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

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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 (R²=0.986) and simulated visible light (R²=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 (89.91%-synthetic wastewater and 55.39%-formulated wastewater) and UV254 (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 handwash, 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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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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ and Ni-TiO₂, respectively. Furthermore, similar ionic radius of Ti³⁺ (0.68 Å) and Ni²⁺ (0.72 Å), could be beneficial in the substitution of Ni²⁺ in the place of Ti⁴⁺ in the crystalline lattice of TiO₂ [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-TiO₂ 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 TiO₂ modification techniques. The work describes the effect of Ni-doping on the photocatalytic activities of TiO₂ under natural sunlight and simulated visible light with respect to degradation of the CHD, the mineralization rate (in terms of TOC) and UV absorbance (UV₂₅₄ and UV₂₈₀). Meanwhile, the presence of Ni-particle in TiO₂ 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-TiO₂. 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-TiO₂ 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 H₂O 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 grade.

2.2. Synthesis of Photocatalyst

The raw material and precursor used for preparation of Ni-doped TiO₂ includes titanium tetra-isopropoxide, Ni(NO₃)₂·6H₂O and HNO₃. 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 ground in an 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 in the TiO2. X-ray diffraction (XRD) were recorded using Cu-Kα (λ = 1.5406 Å) 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 Brunaauer Emmett Teller (BET) model was used to calculate specific area surface the portion (P/Po = 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-Kα = 1,486.7 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 min 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 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 (R2), lack of fit, CV% and R2 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].

\[
y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} X_i X_j
\]

Where y is the response variable, b0 is the constant, b the linear coefficient, b the quadratic coefficient, b the interaction coefficient and Xi dimensional coded variables (X1 for the S/C ratio, X2 for the time and X3 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 (Shimandzu 5000) was used to determine the extent of CHD mineralization. The Langmuir-Hinselwood model has been carried out to study the modelling CHD degradation Eqs. (2) and (3).

\[
\ln \frac{C_t}{C_0} = -k_{obs} t
\]

(2)

\[
r_{obs} = -k_{obs} C_{CHD}
\]

(3)

Where, kobs (Reaction rate constant) was calculated from the slope by plotting a graph between ln(Ct/C0) versus t and robs 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]:

\[
ASI = 0.56 \left( \frac{A_{225} - A_{272}}{A_{230} - A_{230}} \right)
\]

(4)

Where A225, A230, A250 and A272 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 × 4.6 × 100 mm) and connected to a UV-Vis detector. The spectrophotometer was set at 275 nm and 1.5 mL/min. 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 μL and filtered by 0.2 μm syringe filters prior to injection [5]. Liquid Chromatography-Mass Spectrometry 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 ~ 25° and 56° confirm the anatase form of tetragonal structure of pure TiO2 matched with (ICSD reference number 01-086-1155). In addition, the characteristic peaks of NiTiO3 at ~ 27°, 36°, 47° and 54° were ascribed the cubic structure of Ni-TiO2 matched with (ICSD reference number 01-075-0399) [20]. Thus, analysis provides a possible assumption that incorporation of Ni2+ into the TiO2 favours the formation of NiTiO3 [21]. The intensity of peaks of undoped TiO2 decreased and slightly shifted due to the doping of metal; this revealed that Ni enter the TiO2 crystal lattice successfully. This Ni2+ could replace Ti4+ due to the similar ionic radius i.e. 0.72 Å (Ni2+) and 0.68 Å (Ti4+) and cause distortion as well as a defect in their lattice. Cubic crystal structure of Ni-TiO2 demonstrated that doping of nickel modifies the tetragonal crystal structure of TiO2 and Ti4+ lattice sites were occupied by Ni2+ 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 which 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 form the XRD peak to calculate the average crystallite sizes of the photocatalyst (Eq. (5)).

\[ D = \frac{K \lambda}{β \cos θ} \]  

Moreover, it was found that there is decrease in crystallite size of pure TiO2 (3.91 nm) due to doping of nickel in Ni-TiO2 (2.96 nm). Thus, Ni2+ tries to replace Ti4+ which may be better explained by the broadening of peaks due to defects formed by Ni2+ in TiO2 [23]. Fig. 1(b) depicts the prominent peak and shifting of 2θ in prepared material (Ni-TiO2), which verifies the doping of Ni in TiO2 [24]. Doping of Ni2+ in TiO2 inhibits the size of crystallite and enhance the formation of anatase crystalline phase of TiO2. This smaller crystallite size of Ni-TiO2 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 TiO2 particles. The SEM micrographs of undoped TiO2 clearly shows the uniform regular spherical particle distribution (Fig. 2(a), (b)). After loading of Ni, the surface of TiO2 sphere exhibits both spherical and slightly elongated rod-like porous structure (Fig. 2(c)−(h)). Furthermore, EDX analysis was also performed to verify and confirm the elemental composition of undoped TiO2 and the loading of Ni content in Ni-TiO2. The EDS spectrum shows the presence of Ti, O along with Ni were found confirming the undoped and Ni doped TiO2 [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-TiO2 sample [25].

