Removal of chlorhexidine digluconate from aqueous solution by heterogenous photocatalysis using sunlight-driven Ni-doped TiO₂ material

Astha Singh, Brijesh Kumar Mishra[†]

Department of Environmental Science and Engineering, Indian Institute of Technology (Indian School of Mines), Dhanbad-826004, India

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ABSTRACT

Photoactive Ni-TiO₂ was synthesized through green hydrothermal method with preferential photocatalytic performance in visible and solar light for synthetic and formulated wastewater treatment. Incorporation of this transition metal into TiO₂ was examined by XRD, FTIR, UV-visible DRS, XPS, SEM-EDS and HRTEM analysis. According to the Langmuir-Hinshelwood model, the photodegradation of the chlorhexidine digluconate under solar ($R^2=0.986$) and simulated visible light ($R^2=0.982$), follows a pseudo-first-order kinetics. The interaction of operational fractions, such as S/C ratio, irradiation time, and pH of the reaction mixture, were evaluated using the RSM. Although complete mineralization of CHD was not achieved using Ni-TiO₂ under visible light, but the parent compound was mineralized to some extent, as demonstrated by TOC reduction (85.71%-synthetic wastewater and 61.17%-formulated wastewater), UV₂₅₄ (89.91% synthetic wastewater and 55.39%-formulated wastewater) and UV₂₈₀ (68.23%-synthetic wastewater and 68.23%-formulated wastewater) absorbance variations. Based on the identified transformed products, the possible degradation pathway was proposed and bacterial susceptibility test on *Bacillus cereus* DPAML065 was performed to evaluate the toxicity of oxidation intermediates. Comparative studies about energy consumption and removal efficiency during simulated visible light/Ni-TiO₂ and sunlight/ Ni-TiO₂ mediated treatment system for formulated wastewater revealed that sunlight/ Ni-TiO₂ mediated treatment system was high energy efficient (1.67 kWhKg⁻¹) system.

Keywords: Formulated wastewater, Ni -doped TiO₂ catalyst, Power consumption, Solar photocatalysis

1. Introduction

Although personal care products (PCPs) have been used for decades, their fate and discharge into the aquatic environment only has recently been identified as one of the most significant environmental chemistry issues. In accordance with the Water Framework Directive (2000/60/EC of the European Parliament and Council) and other legal statutes (Decision 2455/2001/EC, Directive 2008/105/EC), various organic pollutants including PCPs have been identified as priority pollutants in the environmental strategy of EU against water pollution [1]. These compounds are formulated to be physiologically active and resistant to biodegradation, which significantly increases their presence in aquatic environment and are labelled as “pollutant” [2]. The principal pathway of these

compound into the aquatic ecosystem is through excreta from human or animal urine or faces [3]. The model compound chlorhexidine digluconate (CHD) is widely used as a disinfectant in hand-wash, sanitizer, toothpaste, mouthwash, and cosmetic preservatives. When the COVID-19 pandemic broke out, the use of personal care products such as disinfectants soared dramatically in hospitals, health care facilities, and households all around the world [4]. They are excreted directly into the environment after usage, without being modified or treated in any way. The long-term exposure of CHD is associated with harmful effect on human health. Even though small concentration of CHD has received little attention because it was found that transformed products render the total mineralization of parent compound. Additionally, monitoring programs of the European Union for pharmaceutical and personal

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[†] Corresponding author

E-mail: brijesh@iitism.ac.in

Tel: +91-326-2235752

Fax: +91-326-2296624

ORCID: 0000-0002-4451-1924

care products are not yet defined even though they could be future candidates for causing acute or chronic toxicity in the aquatic ecosystem [5].

Thus, removal of CHD is not adequate effective by conventional treatment process. Therefore, considering the disadvantages of all the conventional treatment, semiconductor nanostructure developed significantly in the field of photocatalytic application for efficient removal of organic pollutant [6]. High quantum efficiency, high chemical stability in aqueous media, inexpensiveness, and nontoxicity of TiO_2 were recognized as a significant reason for their widespread acceptance as photocatalyst compared to another semiconductor. Nevertheless, some of their internal limitations including poor visible light consumption, decreased photo-generated electrons and holes pairs separation, and a lack of active species generation hampered their practical uses. Thus, the development of an efficient and new type visible light-driven (VLD) photocatalysts, as well as extensive synthesis and modification methods, are the main challenges in current studies to maximize the exploration of solar light [7, 8].

Very recently, transition metal/nonmetals (V, Cr, Mn, Fe, Ni, Cu) doped TiO_2 are widely used photocatalysts for the removal of organic pollutant. In addition to this, wide band gap, high oxidation capacity, low cost, and remarkable potential application under visible and solar radiation of Ni doped TiO_2 have been found to be promising photocatalyst [9]. To obtain the sunlight driven photocatalyst, the addition of Ni-content tuned the band gap from 3.03 to 2.54 eV for tetragonal and cubic structure of TiO_2 and Ni- TiO_2 , respectively. Furthermore, similar ionic radius of Ti^{4+} (0.68 Å) and Ni^{2+} (0.72 Å), could be beneficial in the substitution of Ni^{2+} in the place of Ti^{4+} in the crystalline lattice of TiO_2 [10]. Though various studies reported the modification of electrical and optical properties by controlling their microstructure for practical applicability [11]. The development of a simple and cost-effective method for producing high-yield nanostructured Ni- TiO_2 toward sunlight driven photocatalytic application remains a major challenge.

Photodegradation involves number of independent and dependent variables because this manual optimization is quite difficult to carry out. Keeping the above facts, Response surface methodology (RSM) has been used to elaborate the interaction among the operating condition (pH, substrate to catalyst ratio and time) and their subsequent effect on photocatalytic activity with respect to mineralization of CHD, phenolic compound, and reduction of aromaticity during photocatalysis process [12]. The optimization of photocatalysis process has been carried out using Face Centered Central Composite Design (FCCD), resulting in a good estimate of the optimum response.

