Article

Photocatalytic Efficiency of Metallo Phthalocyanine Sensitized TiO₂ (MPc/TiO₂) Nanocomposites for Cr(VI) and Antibiotic Amoxicillin

Melek Koç Keşir ¹, Münevver Sökmen ^{2,*} and Zekeriya Bıyıklıoğlu ¹

¹ Department of Chemistry, Faculty of Science, Karadeniz Technical University, Trabzon 61080, Turkey; kocmelek612013@gmail.com (M.K.K.); zekeriya@ktu.edu.tr (Z.B.)

² Department of Bioengineering, Konya Food and Agriculture University, Konya 42080, Turkey

* Correspondence: munevver.sokmen@gidatarim.edu.tr

Abstract: Dye sensitization on semiconductor catalyst TiO₂ was performed with four different metallophthalocyanine (MPc) derivatives (M: Zn, Cu, Co, and Si) using a modified sol-gel method. MPc derivatives were loaded on TiO₂ at 1% mass ratio aiming to increase its photocatalytic action and to shift the light absorption to higher UV region (365 nm). Non-ionic surfactant Triton X-100 (TX-100) was used to obtain a homogenous and meso pore catalyst structure. The prepared catalysts were characterized by FT-IR, XRD, and SEM to determine the crystal and surface structural properties of nanocomposites. The nanocomposites were used for photocatalytic removal and degradation of Cr(VI) and amoxicillin (AMX) as model pollutants. Photocatalytic reduction capacities of the catalysts were tested for Cr(VI) (10 mg/L) and AMX (20 mg/L) aqueous solutions. ZnPc-TiO₂ catalyst was successful for Cr(VI) photoreduction since all Cr(VI) ions in the solution were successfully removed. Presence of TX-100 in the sol-gel synthesis of ZnPc-TiO₂ had a positive effect by increasing the Cr(VI) removal rate to 97.93% after 150 min exposure period. Prepared catalysts were also tested for photodegradation of AMX, applying similar procedures. In general, all catalysts exhibited low degradation rates under the studied condition but more effective with 254 nm UV light (50.38%). Neither surface modification with TX-100 nor MPc sensitization provided significant degradation of AMX.

Keywords: photocatalysis; dye sensitization; TiO₂; chromium (VI); amoxicillin (AMX); TX-100

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1. Introduction

Several environmental pollutants such as organic, inorganic, and biological waste that come from different industrial segments accumulate in water, air, and soil [1]. Various chemicals are used in many industries and these harmful materials are ultimately collected in aquatic environments, and the combined effect creates critical problems for all living creatures [2,3]. Thereby, the availability of detrimental and toxic materials in our aquatic ecosystem leads to significant risks for not only the health of individuals but also to public safety [4,5]. To generate a sustainable environment, it is necessary to improve methods which remove these pollutants. Various research methods in literature have used centrifugation, sedimentation, flotation, adsorption, biological techniques, filtration, and thermal oxidation, which are collectively known as traditional and classical purification technologies, with the objective of lowering levels of pollutants [6–8]. Unfortunately, common biological techniques are not effective in remediation of toxic materials that do not decompose as biological products. In methods based on adsorption; the pollutant only passes from one medium to another. In conclusion, the scientific world is creating a survey of alternative, game-changing, and promising technologies, seeking to eradicate robust contaminants in wastewater.

In recent years, advanced oxidation processes (AOP) that generate the most reactive radicals, such as hydroxyl radicals (HO[•]), have been experimented among different alterna-

tives [9,10]. It is known that heterogeneous photocatalysis with Titanium dioxide (TiO_2), which is a semiconductor material, along with ultraviolet solar radiation, is one popular process utilized in removing hazardous compounds [11,12]. Being a green technique, photocatalysis has a huge capacity for suppression of toxic materials in the aquatic media due to its impressiveness and extensive practicality.

