Direct Sunlight driven photocatalytic degradation of hazardous organic dyes using TiO$_2$-NiO nanocomposite p-n junction

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Abstract. TiO$_2$ is stable and nontoxic, an effective, low cost, semiconductor photo catalyst to degrade most of the organic pollutants. Nevertheless, the practical application of TiO$_2$ are limited due to two important reasons, while one of the reasons is rapid recombination of electron and hole pair and other one is larger band gap 3.2eV, which permits to absorb 3-4% of solar energy. To enhance photocatalytic activity, several TiO$_2$- metal oxide composites have been used. Due to their electron hole separation ability p-n junction, type semiconductor has become more focused in the last few years. TiO$_2$-NiO nanocomposite is one such catalyst; the presence of NiO facilitates the separation of the hole and the electron pair and encourages the interfacial charge transfer, which facilitates TiO$_2$-NiO a good photocatalyst under direct sunlight. The objective of the study is to synthesise nanocomposite of different mole ratios of NiO and TiO$_2$, to investigate the physicochemical properties such as XRD for phase and purity test, SEM –EDX for morphology and percentage elemental composition, UVDRS for band gap analysis. Photocatalytic activity of TiO$_2$-NiO p-n junction nano structures experiments were carried out under direct sunlight in different systems; using aqueous solution of the dye with effect of pH, concentration of dye, catalyst loading and time on degradation of the organic dye were studied. With increasing the concentration of NiO in to TiO$_2$-NiO composite increases the photocatalytic activity due to narrowing of the band gap attributed to interfacial charge transfer or higher hole mobility.

Keywords: Photo catalyst; p-n junction; nanocomposite; sunlight; degradation; band gap.

1. Introduction

Organic dyes are majorly used in dyeing industry. Effluents of these industries impose a burden on environment, by causing hazardous health issues. Therefore, development of low cost and effective methods to treat and purify contaminated water has been very crucial [1]. Some of the techniques followed to treat water are coagulation, reverse osmosis, membrane filtration, ion exchange, complexometric method. Chemical techniques are reduction, oxidation and biological methods such as aerobic and anaerobic methods. Recently, scientists have demonstrated that TiO$_2$ has the greatest
photocatalytic activity, which is restricted by recombinating the electron hole pairs produced by photo generation arising from the inner electrical field [2,4,]. Doping semiconductors with non-metals and noble metals paves the way for visible light-driven photo catalyst by expanding their wavelength [5]. Visible light-driven photo catalysts are of great interest because of their advantage [6] that complete mineralization of waste water contaminants into environment friendly products that by using low cost and inexhaustible sun light as an energy source operating at ambient temperature. Some of the photo catalyst have drawbacks such as formation of electron and hole recombination centers, thermal instability, and metal leaching. Perovskite based titanium oxides such as YTiO$_3$ ( Y= BSC and Ni, Where BSC means Barium, Strontium and Calcium) gain tremendous attention as a photo catalyst due to stable structure [9,10,11,12,13]. Band gap of NiTiO$_3$ is 2.18eV [14] the decrease in band gap is due to the generation of oxidative species. [15] NiO (p-type semiconductor) in contact with TiO$_2$ (n-type semiconductor) enable to form a composite structure [16, 17], favours the separation of electrons and holes and makes TiO$_2$-NiO an excellent photo catalyst to use under direct sunlight [18].

