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Solid-state, rapid mechanochemical pathway for zinc phthalocyanine-embedded Schiff-Base polymer-TiO₂ nanocomposite for LED assisted efficient photochemical remediation of hexavalent chromium

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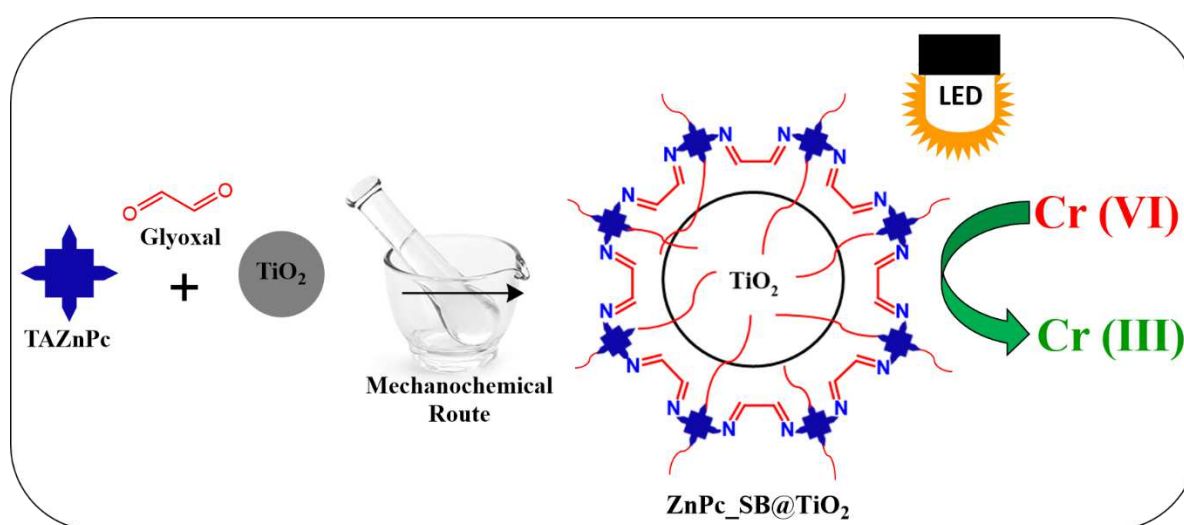
Abstract

The processing and elimination of heavy metals and toxic components from water is indispensable due to its potentially hazardous and carcinogenic impacts on the well-being of people and the environment. Successful heavy metals and toxic components mitigation ensures adequate water quality for consumption, prevents ingestion in to living organisms, and limits the contamination of the environment. The present work details the development of a zinc phthalocyanine based polymeric Schiff-Base encapsulated TiO₂ (ZnPc_SB@TiO₂) nano-

composite via solid-state, mechanochemical pathway for the effective photochemical remediation of Cr(VI) in the presence of energy efficient LED as source of visible light. To comprehensively understand the structure, size, morphology, and optical properties of the newly synthesized photoactive materials, they were subjected to Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Solid-state diffuse reflectance spectrophotometer characterization. The photoreduction of Cr(VI) was carried out under the impact of a 100 W LED as visible light source to investigate the photocatalytic competence of TiO₂ and ZnPc_SB@TiO₂. The implications of several factors on the photocatalytic performance, such as photocatalyst dosage, interaction time, pH of the medium, and photocatalyst re-usage, are investigated. The photocatalytic activity for Cr(VI) photochemical remediation was found to be 88% for ZnPc_SB@TiO₂ where as TiO₂ alone exhibited less than 10%. The findings suggested that photosensitization of TiO₂ with ZnPc_SB significantly boosted photocatalytic activity for Cr(VI) photochemical remediation.

Key words: Solid-state, Mechanochemical, Surface functionalization, Phthalocyanine, Photoreduction, Hexavalent Cr removal.

Graphical abstract:



1 Introduction

Geological weathering, mining operations, industrial processes, agricultural practices, leachate from landfills and dumping sites, fossil fuel combustion, and vehicle emissions constitute a few of the factors that contribute to the discharge of hazardous wastes, especially heavy metal ions, into the environment [1,2]. When heavy metal ions pile up in the environment, it's commonly referred to as heavy metal ion pollution. Various water bodies are susceptible to this accumulation of heavy metal ions, which may lead to environmental issues. This buildup of heavy metal ions can occur in a variety of water bodies, which can cause environmental problems and, more specifically, health problems like cancer, Kidney damage, cardiovascular disease, neurological disorders, birth defects, and respiratory problems [3,4].

