

Scientific paper

Photodegradation of 4-Methylphenol on Palladium Phthalocyaninesulfonate Functionalized Mesopolymer Under Visible Light Irradiation

Rong Xing,* Lin Wu and Zhenghao Fei

Department of Chemistry and Chemical Engineering, Yancheng Teachers University, Kaifang Dadao Rd. 50, Yancheng City, Jiangsu Province 224002, China.

* Corresponding author: E-mail: xingrr@126.com

Fax: +86 -515-88233188

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Abstract

A versatile photocatalyst has been prepared by grafting palladium phthalocyaninesulfonate (PdPcS) onto the FDU-14 mesopolymer with 3-D cubic mesostructure (FDU-14-PdPcS) via multi-step chemical modification processes. The FDU-14-PdPcS was characterized by the X-ray diffraction (XRD), diffuse reflectance UV-vis spectroscopy and inductively coupled plasma (ICP) techniques. In the photodegradation studies of 4-methylphenol, the FDU-14-PdPcS catalyst exhibited excellent visible light photocatalytic activity and reusability in the present of H₂O₂. The photodegradation intermediate of 4-methylphenol was investigated by gas chromatography-mass spectrometry (GC-MS) technique. Quenching experiments with isopropanol, sodium azide and benzoquinone suggested that ¹O₂ and O₂⁻ were the prominent active species during the photodegradation process. A possible mechanism involved in the photodegradation of 4-methylphenol has also been discussed.

Keywords: FDU-14 mesopolymer, phthalocyanine, photocatalysis, visible light

1. Introduction

4-Methylphenol (*p*-cresol) is widely used in the industry as chemical intermediate in the synthesis of the pesticides, pharmaceutical, plastics and phenolic resin products. As one of the toxic organic substances, 4-methylphenol is a carcinogen and can cause hepatotoxicity when it is discharged into the environment, poisoning the water.^{1,2} Moreover, it has poor biodegradability, so efficient removal of 4-methylphenol in wastewater has received significant concerns.

In the water environment treatment processes, photocatalysis is a promising technique for degradation of organic pollutants owing to the advantages of energy-saving and environmentally friendly process.³⁻⁵ Phthalocyanine/vis-light as one of the photocatalysis techniques has attracted particular attention because phthalocyanines (MPcs) are efficient photocatalysts with outstanding photochemical stability and high ability to absorb visible light generating highly active singlet oxygen species.⁶⁻¹⁰ However, soluble MPcs are difficult in separation from

the reaction media and recycle under homogeneous conditions, while insoluble MPcs show a low efficiency for the photodegradation of organic pollutants in aqueous solvent because its aggregate form leads to self-quenching of the excited species and results in deactivation of the photocatalysts.¹¹⁻¹⁵ Much improvement in heterogeneous MPc catalysts has been achieved by using various supports such as chitosan,¹⁶ clays,¹⁷ resins,¹⁸ zeolites,¹⁹ TiO₂,²⁰ silica-based mesoporous materials,^{21,22} etc. Mesopolymer materials with high stability and tunable pore texture possess reactive aromatic moieties in the organic framework, which can be used as an ideal support for the dispersion and stabilization of MPc monomer.

According to the literatures reported, PdPc is the best one in the metal phthalocyanine family in terms of both photoactivity and photostability.²³⁻²⁵ Recently, we reported that the diamine-functionalized FDU-15 mesopolymer with 2-D hexagonal mesostructure (*p6mm*) was used as a promising scaffold for the dispersion of the palladium phthalocyaninesulfonate molecules (PdPcS).²⁶ The obtained PdPcS-functionalized FDU-15 photocatalyst exhibi-

ted excellent photocatalytic activity in the degradation of 4-chlorophenol under visible light. In this study, we synthesized the PdPcS-functionalized FDU-14 with 3-D cubic mesostructure (*Ia3d*). The photocatalytic performance of PdPcS-functionalized FDU-14 photocatalyst was investigated in the degradation of 4-methylphenol under visible light irradiation.

2. Experimental

2. 1. Materials

The FDU-14 mesoporous polymer and diamine-functionalized FDU-14 (denoted as FDU-14-ED) were synthesized as previously reported.^{27,28} Palladium (II) phthalocyanine sulfonate (PdPcS) was prepared according to the literature method.²⁹ 4-Methylphenol was purchased from Shanghai Chemicals Inc, and was used as received.

