Fabrication of Hetero junction \( p \)-LaNiO\(_3\) modified \( n \)-TiO\(_2\) as visible light active catalyst for photocatalytic degradation of 4-Chloro phenol

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**ABSTRACT**

To enhance the photocatalytic efficiency of TiO\(_2\) under UV light captured to visible range in this present work, Visible light active nanocomposites of LaNiO\(_3\) modified TiO\(_2\) in different molar ratios were synthesised by precipitation method. The obtained nanocomposite’s morphology, crystal size and its photocatalytic activity were scrutinized by UV – visible Diffuse Reflectance Spectroscopy (UV –vis-DRS), Fourier Transform Infra red spectroscopy (FT – IR), Photoluminescence Spectroscopy (PL), X – Ray Diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDX), Field emission Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The photocatalytic efficiency and COD of the synthesised catalyst was examined by the degradation of 4-Chlorophenol (4-CP). The influence of various factors on the degradation of 4-Chlorophenol were investigated and in addition reusability and stability of the catalyst was also investigated.

**Keywords:** Nanocomposites, LaNiO\(_3\), TiO\(_2\), photocatalytic efficiency, 4-ChloroPhenol.

**Highlights**

- Hetero junction \( p \)-LaNiO\(_3\) modified \( n \)-TiO\(_2\) has been fabricated by simple precipitation method.
- Photocatalytic activity of the composite has been tested by taking 4-CP as model pollutant under visible light irradiation.
- The synthesised nanocomposites show red shift than other TiO\(_2\) based nanocomposites.
- 25\%TiO\(_2\)/LaNiO\(_3\) nanocomposite shows the maximum degradation efficiency of 91\% in 3-hours of simulated solar light irradiation with 78.21\% COD removal.
- This work confirms that the present fabricated nanocomposites acts as an effective photocatalyst for the degradation of organic pollutant.

1. **INTRODUCTION**

Chemical substances make revolutionary changes in agricultural, industrial productivity and improve the control of the diseases. At same time the waste chemical disposal causes severe hazardous effect to the environment. Different types of chemicals particularly both organic and inorganic compounds are the main sources of pollutant which pollute the ground and surface water technologically and agriculturally [1]. Omni-present chlorophenol (CP) and its derivatives are imperative toxic pollutant in wastewater, groundwater and soils [2-6]. CPs used as intermediates in producing agricultural chemicals, pharmaceuticals, biocides, wood and leather preservatives and dyes. The discharge of the above waste can result in pessimistic effects such as heart disease, carcinogenic, teratogenic, mutagenic and acute toxicity [7]. The conventional thermal, chemical and biological methods also create adverse chemicals.

Research on decontamination of organic pollutants is increasing day by day because of the advantage of photo catalytic action. In the recent decade photocatalysis (by using Advanced Oxidation Processes) has opened a new door for the remediation of toxic organic pollutants [8-10]. TiO\(_2\) acts as an excellent photocatalyst for water splitting, water purification and for the degradation of several organic pollutants, because of its high stability, good photocatalytic activity, inexpensiveness and non-toxicity [11-15]. Unfortunately, the large band gap, high recombination rate of electron-hole pairs and activity under UV light are some of the drawbacks which restrict the practical application of TiO\(_2\). To date a variety of methods such as doping with metals, non-metals, and co-doping with metals [16-21] have been carried out to improve the photocatalytic efficiency of TiO\(_2\) under visible light. Compared to other surface modification methods, fabrication of heterojunction by the combination of two or more semiconductors with different band gap promote the separation of photogenerated charge carriers and greatly improves the photocatalytic activity [22-25]. Several studies have been reported on Fe\(_2\)O\(_3\)/SiO\(_2\)/TiO\(_2\), CuMoO\(_4\)/TiO\(_2\), Carbon-modified...
TiO$_2$, Ag/TiO$_2$/Fe$_2$O$_3$, Ag/MFe$_2$O$_4$ (M= Co, Zn, Cu and Ni) for the degradation of 2/4-Chlorophenol which show enhanced photocatalytic activity [26-30] than pure TiO$_2$.