TiO_2 is one of the well-known semiconductors that is being used by catalytic research, due to being cheap, non-toxic, inert, and its chemical- and photostability [13]. The reason Titanium dioxide is effective in photocatalysis is the electronic transitions between valence (VB) and conduction band (CB) electrons. If the TiO_2 semiconductor is irradiated with light having energy equivalent to or higher than the gap between its VB and CB (e.g., 3.2 eV for anatase and 3.0 eV for rutile), electrons in VB are excited and migration occurs toward CB, which produces electron (e_{CB}^-)-hole (h^+) pairs [14]. While these two active pairs react, as photocatalytic, with water and oxygen adsorbed on the TiO_2 surface, reactive oxygen species (ROS) such as hydroxyl radical ($\text{HO}^\bullet$), hydroperoxyl radical ($\text{HO}_2^\bullet$), singlet oxygen ($^1\text{O}_2$), and superoxide (O_2^-) are generated [15,16]. Whereas positive holes onto photocatalyst TiO_2 can react with water and hydroxyl anions in the solution to compose $\text{HO}^\bullet$ radicals, negative holes (e_{CB}^-) onto the surface can simultaneously react with molecular oxygen adsorbed by the surface of TiO_2 to form O_2^- radicals [17]. Having redox capacity, these active radicals are an important species to facilitate decomposition of jeopardous pollutants until its mineralization. The entire mineralization of organic, inorganic, and biological compounds may be achieved, and formation of secondary or end products are not predominant in many cases. In contrast, it is hoped that the final product, such as CO_2 and H_2O , or if there are nitrogen, sulfur, or chlorine atoms in compounds, formation of salts can occur [10]. In particular, hydroxyl radicals ($\text{HO}^\bullet$) among other free radicals play a vital role for solar detoxification of many contaminants. Since, with the exception of $\text{HO}^\bullet$, potentially oxidizing reagents such as O_2^- and H_2O_2 in solution under a light source are ultimately converted to $\text{HO}^\bullet$ radicals [18]. In addition, AOP has gained big advantages since $\text{HO}^\bullet$ radicals display high reactivity, non-selectivity, are simple to produce, and are non-toxic [19]. The use of photocatalytic properties of TiO_2 is restricted owing to its wide band gap, which causes decreasing visible light beneficiation, and therefore TiO_2 cannot adequately gather visible light [20]. Recently, new attempts in this field have been tried to increase the spectral range of the TiO_2 photocatalyst, mainly shifting it to longer wavelengths, as the amount of solar irradiance reaching the Earth is less than 3–5% and UV irradiation is relatively expensive. Conversely, recombination of conduction band electrons and valence-band holes occur faster than the time needed for chemical interaction between active radicals and existing species [21,22]. Certain examples of these attempts are sensitization of TiO_2 by using organic, inorganic, or organometallic dyes that absorb visible light. Phthalocyanines that are macromolecular heterocyclic compounds (Metallo phthalocyanine: MPc, Free Phthalocyanine: H_2Pc) are dyes. Such various dye types have attracted interest on account of being inexpensive [11]. MPc molecules that are attained from porphyrins exhibit different features that are not only structural but also chemical from porphyrins, and when compared to porphyrins, MPc molecules have perfect resistance to heat, light, and the effect of alkalis [23]. MPc sensitized TiO_2 (Figure 1) has gained the interest of researchers utilizing these compounds, which densely absorb light in the near visible and visible spectral range, are low cost, chemical in nature, and photostable [24].

Figure 1. Schematic illustration of sensitization of TiO_2 with MPc.

There are examples of photocatalysts on the efficiency of composite materials obtained by immobilized MPc onto TiO_2 . Kim et al. [4] reported that mesoporous $ZnPc/TiO_2$ hybrid nanomaterials, which were prepared with different particle sizes, degraded methylene blue solution under an irradiation source. It was stated that obtained spherical $ZnPc/TiO_2$ hybrid improved photocatalytic efficiency because photosensitization of the $ZnPc$ under visible light irradiation supplied the photo-electron injection to the TiO_2 conduction band from the lowest unoccupied molecular orbital (LUMO) of the $ZnPc$. Another Methylene blue degradation-affected $CoPc/TiO_2$ nanostructure has shown that sensitization with $CoPc$ dramatically affected the degradation of Methylene blue in wastewater under UV-vis and visible light irradiation. This may be associated with speedy injection rates and decreasing recombination of e^-/h^+ pairs being photoinduced carriers [2]. MPc/TiO_2 (M:Co, Fe) nanocomposites have also been tested for removal and degradation of selected industrial dyes and an effective catalyst order was reported as following, $CoPc/TiO_2 > FePc/TiO_2 > TiO_2$ [25]. Moreover, it was found that the optical band gap of samples was decreased to be 2.69eV and 2.88eV for $CoPc/TiO_2$, $FePc/TiO_2$, respectively. Paracetamol and ponceau 4R were used as model pollutants in literature that evaluated the photocatalytic activity of $ZnPc/TiO_2$. It was determined that about 50% of dye and 89–91% of paracetamol were mineralized [1,13]. Besides, there are numerous detailed literature related to this aspect for dyes [7,8,26–29], organic compounds [14,30–32], and toxic Cr(VI) [5,17,33–36].

