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Preparation of phthalocyanine/TiO₂ nanocomposites for photocatalytic removal of toxic Cr(VI) ions

Rıza Bayrak^a, Cansu Albay^b, Melek Koç^b, İlknur Altın^b, İsmail Değirmencioğlu^{b,**}, Münevver Sökmen^{b,*}

^a Sinop University, Vocational School of Health Services, Department of Medical Laboratory Techniques, 57000 Sinop, Turkey

^b Karadeniz Technical University, Faculty of Science, Department of Chemistry, 61080 Trabzon, Turkey

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ABSTRACT

In this study, a group of novel metal free azomethine-bridged phenolic phthalocyanines (H₂Pc) was synthesized. These derivatives are completely new and first time reported. Four derivatives at peripheral or non-peripheral substitution on macro cyclic ring were synthesized and characterized employing various spectroscopic methods. H₂Pc derivatives (defined as H₂Pc-1, H₂Pc-2, H₂Pc-3, H₂Pc-4) were immobilized on TiO₂ nanoparticles to obtain photoactive nanocomposites (H₂Pc/TiO₂, 1% of the mass of TiO₂). H₂Pc derivatives were used as photosensitizer to improve the near visible-light photocatalytic efficiency of TiO₂ catalyst in wastewater treatment. Photocatalytic abilities nanocomposites were tested for photocatalytic reduction of chromium (VI) ions (10 mg/L) and compared with neat TiO₂. A near UV light source (365 nm) was used for illumination in a batch reactor and Cr(VI) concentration was monitored during 150 min treatment period. It is clear that H₂Pc sensitized photocatalyst is effective for the reduction of chromium ions. Removal percentages were between 83.70 and 99.75% indicating almost total reduction of toxic Cr(VI) ions. Neat TiO₂ was able to reduce only 55.43% of initial Cr(VI) ions. All phthalocyanine containing TiO₂ composites are significantly more effective and reduce more Cr(VI) ions than TiO₂ itself. Photocatalytic action of the catalysts is decreased in the following order H₂Pc-4/TiO₂ > H₂Pc-2/TiO₂ > H₂Pc-1/TiO₂ > H₂Pc-3/TiO₂.

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1. Introduction

Phthalocyanines (Pc), a blue-green-colored aromatic macrocyclic compounds, have a great deal of attention from scientists in diverse fields such as catalysis, solar energy conversion, photodynamic therapy of cancer, non-linear optics, gas sensors and laser dyes due to their highly delocalized electronic structure (Akçay et al., 2013; Topuz et al., 2013; Przybył and Janczak, 2015; Bilgiçli et al., 2015). Major problem of Pc

molecule is its insolubility in water and this can be enhanced by substitution on its peripheral or non-peripheral positions. Peripheral means substitution of functional group to nitrile carbon at α position and non-peripheral at β position (López Zeballosa et al., 2015).

Photocatalysis is an advanced oxidation technology (AOT) for removal of pollutants in water that usually involves anatase type titanium dioxide (TiO₂) in the presence of light. Because of its partially large band gap energy (e.g., 3.2 eV)

* Corresponding author. Tel.: +90 462 3772532; fax: +90 4623253196.

** Corresponding author. Tel.: +90 462 3773321; fax: +90 4623253196.

E-mail addresses: ismail61@ktu.edu.tr (İ. Değirmencioğlu), msokmen@ktu.edu.tr (M. Sökmen).

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the energy of the light should be high enough for transferring the electron from valance band to conducting band. This electronic excitation is only provided by the light which wavelength is lower than 400 nm. However, sunlight contains only 5% UV light and production of UV light is expensive. On the other hand, hole–electron recombination is high during excitation and quantum yield is low. A group of dye molecules, which are called sensitizer, decrease the band gap energy by improving electron transfer and increase the photocatalytic activity of TiO₂.

Therefore, dye sensitization of TiO₂ produces more effective catalyst system by facilitating the electron transfer and shifting the wavelength of the light to visible region. Basically, special organic or inorganic molecules can transfer the electrons under two circumstances:

- i. if they have π electrons
- ii. if they have substituted Lewis base (such as O, N or S) containing unbounded electrons.

Those molecules have above properties are able to transfer their electrons when they are excited by an external source. Pcs are good candidates since they have 18- π electrons and can be substituted with long chain functional group at either peripheral or non-peripheral position. Most of the Pc are p-type semiconductors and well adsorbed on TiO₂ surface. If a Pc molecule has polar substituted group/groups on its macrocyclic ring the adsorption capacity on TiO₂ surface is better. Not only easing electron transfer ability and the Pc/TiO₂ nanocomposite prevent the e⁻/h⁺ recombination resulting increased photo catalytic activity. Therefore novel Pc derivatives are synthesized to meet above mentioned requirements. Azomethine-bridged phenolic Pc may be a good choice since these derivatives pose higher polarity and have π electrons in substituted groups as well as electron drawing groups.