Recently rare earth ABO$_3$ types of perovskite mixed oxides have attracted the attention because of their electronic, magnetic and catalytic properties. Generally an ideal ABO$_3$ perovskite has a cubic crystal structure. But when the tolerance factor (t) is less than one, it produces a slightly distorted perovskite structure with orthorhombic or rhombohedral symmetry. A wide range of perovskite photocatalysts have been developed for water splitting and organic pollutant degradation under UV or visible light irradiation during the past few decades. Among the different perovskite materials LaNiO$_3$, P-type semiconductor, is one of an important perovskite material, synthesised in different ways [31-38] and widely reported for various applications [39-43].

Despite this research, to the best of our knowledge, LaNiO$_3$ tailored TiO$_2$ has not been reported. Therefore, in this present work it was reported that the hetero junction p- LaNiO$_3$ / n-TiO$_2$ synthesised by co- precipitation method. In addition, UV- vis, FT-IR, XRD, SEM, EDX, and TEM techniques were used to characterize the obtained samples. Also, a series of control experiments were conducted to discuss the catalytic efficiency of the synthesised nanocomposites for the photodegradation of 4-Chlorophenol. The catalytic mechanism was also discussed based on the results of the photocatalyst characterization and activity test.

2. Experimental section
2.1 Materials

TiO$_2$ (P25) was purchased from Sigma-Aldrich and analytical-grade lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), citric acid (C$_6$H$_8$O$_7$·H$_2$O) and 4-CP were purchased from Merck.

2.2. Synthesis of nanocrystalline LaNiO$_3$

Nanocrystalline LaNiO$_3$ was synthesized by sol-gel process. Analytical grade lanthanum nitrate and nickel nitrate (in 1:1 molar ratio) were dissolved in double distilled water. Then citric acid was added to the above transparent solution and pH was adjusted by ammonia. The mixture was held at room temperature for 3 hours under magnetic stirrer to produce sol, which was dried at 100 °C for a day. According to Yuanyuan Li et al the calculations temperature determined the crystal size and surface area of the catalyst of LaNiO$_3$ and further increase in temperature interconnect the particles with each other. So the dried powder was calcined at 700°C for 4 hours [39, 41]. Commercial TiO$_2$-P25 was calcinated at 300°C for further characterization studies.

2.3. Synthesis of LaNiO$_3$ - TiO$_2$

TiO$_2$- LaNiO$_3$ was prepared by the precipitation method. Constant molar amount of TiO$_2$ was added to aqueous lanthanum nickalate solution of different molar ratio under stirring. Then pH of the reaction mixture was adjusted to basic form using aqueous ammonia. After 12 h magnetically stirred condition at room temperature, the product was filtered, washed repeatedly with ethanol and double distilled water, then dried at 100°C for 6 hours followed by calcination at 300°C for 4 hours.

2.4. Characterisation

The synthesised sample was first subjected to UV-Visible diffuse reflectance spectral measurements, carried out in a Shimadzu UV – 2450 spectrophotometer using BaSO$_4$ as the reference at room temperature in the wavelength range of 200–800nm. The Fourier Transform Infra-Red (FT-IR) spectrophotometer measurement of the sample was recorded with JASCO – FT-IR- 4200A using KBr pellet to establish the Surface structure. Powder X-Ray diffraction analysis (XRD) measurement was taken for annealed samples by X-ray diffractometer (D8 Advance ECO XRD system with SSD1601D Detector, Bruker) with Cu K$_α$ radiation at 25 °C and the crystallographic phase assignments were made with reference to the JCPDS powder diffraction files. The surface morphology of the obtained samples and elemental analysis has been studied using scanning electron microscopy in both secondary and back scattered electron modes (SEM Carl Zeiss Evo+8) and energy dispersive X-Ray spectrometer (Quantem 200 with X-Flash Bruker) respectively. Transmission electron microscopy (TEM) images were examined using TEM-CM200 PHILIPS under operating voltage of 20-200kv. The photoluminescence spectra of the photocatalyst were recorded by spectrofluorometer (JASCO-FP-6200). The photocatalytic activity of the prepared sample was also analysed by taking 4-CP as pollutant at different parameters in a HEBER immersion type photoreactor (HIPR-MP125).
2.5. Photocatalytic Activity