One of the hazardous heavy metals, chromium ions, is widely distributed in the environment due to both anthropogenic and non-anthropogenic contributes [5]. Chromium ions can be present in the environment in a number of different forms, including chromate, dichromate, and chromium trioxide [6]. Despite the fact that the majority of chromium is in the +3 oxidation state, there is also chromium in the +6 oxidation state in the environment, which is concerning because of its environmental impact. Chromium ions can enter the body through inhalation, ingestion, or dermal absorption. Once in the body, chromium ions can be distributed to various tissues, including the liver, kidney, lung, and bone, and they can be excreted in the urine, faeces, and sweat [4,7]. Chromium ions have been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) and there is no safe level of exposure to chromium. Its exposure has been associated with an increased risk of lung cancer, kidney damage and impairment, skin ulcers, allergic dermatitis, and respiratory issues such as asthma and bronchitis. According to some research, prolonged exposure to chromium may have an impact on fetal growth and reproductive health. So, to minimize the impacts of chromium (VI) on human beings and on to environment it has to be reduced to chromium (III) [8]. Various techniques can be employed to eliminate heavy metal ions from water, such as adsorption

(carbon-based, polymer-based, MOFs, and magnetic adsorbents), biosorbents, reverse osmosis, coagulation, chemical precipitation, ion exchange, and photocatalysis [9,10]. Each method has its own advantages and disadvantages, and the most appropriate method for a given application will depend on the specific circumstances.

The use of TiO_2 for the photoreduction of Cr (VI) in water is a promising approach for the treatment of Cr (VI) contaminated water [11,12]. TiO_2 is a photocatalyst that is able to reduce Cr (VI) to Cr (III) under ultraviolet (UV) light irradiation. The main advantage of using TiO_2 for the photoreduction of Cr (VI) is that it does not produce any harmful by-products. Additionally, TiO_2 is a very stable photocatalyst and can be reused several times [13].

In order to increase photocatalytic efficiency of TiO_2 semiconductors and to shift absorbance range from UV to visible range, functionalization and composite of TiO_2 has been explored by researchers to increase the photocatalytic efficiency towards photoreduction of Cr (VI) [14]. By functionalizing the TiO_2 surface with different organic and inorganic systems, the photocatalytic activity of TiO_2 can be enhanced [15]. Metal phthalocyanines (MPc's) based functional materials have been extensively investigated as active material in several emergent technologies, encompassing electrocatalysis, energy systems, molecular electronics, sensors, and photocatalysis due to their outstanding stability and fascinating property [16-21].

In recent decades, mechanochemistry has rapidly advanced because to its simple nature, higher efficiency of conversion and productivity, often brief reaction times, straightforward processes for operations, and less environmental impact [22, 23]. Diverse organic and inorganic transformations have been accomplished with mechanochemistry, emerging as a significantly investigated domain for the synthesis of hybrid materials for various applications, including water purification [24-26].

In this context, in the present work, mechanochemically zinc phthalocyanine based polymeric Schiff-Base (ZnPc_SB), and their TiO_2 nanocomposites (ZnPc_SB@ TiO_2) were

successfully synthesized by adopting simple mechanochemical method to examination the photocatalytic effectiveness towards photoreduction of Cr (VI) in the presence of eco-friendly LED as source of visible light source.

2 Materials and methods

Reagents like 4-nitrophthalophthalimide, $(\text{NH}_4)_2\text{MoO}_4$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, TiO_2 , and glyoxal (40 wt. % in H_2O) were supplied by Sigma Aldrich. Merck (India) provided the $\text{K}_2\text{Cr}_2\text{O}_7$, 1, 5-diphenylcarbazine (DPC), p-Toluenesulfonic acid (PTSA), and NaOH. Tetra amino zinc phthalocyanine (TAZnPc) was synthesized by adopting previously well documented procedure [27,28]. Stock and feed solutions were made with DD water.

2.1 Synthesis of zinc phthalocyanine embedded Schiff-base polymer (ZnPc_SB)

TAZnPc (100 mg) and 2 equivalents of glyoxal (40 wt. % in H_2O) were added and the reaction mixture was thoroughly pulverized in an agate mortar and pestle for 30 minutes in the presence of a catalytic amount of PTSA. The product ZnPc_SB obtained was thoroughly washed with distilled water followed by ethanol and dried in an oven at 100 °C for 5 h. Schematic representation for the synthesis of ZnPc_SB is presented in Fig. 1.

2.2 Synthesis of zinc phthalocyanine embedded Schiff-base polymer-TiO₂ composite (ZnPc_SB@TiO₂)

TiO_2 nanoparticles (500 mg), TAZnPc (100 mg) and 2 equivalents of glyoxal (40 wt. % in H_2O) were added and the reaction mixture was thoroughly pulverized in an agate mortar and pestle for an additional 30 minutes in the presence of a catalytic amount of p-Toluenesulfonic acid (PTSA). The product ZnPc_SB@TiO₂ obtained was thoroughly washed with distilled water followed by ethanol and dried in an oven at 100 °C for 5 h.