Surfactants as a stabilizer and template are used in photocatalyst synthesis to achieve modified TiO_2 that has different morphological structures by adding the synthesis media. The intended usage of surfactants is to control the particle size of catalysts, crystal growth, and to avoid other nanoparticles in order to prevent their aggregation or agglomeration [37,38]. Sol-gel method has been used for preparing the nanoparticles for both porous and large surface areas. Surfactants added in the sol-gel solution notably enhance photocatalytic activity by fast molecular transferring between particles [39]. Darzi et al. identified that photocatalytic efficiency in Congo Red degradation was obtained higher than 80% within one hour when the surface of TiO_2 thin layer was modified with P-123 surfactant [40]. Influences on photocatalytic activity of surfactants have been investigated in experiments in which hazardous materials were removed with modified TiO_2 nanoparticles in the scientific world. In order to generate sensitized or non-sensitized

TiO₂ composites, especially with mesoporous structures, surfactant materials were used in the literature. They are Tween-20 [41], Tween-80 [42], polyethylene glycol [43,44], Brij-58 [45], Triton X-100, Pluronic F-127/P-123 [40–46], Acetyl trimethyl ammonium bromide (CTAB) [43–47], and Laurylamine hydrochloride [48,49].

In this paper, MPc materials (M: Zn, Cu, Co, and Si) were exploited to attain dye-sensitized nanocrystalline TiO₂ photocatalysts by means of sol-gel methods, which include titanium isopropoxide (TIP) as the precursor. All the metal-doped TiO₂ nanocomposites were prepared in the presence and absence of surfactants, namely non-ionic Triton X-100 (TX-100) as a template. The efficiency of TiO₂ catalyst can be improved by MPc molecules due to absorbed stimulating light via transition of the singlet and triplet state. The morphology of as-prepared samples was characterized by X-ray diffraction (XRD), Fourier transform infrared spectrophotometer (FT-IR), and scanning electron microscopy (SEM).

Photocatalytic activities of composites were investigated onto the organic and inorganic species as model pollutants under UV light irradiation (365–254 nm). Hence, Cr(VI) and Amoxicillin (AMX) (Figure 2) antibiotic was selected in order to evaluate reduction and oxidation mechanisms of MPc/TiO₂. Cr(VI) ions are found frequently in water sources as being highly toxic and carcinogenic with high mobility [50,51]. Second, AMX, which is one of the most commonly prescribed drugs, is a semi-synthetic and broad-spectrum penicillin analogue of the β -lactams family [52].

Figure 2. UV spectrum and molecular structure of 20 mg/L AMX.

AMX is slowly metabolized by organism and its degradation reactions show particular features at different pH [53]. While reduction from Cr(VI) to Cr(III) was monitored using a UV–vis spectrophotometer, degradation of AMX was monitored by HPLC method.

2. Materials and Methods

2.1. Materials and Reagents

All of the chemical reagents were analytical grade and AMX model pollutant was purchased from Deva Holding Ltd. (Istanbul/Turkey), the pharmaceutical manufacturer. Potassium dichromate (K₂Cr₂O₇, ≥99.9%), titanium isopropoxide (Ti[OCH(CH₃)₂]₄,

99.8%), and Triton X-100 were purchased from Sigma Aldrich. Nitric (HNO_3 , 65%) and phosphoric acid (H_3PO_4 , 85%) were supplied by Sigma Aldrich. Absolute EtOH (EtOH) ($\geq 99.9\%$, HPLC grade), potassium dihydrogen phosphate (KH_2PO_4 , 99.5%), and acetonitrile (ACN, $>99.9\%$, HPLC grade) were obtained from Merck, Carlo ERBA and J.T. Baker. 1,5-Diphenyl Carbazide ($\text{C}_{13}\text{H}_{14}\text{ON}_4$), as the complexing agent, was purchased from LaboChemie. All solutions were prepared using ultrapure water throughout the photocatalytic experiments.