The photocatalytic activity of the obtained samples was investigated by using 4-CP as a pollutant. The experiment was carried out in an immersion type reactor consists of cylindrical glass vessel, which was surrounded by a circulating water jacket to cool the lamp. 200ml aqueous solution of 4-CP (50ppm) with initial concentration of 1g/lit photocatalyst was taken in the photoreactor vessel [24, 25]. Air was bubbling continuously into the aliquot by an air pump in order to provide a constant source of dissolved oxygen. Prior to light irradiation, the suspension was stirred in the dark for 30min to ensure the adsorption−desorption equilibrium between the pollutant and the catalyst. A 150W Xe arc lamp with an ultra violet (λ>400 nm) cut off filter was used as the light irradiation source. During the course of light irradiation, 5mL aliquot was withdrawn at regular time interval of 30min. Then the sample was centrifuged at 5000 rpm for 3min to settle down the pollutant from solution and filtered through a Millipore filter to remove the photocatalyst. The filtrate was analysed by UV−vis spectrophotometer. The photodegradation percentage was calculated by the expression (1) given below

\[
\text{The photodegradation efficiency (\%) } = \frac{C_o - C}{C_o} \times 100 \tag{1}
\]

Where \(C_o\) is the initial concentration of pollutant before irradiation and \(C\) is the concentration after a certain irradiation time.

2.6. Evaluation of chemical oxygen demand (COD)

COD was measured by dichromate method as follows [26]. 20 mL of degraded 4-CP solution was taken in a round bottom flask fitted with a reflux condenser. Then 10 mL of \(K_2Cr_2O_7\) (0.25 N) and 30 mL of silver sulphate/sulphuric acid were added into the reaction vessel under constant stirring. The contents of flask were refluxed for 3 hrs. After the completion of reaction, the condenser was washed carefully with 20 mL of double distilled water. Then the solution was cooled to room temperature and diluted to 140 mL. Finally Ferrous ammonium (II) sulphate (FAS) of 0.25 N was used to measure the unreacted dichromate quantitatively using 1, 10 - phenanthroline as an indicator. The change of colour from yellow to cyan, and to mahogany was the end point of titration. The COD was calculated according to eqn (2)

\[
\text{COD} = \frac{C(V_2 - V_1)}{V} \times 8000 \tag{2}
\]

where, \(C\) is the concentration of FAS, \(V_1\) is the volume of consumed FAS in test sample, \(V_2\) is the volume of consumed FAS in blank titration, and \(V_0\) is the volume of samples taken for analysis.

3. Results and discussion

3.1. Optical absorption study

The optical properties of the synthesised TiO\(_2\), LaNiO\(_3\), 2.5%LaNiO\(_3\)/TiO\(_2\), 5%LaNiO\(_3\)/TiO\(_2\) and 7.5% LaNiO\(_3\)/TiO\(_2\) are investigated by UV- Vis diffuse reflectance spectroscopy and the results are illustrated in Fig.1A. As shown in the figure pure TiO\(_2\) exhibited the absorption edge around 380 nm, at the same time addition of LaNiO\(_3\) in TiO\(_2\) enhanced the light absorption ability. The absorption edge of the nanocomposites showed red shift than pure TiO\(_2\). The observed red shift exhibited the electron-hole transition between TiO\(_2\) and LaNiO\(_3\).