To understand the mineralization process of PCPs such as CHD into their transformed products and conversion of heteroatoms as well as functional group during photocatalysis process are again another challenging task. Monitoring of such intermediate generally carried out with the help of GC-MS, LC-MS and HPLC, which is the time consuming and costly procedural. The present study not only provide ideal scenario for photocatalysis process with different photocatalyst, but also opens a new avenue to understand the mineralisation of emerging pollutant coupled with simultaneous reduction of phenolic as well as aromaticity

through Absorbance Slope Index (ASI) and spectral indices [13]. For example, UV absorbance at specific wavelengths (e.g., UVA 203, 204, 220, 230, 253 254, 260, 265, 272, 275 and 280), and ASI correlate well with the degradation CHD, aromaticity, hydrophobicity and transformed products. In previous studies, employment of spectral indices approach for characterization of DOM (aromatic components) has been demonstrated to be feasible, fast and easy tool [14].

In this research, a green hydrothermal synthesis approach was adopted, which is simple to use and can reduce time as compared to other conventional TiO_2 modification techniques. The work describes the effect of Ni-doping on the photocatalytic activities of TiO_2 under natural sunlight and simulated visible light with respect to degradation of the CHD, the mineralization rate (in terms of TOC) and UV absorbance (UV_{254} and UV_{280}). Meanwhile, the presence of Ni-particle in TiO_2 was validated by XPS, XRD, HRTEM and EDS. Radicals trapping experiment carried out to discuss the prominent radicals in the photodegradation system. A toxicity test of oxidation intermediates, high reusability, and electrical energy consumption, indicating the practical reliability and safe disposal of Ni- TiO_2 . The research also established the efficiency of photo mineralisation of CHD through HPLC and toxicity test of its oxidative by-products on the water bodies. Thus, current study provides the guidance for large scale applicability of Ni- TiO_2 system in the field of pharmaceuticals and personal care products (PPCPs) with special emphasis on personal care products loaded wastewater.

2. Materials and Methods

2.1. Materials

Chlorhexidine digluconate (CAS # 18472-51-0-C9394) of 20% in H_2O was purchased from Sigma-Aldrich. Titanium dioxide and other chemicals were procured from Merck (India) and Sigma-Aldrich. Chlorhexidine digluconate solution and formulated wastewater were prepared using a Milli-Q water system (Millipore). All chemicals are analytical graded.

2.2. Synthesis of Photocatalyst

The raw material and precursor used for preparation of Ni-doped TiO_2 includes titanium tetra-isopropoxide, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HNO_3 . The clear aqueous solution was prepared by adding 10 mL of titanium tetra-isopropoxide into a beaker containing 60 mL of deionized water and 10 mL of isopropanol for 1 h of stirring. This clear solution was then added to 3 mmol of nickel (II) nitrate hexahydrate and 60 mL of 0.02M nitric acid for 2 h of continuous stirring. After obtaining clear solution, later add ammonium hydroxide drop-wise into the solution followed by vigorous stirring for 2 h to obtain a residue. The stirring was maintained for the next 6 h at a steady temperature of 80°C to ensure proper mixing of the solution. The resulting material was washed several times using distilled water to remove the impurities and dried in the air for 24 h. Thus, dried material was grinded in agate mortar and then calcined in the furnace at 600°C for 2 h [10, 15].

2.3. Characterization of Photocatalyst

The crystallinity, morphology, elemental analysis, optical measurement, and bandgap modification of the prepared photocatalyst were analyzed. Scanning electron microscopy (SEM) using Hitachi S-4300 type, High Resolution Transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) patterns were used to examine the morphology, microstructure, distribution, and incorporation of elements on the TiO₂. X-ray diffraction (XRD) were recorded using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation on a Bruker D8 ADVANCE diffractometer to analyze the crystalline phase of the prepared material. The optical properties of the sample were recorded from UV-vis spectrophotometer (Perkin Elmer Lambda 900 spectrophotometer) equipped with BaSO₄ powder was used as a reference for baseline study. Bandgap calculated from the modified Kubelka-Munk plot against wavelength ranging from 200–900 nm using diffuse reflectance spectra (DRS). The Brunauer Emmett Teller (BET) model was used to calculate specific surface area using the linear portion ($P/P_0 = 0.05 - 0.2$). The infrared spectrum of Ni-TiO₂ was scanned through Bruker Vertex- 70 Fourier transform infrared (FTIR) to identify the presence of functional groups of prepared material. X-ray photoelectron spectroscopy (XPS) were used to examine the oxidation state and charge compensation of the element present in the material using a VG 250 Escalab spectrometer equipped with an Al anode (Al-K $\alpha = 1,486.7 \text{ eV}$) as an X-ray source. The textural and optical properties of the synthesized catalysts are given in Table S1.

2.4. Synthetic Wastewater Formulation

The pharmaceutical wastewater was prepared in the laboratory, based on the composition of real wastewater of the pharmaceutical industry with slight modifications [16]. The physiochemical characteristics of formulated wastewater such as pH, TOC, COD, BOD₅ and Ultraviolet (UV) absorbance at 254 nm are presented in Table S2.

2.5. Experimental Setup and Procedures

The photocatalytic activity of Ni-TiO₂ was investigated through CHD degradation using simulated visible light and natural sunlight as a source of irradiation. In a typical photocatalytic degradation experiment using simulated visible light, an aqueous solution of CHD was mixed and stirred well with Ni-TiO₂ powder in a photocatalytic system consisting of a 1 L Pyrex reactor (diameter 96 mm and height 140 mm) with Hg lamp (200 W), mounted inside the system and a beaker with the same dimensions used for sunlight mediated experiment. To compare the performance of Ni-TiO₂ in different light sources, the photocatalytic degradation of formulated wastewater containing CHD was also carried out using UV, visible, and solar light as irradiation sources [17]. The suspension was sonicated for 5 m and then irradiated with simulated visible light (300–420 nm and 40 m-W/cm²) or sunlight (30–40 m-W/cm²). The light intensity was measured by a radiometer (Delta OHM, LP-NET14). Aliquots (3 mL) were taken from the suspension at equal intervals, and centrifuged (4°C, 11,000 X g, 5 min) before being filtered with 0.22 μ m syringe filters for UV absorption spectra and TOC analyses.