At present quite a few researchers have investigated NiO in contact with TiO$_2$ as a p-n junction and splitting of water using TiO$_2$-NiO photo catalyst was widely researched. Chou et, al threw light on the solar cell construction by utilizing TiO$_2$-NiO composite [19, 20, 21, 22]. Also, Sreethawong et, al reported the enhancement in evolution of hydrogen by utilizing TiO$_2$-NiO rather than TiO$_2$. More recently, Karunakaran Chocklingam et al [23] described the selective photo degradation property of TiO$_2$-NiO composite. For, instance the photocatalytic activity of TiO$_2$-NiO on degradation of Sunset Yellow, Rhodamine B, Methylene blue and Methylene orange dyes using UV light is less compared to TiO$_2$ alone. This is due to less number of holes available for oxidation. Though, extensive information is available on degradation of organic dyes using a photo catalyst and UV light, focus on direct sunlight driven photocatalytic activity of TiO$_2$-NiO is still limited. According to Q. Zhu, Na LiU, Nan Zhany and etal 99.9% of Rhodamine B was photocatalytically degraded by Ni/NiO/TiO$_2$ thin film in presence of solar light over a period of 60 min, whereas only 61.9% by pure TiO$_2$ film [33]. V.Vinath, P.Karthik, K. Devan have described that the 30% and 6% of Methyl orange was degraded using ultrasound and diffused sunlight. Also, 4.8 fold increase in the photocatalytic degradation using ultrasound technique in presence of sun light [34]. Lan Ching Sim, Kai Wern Ng have demonstrated that NiO-TiO$_2$ nanotubes show higher degradation efficiency than TiO$_2$ alone. Nearly, 86% of Methylene Blue was removed in 7.5hr under direct sun light [35]. In our present work, we reported the synthesis of p-n junction nanocomposite via low cost sol-gel technique, investigated their physico-chemical properties and studied the direct sunlight driven photocatalytic degradation of hazardous organic dyes such as CV, AO and AY.

2. MATERIALS AND METHOD
Titanium isopropoxide (TTIP), 2-Propanol, Nickel nitrate (NiNO$_2$.6H$_2$O), Acetyl acetone, Alizarin yellow, Acid- orange 7, Crystal violet, Distilled water and HCl were purchased from E-Merck India (Ltd). A digital pH meter with combined glass electrode (ELICO) is the instrument for the pH measurement. A UVDRS (SHIMADZU) instrument was used for band gap analysis by Tauc expression. UV-VIS (SHIMADZU) spectrophotometer to study the degradation of dye samples after irradiation under direct sun light. Sample characterization was carried out by XRD measurements and morphological studies by SEM analysis; percentage composition of individual element was carried out by EDS technique.

Method: Only TiO$_2$ and TiO$_2$ - NiO samples were synthesized by a bottom up approach, a classical method called Sol-Gel. A different weight % (0.5, 1.0, 4.0 and 5.0) NiO doped samples were prepared
by using calculated amount of TTIP and NiNO$_3$.6H$_2$O. A known quantity of TTIP, 6ml of Acetyl acetone (stabilizing agent) and a 30ml of 2-Propanol (hydrolyzing agent were taken in a beaker. The mixture is magnetically stirred for 2 hrs at 25˚C. This is Part A solution. A known quantity of NiNO$_3$.6H$_2$O, 15ml of 2-Propanol is taken in another beaker and pH is adjusted using calibrated digital pH meter and 1M HCl solution. This is Part B solution. Part B is added to Part A in drops with constant stirring for 2hrs, temperature of the reaction mixture is increased to 60˚C and allowed to form a gel, it was dried in a hot air oven over night and annealed at 350˚C for 3hrs to yield powder sample.

3. EXPERIMENTAL

3.1 Characterization of Photo catalyst

Crystalline phases of TiO$_2$ and TiO$_2$-NiO composites are measured using BruckerD8 advanced diffractometer, Cu Kα radiation for a range between 10 to 70˚. Scherrer’s equation: D = kλ/βcosθ, is applied to determine crystallite size. The lattice parameters [24] were calculated using the equation 

\[ \frac{1}{d^2}(hkl) = \frac{h^2 + k^2 + l^2}{a^2 + b^2 + c^2} \]

where h,k,l are interplanar distances and lattice parameters a, b, c for tetragonal anatase phase of TiO$_2$ is a = b ≠ c. The planes, (101) and (200) for anatase JCPDS 21-1272, and the planes (111) for NiO cubic JCPDS: 47-1049, were considered to calculate the lattice parameters.

