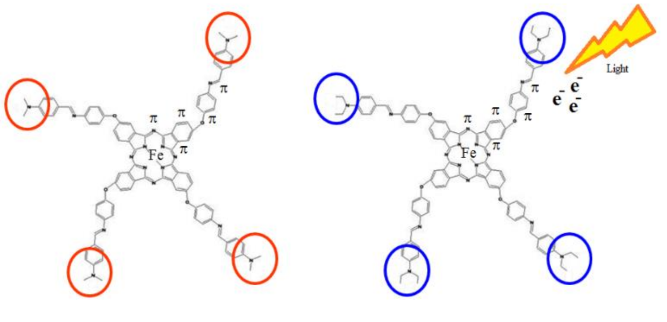


Fig. 7. Peripheral substituted Fe(II)Pc-3 (left) and Fe(II)Pc-4 (right) derivatives for electron transfer.

The excited charge was transferred from excited state of Fe(II)Pc (Fe(II)Pc*) to titania conduction band, followed by formation of the Fe(II)Pc cation radical (Fe(II)$Pc^{\cdot +}$) and conduction band electrons (e_{CB}^-) of TiO_2 (Fig. 8).

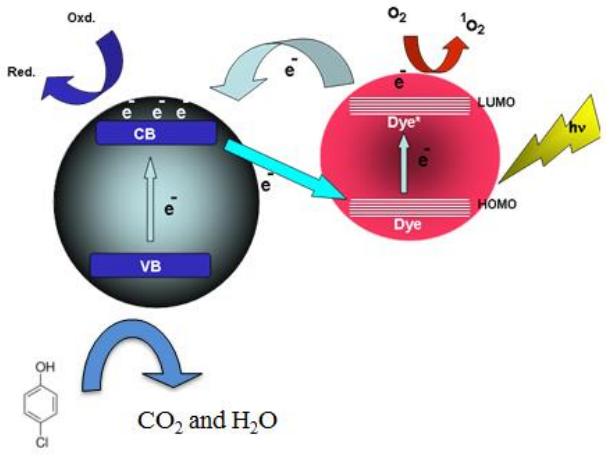


Fig. 8. Mechanistic pathway of dye sensitization.

Consequently, the separation of holes and electrons is promoted because of the migration of more e_{CB}^- to the surface of the photocatalyst. At the same time, the generated electrons react with dissolved oxygen molecule and $^1O_2$ to form hydroxyl radicals for the degradation of 4-CP [36].

The data in Fig. 6 shows that the presence of both of Fe(II)Pc and H_2O_2 oxidant significantly improves the degradation of 4-CP. In particular, Fe(II)Pc-3/TiO_2 (azomethyl bridged phenolic groups substituted at peripheral position) catalyst exhibited the highest photocatalytic activity. The degradation rates of 4-CP reached about 93.21% within 150 min. The degradation efficiency of non-peripheral Fe(II)Pc-1 and Fe(II)Pc-2 immobilized TiO_2 catalysts were also better than TiO_2. Only Fe(II)Pc-4/TiO_2 did not show any positive effect on TiO_2. The presence of an ethyl group in peripheral positions may prevent activation.

Intermediate products are usually formed during the photocatalytic processes, and these structures have been previously determined. Nguyen et al. [20] have reported that the main products formed during the photodegradation of 4-CP are benzoquinone (BQ), 4-chloro-catechol (4-cCat) and hydroquinone (HQ). Similar results were also obtained by Abeish et al. [37] and Cheng et al. [38], and they have proposed a mechanism for the production of intermediate products. Therefore, we have monitored the possible intermediate products after light exposure. HPLC chromatograms were almost clear and none of the intermediates (HQ, BQ and 4-cCat) were determined. It was evaluated as complete mineralization of 4-CP. Production of active species such as ·OH radicals is enhanced by both sensitization and H_2O_2 which can rapidly oxidize 4-CP and its by-products to convert them CO_2, H_2O and inorganic ions.

4. Conclusions

A new series of peripherally or non-peripherally substituted Fe(II) phthalocyanine organometallic complexes was synthesized. The characterization of Fe(II) phthalocyanine derivatives were carried out using FTIR, UV-Vis spectroscopy and mass spectral data. The results of morphological analysis demonstrated that Fe(II)Pc has combined with TiO_2 and could not change crystal size of TiO_2. From the UV-Vis DRS spectra, we could conclude that the immobilization of Fe(II)Pc on TiO_2 particles has expanded the light absorption to visible region. 4-CP photocatalytic degradation capability of TiO_2 was greatly improved after modification with Fe(II)Pc derivatives except for Fe(II)Pc-4. On the other hand, the same peripheral positioned derivative Fe(II)Pc-3 exhibited the highest 4-CP degradation. This derivative has methyl end groups, and possibly attachment on TiO_2 surface greatly affected these groups. Ethyl groups might increase the distance between Fe(II)Pc and TiO_2 particles, which inhibits the electron transfer involved in sensitization process. Consequently, H_2O_2 assisted Fe(II)Pc/TiO_2 composite catalysts have quite high photocatalytic activity and promising material for practical application to remove and degrade the organic pollutants from wastewater.

SUPPORTING INFORMATION

The supplementary material associated with this article is available at www.dergipark.gov.tr/XXXXX.

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