2.2. MPc Sensitizers

The entirety of MPc sensitizers were designed and characterized in our laboratory. Synthesized novel MPc derivatives had special functional groups to increase the UV-vis absorption capacity of the molecule as well as being water soluble. Metal ions Zn, Cu, Co, and Si were located in the center of the Pc ring, and each derivative had a different side functional group on the ring. In general, it was not easy to synthesize stable and pure MPc derivatives. These functional groups containing MPc molecules have unique properties and exhibit superior functions [54–56] such as being water soluble and having higher light absorption capacity. Therefore, these derivatives were specifically chosen in the sensitization of TiO_2 . These molecules were first used for sensitization of TiO_2 and tested in the photocatalytic reduction of Cr(VI) and AMX. Table 1 shows chemical structures of MPc molecules used in the sensitization of TiO_2 . Synthesis and characterization of SiPc [54], ZnPc [55], and CuPc [56] derivatives were previously published but synthesis of CoPc derivative was reported here first.

CoPc: (100 mg, 0.33 mmol) CN and (23 mg, 0.17 mmol) anhydrous CoCl_2 were dissolved in Schlenk flask in 2 mL n-pentanol. Afterward, 4 drops of 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) were added to the solution; this mixture was stirred at the 60°C for hours. 50 mL of diethyl ether was added in green-colored mixture and cooled to room temperature. Raw product was decanted and dried under vacuum. Purification of greenish outputs were fulfilled by column chromatography using aluminum oxide as stationary phase and CHCl_3 :MeOH (100:2) as mobile phase. Yield: 65 mg. IR (ATR) ν (cm^{-1}): 3057 (Ar-H), 2963–2850 (Aliph. C-H), 1592, 1565, 1501, 1455, 1406, 1324, 1298, 1253, 1217, 1118, 1093, 953, 875, 835. UV-Vis (DMSO) λ_{max} nm (log ϵ): 658 (4.99), 598 (4.49), 332 (4.92). MALDI-TOF-MS m/z : 1257.53 $[\text{M} + \text{H}]^+$. Figure 3 shows the main reactions used for CoPc synthesis.

Figure 3. Synthesis stages of CoPc.

Table 1. Pc molecules used in sensitization of TiO₂.

	Metallo Phthalocyanines (MPc)	Substituent R groups	Reference
SiPc			54
ZnPc			55
CoPc			Original
CuPc			56

2.3. Synthesis of MPc/TiO₂ and MPc/TiO₂/TX-100 Nanocomposites

MPc/TiO₂ nanoparticles were synthesized with the sol-gel method in the presence and absence of non-ionic surfactant TX-100. The general procedures were as follows [17]; first, a certain amount of each MPc (the mass ratio of MPc to TiO₂ was 1% *w/w*) was dissolved within 8.4 mL of TIP as a precursor, which was vigorously stirred in 20 mL absolute EtOH solution for 2 h (Solution A). Then, 10 mL of EtOH including 1 mL concentrated HNO₃ and 1 mL H₂O was dripped in solution A (solution B). After solution B was left to stir using a magnetic shaker at ambient temperature for one day in order to provide gel formation, it was dried at 80 °C in a drying oven (Nüve FN120) for 12 h. Obtained rigid yellowish-white gels were calcinated at 300 °C in a furnace (Protherm, Turkey) for 4 h to form the anatase structure and remove residual organic reagents. After calcination as-prepared, each MPc/TiO₂ was cooled down to room temperature and was crushed by agate-mortar to fine powders and placed in the dark.