2.6 Experimental Design Using Response Surface Methodology

Response Surface methodology was used to optimize three variables (S/C ratio, pH and time) with 3 different levels (+1, 0 and -1) for maximum CHD removal as response. The experiment design (DoE) was performed on the basis of the FCCD devised by Design Expert v7.0.0 software (SaMeep 104, State Ease, INC. Minneapolis (USA)). A total of 20 different combinations were obtained with six center points in random order according to Central Composite Design (CCD) configuration for three factors. In this analysis, FCCD was used to model the percentage removal of CHD as quadratic model. Statistical validation was done by using "Analysis of variance" (ANOVA), correlation coefficient (R^2), lack of fit, CV% and R^2_{adj} . A general second order polynomial model was selected and expressed by an Eq. (1) to investigate the effects of individual parameters as well as their synergistic interactive effects on the response variable [12].

$$y = b_0 + \sum_{i=1}^3 b_i X_i + \sum_{i=1}^3 b_{ii} X_i^2 + \sum_{j=1}^3 \sum_{i=1}^3 b_{ij} X_i X_j \quad (1)$$

Where y is the response variable, b_0 is the constant, b_i the linear coefficient, b_{ii} the quadratic coefficient, b_{ij} the interaction coefficient and X_i dimensional coded variables (X_1 for the S/C ratio, X_2 for the time and X_3 for the reaction medium pH).

2.7. Analytical Procedure

The quantitative measurements of concentration of CHD and their degradation products were monitored by UV-vis spectrophotometer (Lab-tech, China) at 275 nm wavelength and LC-MS analysis (Thermo Scientific TSQ 8000 liquid chromatograph-mass spectrometer). TOC analyser (Shimadzu 5000) was used to determine the extent of CHD mineralization.

The Langmuir-Hinshelwood model has been carried out to study the modelling CHD degradation Eqs. (2) and (3).

$$\ln \frac{C_t}{C_0} = -k_{obs} t \quad (2)$$

$$r_{obs} = -k_{obs} C_{CHD} \quad (3)$$

Where, k_{obs} (Reaction rate constant) was calculated from the slope by plotting a graph between $\ln \frac{C_t}{C_0}$ versus t and r_{obs} is the observed CHD degradation rate (mg L⁻¹ min) in the photoreactor [18].

UV absorbance at various wavelengths (203, 204, 220, 230, 253, 254, 260, 265, 272, 275 and 280) were employed to investigate the reduction in aromaticity of compound, residuals of phenols and ASI, calculation can be represented as [19]:

$$ASI = 0.56 \left[\frac{A_{254} - A_{272}}{A_{220} - A_{230}} \right] \quad (4)$$

Where A_{220} , A_{230} , A_{254} and A_{272} are the representative of UV absorbance at wavelength 220, 230, 254 and 272 nm, respectively.

The quantitative measurements of the conversions of CHD and

the degradation products were validated on a High-Performance Liquid chromatograph (Phenomenex UK) equipped with a hyperclone (Eclipse plus C18 column; $3.5 \times 4.6 \times 100$ mm) and connected to a UV-ViS detector. The spectrophotometer was set at 275 nm and 1.5 ml/mi. flow rate for 10 min. of retention time was used for the chromatograph. As a mobile phase solution of acetonitrile (70% v/v) and ultrapure water (30% v/v) was selected. Sample injection volumes were 10 μ L and filtered by 0.2 μ m syringe filters prior to injection [5]. Liquid Chromatography-Mass Spectrophotometer was used to investigate degradation pathway of CHD and its metabolites formation.

2.8. Bacterial Susceptibility Test

Bacillus cereus DPAML065 was used in a susceptibility test to determine the toxicity of partially/fully mineralized CHD using autoclaved Muller Hinton agar medium and petri plates at 121°C for 20 min. Approximately 1 mL of *Bacillus cereus* culture broth suspension was added to fresh medium and mixed. After incubation, this homogeneously mixed culture solution of bacteria and medium displays a confluent lawn of growth. Prior to the observation of the inhibition zone, the bacterial growth was incubated for 24 h at 37°C.

3. Results and Discussion

3.1. Characterization of the Photocatalysts

The XRD pattern showed the phase structure of the prepared photocatalyst in (Fig. 1(a)). The observed peaks at $\sim 25^\circ$ and 56° confirm the anatase form of tetragonal structure of pure TiO_2 matched with (ICSD reference number 01-086-1155). In addition, the characteristic peaks of NiTiO_3 at $\sim 27^\circ$, 36° , 47° and 54° were ascribed the cubic structure of Ni-TiO_2 matched with (ICSD reference number 01-075-0399) [20]. Thus, analysis provides a possible assumption that incorporation of Ni^{2+} into the TiO_2 favouring the formation of NiTiO_3 [21]. The intensity of peaks of undoped TiO_2 decreased and slightly shifted due to the doping of metal; this revealed that Ni enter the TiO_2 crystal lattice successfully. This Ni^{2+} could replace Ti^{4+} due to the similar ionic radius i.e. $0.72 \text{ \AA}$ (Ni^{2+}) and $0.68 \text{ \AA}$ (Ti^{4+}) and cause distortion as well as a defect in their lattice. Cubic crystal structure of Ni-TiO_2 demonstrated that doping of nickel modifies the tetragonal crystal structure of TiO_2 and Ti^{4+} lattice sites were occupied by Ni^{2+} as a substitutional impurity [11]. This phase transformation was observed with incorporation of Ni content can be explained by the fact that when Ni and Ti bond attached to O atom, Ti loses electron more easily than Ni atom due to the difference of electronegativity between Ti (1.54) and Ni (1.91). Thus, the large angle was found between the among Ni-O bonds than the Ti-O bonds this leads to the stronger interaction between the second Ti-O bonds and also due to the stronger polarity of the Ni-O bonds and hence results in deviation of crystal structure from tetragonal to cubic [22]. The Debye-Scherrer formula used FWHM data from the XRD peak to calculate the average crystallite sizes of the photocatalyst (Eq. (5)).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (5)$$