3.2 Band gap

The band gap energies of [14, 25,] TiO$_2$-NiO powders were determined using UV-Vis DRS method. Data extracted is well fitted in Tauc relation \[(\alpha h\nu)^n = C(h\nu - E_g)\], where C is a constant, \(\alpha\) is the absorption coefficient, \(E_g\) is the band gap and \(n=2\) or \(\frac{1}{2}\) and \(h\) is the Plank’s constant, and \(\nu\) is the frequency of photons. The average band gap energies were predicted, from the linear portions of the \((\alpha h\nu)^2\) or \((\alpha h\nu)^{1/2}\) versus \(h\nu\) of plots, respectively and band-gap wavelength is derived by extrapolating along-wavelength axis.

3. 3 Photocatalytic Experiment

Photocatalysis driven by visible light using semiconductor is of excellent concern [5]. Complete mineralization of dye molecules were carried out by using low cost and effective photo catalyst in presence of inexhaustible sun light, operating at room temperature without the use of additional chemicals. Photocatalytic studies were conducted at the bright sunny days using crystal violet, acid-orange 7 and alizarin yellow as model pollutants. Individually, the dye solutions were prepared by dissolving in 1000ml of distilled water. All chemicals are of analytical grade, 100ml of 10ppm of the dye solutions with different catalytic loading from 10mg to 50mg was used to prepare a suspension. Adsorption and desorption equilibrium between dye molecules and catalyst surface is obtained by dark reaction. The concentration at this condition is measured as initial concentration \(C_0\). 5ml of solution is withdrawn periodically after irradiation under direct sun light, centrifuged, and filtered to remove catalyst, and the concentration was measured using UV-Vis spectrophotometer. The percentage degradation of dye has been determined using the formula.

\[ \% \text{ Degradation} = \frac{C_0 - C_f}{C_0} \times 100 \]

Unless otherwise stated, the entire dye solutions test was conducted at natural pH 6.5. The impact on the speed of photocatalytic degradation of catalyst loading variation and pH of the solution were researched. Desired pH of the solution was adjusted with the addition of either dil.NaOH or dil. HCl.
Dye decolouration was tracked by using UV-Vis spectroscopic analysis (Shimadzu UV-Vis 1601). The double beam spectrophotometer has built-in tungsten and deuterium lights that provide optical density (OD) measurement within 200-1100nm range. Quartz cuvette is used because they have zero absorption in the wavelength regions 200 to 1100nm. The dye derivatives concentration was calculated using the standard calibration curve obtained at different concentration of the dye. The change in the absorbance of the dye solution was followed as a function of the irradiation time at their fixed wavelength [26] $\lambda_{\text{max}} = 352 \text{ nm}$ and 346 nm. The observed absorbance is proportional to the range of concentration of dye studied by Beer-Lambert’s law.

4. Results and discussion

4.1 XRD

Fig:1 Show XRD pattern for all samples, diffraction peaks can be assigned as a 100% anataseTiO$_2$ and TiO$_2$-NiO composite annealed at 350˚C does not shown any phase change in TiO$_2$ for varying concentration of NiO. TiO$_2$ anatase phase are tetragonal (JCPDS 21-1272) appeared at $\theta$ of 25.3˚, 36.9˚, 37.9˚, 38.2˚, 48.1˚, 54˚,62.8˚, 69.9˚, 70.2˚, 75.3˚ corresponding to (1 0 1), (1 0 3), (0 0 4) , (2 0 0), (1 0 5), (2 1 1), (1 1 6) and (2 1 5) crystal planes respectively. NiO is found at 43.2˚ (2 0 0) plane (JCPDS no21-1272) for cubic structure. The lattice parameters of all the samples and crystallite size of all the samples are calculated using the formula Scherrer equation; $D = \frac{k\lambda}{\beta\cos\theta}$, here is the wavelength $\lambda$ of X-ray (0.15nm),

![X-ray pattern](image)