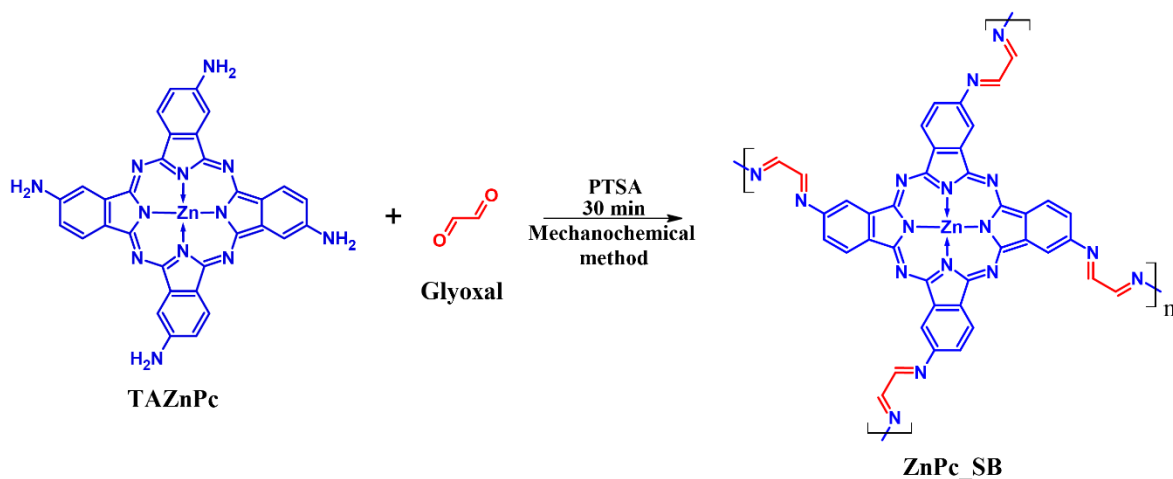


Fig. 1 Schematic representation for the synthesis of zinc phthalocyanine embedded Schiff-base polymer (ZnPc-SB)

2.3 Photocatalytic experiment

The photocatalytic activity of the pristine TiO₂ and synthesised ZnPc_SB@TiO₂ in the photoreduction of hexavalent chromium in an aqueous medium under the impact of a 100 W LED light source was examined. Hexavalent chromium solution was prepared by dissolving a suitable amount of K₂Cr₂O₇ in DD water to obtain a solution of 10 ppm concentration. The photoreduction of hexavalent chromium was accomplished in a photoreactor equipped with a 100 W LED and magnetic stirrer. Typically, 100 mL of Cr (VI) solution containing a known amount of photocatalyst was stirred for 30 min in the dark to establish adsorption-desorption equilibrium between the photocatalyst and Cr (VI). During irradiation, at predetermined time intervals, a 3 mL aliquot was collected, and the photocatalyst was separated by centrifugation. The Cr (VI) content in the reaction solution was determined by UV-vis spectrophotometer using the standard diphenylcarbazide method. The percentage conversion of Cr (VI) to Cr (III) was calculated using the following equation,

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the concentration of Cr (VI) at the 0th time and C_t the concentration of Cr (VI) at t minutes. The operational factors that impact the photocatalytic reduction of Cr (VI) to Cr (III) were examined, including the effects of pH, interaction time, and photocatalyst catalyst dosage.

2.4 Estimation of Cr (VI) by the Diphenylcarbazide method

The Diphenylcarbazide procedure was used to determine the chromium concentration [25]. Briefly, in a 10 ml glass container, 9 ml of 0.2 mol L⁻¹ H₂SO₄ was mixed with 1 ml of Cr (VI) solution, followed by the addition of 0.2 ml of freshly prepared 0.25% diphenylcarbazide in acetone. The reaction mixture was mixed thoroughly for 1 min and allowed to stand for 10 min. The absorbances of the Cr (VI)-diphenylcarbazide complex mixture were measured at $\lambda_{\text{max}} = 540$ nm.

3 Results and discussion

3.1 FTIR analysis

The FTIR analysis was used to determine the functional groups that were present in the newly synthesized composite and its pristine constituents. The FTIR spectra of TiO₂, TAZnPc, ZnPc_SB, and the ZnPc_SB@TiO₂ composite are shown in Fig. 2(a). The FTIR spectrum of TiO₂ displays a broad peak at 3659-3059 cm⁻¹ for OH vibrational stretching for adsorbed H₂O molecules. The characteristic peaks at 1623 cm⁻¹ and 483 cm⁻¹ correspond to the stretching vibration of Ti-OH and Ti-O (metal to the hydroxide, and MOxs). The FTIR spectrum of TAZnPc shows a peak at 3350 cm⁻¹ corresponding to peripheral substituted free N-H stretching vibrations. Peaks at 2951-2828 cm⁻¹, 1606 cm⁻¹, 1347 cm⁻¹, 1249 cm⁻¹, and 1143-1016 cm⁻¹ correspond to the C-H, C=C, C-C, C-N, and N-H stretching vibrations of the phthalocyanine ring skeleton. The characteristic fingerprint stretching vibration of iso-indole nitrogen with the core metal atom Zn-N of the phthalocyanine ring can be observed at 825 cm⁻¹. The peak at 740 cm⁻¹ is due to the C-H in-plane bending vibration. In the case of ZnPc_SB, the FTIR spectrum demonstrates all the characteristic peaks of TAZnPc with a broad peak in the region of 3676-

3026 cm^{-1} suggesting the absence of peripheral free amine, which further confirms the utilization of the amine group during the reaction. The FTIR spectrum of the ZnPc_SB@TiO₂ composite shows all the characteristic peaks of ZnPc_SB and TiO₂ in its pristine form with a slight shift in the wave number, suggesting the effective functionalization of TiO₂ with phthalocyanine.