The band gap of semiconductor is related to its absorption wavelength and the band gap decreases with increase of absorption edge. The absorption range of LaNiO\(_3\)/TiO\(_2\) nanocomposite is broadened to visible light range and for this reason the photocatalytic properties of the samples are improved considerably. The band gap energy of the synthesised nanoparticles and nanocomposites are calculated by Tauc approach [27].

\[
(\alpha h \nu)^{1/2} = A (h \nu - E_g) \tag{3}
\]

In eqn (3) \(\alpha\) is the absorbance, \(h\nu\) is the incident photon energy, and \(A\) is a constant. The band gaps \((E_g)\) are determined from extrapolation of linear fit onto the X-axis. The absorption edge and band gap energy of pure TiO\(_2\), LaNiO\(_3\), 2.5%LaNiO\(_3\)/TiO\(_2\), 5%LaNiO\(_3\)/TiO\(_2\) and 7.5% LaNiO\(_3\)/TiO\(_2\) is presented in Fig.1 (I-V). According to the above equation the band gap energy of the synthesised samples are 3.19eV, 2.2eV, 3.08eV, 3.10eV and 3.13eV respectively. The band gap energy values of TiO\(_2\) and LaNiO\(_3\) are match with reported literature value [41]. In the absence of TiO\(_2\), an easily induced photogenerated and holes activated by visible light in the photocatalyst of LaNiO\(_3\) recombine rapidly. But heterojunction semiconductor inhibits the rapid recombination of photogenerated and holes, leading to the strong response in visible region. The nanocomposite show red shift and ceiling absorption edge shift is observed. When the amount of dopant is stumpy that nanocomposite absorbs more visible light than the corresponding composites are evidence for highest photocatalytic efficiency.
The photocatalytic effect and the separation efficiency of the photogenerated electron–hole pairs of the synthesised samples are investigated by photoluminescence (PL) spectra and the results are described in Fig.2. A decrease in PL intensity indicates the recombination of photon instigate electron–holes are repressed [44]. From the data it is understood that the decrease in intensity of LaNiO₃ modified TiO₂ (shown in Fig.2 -II) than pure TiO₂ (I) and LaNiO₃ (II). This confirmed the maximum photocatalytic activity of nanocomposite attributed due to synergistic effect between TiO₂ and LaNiO₃.

3.2. FT-IR analysis

The FT-IR spectra are taken to analyse the information about the structure and interaction between binary composite oxide TiO₂ - LaNiO₃. Fig.3, symbolizes the FT-IR spectra of the prepared samples. As seen in Fig.3 (a), pure TiO₂ shows a very broad band in the range of 700-500 cm⁻¹ which shows the formation of Ti-O bond. The peak above 1460 cm⁻¹ represents the Ti-O-Ti stretching vibration [45-46]. Two characteristic broad peaks observed at 1603 and 3577 cm⁻¹ which specify the stretching and bending vibration of OH group which may originate due to water adsorbed from atmosphere. As presented in Fig.3 (b), the peaks appear in the range from 400-600 cm⁻¹ is a sign of metal-oxygen bonds indicate the existence of LaNiO₃ [47]. The vibration band in the range of 1400-1500 also confirmed the presence of Ni³⁺ coordination with rare-earth element [48]. The characteristic peak corresponding to TiO₂ and LaNiO₃ shift relatively to higher or lower wavenumber ascribed the interaction between nanoparticles presented in Fig.3 (c-e). It is also observed that the increased quantity of LaNiO₃ increases the peak intensity shown in the curve c-e. These results are further confirmed by XRD.