Moreover, it was found that there is decrease in crystallite size of pure TiO_2 (3.91 nm) due to doping of nickel in Ni-TiO_2 (2.96 nm). Thus, Ni^{2+} tries to replace Ti^{4+} which may be better explained by the broadening of peaks due to defects formed by Ni^{2+} in TiO_2 [23]. Fig. 1(b) depicts clearly the prominent peak and shifting of 2θ in prepared material (Ni-TiO_2), which verifies the doping of Ni in TiO_2 [24]. Doping of Ni^{2+} in TiO_2 inhibits the size of crystallite and enhance the formation of anatase crystalline phase of TiO_2 . This smaller crystallite size of Ni-TiO_2 particles were further validated by the scanning electron microscopy (SEM) and our findings are consistent with previous studies [10].

The SEM and High-resolution transmission electron microscopy (HRTEM) confirmed the smaller crystallite sizes of Ni-doped TiO_2 particles. The SEM micrographs of undoped TiO_2 clearly shows the uniform regular spherical particle distribution (Fig. 2(a), (b)). After loading of Ni, the surface of TiO_2 sphere exhibits both spherical and slightly elongated rod-like porous structure (Fig. 2(c)~(h)). Furthermore, EDS analysis was also performed to verify and confirm the elemental composition of undoped TiO_2 and the loading of Ni content in Ni-TiO_2 . The EDS spectrum shows the presence of Ti, O along with Ni were found confirming the undoped and Ni doped TiO_2 [10]. The content of observed element in sample are mentioned in Table S1. HRTEM images and selected area electron diffraction (SAED) patterns show the presence of the lattice fringes and crystallinity of prepared material. Additionally, mapping shows the successful incorporation and equal distribution of metal ion onto Ni-TiO_2 sample [25].

FTIR spectrum was recorded to elucidate the presence of chemical group on the surface of TiO_2 and formation Ni-TiO_2 (Fig. 1(d)). The broad hump on TiO_2 and Ni-TiO_2 showed absorption peak around $3,402.71 \text{ cm}^{-1}$, which is characteristic peak of the OH-stretching vibration of surface absorbed water molecules. The peak representing Ti-O stretching bond were identified at 544 cm^{-1} , which is the characteristic band of pure TiO_2 sample [26]. Interestingly, characteristic peak of metal-oxygen vibrational bond were observed in the range of $700\text{--}400 \text{ cm}^{-1}$, thus sharp absorption peaks around $500\text{--}450 \text{ cm}^{-1}$ confirms the characteristic peak of metal titanate bond Ti-O-Ni [9]. Additionally, the characteristic peaks of Ni-OTiO₂ and O-O stretching vibration were identified around 609.88 and 854.49 cm^{-1} . The peaks around $1,380 \text{ cm}^{-1}$ caused by substitution of the Ni^{2+} in place Ti^{4+} lattice sites [27, 28]. On other hand, the physically adsorbed water from H-O-H bending vibration, which was identified from the sharp peak at $1,630 \text{ cm}^{-1}$. In contrast to pure TiO_2 , the Ti-O peaks for Ni doped TiO_2 occurred at higher wavenumbers. For instance, Ti-O stretching bond of pure TiO_2 and Ni-OTiO_2 were identified at 544 and 609.88 cm^{-1} , respectively. This could be due to the incorporation of Ni^{2+} into the TiO_2 crystal structure which was further validated by XPS and confirmed by XRD. The high-resolution XPS spectra showed the chemical state of the elements and its effect in pure TiO_2 and Ni-doped TiO_2 (Fig. 3). The characteristics peak of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ found at 458.89 and 464.77 eV , respectively indicated the existence of Ti^{4+} species [29]. On comparison of undoped TiO_2 , two distinct

Fig 1. (a) XRD; (b) magnified XRD; (c) Nyquist plot; (d) FTIR; (e) DRS-spectra; and (f) Kubelka - Munk function photocatalysts TiO₂ and Ni-TiO₂.

peaks attributed to Ni 2p_{3/2} and Ni 2p_{1/2} at binding energies of 854.3 and 872.1 eV were observed. The presence of a Ni-O band is suggested by the difference between these peaks, which is 17.6 eV [30]. This slightly shifting of the binding energy of Ti 2p corresponding to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively in Ni-TiO₂ (Fig. 3(b)). The photoelectron peaks of the oxygen lattice (O 1s) in Ni-doped TiO₂ i.e 529.76 is slightly lower than 530.15 eV of undoped TiO₂ (Fig. 3(d)). Thus, change in state of oxygen and intensity of peak slightly toward the higher binding energy due to the difference in electronegativity of both element (Ti = 1.54 and Ni = 1.91) [31]. Consequently, transformation of titanium ions to higher valent state takes place by releasing plethoric electron to achieve charge balance in the TiO₂ lattice following the introduction of Ni²⁺ [32]. Thus, this indicated the incorporation of Ni²⁺ ions in TiO₂ lattice of Ni-doped TiO₂ sample [25]. The surface hydroxyl

group or chemisorbed water molecules also reflects peak in Ni-doped TiO₂ at 532.30 eV [33]. These observation has been ascribed the successful formation of bond among Ni-O-Ti in the Ni-TiO₂ material [10].