**Figure 1.** X-ray pattern for TiO$_2$, TiO$_2$-NiO (99:1) and TiO$_2$-NiO (95:5) nano composites annealed at 350˚C

k is 0.89 for calculations, diffraction angle is $\theta$ and FWHM is $\beta$ for the 20 peak. The lattice parameters of nanostructures is calculated for (200) plane of NiO cubic system and (200) and (101) in anatase
crystal planes, by using Braggs equation \( D = \frac{\lambda}{2 \sin \theta} \). Tetragonal formula is \( \frac{1}{d_{2hkl}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \), where \( a=b\neq c \) and cubic system \( \frac{1}{d_{hk0}} = \frac{h^2 + k^2}{a^2} \), (h k l) interplanar distance is \( a=b=c \), diffraction angle \( \theta \), \( \lambda \) is the x-ray wavelength, and \( a, b, c \) are lattice parameters. The location of XRD peaks is slightly shifted with increase in NiO doping relative to the normal anatase peak. Anatase tetragonal lattice parameters did not vary much as \( \text{Ni}^{2+} \)(0.72Å) and \( \text{Ti}^{4+} \)(0.68Å). All samples lattice parameters remain almost unchanged along the ‘a’ and ‘b’- axis, whereas the value along ‘c’- axis is experiencing a slight decline with rise in concentration of NiO.

### Table 1. Comparison of standard and experimental values of lattice parameter

| Sample ID | a=b  | C       | ERROR in "a" & “b” | ERROR in “c” |
|-----------|------|---------|---------------------|--------------|
| Standard  | 3.785| 9.513   |                     |              |
| Only TiO2 | 3.787| 9.5264  | 0.002               | 0.0134       |
| TiO2-NiO (99:1) | 3.788 | 9.4796 | 0.003               | 0.0334 |
| TiO2-NiO (96:4) | 3.781 | 9.4548 | 0.004               | 0.0582 |
| TiO2-NiO (95:5) | 3.774 | 9.429  | 0.011               | 0.084 |

The decrease in the size of the lattice parameter along the “c” axis is due to the existence of \( \text{Ni}^{2+} \) ions in the anatase crystal structure, where the \( \text{Ti}^{2+} \) ionic radius is 100pm, \( \text{Ti}^{3+} \) is 67pm, \( \text{Ti}^{4+} \) is 61pm and \( \text{Ni}^{2+} \) is 69pm. There is no huge difference between both the metal ions. The change in size of ‘c’-value is noticeable only when the concentration of NiO is more. Since \( \text{Ni}^{2+} \), the size of ‘c’, replaces \( \text{Ti}^{3+} \) ions-axis decreases, intensity of a doublet between 2θ values of 68-70 is decreasing with increasing the concentration of NiO. Calculated lattice parameters are compared with standard values and listed in Table No:1.

4.2 UV-Vis diffuse reflectance spectra

Key considerations for enhancing TiO2’s photo degradation effectiveness are inhibiting photo-induced (e- & h+) pair recombination and extending absorption to visible light region. Fig: 2b shows the diffuse reflectance spectrum of different TiO2-NiO composite structures. The TiO2 samples display an absorption band below 380nm owing to transfer of “O”.-2p valence band electrons to the “Ti”-3d conduction band. An abrupt increase in the absorbance for the samples TiO2-NiO (96:4), TiO2-NiO (95:5) and TiO2-NiO (99:1), only TiO2 remain same, as TiO2-NiO (99:1) is not significant to bring change in the crystal structure. Increase in absorption could be explained as the overlap of 3d level of \( \text{Ti}^{4+} \) and d level of \( \text{Ni}^{2+} \) favours charge transfer transition in the junction region. The optical band gaps [27] of TiO2 and TiO2-NiO composites (Direct-gap semiconductor) could be roughly estimated using Tauc plot, and the expression \( (ahv)^2 = A(hv - Eg)^n \), where \( v \) is the frequency, \( h \) is the Plank constant, \( E_g \) is the optical band gap energy, the value \( A \) is a constant depends on the probability. Extrapolation of a straight line to the \( (ahv)^2 = 0 \) axis in the plots of the \( (ahv)^2 \) versus optical band gap energy is used to determine \( E_g \) of only TiO2 and TiO2-NiO nanostructure [28]. It also reduces the band gap energy between NiO and TiO2 as a result of the oxides being dispersed. Band gap values are
display in the plot for only TiO\textsubscript{2} and TiO\textsubscript{2}-NiO composites. Band gap of TiO\textsubscript{2}, TiO\textsubscript{2}-NiO (99:1), TiO\textsubscript{2}-NiO (96:4) and TiO\textsubscript{2}-NiO (95:5) composites are shown in the Fig:2a, band gap of only TiO\textsubscript{2} is 3.22eV and 2.1eV for NiO (95: 5) narrowing down in the band gap attributed to interfacial charge transfer and favours generation of oxidative species which are required for degradation of dye molecule. In addition, higher mobility of p-type NiO favours the separation of electron and holes, which facilitates TiO\textsubscript{2}-NiO a good photocatalyst under direct sunlight. It also reduces the band gap energy between NiO and TiO\textsubscript{2} as a result of the oxides being dispersed.