2. 2. Preparation of PdPcS-functionalized FDU-14

FDU-14-ED (0.30 g) was stirred in 150 mL of PdPcS solution (corresponding to 0.10 wt % loading) at room temperature until the suspension turned to be colorless. The obtained material was washed with distilled water. It was finally dried at 60 °C for 12 h, leading to FDU-14 mesopolymer supported PdPcS, which is denoted as FDU-14-PdPcS.

2. 3. Measurements

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-K α radiation ($\lambda = 0.15418$ nm) at 35 kV and 25 mA. UV-visible spectra of solid and liquid samples were recorded on a PerkinElmer Lambda 35 UV/VIS spectrometer with a mode of diffusion reflectance using polytetrafluoroethene as a reference and a SPECORN-S600 equipped with 1.0 cm quartz cells, respectively. The amount of Pd in the photocatalyst was quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

2. 4. Photocatalytic Test

The photocatalytic reaction was performed in a glass reactor using a Halogen lamp (500 W, Shanghai Yamin) through a glass filter ($\lambda \geq 450$ nm) as irradiation source. In a typical experiment, 50 mL of 4-methylphenol solution and 0.01 g of catalyst were stirred in an air-saturated aqueous solution at room temperature under dark overnight until reaching adsorption equilibrium. An appropriate amount of H₂O₂ was then added into the reactor and the suspension was irradiated to start the photo-

reaction. During the irradiated photoreaction, a proportion of reaction mixture (ca. 2 mL) was sampled. After removing the solid catalyst by filtration through a membrane (0.45 μ m), the amount of 4-methylphenol remaining in the solution was analyzed by high performance liquid chromatography (Waters 2695-2489 HPLC, C 18 reverse column, 5 μ m, 250 mm \times 4.6 mm) using CH₃OH-H₂O (60% : 40%, pH 5 by acetic acid) as an eluent. The photodegradation intermediates were identified by GC-MS on an Agilent Technologies 7890A instrument equipped with a DB-624 capillary column (60 m \times 0.25 mm \times 1.4 μ m). The reaction filtrate was acidified to pH 1–2 and then its volume reduced to about 5 mL via rotatory evaporation. Then 5 mL of CH₃OH and 0.5 mL of concentrated sulfuric acid were added to the residue. After the resulting mixture was refluxed for 3–4 h, it was saturated with NaCl and further extracted with dichloromethane. The organic liquor was dried over anhydrous MgSO₄ and then evaporated to about 2 mL under reduced pressure before GC-MS analysis. The carbon dioxide was detected by Ba(OH)₂ method. Isopropanol (0.05 mol L⁻¹), sodium azide (0.01 mol L⁻¹) and benzoquinone 0.02 mmol L⁻¹) were used as OH \cdot , ¹O₂ and O₂⁻ scavenger, respectively in the photodegradation reactions. The used catalyst was washed repeatedly with distilled water and ethanol, and dried at 60 °C. The recycling experiments of FDU-14-PdPcS were carried out under the above mentioned conditions.

3. Results and Discussion

FDU-14 mesopolymer with a phenolic resin framework (containing aromatic sections) and the cubic *Ia3d* mesostructure, was prepared by a soft templating method from the sources of phenol, formaldehyde and Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) triblock copolymer.³⁰ Palladium phthalocyaninesulfonate functionalized FDU-14 mesopolymer was prepared following the procedures set out in scheme 1. First, as our previously reported, the FDU-14 was chloromethylated with chloromethyl methyl ether and subsequently reacted with ethylenediamine (ED) to produce diamine-functionalized FDU-14 (denoted as FDU-14-ED). Second, the obtained FDU-14-ED was stirred in a solution of PdPcS at room temperature and exhibited the ability for PdPcS scavenging into its mesoporous channels. The resulting PdPcS-functionalized FDU-14 material can be denoted as FDU-14-PdPcS.

3. 1. Characterization of FDU-PdPcS

Figure 1 presents the small-angle X-ray diffraction patterns of FDU-14, FDU-14-ED and FDU-14-PdPcS. The XRD patterns of the parent FDU-14 and the corresponding modified samples showed three well-resolved diffraction peaks indexed to the 211, 220 and 420 reflec-

which caused by the π - π interaction between PdPcS and the FDU-14 mesopolymer. This result is well consistent with the reported data.²⁴ Two relatively broad peaks at 608 and 552 nm associated with the aggregate forms of PdPcS. This evidence directly demonstrated that most of the monomeric PdPcS molecules were successfully attached to the mesoporous channels of FDU-14, and a small portion of PdPcS aggregates may be located on the outer surface of FDU-14.