In the case of MPc/TiO₂ preparation in the presence of TX-100 surfactant, a similar procedure was used. An amount of 8.4 mL of TIP reagent was regularly inset dropwise to a certain amount of TX-100 dissolved in 20 mL of EtOH by being stirred intensively to supply homogenization and formation of inverse micelles for 2 h via a magnetic stirrer (solution C). After mixing for a while, solution B was added drop by drop into solution C and newly obtained suspension was exposed to blend for one day. After formation of the gel, it was dried at 80 °C in a drying oven for 12 h to remove remaining TX-100 and organic reagents. The rest of the procedure was performed in a similar manner as described for the MPc/TiO₂ nanocomposites (the mole ratio of TIP, EtOH, and TX-100; 1:5:1, respectively).

2.4. Structural and Surface Analyses

Histograms of all obtained nanocomposites for crystal structures were determined with a Rigaku Smart lab X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range $2\theta = 20\text{--}80^\circ$ at room temperature. The morphologies of the photocatalysts were examined using a JEOL (JSM-6610) scanning electron microscope (SEM) under an applied voltage of 3.0 kV. IR spectra were gathered over the range of 4000 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1} by performing Perkin Elmer 1600 FT-IR spectrometer that was connected with integrated ATR. The optical properties of pure MPc molecules were obtained using Shimadzu UV-vis 1240.

2.5. Photocatalytic Performance Tests

Photocatalytic activity of each catalyst was tested for both inorganic Cr(VI) ions (10 mg/L) that was aimed at the reduction from Cr(VI) to Cr(III) and pharmaceutical compound AMX (20 mg/L), which can be degraded by photocatalytic oxidation. A UV light source Spectro line ENF260 was employed, equipped with a nominal power of 6W (X2) lamp, emitting radiation at 254/365 nm (light intensity 350 mW/cm^2). The light source was placed at about 15 cm from reaction solution (50 mL) that includes photocatalyst and pollutant. In every experiment, a portion of samples were removed from the quartz cell in the presence and absence of light. The reduction experiment of Cr(VI) was conducted at pH 2 because of being more effective for the reduction of Cr(VI) to Cr(III). The Cr ions are present as Cr(VI) oxidation state at this pH [57]. Thus, initial pH of Cr(VI) solution was adjusted with H_3PO_4 . The concentration of MPc/ TiO_2 was 1 g/L for each test medium. Before the light exposure, the mixture containing catalyst and contaminant was placed in the dark for 30 min and stirred to provide adsorption and desorption equilibrium between the catalyst and pollutant. Afterward, the suspension medium was exposed to light (365 nm) for 150 min. An amount of 10 mL of irradiation solution was regularly withdrawn and centrifuged (Eppendorf, 3000 rpm, 20 min) to separate from the MPc/ TiO_2 solid at different time intervals during the runs (every 30 min).

Cr(VI) suspension was decanted as soon as possible and the remaining ion concentration in the supernatant was measured by standard photometric method, which is based on complexation reactions between Cr(VI) and 1,5 diphenyl carbazide. Absorbance of formed complex was monitored at the wavelength 540 nm by UV-Vis spectrophotometer.

Photocatalytic reaction of AMX was performed, applying a similar procedure reported above. After centrifuge periods, 2 mL of AMX supernatant was filtered through 0.22 μm membrane filter using a syringe to determine the remaining AMX concentration by HPLC. The HPLC instrument was equipped with a DAD detector (Waters) and C_{18} (ACE 5, $150 \times 4.6 \text{ mm} \times 5 \mu\text{m}$ particle size) column. A previous chromatographic method was modified for these analyses [58]. The mobile phase was delivered at a flow rate of 0.5 mL min^{-1} in isocratic mode, composed of a mixture of acetonitrile/phosphate buffer (0.025 M of KH_2PO_4), (70:30 %, *v/v*). The column temperature was 40 $^\circ\text{C}$ and diode array detector set at 235 nm. Run time was determined at 7 min.

$$\text{Degradation \%} = ([C]_0 - [C]_t / [C]_0) \times 100 \quad (1)$$

The removal percentage of both pollutants was calculated from the above equation where $[C]_0$ shows the initial concentration of pollutants (AMX, Cr(VI)) while $[C]_t$ is the final concentration after irradiation treatment.