![Figure 2.a](image1.png)  
**Figure 2.a.** UV-DRS spectra depicting the band gap values of TiO\textsubscript{2}, TiO\textsubscript{2}-NiO (99:1) TiO\textsubscript{2}-NiO (96:4) and TiO\textsubscript{2}-NiO (95:5) composites.

![Figure 2.b](image2.png)  
**Figure 2.b.** UVDRS spectral data represented as a function of absorbance Vs wavelength for the samples TiO\textsubscript{2}, TiO\textsubscript{2}-NiO (99:1), TiO\textsubscript{2}-NiO (96:4) and TiO\textsubscript{2}-NiO (95:5) composites.

| Table 2. Tabulation of elemental composition Oxygen, Titanium and Nickel |
|-------------------------|-------------------------|-------------------------|-------------------------|
|                         | Only TiO\textsubscript{2} | TiO\textsubscript{2}-NiO |                         |
| Element                 | Wt %   | Atom %   | Element                 | Wt %   | Atom %   |
| O                       | 23.32  | 47.66    | O                       | 52.39  | 75.98    |
| Ti                      | 76.68  | 52.34    | Ti                      | 43.63  | 21.14    |
| Ni                      | 3.98   | 2.88     |                         |        |          |

**4.3 Structural and Morphological Characterization:**

Morphological studies of only TiO\textsubscript{2} represent the possibility of agglomeration of particles, whereas TiO\textsubscript{2}-NiO composite shows growth in its size indicating the possibility of a cover of NiO over TiO\textsubscript{2}. Furthermore, significant morphological changes are found with addition of NiO except in its growth in TiO\textsubscript{2}-NiO composites. EDS assessment offers elementary evaluation of a sample within a SEM, information extracted from EDX analysis comprises of spectra displaying peaks corresponding to the component making up real structure of the sample being analysed, particularly since Ni guarantees
NiO dispersion uniformly. Analysis of EDS in Fig: 4 shows the existence of NiO in composite TiO$_2$-NiO. The comprehensive structure of elements in it is tabulated in Table: 2.