To clarify Pd content in the FDU-14-PdPcS sample, inductively coupled plasma (ICP) analysis was performed. The Pd content of the FDU-14-PdPcS was ca. 0.011 wt % (corresponding to 0.10 wt % PdPcS loading).

3. 2. Photocatalytic Decomposition of 4-methylphenol

3. 2. 1. The Effect of pH

The photocatalytic activity of the FDU-14-PdPcS was evaluated by the degradation of 4-methylphenol under visible-light irradiation. It is known that pH value can affect the photocatalytic activity of catalysts and the degree of ionization of phenolic compounds.^{31,32} Therefore, the effect of pH on photocatalytic reactions was first investigated and illustrated in Figure 3. The photodegradation of 4-methylphenol was carried out under visible light irradiation in acidic, neutral and basic aqueous solution, respectively. After irradiation for 3 h, 4-methylphenol was photodegraded 76% and 79% in acidic and neutral aqueous solution, respectively. This indicated that the photodegradation rates of 4-methylphenol was negatively affected in acidic and neutral aqueous solution. In a basic aqueous solution, 4-methylphenol was degraded 97% after irradiation for 3 h, suggesting that the basic media favors the photodegradation of 4-methylphenol. This can be explained that the 4-methylphenol was deprotonated in basic en-

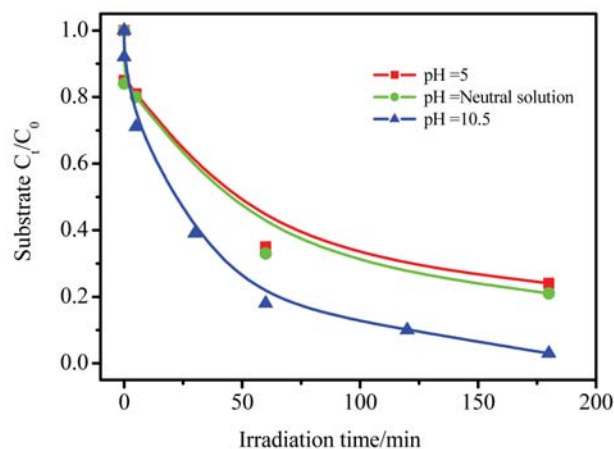


Figure 3. Effect of pH value on the photodegradation rate of 4-methylphenol. Reaction conditions: 0.01 g FDU-14-PdPcS, 50 mL 4-methylphenol (0.6 mmol L⁻¹), H₂O₂ (20 mmol L⁻¹).

vironments to produce methylphenolate, which was more oxidizable by active species. Therefore, the subsequent photodegradation of 4-methylphenol was carried out at the optimum pH value (pH = 10.5).

3. 2. 2. The Effect of H₂O₂

According to the literatures reported, H₂O₂ can not only greatly accelerate the photodegradation rates of organic pollutants, but also eliminate the colored intermediates formed in the photodegradation reactions.³³ Accordingly, the effect of H₂O₂ concentration has been studied and discussed. As shown in Figure 4, the photodegradation of 4-methylphenol could effectively occur in the presence of both H₂O₂ and photocatalyst under visible light irradiation. After 3 h of irradiation, the photodegradation rate of 4-methylphenol (0.6 mmol L⁻¹) aqueous solution was similar and about 97%, 98% and 98% in the present of 10, 20 and 30 mmol L⁻¹ H₂O₂, respectively. However, in the reaction time 2 hours, the photodegradation rate of 4-methylphenol (0.6 mmol L⁻¹) aqueous solution was higher in the present of 20 mmol L⁻¹ H₂O₂ than in the present of 10 or 30 mmol L⁻¹ H₂O₂. This can be explained that H₂O₂ could increase the degradation rate of 4-methylphenol at low concentration, but probably competed with the 4-methylphenol for adsorption and diffusion at catalytic active sites at high