3. Result and Discussion

3.1. Spectral Features of MPc Molecules

MPc molecules show characteristic peaks in the UV-visible range because of having double bonding electrons in their structures. Especially, MPc molecules have intensely two different band types called Q and B (Soret) which show absorption in the electronic spectrum (Figure 4). Q band is monitored with electron transition between HOMO orbital

in the a_{1u} (π) symmetry and LUMO orbital in the e_g (π^*) symmetry under red/near-IR (600–750 nm) while B (Soret) band happens through migration of electron from orbitals in a_{2u} and b_{2u} symmetry to orbital in e_g symmetry under UV/Blue (300–500 nm).

Figure 4. The UV-vis spectrum of MPc derivatives (concentration = 1×10^{-5} mol/L).

As a result of overlapping of B1 and B2 bands, B band is observed as one broad-band [34,59]. Before sensitization of TiO_2 , MPc samples were dissolved in a desired solvent at 1×10^{-5} mol/L concentration that can utilize their light absorption spectrum in a wide range. Due to steric hindrance of macrocyclic ring of four substituent-linked CoPc, absorbance of CoPc was shown to decrease. Originating from $\pi \rightarrow \pi^*$ transitions, Q bands were sighted at 661, 678, 683, and 688 nm for CoPc, SiPc, CuPc, and ZnPc, respectively. Soret bands were tracked to 332, 365, 339, and 351 nm for CoPc, SiPc, CuPc, and ZnPc, respectively. When reviewing these transitions, ZnPc sensitizer was aroused from richer electron density versus other Pc molecules since both migration of electron can be easy from on the aliphatic chain to Pc ring, and there was a lack of any obstacle compelling electron transition, such as steric hindrance. ZnPc sensitizer is thought to be promising regarding sensitization of TiO_2 to remove both pollutants.

3.2. X-ray Diffraction Analysis (XRD)

In order to obtain information about crystal structures of prepared catalysts, XRD analyses were performed. Figure 5 shows XRD patterns for the prepared powders MPc/ TiO_2 (left) and MPc/ TiO_2 /TX-100 (right) nanoparticles.

Figure 5. XRD spectra of (a) TiO_2 , (b) SiPc/TiO_2 , (c) ZnPc/TiO_2 , (d) CuPc/TiO_2 , and (e) CoPc/TiO_2 ((left): without TX-100, (right): with TX-100).

All MPc/TiO_2 samples demonstrated characteristic sharp peaks well, matching with and related to a pure bulk anatase crystal structure. The Bragg Peaks of Pc/TiO_2 nanocomposites at 2θ of 25.3° , 38° , 48° , and 54.4° confirmed the anatase phase of MPc/TiO_2 nanocomposites and impurities not observed. Based on (101), (004), (200), and (105) (JCPDS Card no. 21-1272), miller indices are second evidence of diffraction peaks corresponding with crystalline nature of the TiO_2 anatase nanocomposites [7,8]. In the presence of TX-100 surfactant molecules (right Figure 5), miller indices and data were monitored in the manner of weak and relatively broad peaks that indicate a lightly amorphous TiO_2 crystal structure. This may be due to residues of TX-100 after calcination potentially causing diffraction peaks at low intensity or size effect [60]. The Scherrer equation was used to calculate crystallite sizes of all samples by fitting the (101) sharp diffraction peak of the anatase phase. This equation is given as

$$D_{hkl} = 0.89 \lambda / \beta \cos \theta \quad (2)$$

where, D_{hkl} is the crystal thickness in the hkl direction, λ is the wavelength of X-ray diffraction ($\text{Cu K}\alpha = 0.15406 \text{ nm}$), β is the peak width at half maximum fixed for instrumental broadening, and θ is the Bragg angle of the diffraction peak. When the equation above was used to determine the production of both TiO_2 and MPc/TiO_2 , it observed that their particle size changed between 2.01 and 4.43 nm. Particle size of MPc/TiO_2 was almost the same as neat TiO_2 . Therefore, surface modification with MPc derivatives had no clear effect on the crystallite structure as stated before [4,5,25,27].