3.2 X-ray diffraction (XRD) analysis

To study the morphology and crystalline nature of the synthesized composite and its pristine components, powder X-ray diffraction analysis was performed. Fig. 2(b) shows the X-ray diffraction pattern of TiO₂, TAZnPc, ZnPc_SB, and the ZnPc_SB@TiO₂ composite. The diffraction for TiO₂ shows peaks at 2θ values of 25.42°, 38.02°, 48.18°, 54.16°, 55.22°, 62.90°, 69.00°, 70.45°, and 75.23° for the crystal planes 101, 004, 200, 105, 211, 204, 116, 220, and 215, respectively. The obtained diffraction peaks match the JCPDS file of 89-4921 of anatase TiO₂ in its purest form [29]. The small diffraction peak at 2θ values of 17.92° (202), 20.96°, 23.34°, 26.95°, and 29.15° corresponds to the crystalline nature of the synthesized TAZnPc. The broad peak at 2θ value of 26.12° corresponds to the parallelly aligned phthalocyanine molecules to the sample surface, and the amorphous nature of the molecule suggests the semi-crystalline nature of TAZnPc. Following the polymerization of TAZnPc, less intense diffraction peaks at 18.32°, 20.88°, 24.54°, 26.53°, and 28.89°, with a broad peak at 26.12°, can be observed, indicating ZnPc_SB has maintained a comparable crystal structure. The diffraction peaks for the ZnPc_SB@TiO₂ composite observed at 2θ values of 23.53°, 25.47°, 26.00°, 38.76°, 48.71°, 55.69°, 56.82°, 61.52°, 68.04°, 72.41°, and 75.07° correspond to combined crystal planes of the ZnPc_SB polymer and TiO₂. The diffraction peaks of the composite material retained all the characteristic peaks with a slight shift in the 2θ values, suggesting the effective interaction of TiO₂ and ZnPc_SB Polymer.

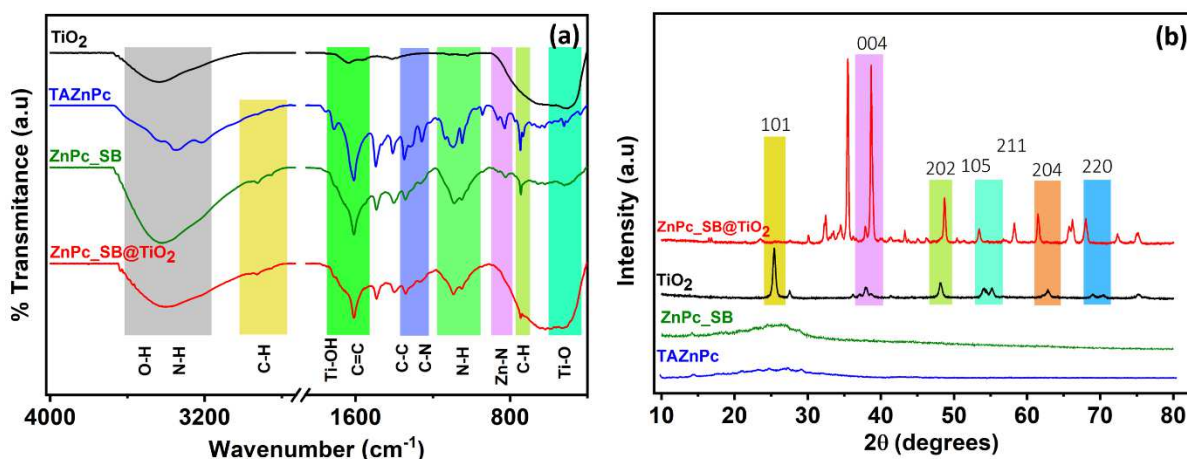


Fig. 2 (a) FTIR spectra of TiO₂, TAZnPc, ZnPc_SB, and ZnPc_SB@TiO₂; b) X-ray diffraction study of TiO₂, TAZnPc, ZnPc_SB, and ZnPc_SB@TiO₂

3.3 Solid-state diffuse reflectance spectra

The solid-state diffusive reflectance spectra of TiO₂, ZnPc_SB, and the composite ZnPc_SB@TiO₂ are presented in Fig. 3. The diffuse reflectance spectra of TiO₂ presented in Fig. 3(a) exhibited its characteristic peak at around 325 nm, and the estimated band gap was found to be 3.26 eV [Fig. 4(a)]. The diffuse reflectance spectra of ZnPc_SB presented in Fig. 3(b) revealed two bands, i.e., a Soret band at 374 nm and a Q band at 626 nm, and the estimated band gap for ZnPc_SB is found to be 3.03 eV [Fig. 4(b)]. The diffuse reflectance spectra presented in Fig. 3(c) for ZnPc_SB@TiO₂ demonstrated peaks at 279 nm and 678 nm with a band gap of 3.01 eV [Fig. 4(c)]. The assessed band gap was discovered to be in the following order: TiO₂ (3.26 eV) > ZnPc_SB (3.03 eV) > ZnPc_SB@TiO₂ (3.01 eV). Effective electronic interaction between TiO₂ and ZnPc_SB can be witnessed by the observed red shift in the visible region and reduced band gap in ZnPc_SB@TiO₂ as compared to pristine TiO₂. This is most probably driven by molecular orbital hybridization that modulates the electronic structure.