Figure 3. a SEM images of only TiO$_2$ and TiO$_2$-NiO (99:4) nanocomposite

4.4 Photocatalytic Activity of TiO$_2$-NiO Composite:

TiO$_2$ and TiO$_2$-NiO composite, photocatalytic activity is driven by direct sunlight and is studied using crystal violet, acid- orange 7 and alizarin yellow as model pollutants. The initial concentration ($C_0$) is the concentration of crystal violet, acid – orange 7 and alizarin yellow after adsorption and desorption equilibrium. 2% of crystal violet, 5% of acid orange and 8% of alizarin yellow dye is removed in the dark reaction. The adsorption and photocatalytic degradation efficiencies of crystal violet, acid-orange and alizarin yellow on TiO$_2$ and TiO$_2$-NiO is evaluated by determining the percentage decrease of the absorbance at 548nm, 346nm and 352nm. Fig:5 shows the % degradation of different dyes at the fixed parameters, 100ml of 10ppm dye solution, natural pH 6.5 and normal temperature. Controlled photocatalytic experiment using TiO$_2$-NiO composite 5% wt demonstrates the greatest effectiveness of degradation relative to TiO$_2$ alone. TiO$_2$-NiO band gap is 2.49eV and favours the separation of charge carriers and retains electrons in the conduction band, holes in the valence band to form a p-n junction in which NiO is p-type and TiO$_2$ is a n-type semiconductor. In addition, NiO in TiO$_2$-NiO composite extends the photo responding range. Charge carriers hole (+) and e$^-$ facilitates the formation of energetic reactive intermediates such as oxygen superoxide and $^{\ddagger}$OOH free radical to interact with adsorbed dye molecules. The degradation of the dye is noticeable through decrease in the intensity of the solution and decrease in concentration is measured using UV-Vis spectrophotometer, % degradation is calculated using the formula:

$$\% \text{Degradation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$

The advancement of effectiveness of degradation of dyes using TiO$_2$-NiO photocatalyst is primarily due to the separation of charges and effective visible light absorption. NiO’s presence develops p-n junction to effectively separate electron-hole pairs, while the energy of visible-light permits charge transfer transitions from the 3d orbital of substituted Ni$^{2+}$ to the TiO$_2$ conduction bands. Furthermore, a competitive adsorption between the catalyst and the intermediate products on the active sites reduces the rate of degradation at the end of reaction. Consequently, availability of active sites impact degradation effectiveness for all TiO$_2$-NiO samples at the end of reactions. Overall, it could be found that higher concentration of NiO in TiO$_2$-NiO enhances direct sun light induced photocatalytic activity efficiently.
Figure 3.b Particle size distribution plot of TiO$_2$ and TiO$_2$-NiO (96:4) composite

Figure 4. EDS graph showing elemental composition of TiO$_2$ and TiO$_2$-NiO (96:4) composite

TiO$_2$-NiO with greater NiO concentration has better visible light absorption capacity. Experimentally, it is evident that TiO$_2$-NiO shows higher degradation capacity than undoped TiO$_2$. 82% of crystal violet, 66% of acid orange and 65% of alizarin yellow was degraded by undoped TiO$_2$ in comparison with 93% of crystal violet, 77% of acid orange and 97% of alizarin yellow was removed by TiO$_2$-NiO (95:5) nanostructures.

Mechanism:

Illumination of photons on semiconductor promotes electrons from valence band to conduction band only when energy of incident photon is greater than energy of band gap. Further, holes left in the valence band facilitate the formation of hydroxyl radicals. These powerful hydroxyl radicals are responsible to oxidise organic pollutants, while, electrons of conduction band helps in the formation of superoxide ions. When reacts with dissolved oxygen, chain reactions takes place due to holes and electrons, which are adsorbed on the surface of catalyst.

4.5 Effect of initial dye concentration:

The impact of initial dye concentration on the photocatalytic degradation is studied by changing the concentration of dye from 2 ppm to 10 ppm, at a fixed loading of 50mg for 45min. It has been discovered that percentage degradation is mostly affected by initial dye concentration from 2ppm to 10ppm. The rate of degradation is expounded to the accessible catalyst surface for the generation of electron and hole pair, that successively generated by hydroxyl group radicals. At constant catalyst loading number of OH radicals generated remains same, whereas increase in dye concentration decreases the attack by hydroxyl radicals so, the rate of degradation decreases.
Figure 5 Change in absorption intensity at different intervals of time on irradiation of aqueous solution of crystal violet and acid-orange 7 in presence of TiO$_2$ and TiO$_2$–NiO composite.