UV-vis spectrum analysis was used to determine the electronic structure of the samples, which provides the optical properties (such as absorption and band gap) through the irradiating light intensity. Kubelka-Munk and Tauc's plots were used to convert the reflectance spectra for bandgap estimation (Fig. 1(e) and (f)). Undoped TiO₂ and Ni doped TiO₂ showed absorption bands ranging from 200 to 300 nm and 400 to 500 nm, respectively. It has also been observed that photocatalytic efficiency of Ni doped TiO₂ is significant in the UVA lamp used in the experiment. Undoped TiO₂ (3.03 eV) showed significant absorption below 400 nm due to the charge transfer between ligand (O²⁻) and metal

Fig. 2. (a), (b) SEM, TEM, SAED and EDS images of photocatalysts TiO_2 ; and (c)–(h) Ni-TiO_2 .

ion (Ti^{4+}) [34]. However, doping of nickel ion causes new electronic states in TiO_2 , which led to the narrowing of band gap and shifting of absorption into the visible region of Ni-TiO_2 (2.54 eV). This electronic transition occurs from the valence band (2p level of oxygen) to conduction band (3d level of titanium) in pure TiO_2 . As a result of doping Ni^{2+} ions into the TiO_2 lattice, a Schottky barrier forms at the interface, which inhibiting electron-hole recombination. The electron transport from Ni^{2+} (3d) to TiO_2 conduction band is aided by this interfacial barrier [35]. Thus, obtained results demonstrated that Ni^{2+} doping could alter the crystalline structure, lowers the band energies, and widen the optical properties to the visible light.

The electrochemical impedance spectroscopy (EIS) provides information about the electrical property of material. The charge

transfer process and the solid electrolyte interface film are responsible for the two semicircles in the high-to-medium frequency range, respectively. The Nyquist plot is drawn between the real and imaginary parts of the impedance, and a smaller arc radius indicates that photogenerated electron-hole pairs are effectively separated, and that interfacial charge transfer is rapid. The result shows the smallest arc radius of EIS Nyquist plot in Ni -incorporated material, which is indicating the most effective separation of electron-hole pairs and the fastest interfacial charge transfer (Fig. 1(c)) [36].

The surface area of pure TiO_2 was $5.71 \text{ m}^2\text{g}^{-1}$ and increased to $12.19 \text{ m}^2\text{g}^{-1}$ for Ni-TiO_2 materials. The increase in surface area implying the presence of Ni^{2+} in TiO_2 lattice with their small crystallite sizes of Ni-TiO_2 materials [37].

Fig. 3. XPS spectra of photocatalysts TiO_2 ; and Ni-TiO_2 .

3.2. Regression Analysis for Photocatalytic Activity of Photocatalyst on CHD Removal

ANOVA is one of the statistical tools which is used to determine the significance and accuracy of quadratic model developed through response surface methodology. The regression analysis was carried out in order to obtain a good fit in the response function and to predict the catalytic behaviour of the photocatalyst using quadratic equation in terms of CHD removal efficiency. The three-dimensional response surface plots of CHD reduction over different catalyst have been shown in Fig. S1. The quadratic model has been developed to predict the catalytic activity and CHD removal as a function of X_1 (S/C), X_2 (pH), X_3 (Time) and calculated as three first order effect (X_1 , X_2 and X_3), interaction effect (X_1X_2 , X_1X_3 and X_2X_3) and three second order effect (X_1^2 , X_2^2 and X_3^2). A polynomial model was used to represent the effects of individual parameters as well as their synergistic interactive effects on the response variable in Eqs. (6) and (7).

$$\begin{aligned} \text{CHD removal \% (TiO}_2\text{)} \quad \gamma = & 44.97 - 3.35X_1 + \\ & 8.69X_2 + 3.42X_3 + 0.92X_1X_2 - 0.044X_2X_3 - 12X_1^2 - \\ & 0.84X_2^2 - 1.79X_3^2 \end{aligned} \quad (6)$$

$$\begin{aligned} \text{CHD removal \% (Ni-TiO}_2\text{)} \quad \gamma = & 47.19 - 2.66X_1 + \\ & 9.32X_2 + 4.02X_3 - 2.26X_1X_2 - 0.54X_1X_3 + \\ & 1.17X_2X_3 - 14.32X_1^2 - 2.41X_2^2 - 2.62X_3^2 \end{aligned} \quad (7)$$

The results of the analysis of variance (ANOVA) (Table S3) represent the suitable model for photocatalyst during photocatalysis process. The P-value of the model, for both the photocatalyst, was < 0.0001 , and the F-value was 27.84 and 396.87 for TiO_2 and Ni-TiO_2 respectively. These results confirmed that the model was highly significant, which is supported by the close agreement between the predicted and observed values. The R^2 values were obtained 0.9616, and 0.9970 for TiO_2 and Ni-TiO_2 , respectively, which implies good correlation in actual and predicted values for CHD removal and further confirmed the reliability of model [38]. Smaller $P > F$ (< 0.05) values show the significance of the particular model and the higher contribution towards the response variable, while the greater P-value of terms indicates the insignificance of the model.

3.3. Photocatalytic Degradation and Mineralization Efficiency

The photocatalytic performance of prepared catalyst compared to

Fig 4. Photocatalytic removal of (a) CHD under solar and visible light; (b) pseudo-first order kinetic model under solar light; (c) pseudo-first order kinetic model under visible light; (d) TOC removal; (e) UV absorbance reduction and (f) Trapping experiment of photocatalysts TiO_2 and Ni-TiO_2 .

TiO_2 was investigated under simulated visible light and natural sunlight (winter season) for removal of CHD from synthetic water and formulated wastewater under optimized conditions. The results showed higher removal efficiency of Ni-TiO_2 (90.34%-visible and 79.26%-solar light) as compared to TiO_2 (23.64%-visible and 15.69%-solar light) under both simulated visible and solar light (Fig. 4(a)).