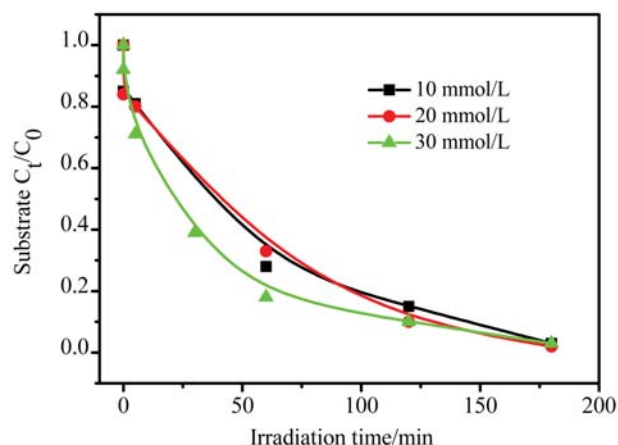


Figure 4. Effect of H₂O₂ concentration of: (a) 10 mmol L⁻¹, (b) 20 mmol L⁻¹ and (c) 30 mmol L⁻¹ on the photodegradation rate of 4-methylphenol. Reaction conditions: 0.01 g FDU-14-PdPcS, 50 mL 4-methylphenol (0.6 mmol L⁻¹), pH = 10.5.

concentration. The above results were similar to the literatures reported.^{16, 34–37} From this standpoint, the optimal H₂O₂ concentration of 20 mmol L⁻¹ was selected for the following photodegradation of 4-methylphenol.

3. 2. 3. Photodegradation of 4-methylphenol

Figure 5 shows the concentration of 4-methylphenol versus irradiation time under various reaction condi-

tions. It can be observed that H_2O_2 alone did not degrade 4-methylphenol in the dark or ever under visible light irradiation, suggesting that H_2O_2 alone could not produce free radicals in the absence of photocatalyst (Figure 5a and b). In the experiments without visible light irradiation, FDU-14-PdPcS did not degrade 4-methylphenol in the dark in the presence of H_2O_2 , and only absorbed about 12 % of 4-methylphenol from aqueous solution (Figure 5c). However, in the experiment under visible light irradiation, FDU-14-PdPcS exhibited a high photocatalytic activity for the oxidation of 4-methylphenol, which was degraded 97% and 89% after irradiation for 3 h in the presence and absence of H_2O_2 , respectively (Figure 5d and 5e). Moreover, in the absence of H_2O_2 , almost 95% of 4-methylphenol was degraded using FDU-14-PdPcS as photocatalyst when the irradiation time was prolonged to 4 h. Under the same photoreaction condition, the degradation reaction of 4-methylphenol did not occur at all using the parent FDU-14 as photocatalyst, indicating that FDU-14 was no photocatalytic activity. Above findings indicated that FDU-14-PdPcS and visible light were essential for degradation of 4-methylphenol. The control experiment with FDU-14-PdPcS in the presence and absence of H_2O_2 exhibited that H_2O_2 was beneficial to the degradation rate increased and elimination of the colored intermediates produced in the photoreactions. The FDU-14-PdPcS catalyst exhibited high photocatalytic activity at low molar ratio of PdPcS/4-methylphenol during the photodegradation of the 4-methylphenol, which can be attributed to high dispersion of the PdPcS monomer inside mesoporous channels stabilized by π -electron of FDU-14 mesopolymer. In addition, FDU-14-PdPcS with a cubic structure could provide good effects

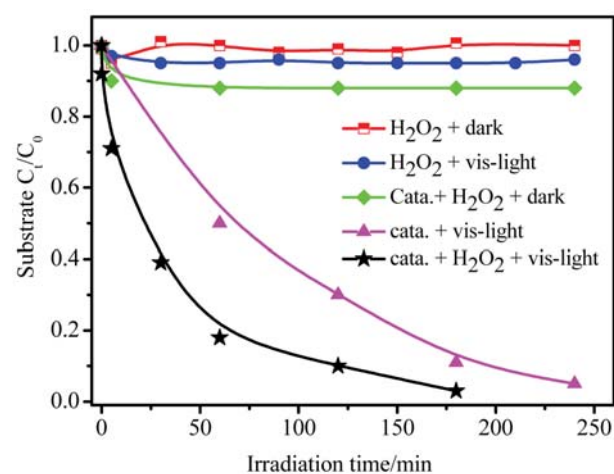


Figure 5. The changes of 4-methylphenol concentration with reaction time under various conditions: (a) H_2O_2 + dark, (b) H_2O_2 + vis-light, (c) FDU-14-PdPcS + H_2O_2 + dark, (d) FDU-14-PdPcS + vis-light and (e) FDU-14-PdPcS + H_2O_2 + vis-light. Reaction conditions: 0.01g FDU-14-PdPcS, 50 mL 4-methylphenol (0.6 mmol L^{-1}), H_2O_2 (20 mmol L^{-1}), pH =10.5.

on photocatalysis because it could more effectively promote the diffusion or adsorption of molecular oxygen and/or 4-methylphenol to the catalytic active sites.