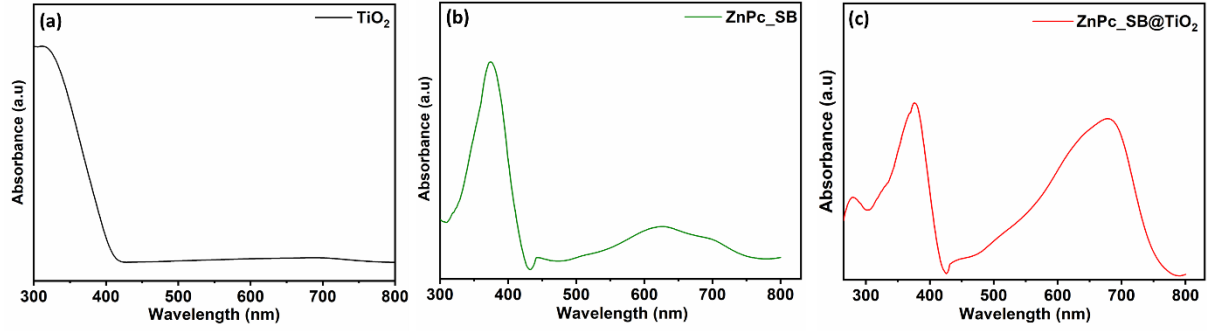


Fig. 3 Solid state diffuse reflectance spectra of (a) TiO_2 , (b) ZnPc_SB , and (c) ZnPc_SB@TiO_2

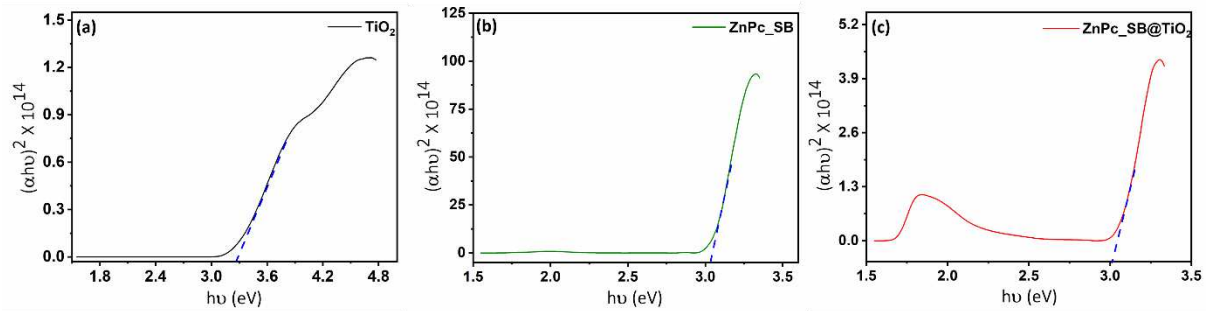


Fig. 4 Band gap estimation of (a) TiO_2 , (b) ZnPc_SB , and (c) ZnPc_SB@TiO_2

3.4 FESEM and EDX analysis

The surface morphology of TiO_2 and ZnPc_SB@TiO_2 was examined by employing FESEM, and the images are presented in Fig. 5. As evident in Fig. 5(a), the spherical, densely packed TiO_2 nanostructures have a diameter of less than 50 nm. Whereas, in Fig. 5(b) ZnPc_SB@TiO_2 had a morphology that appeared quite similar to that of TiO_2 , but with more agglomeration due to the additional existence of ZnPc_SB . EDX analysis of TiO_2 and ZnPc_SB@TiO_2 are presented in Fig. 5(c) and (d), respectively. EDX analysis validates the presence of Ti and O in TiO_2 nanomaterial, and the presence of C, N, Zn, Ti, and O in ZnPc_SB@TiO_2 indicates the successful formation of the composite. The noticed elemental fraction for TiO_2 was Ti (26.58 %) and O (73.42 %) whereas in the case of ZnPc_SB@TiO_2 it was found to be C (27.29%), N (6.02%), O (46.21%), Ti (19.95%), and Zn (0.53%).