These photocatalytic results demonstrated that doping of transition metal onto TiO_2 could improve the optical properties of

Ni-TiO_2 to visible range and give rise to new energy level in the bandgap of TiO_2 , which facilitates the inhibition of electron-hole recombination. SEM, EDX and TEM results demonstrated the modification of TiO_2 and revealed the shape of synthesised material as a slightly elongated particle, with presence of characteristic element. XPS and XRD results revealed the amount and state of Ni^{2+} in TiO_2 lattice that could promote the photocatalytic performance of prepared material. These results suggested that photocatalytic performance enhanced by doping

Fig 5. (a) Cycle experiment of Ni-TiO₂ in photocatalytic degradation of CHD under optimized condition; (b) Zeta potential of TiO₂ and Ni-TiO₂ at different pH and (c) Effect of pH on CHD degradation Ni-TiO₂.

of cationic metal in TiO₂ with small radii, which could occupy the lattice site of Ti⁴⁺ with more oxygen vacancies [39]. Therefore, extended light absorption properties of Ni-TiO₂ to visible region leads to the investigation of photocatalytic activity of Ni-TiO₂ under natural sunlight. The results depicted slight decrease in the removal efficiency of Ni-TiO₂ as compared to the visible region due to the variation in the intensity of sunlight [17]. This decreased solar intensity occurs due to the decrease in solar altitude and less transparency in the path of sunlight in the winter season [40]. Since, intensity of light is an important factor for the performance evaluation of a photocatalyst. Doping of metal on the surface of TiO₂ can be accessible by hydroxyl group present on the surface of a material, which can trap both electron and hole generated. Evidently, trapping experiment has been carried out to evaluate the active radicals responsible for the mineralization process [41]. Isopropanol (IPA) (1%), 1.0 mM of potassium persulfate (K₂S₂O₈) and ethylenediaminetetraacetic acid (EDTA) were used as scavengers of hydroxyl radicals ([•]OH), electron (e⁻), and holes (h⁺), respectively (Fig. 4(f)). This result indicates that IPA and EDTA inhibited the CHD degradation and further confirms that [•]OH and h⁺ were dominating reactive species. Therefore, the effect of photogenerated reactive species was found as de-

creased in order of [•]OH > h⁺ > e⁻. Therefore, it can be assumed that the generation of reactive species was influenced by intensity of sunlight which led to lowers the photocatalytic activity of Ni-TiO₂ sample.

Apart from light absorption, solution pH, surface charge and surface area of the catalyst are also responsible for high photocatalytic activity of Ni-TiO₂ compared to TiO₂. The point zero charge (pH_{PZC}) was measured to evaluate the surface charge of TiO₂ (6.2) and Ni-TiO₂ (6.8), respectively (Fig. 5(b)). The surface of catalysts was positively charged at the pH lower than their pH_{PZC} values and negatively charged at the pH higher than their pH_{PZC} values. Thus, higher degradation and mineralization of CHD takes place in alkaline condition (pH = 9.5), where surface of catalyst is negatively charged i.e. pH > pH_{PZC} and CHD (pK_a = 2.2 and 10.8) remain protonated which facilitates the interaction of catalyst and pollutant through electrostatic interaction [42]. Hence, alkaline condition enhances the photocatalysis process because the formation of hydroxyl radicals increased due to sufficient availability of OH⁻ in the reaction mixture.

The photocatalytic performance of Ni-TiO₂ was investigated by using Langmuir–Hinshelwood (L-H) kinetic model, based on pseudo-first-order kinetics (Eq. (2), (3)) for a solid-liquid interface.

Fig. 6. Photocatalytic removal of formulated wastewater (a) CHD; (b) pseudo-first order kinetic model under solar light; (c) pseudo-first order kinetic model under visible light; (d) TOC removal; (e) UV absorbance reduction using TiO_2 ; and Ni-TiO_2 .

Rate of reaction found by plotting the graph among $\ln(C/C_0)$ versus t (Fig. 4). The rate of reaction decreases under solar light due to the variation of light intensity during the experiment. The results showed that photocatalysis of synthetic wastewater using Ni-TiO_2 under simulated visible light and sunlight well fitted with pseudo-first kinetic order (Table 1). Among various photocatalytic conditions, Ni-TiO_2 showed highest k_{CHD} of 0.024 min^{-1} under optimized condition. Considering the fact that increasing the surface area enhanced the photocatalytic reaction rate because photocatalysis mainly occur on the surface of cata-

lyst [43].

For industrial application and better understanding of the photocatalytic efficiency of prepared catalyst, comparative studies have been carried out to treat formulated wastewater. The results demonstrated that removal efficiency of Ni-TiO_2 deduced for formulated wastewater treatment due to interference of other ions (Fig. 6(a)~(e)). The use of Ni-TiO_2 for the removal of organic pollutant could be scaled-up under sunlight because of cost effective, reusability and easy applicability even though removal efficiency decreased.

Table 1. PFO Model Kinetic Parameters of Chlorhexidine Digluconate (CHD) Degradation by Different Photocatalyst during UV, Visible and Solar Photocatalysis