3.3. XRD investigation

X-ray diffraction analysis is employed to investigate the crystallinity and orientation of the synthesized samples. Fig.4 (a-e) represents the X-Ray diffraction peak of all set of samples. As shown in Fig.4a XRD shows several peaks at 2θ = 25.15, 37.65, 48.17, 53.82, 55.17 and 60.00 for pure TiO₂ and the peaks are perfectly harmonized with the anatase phase which unmistakably matched (with JCPDS 21-1272) and the nanoparticle shows hexagonal structure. LaNiO₃ form sharp and well defined peaks at 2θ = 32.81, 47.24 and 58.52 (represented by curve b) has good agreement with rhombohedral phase (JCPDS: 01-088-0633). Fig.4 (c-e) seemed that the important peak patterns of TiO₂-LaNiO₃ composites are similar to that of pure TiO₂ and LaNiO₃. It is noted that the peak intensities of LaNiO₃ increase with increasing of its concentration. There are no other characteristic peaks observed in XRD analysis which confirmed that all the sample exist in pure form and the sharp peaks suggest that the catalysts are well crystallised. The crystallite size of the prepared samples is calculated by Debye-Scherer equation (4).

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Where, D is crystallite size of nanoparticle, \(\lambda\) is Wave length of X-ray source (0.1541 nm), \(\beta\) is full width at half maximum of the diffraction peak, K is Scherrer constant (0.9) and \(\theta\) is Bragg angle. The average crystallite size of TiO₂ and LaNiO₃ samples are 15.59 nm [24] and 31nm [32].

3.4. Morphology and elemental study

SEM and TEM study's carried out to examine the morphology and micro structure of the heterojunction semiconductor synthesized. Fig.5 (a-c) represent the SEM micrographs of TiO₂, LaNiO₃ and 2.5% LaNiO₃/TiO₂ nanocomposite and they signify that the obtained samples have uniform shape and size and synthesised nanoparticles are agglomerated. The energy dispersive X-ray spectrum (EDX) analysis was used to investigate the elements present in the material. Fig. 5 (d-f) shows the EDX of TiO₂, LaNiO₃ and 2.5% LaNiO₃/TiO₂ nanocomposite. The spectrum authenticates the existence of elements of titanium, lanthanum, nickel and oxygen. From the EDX analysis it also inveterate that there is no other element and fabricated sample are highly pure.

TEM image of the 2.5% LaNiO₃/TiO₂ binary nanocomposite of different magnification is shown in Fig.6 (a-b) which presents the detailed information about the crystalline structure. It can be seen from the figure that the rhombohedral perovskite particles stretch on the surface of spherical TiO₂ are observed as dark spots. The TEM results are in good agreement with the XRD and SEM results.

3.5. Photocatalytic efficiency

Photocatalytic degradation efficiency of the synthesised samples is evaluated by taking 4-CP as model pollutant at different experimental condition under visible light irradiation and the results are indexed in Fig.7 (a-e). The effect of different catalyst TiO₂, LaNiO₃, 2.5%LaNiO₃/ TiO₂, 5%LaNiO₃/ TiO₂ and 7.5%LaNiO₃/ TiO₂ on the degradation of 4-CP are tested at constant pollutant concentration and pH of 9 depicted in the Fig.7-a which specifies that 2.5%LaNiO₃/TiO₂ show higher photocatalytic degradation. The percentage of photocatalytic degradation efficiency of LaNiO₃/TiO₂, 2.5%LaNiO₃/TiO₂, 5%LaNiO₃/TiO₂, and 7.5%LaNiO₃/TiO₂ are 49%, 11%, 91%, 37% and 33% respectively.
When TiO$_2$ is doped with LaNiO$_3$ which is loaded on the surface of TiO$_2$ can be easily excited and generate mobile electrons. These mobile electrons are conceded to conduction band of TiO$_2$ and then the electrons in the conduction band are readily reacting with surface adsorbed oxygen and create more reactive oxygen species which up-grade the catalytic activity [46-47] and degrade the pollutant through the intermediates Hydroquinone (HQ), benzoquinone (BQ) and hydroxyhydroquinone (HHQ) into H$_2$O and CO$_2$. The overall photocatalytic reactions taking place on the surface of LaNiO$_3$/ TiO$_2$ would be described as follows:

\[
\text{LaNiO}_3(\text{photosensitizer}) + h\nu \rightarrow \text{LaNiO}_3(h^+) + e^- \\
\text{TiO}_2 + e^- \rightarrow \text{TiO}_2(e^-) \\
\text{TiO}_2(e^-) + O_2 \rightarrow O_2^- \\
O_2^- + H^+ \rightarrow HO_2^- \\
\text{OH}^- + 4-\text{CP} \rightarrow \text{HQ} + \text{BQ} + \text{HHQ} \\
\text{H}_2\text{O} + \text{CO}_2
\]