FTIR spectrum was recorded to elucidate the presence of chemical group on the surface of TiO2 and formation Ni-TiO2 (Fig. 1(d)). The broad hump on TiO2 and Ni-TiO2 showed absorption peak around 3,402.71 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 TiO2 sample [26]. Interestingly, characteristic peak of metal-oxygen vibrational bond were observed in the range of 700−400 cm⁻¹, such sharp absorption peaks around 500−450 cm⁻¹ confirms the characteristic peak of metal titane bond Ti-O-Ni [9]. Additionally, the characteristic peaks of Ni-OTiO2 and O-O stretching vibration were identified around 609.88 and 654.49 cm⁻¹. The peaks around 1,380 cm⁻¹ caused by substitution of the Ni2+ in place Ti4+ 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 cm⁻¹. In contrast to pure TiO2, the Ti-O peaks for Ni doped TiO2 occurred at higher wavenumbers. For instance, Ti-O stretching bond of pure TiO2 and Ni-OTiO2 were identified at 544 and 609.88 cm⁻¹, respectively. This could be due to the incorporation of Ni2+ into the TiO2 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 TiO2 and Ni-doped TiO2 (Fig. 3). The characteristics peak of Ti 2p1/2 and Ti 2p3/2 found at 458.89 and 464.77 eV, respectively indicated the existence of Ti4+ species [29]. On comparison of undoped TiO2 two distinct
peaks attributed to Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{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\textsubscript{3/2} and Ti 2p\textsubscript{1/2}, respectively in Ni-TiO\textsubscript{2} (Fig. 3(b)). The photoelectron peaks of the oxygen lattice (O 1s) in Ni-doped TiO\textsubscript{2} i.e 529.76 is slightly lower than 530.15 eV of undoped TiO\textsubscript{2} (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 TiO\textsubscript{2} lattice following the introduction of Ni\textsuperscript{2+} [32]. Thus, this indicated the incorporation of Ni\textsuperscript{2+} ions in TiO\textsubscript{2} lattice of Ni-doped TiO\textsubscript{2} sample [25]. The surface hydroxyl group or chemisorbed water molecules also reflects peak in Ni-doped TiO\textsubscript{2} at 532.30 eV [33]. These observation has ascribed the successful formation of bond among Ni-O-Ti in the Ni-TiO\textsubscript{2} 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 TiO\textsubscript{2} and Ni doped TiO\textsubscript{2} 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 TiO\textsubscript{2} is significant in the UVA lamp used in the experiment. Undoped TiO\textsubscript{2} (3.03 eV) showed significant absorption below 400 nm due to the charge transfer between ligand (O\textsuperscript{2-}) and metal.

Fig 1. (a) XRD; (b) magnified XRD; (c) Nyquist plot; (d) FTIR; (e) DRS-spectra; and (f) Kubelka–Munk function photocatalysts TiO\textsubscript{2} and Ni-TiO\textsubscript{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 m$^2$g$^{-1}$ and increased to 12.19 m$^2$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].
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 X1(S/C), X2(pH), X3(Time) and calculated as three first order effect (X1, X2 and X3), interaction effect (X1X2, X1X3 and X2X3) and three second order effect (X1^2, X2^2 and X3^2). 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).

\[
CHD \text{ removal } \% (TiO}_2 \gamma = 44.97 - 3.35X_1 + 8.69X_2 + 3.42X_3 - 0.92X_1X_2 - 0.044X_1X_3 - 12X_1^2 - 0.84X_2^2 - 1.79X_3^2
\]  

\[
CHD \text{ removal } \% (N - TiO}_2 \gamma = 47.19 - 2.66X_1 + 9.32X_2 + 4.02X_3 - 2.26X_1X_2 - 0.54X_1X_3 + 1.17X_2X_3 - 14.32X_1^2 - 2.41X_2^2 - 2.62X_3^2
\]  