Photocatalysts	Experimental conditions	Removal efficiency	R ²	k _{obs} value (min ⁻¹)	Light source
TiO ₂	C ₀ = 30 mgL ⁻¹ , S/C = 1.8, pH = 7.6, Synthetic water	23.64	0.974	0.003	visible light
	C ₀ = 30 mgL ⁻¹ , S/C = 1.63, pH = 8.2, Synthetic water	15.69	0.92	0.001	sunlight
	C ₀ = 30 mgL ⁻¹ , S/C = 1.8, pH = 7.6, formulated wastewater	20.07	0.97	0.0028	visible light
	C ₀ = 30 mgL ⁻¹ , S/C = 1.63, pH = 8.2, formulated wastewater	9.45	0.962	0.0035	sunlight
Ni-TiO ₂	C ₀ = 30 mgL ⁻¹ , S/C = 1.54, pH = 9.2, Synthetic water	90.34	0.982	0.0245	visible light
	C ₀ = 30 mgL ⁻¹ , S/C = 1.98, pH = 7.89, Synthetic water	79.26	0.986	0.0119	sunlight
	C ₀ = 30 mgL ⁻¹ , S/C = 1.54, pH = 9.2, formulated wastewater	90.34	0.976	0.022	visible light
	C ₀ = 30 mgL ⁻¹ , S/C = 1.98, pH = 7.89, formulated wastewater	79.26	0.986	0.239	sunlight

3.4. Possible Pathway and Toxicity Test

The performance of photocatalyst was also estimated in terms of TOC removal and reduction of UV₂₅₄. The oxidation process produces more harmful intermediates than the parent compound, which can be assessed using UV absorbance. The reactive organic fraction of wastewater loaded with organic pollutant is measured at a wavelength of UV₂₅₄ nm.

The overall reaction during photo mineralization of CHD in the excess of oxygen under optimized experimental condition is validated by the equation (Eq. (8)) given below:

As can be observed, reduction in reactive organic fraction increased rapidly after 20 min during the photocatalytic process using Ni-TiO₂ under visible (89.92%) and solar light (57.15%) (Fig. 4(e)). This difference in removal efficiency may be explained by the availability of sufficient solar light to generate a significant number of reactive species for the degradation of parent compound and their intermediate. Moreover, leftover reactive organic species in reaction mixture after photocatalysis process may be due to the formation of intermediate, which need more time to be removed [44]. A similar trend of mineralization was observed, where Ni-TiO₂ (85.71%-visible and 71.79%-solar light) showed highest TOC removal as compared to TiO₂ (21.70%-visible and 17.06%-solar) under visible and solar light, respectively (Fig. 4(d)). The results were validated using chromatogram of HPLC (Fig. S6). The toxicity test has been carried out for the successful applicability of photocatalyst in solar as well as visible light.

The possible degraded by-product and pathway during Ni-TiO₂ mediated photocatalysis of formulated wastewater under simulated visible light and solar light was investigated by LC-MS spectroscopy. The peak at 505 and 507 m/z shows two isotopes of Cl atoms (35 and 37) attached to CHD in aqueous solution. This characteristics

peak disappeared upon increasing the time during photocatalysis of formulated wastewater using Ni-TiO₂ under visible light process. According to LC/MS results, transformation of the characteristics peak to 453,316,221,127 and 200 m/z belongs to the intimidated products of photooxidation process. According to LC/MS results and literature available, a possible pathway was proposed by substitution and addition [45, 46] (Fig. S2(a) and S3). OH[•] and h⁺ were produced as a reactive species in Ni-TiO₂ mediated photocatalysis process, where OH[•] was dominating in the photocatalytic oxidation was investigated by trapping experiment. OH[•] attacked on benzene ring of CHD and involve breaking of C-Cl bond i.e., dichlorination of aromatic ring takes place by addition of OH[•]. Finally, resulted to the breakdown of biguanide moiety leads to the formation of smaller molecules of transformed products. In addition, quantification and mass identification of transformed product are beyond the scope of study.

Toxicological studies have been carried out to investigate the toxicity of transformed products. *Bacillus cereus* was subjected to bacterial susceptibility test, which is commonly found in human oral cavities. Inhibition zone of a standard solution of CHD, 30 mg/L concentration of sample, ciprofloxacin and amoxicillin antibiotics was 30, 15, 50 and 3 mm in diameter (Fig. S4). Negligible inhibition zone was observed for the degraded product after photocatalytic degradation of CHD. From the obtained results, it can be foreseen that the transformed products after photocatalytic degradation of CHD using Ni-TiO₂ as a photocatalyst are non-toxic upon release in the environment.

Thus, higher mineralization of CHD was found using Ni-TiO₂ as a photocatalyst under simulated visible light because modification of TiO₂ enhanced the absorption of light with the wavelength > 400 nm and promotes the formation of sufficient number of reactive species. This reactive species attack phenyl ring of CHD during oxidation process and break up into short-carbon compounds. Atomic adsorption analysis of treated wastewater has been carried out to check the metal leaching during photocatalysis

Table 2. Energy Consumption in Synthetic and Formulated Wastewater Treatment Using Photocatalyst under Different Treatment Condition

Photocatalysts	Experimental conditions	Removal efficiency	Working volume (L)	Reaction time (h)	Power Consumption (W)	Power consumed/ CHD removal (kWhkg ⁻¹)
TiO ₂	C ₀ = 30 mgL ⁻¹ , S/C = 1.8, pH = 7.6, Synthetic water and visible light	23.64	0.2	0.003	0.2	7.55
	C ₀ = 30 mgL ⁻¹ , S/C = 1.63, pH = 8.2, Synthetic water and sunlight	15.69	0.2	0.001	1.17	70.66
	C ₀ = 30 mgL ⁻¹ , S/C = 1.8, pH = 7.6, formulated wastewater and Visible light	18.79	0.2	0.0028	0.2	11.96
	C ₀ = 30 mgL ⁻¹ , S/C = 1.63, pH = 8.2, formulated wastewater and sunlight	9.49	0.2	0.0035	1.17	44.58
Ni-TiO ₂	C ₀ = 30 mgL ⁻¹ , S/C = 1.54, pH = 9.2, Synthetic water and visible light	90.34	0.2	0.0245	0.2	1.88
	C ₀ = 30 mgL ⁻¹ , S/C = 1.98, pH = 7.89, Synthetic water and Sunlight	79.26	0.2	0.0119	1.17	14.59
	C ₀ = 30 mgL ⁻¹ , S/C = 1.54, pH = 9.2, formulated wastewater and visible light	84.34	0.2	0.022	0.2	1.94
	C ₀ = 30 mgL ⁻¹ , S/C = 1.98, pH = 7.89, formulated wastewater and sunlight	71.51	0.2	0.239	1.17	14.68

process. The analysis result indicated that the leaching concentration of Ni in treated water was found to be below detection limit depicting the stability of prepared catalyst during photocatalysis process [47].