The linear relation [29, 30] of the natural logarithm of the proportion between the original concentration of the dye and the concentration after photocatalytic degradation \[ \ln(C_0/C) \] versus the respective irradiation time is plotted in Figure: 5 qualitatively assess the rate of photodegradation of separate dyes under direct sunlight illumination using TiO$_2$-NiO(95:5) photocatalyst. The photocatalytic degradation kinetics of dye can be portrayed through a pseudo first order equation. Straight lines are drawn between the \( \ln(C_0/C) \) against time ‘t’. The outcomes acquired are shown in Fig: 5. In addition, the constant of pseudo-first order rate is assessed at distinct concentrations. It is evident from the table that with a rise in concentration of dye solutions, the apparent pseudo first order rate constants are decreased. Therefore, using TiO$_2$-NiO nanostructures, the decreased concentration of alizarin yellow is discovered to be effective in photodegradation. Pseudo first order kinetics describes the impact of initial dye concentration on the photocatalytic degradation of organic compounds. This is rationalized in terms of the Langmuir–Hinshelwood model modified to accommodate responses that occurring at a solid liquid interface and therefore the final form can be portrayed as

\[
\ln[C_0/C] = k_t K_1 = K_1 t
\]

Where, \( t \) = time required for the initial concentration of solute \( C_0 \) to decrease to \( C \) expressed in ‘min’
\( K \) = equilibrium constant for adsorption of the dye molecule on to TiO$_2$–NiO nanostructure (mg/L)
\( k_t \) = limiting rate of reaction after maximum coverage under the experimental condition(mgL$^{-1}$min$^{-1}$)
\( K_1 \) = apparent rate constant of photocatalytic degradation (min$^{-1}$) s
The natural logarithm plot of the normalised dye concentration versus irradiation time indicates a sorption variation from 2 ppm to 10 ppm dye concentration. Fig: 7 adsorption from 2ppm to 10ppm dye concentration [31]. This indicates that as the initial dye concentration increases the catalyst surface requirement necessary to boost the degradation increases. Since the irradiation time and catalyst loading are constant, the radical created on the TiO₂-NiO surface are also constant.

4.6 Effect of catalyst loading

Overall, the rate of photocatalytic degradation of organic dye increases with photocatalyst dosage [15], owing to increase in active sites. This is primarily owing to the increase in radicals of hydroxyl generated by irradiated photocatalyst. To study the impact of catalyst loading on the photodegradation of dyestuff alizarin yellow, the amount of TiO₂-NiO catalyst was enhanced from 20mg to 100mg at a constant dye concentration of 10ppm.

Figure 7. A graph drawn between the C₀/Cₜ against time ‘t’ and ln (C₀/Cₜ) against time ‘t’ following pseudo first order reaction.

Fig: 8 indicates the ln(C₀/Cₜ) vs time plot for different TiO₂-NiO composites. The steady rate change with change in loading of the catalyst is shown in Fig: 8. It can be seen that with an increase in catalyst loading rate constant improves as listed in Table: 3.
The increase in number of active sites on the surface of photocatalyst increases the number of hydroxyl radicals, resulting in increase in degradation of dye molecules. The increase in loading of TiO$_2$-NiO (95:5) from 20mg to 100mg improved the obvious steady rate from 0.00194 to 0.0061. Experimental studies have shown that increase in catalyst loading increases the photo catalytic degradation.

4.7 Effect of pH on photocatalytic degradation of dyes.

After checking the dosage, pH was varied for the best dosage, stirred well for 30min and absorbance is measured for diff pH. Finally, the effect of time is studied for that particular dosage and the best pH as represented in Fig: 9. Effective degradation was noticed for the dosage 100mg. This is maintained to study adsorption capacity of alizarin yellow dye, which is discussed in the section.