The proposed mechanism also explained by using schematic diagram of electron transfer in LaNiO$_3$ and TiO$_2$ under UV-visible light irradiation, shown in Fig.9. In the coupled semiconductor the photoexcited charge carrier is determined by the position of valence band (VB) edge and the conduction band edge. The band-edge potential level of two components LaNiO$_3$ and TiO$_2$ can be calculated from the following empirical formula [48].

\[
E_{VB} = X - E_{e} + 0.5 E_{g} \\
E_{CB} = E_{e} - E_{VB}
\]

Where X is the absolute electro negativity of the semiconductor, expressed as the geometric mean of the absolute electro negativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy. $E_{VB}$ is the valence band edge potential, $E_{CB}$ is the conduction band edge potential, $E_{e}$ is the band gap energy of the semiconductor, $E_{e}$ is the free electron on the hydrogen scale ($\sim$ 4.5 eV). The calculated band edge position of LaNiO$_3$ and TiO$_2$ by the above equation is shown in Table 2.

**3.5.2. Effect of catalyst concentration**

The degradation efficiency of varying photocatalytic dosage from no catalyst to 0.15g/L at constant pollutant concentration and pH of 9 is presented in Fig.8.b. In the absence of catalyst, 4-CP degradation rate is negligible, while when the dosage is increased from 0.5g/L to 1.0g/L it shows highest degradation (91%). During the increase of dosage of catalyst, the active sites on the catalyst surface enlarged the generation of electron-hole pairs. However the evaluation with further boost pointed out the decrease in degradation which may be explained as due to the increases of the dosage of the catalyst, the transparency of the solution decreases and the amount of light penetration decreases, catalyst also caught up in agglomeration. The degradation percentage at different dosage of catalysts (no catalyst, 0.5g/L, 1g/L and 0.15g/L), constant pollutant concentration and pH of 9 are 0.89%, 71%, 91% and 50% respectively.

**3.5.3. Effect of pH**

The pH of the suspension has a well-built effect on the the electrostatic nature of a catalyst surface and its surface properties [49]. Both O$_2$ and OH radicals have been recognized as responsive for the oxygenation and hydroxylation of pollutant in water, and ultimately important to the mineralization of 4-CP. In general the free radical generation depends on the influence of pH of the photo-catalytic system [50]. Photodegradation rate and the results are represented in Fig.7.c. It indicates that at pH 5 and 7, the effect of pH has not been found to be noteworthy and the degradation efficiency is 33% and 50% only. The degradation achieves maximum degradation efficiency of 91% at pH 9 and further increase of pH does not produce significant change in degradation of 4-CP, because the protons are potential determining ions for TiO$_2$, and the surface charge development is exaggerated by the pH [27]. Upon hydration, surface hydroxyl groups (TiOH) are formed on TiO$_2$. These surface hydroxyl groups can experience proton association or dissociation reactions, there-by bringing about surface charge which is pH-dependent and photodegradation occurs.

**3.5.4. Effect of change of pollutant concentration**

The change of photo degradation with different concentration of pollutant is shown in Fig.7.d. The ranges from 10ppm to 80ppm are tested under optimum condition. The maximum degradation efficiency is observed when the pollutant concentration is increased from 10 ppm to 50 ppm and further, the efficiency is comes down from 91% (for 50ppm) to 36% and 31% with pollutant concentration of 70ppm and 80ppm.
respectively. Even though the catalyst amount, pH and irradiation time are maintained constant due to increase of pollutant concentration reduces the reacting probability of the catalyst. The reason for the reduction in reaction rate is the opacity caused by surplus photocatalyst clusters at pollutant overdose [29].