3.5. Correlation between Spectroscopic indices and mineralization of CHD using TiO₂ and Ni-TiO₂

CHD is composed of phenyl aromatic carbon, presence of reactive and aromatic components in water after treatment referred as left-over organic compound. ASI could be the best way to quantify the left-over reactive organic compound in treated water in Eq. (4). Formation of aliphatic compounds and reduction in ASI, UV₂₈₀ and TOC values in treated wastewater confirms the mineralization of CHD during photocatalysis reaction. ASI and TOC are considered as reactivity of activated aromatic group and oxidized organic carbon in terms of CO₂ release. This spectral approach has been introduced to understand the cleavage of aromatic C=C and decrease in hydrophobic compound in treated water during photocatalysis process, which is measured at 280 nm in UV-spectroscopy. This reduction in the value of aromatic C=C content present in CHD with respect to time validated the reduction of TOC and mineralization of CHD.

Reduction of ASI and UV₂₈₀ was observed, which validates mineralisation process of organic compound through spectral approach. Due to the solubility of phenol, removal of phenyl containing compound might have one reason for drastic reduction in TOC through photocatalysis. However, dominating reactive species such as OH[•] and holes produced using TiO₂ and Ni-TiO₂ mediated photocatalytic degradation of CHD (Fig. S5), the mineralization of CHD (90.34%) with respect to TOC reduction (85.71%), aromaticity reduction (ASI-59.66%) and hydrophobic compound reduction (UV₂₈₀-68.23%) was observed.

The comparative studies for photodegradation efficiencies of both the synthesised photocatalysts (TiO₂ and Ni-TiO₂), it was found that doped- TiO₂ photocatalyst was efficient for removal of recalcitrant

organic pollutant with respect to mineralization of targeted compound and also remove reactive hydrophobic as well as aromatic compound from organic pollutant loaded wastewater.

The mineralisation process of CHD through spectral approach with respect to TOC reduction, aromaticity reduction (ASI) and hydrophobic compound reduction (UV₂₈₀) was validated with HPLC results. The results showed decrease in characteristic peak of CHD with time after photocatalytic degradation process. Additionally, chromatogram of LC-MS confirms the breakdown of complex structure of CHD into smaller molecules due to presence of new peaks in the treated water. The interference and toxicity of transformed products were investigated with respect of reduction in ASI, TOC and UV₂₈₀.

3.6. Comparison of Degradation Efficiency of Photocatalyst under Simulated and Sunlight with Energy Consumption in Treatment Process

The photocatalytic treatment of CHD using TiO₂ and Ni-TiO₂ under simulated and solar light were depicted the higher mineralization in visible light. In order to cost-effectiveness and large-scale applicability of treatment process, energy consumption was investigated using Eq. (9) and (10), respectively [17].

$$\text{Total power consumed (kWh)} = \frac{\text{Power used (kW)} \times \text{Reaction time (h)}}{60 \times 1000} \quad (9)$$

$$\text{Total power consumption per CHD removal (kWhKg}^{-1}\text{)} = \frac{\text{Power Consumption (kWh)}}{[(C_0 - C_f) \times (\text{working volume (L)})]} \quad (10)$$

Where, C₀ and C_f are the initial and final concentration of CHD in KgL⁻¹. The energy consumption during photocatalytic treatment

process for synthetic and formulated wastewater under simulated visible and sunlight was calculated. The experimental results showed higher mineralization for visible light as compared to the solar, which may be due to variation in intensity of solar light during the experiment led to the insufficient production of reactive species. Furthermore, energy was used simply for stirring during solar treatment, whereas visible mediated photocatalytic treatment required a high-powered lamp and stirrer. On comparing the treatment condition, sunlight mediated photocatalysis of synthetic wastewater using Ni-TiO₂ showed lower energy consumption (1.87 kWhkg⁻¹) with comparable CHD removal (79.26%) than other treatment condition (Table 2). The reusability of prepared catalyst was also investigated, and results showed good stability even after 3 cycles. Additionally, pH of the treated water was found near 7 to 7.8, which can be reused for a different purpose other than drinking (Fig. 5(a)).

Thus, results demonstrated that photocatalytic treatment of organic pollutant using Ni-TiO₂ under sunlight could be used as economical and energy-efficient treatment process for large scale treatment system.

4. Conclusions

The synthesized Ni-TiO₂ photocatalyst showed improved photocatalytic treatment due to the incorporation of Ni into the TiO₂ lattice, exhibiting superior properties such as phase structure, crystallinity, crystallite size, morphology, separation of charge carriers and favourable for the shift of the bandgap into the visible region. SEM and TEM images confirmed the aggregation of particles and enhanced optical property due to the formation of bond between Ni and O atoms. The experimental results indicated removal of CHD using Ni-TiO₂ under simulated visible light and natural solar light was ~90.34 and 79.26%, respectively. In addition, toxicity assessment of photooxidation products show the efficiency of treatment system and indicating the safe disposal of treated water into the aquatic environment. Thus, the preferential removal efficiency with lower energy consumption (1.87 kWhKg⁻¹) indicated that Ni-TiO₂ mediated heterogeneous photocatalysis under sunlight could be used for a large-scale treatment system.

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Conflict-of-Interest

The authors declare that they have no conflict of interest.

Author Contributions

A.S. (Ph.D. student) did Conceptualization, Methodology, Investigation, Formal analysis & Writing-Original Draft.
B.K.M. (Associate Professor) did Supervision, Conceptualization, Writing - Review & Editing.

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