4.8 Adsorption studies of alizarin yellow

Alizarin yellow dye solution 100ml (10ppm) was taken in 500ml of glass beaker and a known quantity of catalyst (20mg, 40mg, 60mg, 80mg and 100mg) was added and mixed well. Immediately 5ml of the solution was withdrawn and absorbance was measured at 352nm. The concentration of this solution is $C_o$. The resulting solution is stirred after centrifugation; the absorption of all solutions is measured [32]. The concentration of the solution after time $t$ is given by $C_t$. Same experiment was performed with 40mg, 60mg, 80mg and 100mg of the catalyst. Results are well fitted in Longmuir and Freundlich curves represented in Fig: 10 and 11.

| catalyst in ‘:mg’ | $K^1$ Min | $R^2$ |
|-------------------|------------|------|
| 20mg              | 0.00194    | 0.8337 |
| 40mg              | 0.00278    | 0.8936 |
| 60mg              | 0.00385    | 0.8132 |
| 80mg              | 0.00425    | 0.7532 |
| 100mg             | 0.00610    | 0.7317 |

Table 3 Effect of TiO$_2$-NiO loading
4.9 Study of Langmuir and Freundlich adsorption isotherms

When the adsorbent and adsorbate are contacted long enough. An equilibrium will be established between the amounts of adsorbate in solution. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, $q_e$, in solution at a given temperature. $q_e$ is the amount of solute adsorbed per unit weight of solid at equilibrium (mg/g) and $C_e$ is the concentration of solute remaining in solution when amount adsorbed equals $q_e$.

![Figure 10. Representation of Langmuir isotherm](image)

![Figure 11. Representation of Freundlich isotherm](image)

| Table 4 | Comparison of Langmuir and Freundlich isotherm |
|---------|-----------------------------------------------|
| Langmuir isotherm | Freundlich isotherm |
| Alizarin Yellow | |
| $Q_m$(mg/g) | $R_L$(L/mg) | $R^2$ | $K_F$(mg/g) | $1/n$ | $R^2$ |
| 64.30 | 0.466 | 0.986 | 8.6846 | 0.577 | 0.93 |
| 8 | 7 | 1 | 0 | 87 |

Langmuir isotherm assumes that dye molecules adhere to definite sites with the same energy, from the $R^2$ value, it shows it is a unilayer deposition. The Freundlich isotherm, on the other hand to assumes heterogeneous adsorption of solute to an adsorbent surface and an exponential distribution of solute to an adsorbent surface and an exponential distribution of active sites and heterogeneous energy level. The applicability of the isotherms are evaluated and listed in the table 4 and 5.
**Table 5.** Terms involved in Langmuir and Freundlich isotherm

| Langmuir Adsorption isotherm | Freundlich Adsorption isotherm |
|-----------------------------|--------------------------------|
| $Q_m$: Maximum adsorption capacity for forming mono layer. | Intercept = $\log K_F$ |
| $K_{ad}$ or $b$ has units of $L/mg$ | log $K_F$ = 0.9375 |
| Intercept = $\frac{1}{Q_m} = 0.0155$ | $K_F = 8.6846$ |
| Slope = $\frac{1}{n} = 0.57702$ | $n = 1.733$ |
| $Q_m = 64.3086mg/g$ | $R^2 = 0.93875$ |
| Slope = $\frac{1}{K_m Q_m} = 0.13609$ | $R^2 = 0.98613$ |

**5. Conclusion**

TiO$_2$-NiO photocatalyst synthesized by low cost technique, a solgel method and XRD data obtained confirms the structure of TiO$_2$-NiO photo catalyst and it is best suited for degradation of alizarin yellow under direct sunlight. Rate of degradation increases with increasing catalytic loading for TiO$_2$-NiO (95: 5) catalyst and concentration of alizarin yellow dye used for the study is 10ppm at a pH 6.5 and temperature 25°C. The photo degradation of dyes follows the pseudo first-order reaction; the experimental findings have been well matched with Langmuir, Freundlich isotherms which clears shows it is a unilayer, heterogeneous catalysis, and the information show that the kinetics of adsorption follows the pseudo first-order rate. The current study concludes that the TiO$_2$-NiO (95:5) could be employed as low-cost and effective photo catalyst for the removal of colourured dyes from wastewater.

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