3.3. FT-IR Spectra

Figures 6 and 7 demonstrate that FT-IR spectra of TiO_2 modified MPc derivatives synthesized the sol-gel procedure in the presence or absence of non-ionic surfactant TX-100. When examining FT-IR data of both type catalysts, characteristic aliphatic -C-H fundamental stretching vibration appeared in the $2988\text{--}2900 \text{ cm}^{-1}$ region, which are associated with the addition to MPc derivatives [61]. The stretching vibration of -N-H peaks emerged due to MPc rings, which are rich in terms of N atoms, and were observed at around 3676 and 3663 cm^{-1} ranges [4]. The peaks at around $1534\text{--}1408 \text{ cm}^{-1}$ are referred to as -C=C stretching bands of aromatic groups for the phthalocyanine structure [7]. A broadband at approximately $3650\text{--}2800 \text{ cm}^{-1}$ is typically assigned to Ti-O-H and O-H vibration of absorbed water molecules on TiO_2 surface [62].

Figure 6. FT-IR spectrums of TiO_2 and MPc/ TiO_2 catalysts prepared without TX-100.

Figure 7. FT-IR spectrums of $\text{TiO}_2/\text{TX-100}$ and MPc/ $\text{TiO}_2/\text{TX-100}$ catalysts prepared in the presence of surfactant.

Stretching and vibration between Ti and O are ranked in the fingerprint region described at 1250 cm^{-1} and below this value. Diaristic peaks rising at about 690 cm^{-1} and $800\text{--}450\text{ cm}^{-1}$ are remarked, respectively, as Ti-O-Ti and Ti-O stretching peaks as already given in the current literature [14,24,61].

Except for CuPc, relative increase in the peaks intensity and decrease in the transmittance were observed, which was a distinct evidence of successful immobilization of MPc onto TiO_2 [21]. All catalysts were regenerated (thermally at $300\text{ }^\circ\text{C}$) after photocatalytic treatment and their FT-IR spectrums were compared with freshly prepared ones. Characteristic peaks representing the presence of MPc in the structure were seen (the stretching vibration of -N-H peaks and $1534\text{--}1408\text{ cm}^{-1}$ -C=C stretching band) in the spectrum. It shows that MPc is quite stable and not degraded during photocatalytic process.

3.4. SEM Analysis

SEM imaged showed that all of the MPc samples had accumulated through agglomeration on the TiO_2 surface. Similar surface morphologies were observed in the presence or absence of TX-100 (Figure 8).

Figure 8. SEM images of produced catalysts. (a) SiPc/TiO₂, (b) ZnPc/TiO₂, (c) CuPc/TiO₂ and (d) CoPc/TiO₂ without TX-100 and (a₁) SiPc/TiO₂, (b₁) ZnPc/TiO₂, (c₁) CuPc/TiO₂ and (d₁) CoPc/TiO₂ with TX-100.

Contrary to expectations [4,8,26], MPc-modified TiO₂ nanoparticles exhibited random orientation instead of spherical type. It may be because of both macrocyclic structure of MPc molecules and long chain structure of TX-100. All MPc sensitized TiO₂ samples had not undergone major alterations [62,63]

3.5. Photocatalytic Assessment of MPc/TiO₂ Nanocomposites

The photocatalytic activities of the as-prepared nanoparticles in the absence and presence of TX-100 were investigated for reduction of 10 mg/L Cr(VI) and degradation of 20 mg/L of AMX under 365 nm light using 50 mL pollutant solution and 1 g/L catalyst amount. Control experiments were applied under similar conditions (no catalyst and light). Additionally, the same photocatalytic reduction experiments were repeated with 254 nm light exposure to see the effect of sensitization and removal and degradation with longer wavelength light source. The calculated removal percentages for Cr(VI) ions are shown in Figure 9.