3.5.5. Kinetics of Photodegradation

Kinetics of the photodegradation of 4-CP under visible light and optimum condition over the photocatalyst was investigated by applying the Langmuir-Hinshelwood model.

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

Here \( C_0 \) is initial concentration, \( C \) is concentration of pollutant after time \( t \) and \( k \) is the rate constant of the reaction. The plot of \( \ln \left( \frac{C_0}{C} \right) \) vs time is linear and suggests that the degradation follows the pseudo first order kinetics. The experimental rate constant for the reaction offered in Fig.8.A correspond to \( \text{TiO}_2 \), \( \text{LaNiO}_3 \), 2.5%\( \text{LaNiO}_3 \)/\( \text{TiO}_2 \), 5% \( \text{LaNiO}_3 \)/\( \text{TiO}_2 \) and 7.5% \( \text{LaNiO}_3 \)/\( \text{TiO}_2 \) are 0.8* \( 10^{-3} \text{s}^{-1} \), 3.2* \( 10^{-3} \text{s}^{-1} \), 1.36* \( 10^{-2} \text{s}^{-1} \), 3.10* \( 10^{-3} \text{s}^{-1} \) and 2.0* \( 10^{-3} \text{s}^{-1} \) respectively.

3.5.6. COD removal experiments

2.5% \( \text{LaNiO}_3 \)/\( \text{TiO}_2 \) confirmed remarkable photocatalytic activity with a degradation of 91% and COD removal of 78.21% for 4-CP. COD measurements is carried out under optimum reaction conditions of catalyst concentration (1g/L), pollutant concentration (50 ppm), pH=9 and irradiation time (180min) to estimate the toxicity of the photodegraded organic solutions and the results are shown in Fig.8.B. From the figure, it is observed that the solutions obtained after photodegradation showed significant removal in COD (78.21%). These results suggested that most of the pollutant molecules are mineralized during the photodegradation process.

3.5.7. Photocatalytic stability evaluation

The reusability and stability of photocatalyst also tested under the optimum condition of catalyst, pollutant, \( \text{pH} \) and irradiation time (1g/lit, 50ppm, \( \text{pH} = 9 \) and 3 hrs visible light irradiation) respectively. The reusability of catalyst is verified by running the experiment for 4-cycle. After the completion of the first cycle, the suspension is collected and subjected to centrifugation then the catalyst is collected by filtering and washed with deionised water three times, dried in an air oven, then used for next cycle. The procedure is repeated up to 4-cyclic experiments. The results are presented in Fig.8.C. The photodegradation dose of the catalyst decreases a little turn due to the washing of catalyst, while stability and catalyst effect also maintained.

The samples before and after the degradation of 4-CP are also investigated by XRD and the patterns presented in Fig.8.D which is a sign of that there is no remarkable adaptation in the crystal structure of the catalyst before and after photo reaction. The result shows that there is no photocorrosion and photodissolution of catalyst and the 2.5%\( \text{LaNiO}_3 \)/\( \text{TiO}_2 \) nanocomposite has good stability and reusability for the photocatalytic reaction. 2.5%\( \text{LaNiO}_3 \)/\( \text{TiO}_2 \) establish maximum degradation than pure \( \text{TiO}_2 \) and phosphate anchored \( \text{TiO}_2 \) shows 46% and 68% degradation [51], \( \text{Ag/ TiO}_2/ \text{Fe}_3 \text{O}_4 \) nanocomposites which degraded 82% of 4-CP[29] with enhanced COD removal.