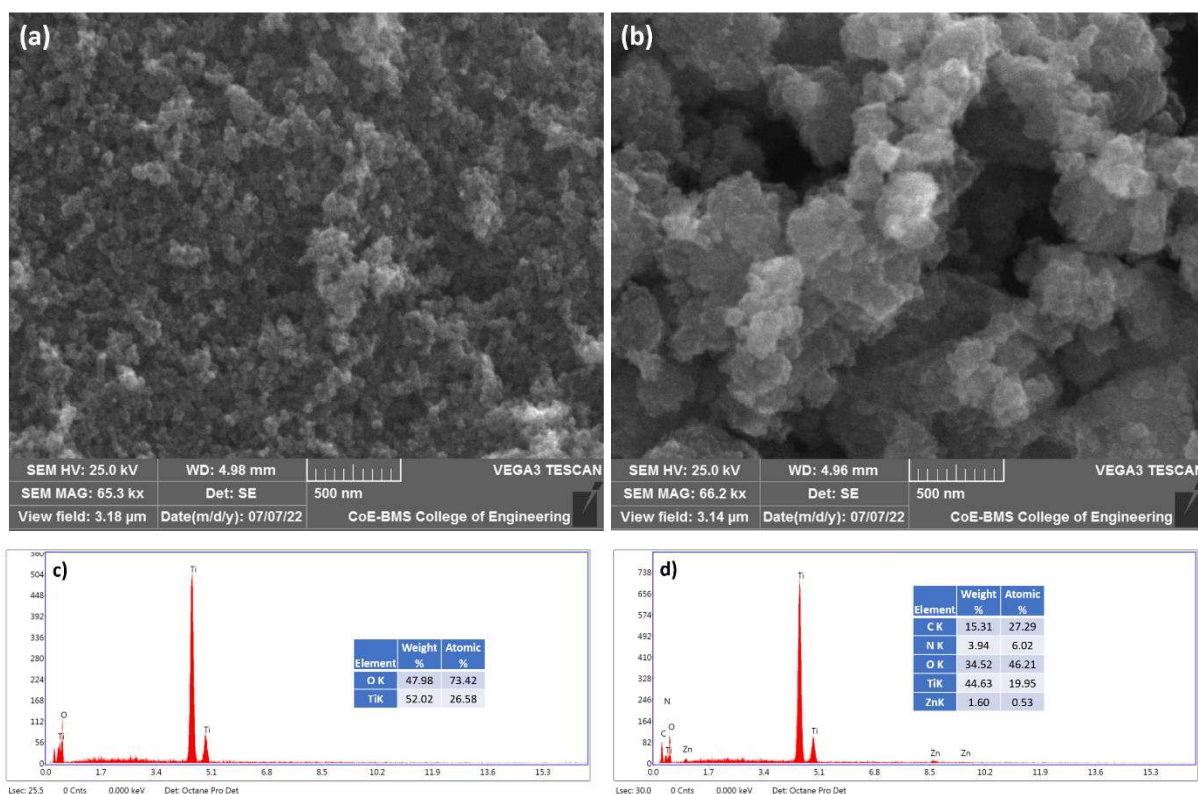


Fig. 5 FESEM images of (a) TiO₂ and (b) ZnPc_SB@TiO₂; Energy-dispersive X-ray spectrum (EDX) of (c) TiO₂ and (d) ZnPc_SB@TiO₂.

3.5 Photocatalytic activity

The photocatalytic activity of TiO₂ and ZnPc_SB@TiO₂ for the photoreduction of Cr (VI) to Cr (III) in aqueous media was examined under the influence 100 W LED. Potassium dichromate (K₂Cr₂O₇) was selected as a model reagent for Cr (VI). The initial investigation was undertaken to recognize the contribution of light and photocatalyst in the transformation of Cr (VI) to Cr (III) under the following conditions: (i) in the absence of a light source and in the presence of photocatalyst. (ii) in the absence of photocatalyst and in the presence of light source. The preliminary assessment depicted that no transformation of Cr (VI) to Cr (III) was observed in the absence of light source and photocatalyst.

UV-vis absorption spectra of Cr (VI) in the presence of 30 mg of ZnPc_SB@TiO₂ photocatalyst at pH 2 under the stimulus of a 100 W LED as a visible light source can be seen in Fig. 6(a). It is evident from the spectra that the characteristic absorption peak intensity of Cr (VI) decreases considerably with an increase in the irradiation time, indicating successful

transformation of Cr (VI) to Cr (III) owing to the photocatalytic activity of ZnPc_SB@TiO₂ photocatalyst. The photocatalytic reduction of Cr (VI) to Cr (III) in the presence of 30 mg of ZnPc_SB@TiO₂ photocatalyst at pH 2 under the stimulus of a 100 W LED as a visible light source was found to be 88% after 90 minutes. Under similar experimental conditions, TiO₂ alone exhibited less than 10% transformation of Cr (VI) to Cr (III), indicating superior photocatalytic activity of ZnPc_SB@TiO₂ photocatalyst.

The rate constant for the photocatalytic reduction of Cr (VI) to Cr (III) by ZnPc_SB@TiO₂ photocatalyst was assessed by considering the slope obtained by plotting $\ln \frac{C_0}{C_t}$ vs light irradiation time. Fig. 6(b) shows a linear relationship between $\ln \frac{C_0}{C_t}$ and light irradiation time t , indicating that the photocatalytic reduction of Cr (VI) to Cr (III) by ZnPc_SB@TiO₂ photocatalyst follows a 1st order kinetics model. The reaction rate constant (k) determined by the slope obtained by plotting $\ln \frac{C_0}{C_t}$ vs light irradiation time t was found to be 0.0227min⁻¹.

The exceptional photocatalytic activity of ZnPc_SB@TiO₂ photocatalyst compared to TiO₂ can be attributed to the fact that TiO₂ alone is not visible light active; nevertheless, when the TiO₂ is sensitized with highly conjugated ZnPc_SB, the system becomes visible light active and demonstrates superior photocatalytic activity. In addition, the presence of imine groups in ZnPc_SB gains positive charge at pH 2 which greatly facilitates the adsorption of Cr (VI) on the photocatalyst surface. The present investigation demonstrates explicitly that surface functionalization of TiO₂ with ZnPc_SB results in an efficient visible light active photocatalyst for heavy metal remediation.