3. 2. 4. The Effect of 4-methylphenol Concentration

The effect of the initial concentration on the photodegradation of 4-methylphenol was studied. The pseudo-first-order model was introduced to illuminate the reaction kinetic of the photodegradation of 4-methylphenol, which can be expressed as:

$$\ln(C_0/C_t) = k_{\text{obs}} t$$

where C_0 and C_t are the initial concentration and concentration at reaction time (t), respectively. k_{obs} is the apparent rate constant and obtained from the slope of the straight lines of $\ln(C_0/C_t)$ versus reaction time t . As shown in Figure 6 and Table 1, the experimental data were presented by the linear plot of $\ln(C_0/C_t)$ versus reaction time t . From the Table1, as the initial concentration of 4-methylphenol increased from 0 to 0.2, 0.4, 0.6 and 1.0 mmol L^{-1} , the values of k_{obs} decreased from 0.0305, 0.0257, 0.0132 and 0.0123, respectively, indicating that the photodegradation of 4-methylphenol was faster in lower concentration solution. In diluted solution, the reactants were considered to diffuse rapidly to the catalytic active sites, while the obtained products diffused rapidly out of the mesopores during the reaction process.

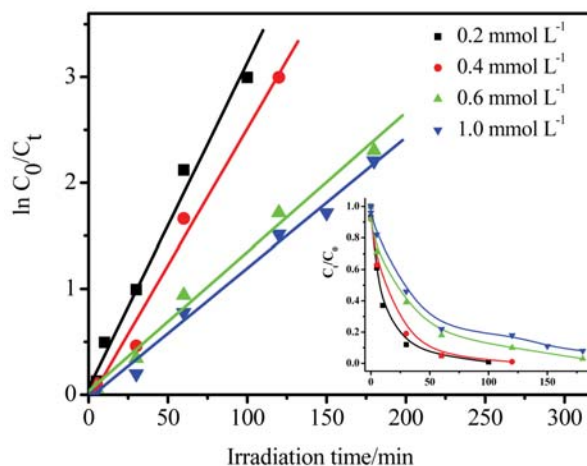


Figure 6. Effect of initial concentration on the photodegradation of 4-methylphenol.

Table 1 Rate constant (k_{obs}), half-life ($t_{1/2}$), at various concentrations of 4-methylphenol

Concentration (mmol L^{-1})	R^2	k_{obs} (min^{-1})	$t_{1/2}$ (min)
0.2	0.9872	0.0305	22.73
0.4	0.9847	0.0257	26.97
0.6	0.9901	0.0132	52.51
1.0	0.9916	0.0123	56.35

3. 2. 5. Products and Mechanism of 4-methylphenol Photodegradation

To confirm the intermediates composed of the highly polar molecules and formed during the photodegradation of 4-methylphenol process, the intermediates need to be esterified with methanol using concentrated sulfuric acid as the catalyst before it was identified by GC-MS. Figure 7 shows major reaction intermediate containing methyl acetoacetate, indicating that photodegradation products were composed of simple organic acids, which could be further photodegraded to CO_2 . The $\text{Ba}(\text{OH})_2$ method was used to confirm CO_2 , which was the final product of the mineralization of 4-methylphenol.

ce of both NaN_3 and benzoquinone (Figure 9a). The addition of benzoquinone alone retarded distinctly the photodegradation rate (Figure 9b), which was about 70 % after irradiation for 6 h. The 4-methylphenol was degraded 79 % after irradiation for 4 h in the presence of NaN_3 (Figure 9c). The addition of isopropanol showed a little influence on the degradation of 4-methylphenol (Figure 9d) in comparison to a typical photocatalysis (Figure 9e). The above results indicated that both $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ may be the outstanding active species in the photodegradation of 4-methylphenol in the presence of FDU-14-PdPcS with H_2O_2 under visible light irradiation. In addition, a small amount of OH^\cdot could attend the photodegradation of 4-methylphenol under visible light