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 TiO2 and Ni-TiO2 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 TiO2 and Ni-TiO2 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
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
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 decreased 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 (pHₚzца) 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 pHₚzца values and negatively charged at the pH higher than their pHₚzца 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 > pHₚzца and CHD (pKa = 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.
Rate of reaction found by plotting the graph among ln(Ct/C0) 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-TiO2 under simulated visible light and sunlight well fitted with pseudo-first kinetic order (Table 1). Among various photocatalytic conditions, Ni-TiO2 showed highest kCHD 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 catalyst [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-TiO2 deduced for formulated wastewater treatment due to interference of other ions (Fig. 6(a)~(e)). The use of Ni-TiO2 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.
validated by the equation (Eq. (8)) given below:

\[
C_34H_54Cl_2N_{10}O_7 + 36O_2 + h^\gamma \rightarrow 34CO_2 + 10NH_3 + 2HCl + 11H_2O
\]  

(8)

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:

\[
C_34H_54Cl_2N_{10}O_7 + 36O_2 + h^\gamma \rightarrow 34CO_2 + 10NH_3 + 2HCl + 11H_2O
\]  

(8)

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)). The 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 the 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 light) under visible and solar light, respectively (Fig. 4(e)). 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 transformed products of photooxidation process. According to LC/MS results and literature available, a possible pathway was proposed by substitution and addition modification and substitution [45, 46] (Fig. S2(a) and S3). OHo and h+ were produced as a reactive species in Ni-TiO2 mediated photocatalysis process, where OHo was dominating in the photocatalytic oxidation was investigated by trapping experiment. OHo attacked on benzene ring of CHD and involve breaking of C-Cl bond i.e., dichlorination of aromatic ring takes place by addition of OHo. 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.

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**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 | R² | kobs value (min⁻¹) | Light source |
|---------------|------------------------|--------------------|----|-------------------|--------------|
| TiO₂          | C₀ = 30 mg/L⁻¹, S/C = 1.8, pH = 7.6, Synthetic water | 23.64 | 0.974 | 0.003 | visible light |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.63, pH = 8.2, Synthetic water | 15.69 | 0.92 | 0.001 | sunlight |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.8, pH = 7.6, formulated wastewater | 20.07 | 0.97 | 0.0028 | visible light |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.63, pH = 8.2, formulated wastewater | 9.45 | 0.962 | 0.0035 | sunlight |
| Ni-TiO₂       | C₀ = 30 mg/L⁻¹, S/C = 1.54, pH = 9.2, Synthetic water | 90.34 | 0.982 | 0.0245 | visible light |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.98, pH = 7.89, Synthetic water | 79.26 | 0.986 | 0.0119 | sunlight |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.54, pH = 9.2, formulated wastewater | 90.34 | 0.976 | 0.022 | visible light |
|               | C₀ = 30 mg/L⁻¹, S/C = 1.98, pH = 7.89, formulated wastewater | 79.26 | 0.986 | 0.239 | sunlight |
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 TiO$_2$ and Ni-TiO$_2$

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, UV$_{280}$ 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 CO$_2$ 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 UV$_{280}$ 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 TiO$_2$ and Ni-TiO$_2$ 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 (UV$_{280}$-68.23%) was observed.

The comparative studies for photodegradation efficiencies of both the synthesised photocatalysts (TiO$_2$ and Ni-TiO$_2$), it was found that doped- TiO$_2$ 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 (UV$_{280}$) 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 UV$_{280}$.

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

The photocatalytic treatment of CHD using TiO$_2$ and Ni-TiO$_2$ 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].

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

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

Where, $C_0$ and $C_f$ are the initial and final concentration of CHD in KgL$^{-1}$. The energy consumption during photocatalytic treatment

### 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$_2$       | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.8, pH = 7.6, Synthetic water and visible light | 23.64 | 0.2 | 0.003 | 0.2 | 7.55 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.63, pH = 8.2, Synthetic water and sunlight | 15.69 | 0.2 | 0.001 | 1.17 | 70.66 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.8, pH = 7.6, formulated wastewater and Visible light | 18.79 | 0.2 | 0.0028 | 0.2 | 11.96 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.63, pH = 8.2, formulated wastewater and sunlight | 9.49 | 0.2 | 0.0035 | 1.17 | 44.58 |
| Ni-TiO$_2$    | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.54, pH = 9.2, Synthetic water and visible light | 90.34 | 0.2 | 0.0245 | 0.2 | 1.88 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.98, pH = 7.89, Synthetic water and Sunlight | 79.26 | 0.2 | 0.0119 | 1.17 | 14.59 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.54, pH = 9.2, formulated wastewater and visible light | 84.34 | 0.2 | 0.022 | 0.2 | 1.94 |
|               | $C_0 = 30\ mg\cdot L^{-1}$, S/C = 1.98, pH = 7.89, formulated wastewater and sunlight | 71.51 | 0.2 | 0.239 | 1.17 | 14.68 |
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 system. The authors declare that they have no conflict of interest.

Conflict-of-Interest

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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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