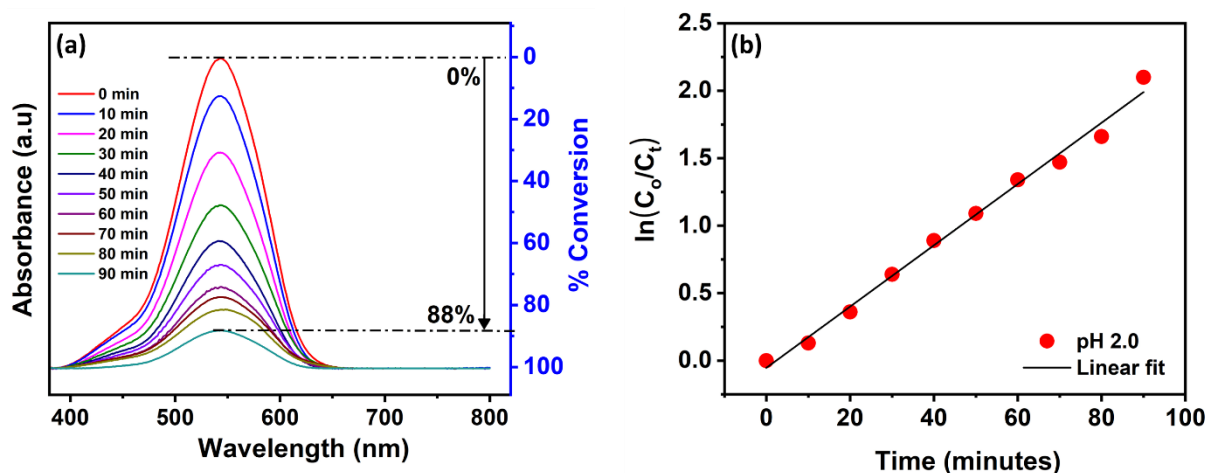


Fig. 6 (a) UV-visible absorption spectra of Cr (VI)-diphenylcarbazide complex in the presence of ZnPc_SB@TiO₂ as photocatalyst. (b) Kinetic study, Plot of $\ln \frac{C_0}{C_t}$ as a function of light irradiation time for of Cr (VI)-diphenylcarbazide complex in the presence of ZnPc_SB@TiO₂ as photocatalyst.

3.6 Impact of catalyst loading

One of the primary parameters that vividly impacts photoreduction of Cr (VI) to Cr (III) is catalyst loading. In order to recognize the optimal photocatalyst loading, the effect of photocatalyst loading on the photoreduction of Cr (VI) to Cr (III) was assessed. To understand the effect of catalyst dosage, Cr (VI) photoreduction was carried out with catalyst dosages of 10, 20, 30, 40, and 50 mg of ZnPc_SB@TiO₂. Photocatalytic effectiveness is amplified with a rise in catalyst quantity due to the increased availableness of active sites on the surface of ZnPc_SB@TiO₂ for Cr (VI) adsorption. The percentage of Cr (VI) to Cr (III) reduction was found to be 88% at a catalyst dosage of 30 mg, and no significant increase in photocatalytic efficiency was observed above 30 mg. As a result, the optimum photocatalyst loading was identified to be 30 mg.

3.7 Impact of the pH

The photocatalytic reduction of Cr (VI) to Cr (III) depends on the surface charge of the photocatalyst, whereas maintaining the surface charge depends on the pH of the solution. It has

been well documented that an acidic environment boosts electrostatic interaction between the photocatalyst and chromate ion, which facilitates Cr reduction (VI) [30]. The reduction rate of Cr (VI) is higher under acidic pH because Cr (VI) exists as $\text{Cr}_2\text{O}_7^{2-}$ in the acidic pH, whereas in the alkaline pH it exists as CrO_4^{2-} or HCrO_4^- . An acidic medium favors the Cr (VI) reduction, whereas an alkaline medium induces the opposite result because of the presence of OH^- ions. At higher pH, the catalyst surface will be negatively charged, and the adsorption of Cr (VI) will be weak. Thus, the photocatalytic reduction efficiency is poor in alkaline media. Therefore, the impact of pH on the photocatalytic reduction process of Cr (VI) to Cr (III) was investigated at various pH of 2, 4, and 6, and the results are presented in Fig. 7 (a). As expected, at lower pH, the maximum photocatalytic transformation of Cr (VI) to Cr (III) was achieved when compared to the higher pH of the medium for the ZnPc_SB@TiO_2 photocatalyst. At pH 2, maximum photoreduction of 88% was achieved, followed by 42% at pH 4 and 18% at pH 6. Kinetic studies established that photocatalytic reduction of Cr (VI) to Cr (III) at different pH levels follows pseudo-first-order kinetics, and the observed slopes were found to be 0.0227 min^{-1} , 0.0059 min^{-1} , and 0.0024 min^{-1} for pH 2, 4, and 6, respectively.

3.8 Photo catalyst re-usability

The photocatalyst's stability and reusability are critical for practical use in an economical and effective manner. Reusability studies for the photocatalytic reduction of Cr (VI) under similar experimental conditions were carried out to investigate the stability and endurance of the ZnPc_SB@TiO_2 photocatalyst. In reusability experiments, the used photocatalyst was collected by ultracentrifugation, treated with 0.01 N NaOH, water, and ethanol, and then dried before reusing. The photocatalytic reduction studies for Cr (VI) were carried out under optimal experimental conditions for four consecutive cycles, and the results are shown in Fig. 7 (b). It can be observed that the competence of the ZnPc_SB@TiO_2 photocatalyst declined gradually to 88, 83, 80, and 74% for the first, second, third, and fourth

cycles, respectively. According to the results, the ZnPc_SB@TiO₂ photocatalyst exhibited a slight drop in photocatalytic efficiency up to the third cycle, indicating ZnPc_SB@TiO₂ photocatalyst has comparatively good stability and can be reused.