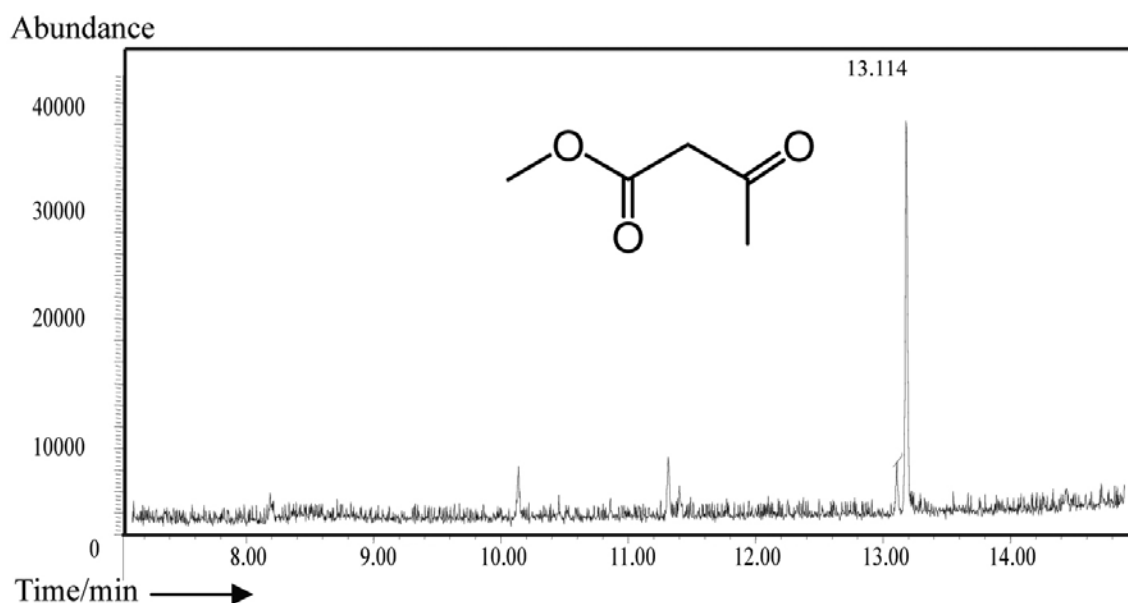


Figure 7. GC-MS chromatogram of degradation of 4-methylphenol. Reaction conditions: 0.01 g FDU-14-PdPcS, 50 mL 4-methylphenol (0.6 mmol L^{-1}), H_2O_2 (20 mmol L^{-1}), $\text{pH} = 10.5$, irradiation 2 hours.

Figure 8 shows the possible mechanism for the photodegradation of 4-methylphenol. In alkaline condition, the photocatalytic oxidation of 4-methylphenol possibly included several steps. Methylphenolate was first oxidized to 4-hydroxy benzaldehyde, which was further oxidized to 4-hydroxybenzoic acid. The active oxygen species could oxidize 4-hydroxybenzoic acid to hydroquinone or benzoquinone, which could be further degraded to CO_2 and H_2O .

Active species in the photodegradation processes were investigated. The isopropanol, NaN_3 and benzoquinone were used as hydroxyl radical (OH^\cdot), singlet oxygen ($^1\text{O}_2$) and superoxide radical ($\text{O}_2^{\cdot-}$) scavengers, respectively. Figure 9 shows that the lowest degradation rate was about 65 % after irradiation for 6 h in the presen-

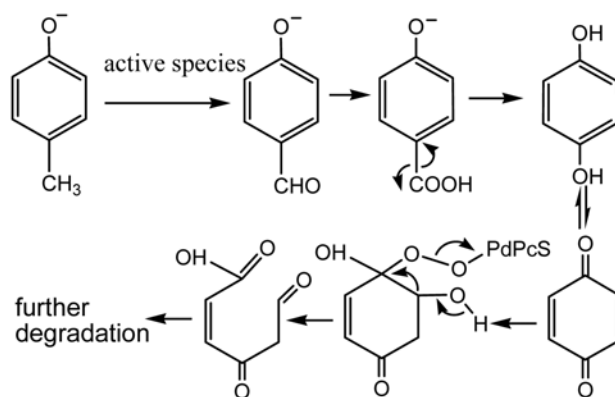


Figure 8. Possible mechanism for the photodegradation 4-methylphenol.