There is a number of applications on photocatalytic removal of specific pollutants employing Pc modified TiO₂ (Pc-TiO₂) (Iliev et al., 2003; Ganem, 2007; Machado et al., 2008; Xu, 2009; Rehman et al., 2009; Zanjanchi et al., 2010; Shang et al., 2011; Fa et al., 2011; Oliveira et al., 2012; Wang et al., 2011, 2012). Various Pc derivatives have been used as photosensitizer to improve the visible-light photocatalytic efficiency of TiO₂ catalyst in wastewater treatment (Yu et al., 2014). The sensitization mechanism has been evaluated in details (Iliev, 2002; Sun and Xu, 2009). It is well known that TiO₂ has ability to oxidize/reduce the organic and inorganic substrates in air and water through redox processes. If the Pc modification facilitates the electron transfer it should prove the reduction ability of TiO₂. A measure of this enhancement is to test the composite catalyst (Pc-TiO₂) for reduction of hexavalent chromium ions (Cr(VI)) ions that causes serious problems in aqueous and terrestrial environment. Photocatalytic reduction of Cr(VI) ions with TiO₂ suspensions have been investigated by several researchers and recent studies were summarized previously (Akkan et al., 2014). TiO₂ itself is an effective photocatalyst for reductive removal of Cr(VI) ions.

This study is mainly concentrated on the synthesis of a group of novel metal free azomethine-bridged phenolic phthalocyanines (H₂Pc). Two different substituted groups namely methylated and ethylated peripheral/nonperipheral Pc derivatives were used as sensitizer dye. The paper comprises largely synthesis of these molecules, details of synthesis steps and structural confirmation. These derivatives are completely new, synthesis and characterization studies are

first time reported in this study. Synthesized derivatives were immobilized on TiO₂ nanoparticles (defined as H₂Pc/TiO₂) and the composite catalysts were tested for their photocatalytic reduction abilities. Catalyst characterization and structural evaluation will be discussed elsewhere (under preparation). Photocatalytic ability of the produced nanocomposites was tested for photocatalytic reduction of chromium (VI) ions and compared with neat TiO₂.

2. Experimental

2.1. Materials

All reactions were carried out under dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. (E)-4-(4-(dimethylamino)benzylideneamino) phenol (1) and (E)-4-(4-(diethylamino) benzylideneamino) phenol (2) were synthesized according to literature (Ha et al., 2010). All solvents were dried and purified as described by Perrin and Armarego (1989) before use (Perrin and Armarego, 1989). 4-Nitrophthalonitrile and 3-nitrophthalonitrile were purchased from Fluka. TiO₂ powder (44 nm particle size) was purchased from Sigma–Aldrich (Darmstadt, Germany) in anatase form.

2.2. Equipments

¹H NMR and ¹³C NMR (for phthalonitrile compound) spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl₃ and DMSO-d₆, and chemical shifts were reported (δ) relative to Me₄Si as internal standard. FT-IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer. The mass spectra were measured with a Micromass Quattro LC/ULTIMA LC–MS/MS spectrometer using chloroform–methanol as solvent system. All experiments were performed in the positive ion mode. Melting points were measured on an electrothermal apparatus and are uncorrected. Absorption spectra in the UV–vis region were recorded with a Shimadzu 2101 UV–Vis spectrophotometer.

Photocatalytic experiments are carried out in a batch reactor and solutions were treated with light in a quartz reaction vessel. A UV lamp (Spectroline ENF-260, 2 × 8 W) producing 365 nm near visible light was used for photocatalytic treatments.

2.3. Synthesis of H₂Pc derivatives

Series of routes were followed for the synthesis of starting materials and target azomethine-bridged phenolic phthalocyanines (H₂Pc). Scheme 1 shows the main reactions used for the synthesis.

Details of the synthesis reactions are given below.

2.3.1. (E)-3-(4-(4-(Dimethylamino)benzylideneamino)-phenoxy)phthalonitrile (3)

In a 100 mL round bottomed flask compound 1 (2.40 g, 0.01 mol) was dissolved in 40 mL of dry N,N-dimethylformamide (DMF) and 3-nitrophthalonitrile (1.73 g, 0.01 mol) was added to this solution. After the temperature was raised to 60 °C dry potassium carbonate (1.38 g, 0.01 mol) was added to the medium in eight equal portions at 15 min intervals. The reaction mixture was kept at this temperature for five days under N₂ atmosphere with efficient stirring. After the completeness of the reaction, the mixture was poured into ice-water and precipitate was filtered and dried under vacuum over P₂O₅.

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