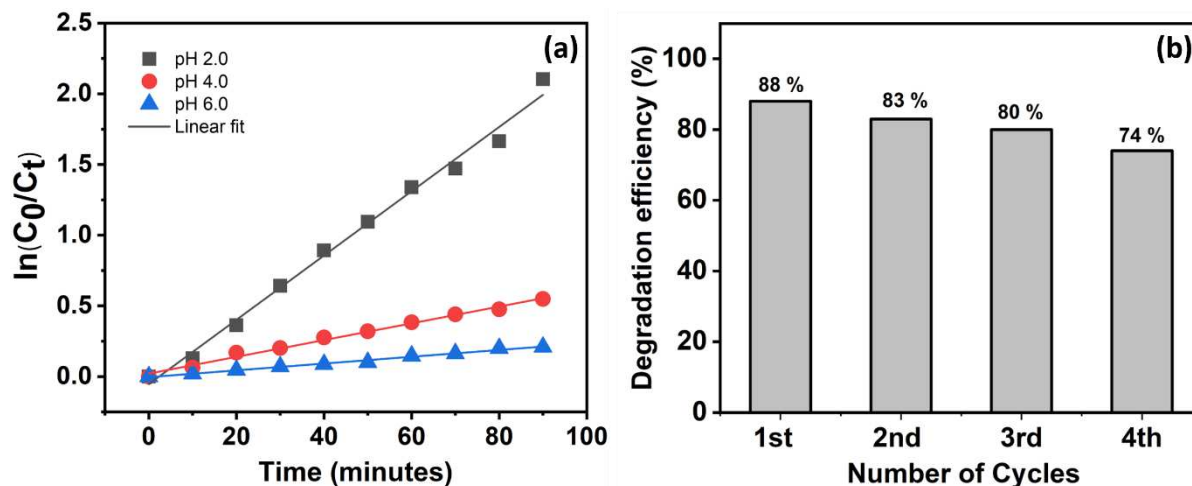


Fig. 7 (a) Kinetic study, Plot of $\ln \frac{C_0}{C_t}$ as a function of light irradiation time for of Cr (VI)-diphenylcarbazide complex in the presence of ZnPc_SB@TiO₂ as photocatalyst at different pH. (b) Reusability valuation of the ZnPc_SB@TiO₂ as photocatalyst for photocatalytic reduction of Cr (VI) at pH 2.

4 Conclusion

The current study aims to examine the impact of surface sensitization of TiO₂ nanoparticle by ZnPc embedded Schiff-Base polymer (ZnPc_SB) on photocatalytic remediation of pollutants in water. The sequence of the determined band gap by solid-state diffusive reflectance spectra was found to be TiO₂ (3.26 eV) > ZnPc_SB (3.03 eV) > ZnPc_SB@TiO₂ (3.01 eV). The observed red shift in the visible region and decreased band gap in ZnPc_SB@TiO₂ compared to pristine TiO₂ demonstrate the impact of surface sensitization and effective electronic interaction between TiO₂ and ZnPc embedded Schiff-Base polymer. To explore the photocatalytic competence of the TiO₂ and ZnPc_SB@TiO₂, under the influence of energy efficient LED light source, photoreduction of hexavalent chromium was under taken. The complex forming ability of diphenylcarbazide was used to determine the Cr ion concentration

during the course of investigation. After 90 minutes, it was discovered that 88% of the photocatalytic reduction of Cr (VI) to Cr (III) in the presence of ZnPc_SB@TiO₂ photocatalyst at pH 2 under the stimulus of 100 W LED. TiO₂ alone showed less than 10% transformation of Cr (VI) to Cr (III) under identical experimental conditions, indicating superior photocatalytic activity of ZnPc_SB@TiO₂ photocatalyst. The ZnPc_SB@TiO₂ photocatalyst demonstrated admirable photocatalytic activity and stability even after multiple reuses. Therefore, ZnPc_SB@TiO₂ can be considered as a viable option for removing hazardous pollutants from wastewater.

Author Contributions:

Shwetha Rajappa: Writing - Original Draft, investigation, methodology, Data Curation, Validation. Poornima Gubbi Shivarathri: investigation, methodology. P V Midhunlal: investigation, methodology. Praveen Kumar M V: investigation, methodology. Bhagyashree B Jahagirdhar: investigation, methodology. Viswanatha Handhvinahalli Mariswamy: investigation, methodology. Mruthyunjayachari Chattanahalli Devendrachari: Formal Analysis, Data Curation, Writing - Original Draft. Harish Makri Nimbegondi Kotresh: Supervision, Resources, Conceptualization, Data Curation, Validation, Writing - Original Draft, Review & Editing.

Data Availability

No data was used for the research described in the article.

Declarations

The authors declare no conflict of interest.

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