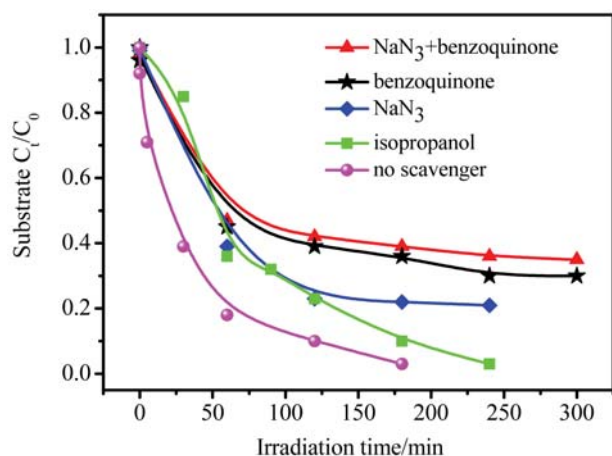


Figure 9. Effect of scavengers on the photodegradation of 4-methylphenol (a) NaN_3 + benzoquinone, (b) benzoquinone, (c) NaN_3 , (d) isopropanol and (e) no scavenger.

irradiation, which probably formed by the H_2O_2 reaction with $\text{O}_2^{\cdot-}$ or via hemolytic cleavage of putative PcSPdO-OH intermediate.^{8, 38–40}

3. 4 Catalyst Recycling

Heterogeneous catalysts are particularly attractive due to its stability and recyclability. As shown in Figure 10, FDU-14-PdPcS catalyst has been reused for the photodegradation of 4-methylphenol. No loss of photocatalytic activity in FDU-14-PdPcS was observed after four cycles for photodegradation of 4-methylphenol under the same experiment conditions. The highly reusable ability of the FDU-14-PdPcS can be attributed to high stability of mesopolymer in basic aqueous solution and tight attachment of the monomeric PdPcS molecules inside the confined mesopores, which be further stabilized by π -electron of mesopolymer.

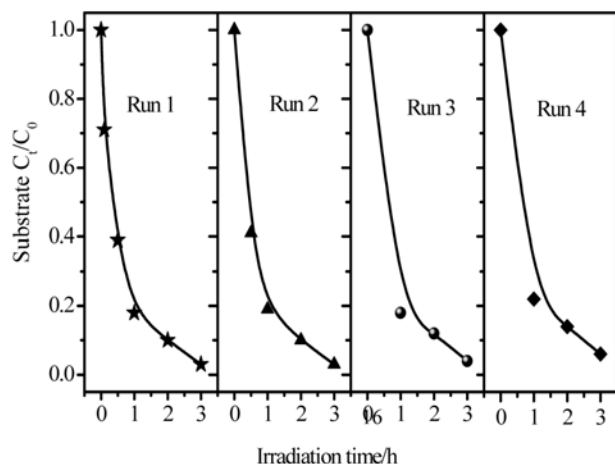


Figure 10. Cyclic use of FDU-14-PdPcS for the photodegradation of 4-methylphenol.

4. Conclusions

A novel efficient photocatalyst, FDU-14-PdPcS, was prepared by the effective electrostatic interactions. The monomeric PdPcS molecules were included to the mesoporous and further stabilized by the π -electrons of the benzene rings, which could benefit for the photodegradation of 4-methylphenol reactions under visible light irradiation. Control experiments proved that $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ were probably the main active species during the photodegradation process. FDU-14-PdPcS is able to act as an eco-friendly photocatalyst, and is expectable for efficient removal of organic pollutants using the sunlight as the energy source.

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Povzetek

Pripravili smo vsestranski fotokatalizator z metodo presejanja paladijevega ftalocianinsulfata (PdPcS) na FDU-14 mezopolimer s tridimenzionalno kubično mezostrukturo (FDU-14-PdPcS) s pomočjo večstopenjskega kemično-modifikacijskega procesa. FDU-14-PdPcS smo karakterizirali s pomočjo rentgenske difrakcije, difuzne odsevnosti, UV-Vis spektroskopije in induktivnostno-plazemske tehnike (ICP). Pri fotodegradaciji 4-metilfenola je FDU-14-PdPcS katalizator izkazal izvrstno fotokatalitsko aktivnost v območju vidne svetlobe in ponovljivost v prisotnosti vodikovega peroksida. Eksperimenti z izopropanolom, natrijevim azidom in benzokinonom so pokazali, da sta $^1\text{O}_2$ in $\text{O}_2^{\cdot-}$ pomembni aktivni komponenti med fotodegradacijskim procesom.