As seen in Figure 9, after 150 min. under dark conditions, all nanocomposites showed high adsorption capacity. Among the nanocomposites, ZnPc/TiO₂, TiO₂ and SiPc/TiO₂ including TX-100 provided more adsorption capacity at 36.49%, 24.32%, and 23.16%, respectively. Removal percentage of Cr(VI) was higher with MPc/TiO₂/TX-100 than those catalysts prepared without TX-100, in all cases. Surfactant TX-100 certainly had a positive effect on photocatalytic action of the catalysts. TiO₂ (77.48%), SiPc/TiO₂ (89.04%), and ZnPc/TiO₂ (97.93%) catalysts prepared with TX-100 surfactant were more effective under 365 nm light exposure. The same catalysts were less effective when test solution was exposed with 254 nm light, in which removal rates were 93.50%, 82.98%, and 90.30%, respectively. Both dye sensitization and surface modification with TX-100 caused a significant increase on the photocatalytic reduction process of Cr(VI). As already discussed in Section 3.1, structural properties of MPc also have an impact on the sensitization of TiO₂. Electrons migrate from HOMO to LUMO level when Pc/TX-100 nanocomposites are illuminated and then electrons onto LUMO move in CB of TiO₂ and increase the electron density on the band, which may contribute to and increase the reduction percentage of Cr(VI) due to the rise of electron amount. To sum up, both dye sensitization, surface modification with TX-100, and electrostatic force caused an increase in the photocatalytic reduction process of Cr(VI). ZnPc molecule exhibit unique properties on the basis of electron transfer (Figure 4), therefore ZnPc/TiO₂/TX-100 catalyst is more effective for electron transfer mediated photocatalytic reaction. Unfortunately, other MPc molecules were not adequate for sensitization of TiO₂.

Figure 9. Comparison of photocatalytic removal of Cr(VI) ($[\text{Cr(VI)}]_0 = 10 \text{ mg/L}$, mass = 1 g/L, $t = 150 \text{ min}$). Cr(VI) reduction is lower than 0.5% in the presence of MPc alone under the same condition.

Similar analytical procedures were performed for degradation of 20 mg/L AMX antibiotic solution. Degradation of AMX was monitored using HPLC. The removal rate of AMX was calculated in the dark and light exposure (365 nm and 254 nm) and is shown in Figure 10. Only slight degradation rates were observed in dark experiments as well as 365 nm exposure for all catalyst types.

Figure 10. Comparison of photocatalytic degradation of AMX ($[\text{AMX}]_0 = 20 \text{ mg/L}$, mass = 1 g/L, $t = 150 \text{ min}$.).

As seen in Figure 10, illumination under 254 nm enhanced the degradation of AMX. While the degradation percentage of AMX with neat TiO₂ was about 12.50% with a 365 nm

light source, this rate increased to 39.65% after 150 min of irradiation with 254 nm light. Only ZnPc/TiO₂ (50.38%) and ZnPc/TiO₂/TX-100 (43.87%) provided significantly higher degradation among studied catalysts. It was seen as small peaks as well as the peak of the AMX in the chromatogram. The detection limit of the device is known to be a significant parameter in terms of chromatographic runs because determination of degradation products or metabolites of AMX is correlated with the detection limit [64]. It can be concluded that species belonging to AMX can overlap with the basic peak of AMX at the retention time, thus the degradation peak area can result from higher versus basic peak area.

4. Conclusions

The novel nanocomposites were synthesized via the sol-gel method in the presence or absence of non-ionic TX-100 surfactant. In the dye sensitization process, phthalocyanine derivatives containing various metal atoms (M: Zn, Cu, Co, and Si) were used in the sensitization process. Structural and morphological characterization of prepared catalysts were completed using UV-vis, FT-IR, SEM, and XRD. Each of the MPc/TiO₂ samples exhibited the Bragg Peaks coherent to pristine anatase structure of TiO₂. Usage of TX-100 during the catalyst preparation had a structural effect to shifting more amorphous structures in XRD pattern. FT-IR spectrums showed that MPc samples that had specific functional groups such as -NH, -OH and C=C were located on the TiO₂ surface. SEM images reflected that the new photocatalytic materials showed identical shapes and dimensions. It was conferred that surface modification with TX-100 did not change the surface property of TiO₂ photo materials, and macro-structured MPc dispersed randomly. All novel catalysts were applied to remove Cr(VI) and degrade amoxicillin (AMX) as organic and inorganic model pollutants. The highest photocatalytic removal was obtained with ZnPc/TiO₂/TX-100 nanocomposite under 6 W 365 nm irradiation after 150 min treatment. Conversely, 50.38% of AMX solution was degraded with ZnPc/TiO₂ material with 254 nm light exposure. It can be concluded that studied MPc molecules are promising sensitizers for photocatalytic degradation, especially for Cr(VI) removal from polluted water media.

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