4. Conclusion

Hetero junction p-\( \text{LaNiO}_3 \) modified n-\( \text{TiO}_2 \) has been fruitfully fabricated by precipitation method and the photocatalytic activity of the composite has been tested by taking 4-CP as model pollutant under visible light irradiation. TEM, SEM and XRD spectra confirmed the incorporation of \( \text{LaNiO}_3 \) with \( \text{TiO}_2 \). The synthesised nanocomposites of \( \text{LaNiO}_3 \) and \( \text{TiO}_2 \) have mixed structures of rhombohedra and hexagonal phase. UV-Vis DRS and PL are the evidences for extending light absorption in the visible region, improved photocatalytic activity of 2.5%\( \text{TiO}_2/ \text{LaNiO}_3 \) (than 5% and 7.5% of nanocomposites) and its degradation rate is higher than pure \( \text{TiO}_2 \) and \( \text{LaNiO}_3 \) respectively. 25%\( \text{TiO}_2/ \text{LaNiO}_3 \) nanocomposite shows the maximum degradation efficiency of 91% in 3-hours of simulated solar light irradiation with 78.21% COD removal. A possible photocatalytic mechanism has also been proposed and degradation follows pseudo-first order kinetics. The photocatalytic activity is obviously affected by catalyst concentration, \( \text{pH} \) and pollutant dosage. This work confirms that the present fabricated nanocomposites acts as an effective photocatalyst for the degradation of organic pollutant.

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Figure captions

**Fig. 1** A) UV-vis-DRS of a) TiO\(_2\), b) LaNiO\(_3\), c) 2.5%LaNiO\(_3\)/TiO\(_2\), d) 5%LaNiO\(_3\)/TiO\(_2\) and e) 7.5%LaNiO\(_3\)/TiO\(_2\). Tauc plots of I) LaNiO\(_3\), II) TiO\(_2\), III) 2.5%LaNiO\(_3\)/TiO\(_2\), IV) 5%LaNiO\(_3\)/TiO\(_2\) and V) 7.5%LaNiO\(_3\)/TiO\(_2\).

**Fig. 2** PL spectra of I) TiO\(_2\), II) LaNiO\(_3\) and III) 2.5% LaNiO\(_3\)/TiO\(_2\).

**Fig. 3** FTIR of a) TiO\(_2\), b) LaNiO\(_3\), c) 2.5%LaNiO\(_3\)/TiO\(_2\), d) 5%LaNiO\(_3\)/TiO\(_2\) and e) 7.5%LaNiO\(_3\)/TiO\(_2\).

**Fig. 4** XRD of a) TiO\(_2\), b) LaNiO\(_3\), c) 2.5%LaNiO\(_3\)/TiO\(_2\), d) 5%LaNiO\(_3\)/TiO\(_2\) and e) 7.5%LaNiO\(_3\)/TiO\(_2\).

**Fig. 5** FE-SEM of a) TiO\(_2\), b) LaNiO\(_3\), c) 2.5% LaNiO\(_3\)/TiO\(_2\) and EDX analysis of d) TiO\(_2\), e) LaNiO\(_3\) f) 2.5% LaNiO\(_3\)/TiO\(_2\).

**Fig. 6** TEM image of a,b) 2.5%LaNiO\(_3\)/TiO\(_2\) with different magnification.

**Fig. 7** Photocatalytic degradation efficiency of 4-CP observed in the presence of different catalyst (a), 2.5%LaNiO\(_3\)/TiO\(_2\) catalyst concentration variation (b), different pH variation (c), pollutant concentration variation (d) and absorption spectra of 4-CP degradation in aqueous solution in the presence of 2.5% LaNiO\(_3\)/TiO\(_2\) catalyst.

**Fig. 8(A)** Kinetic plot of ln \((C_0/C)\) versus irradiation time \(t\) for the photodegradation of 4-CP, (B) Comparison of photodegradation and COD removal percentage of 4-CP in the presence of TiO\(_2\), LaNiO\(_3\), 2.5%LaNiO\(_3\)/TiO\(_2\), 5% LaNiO\(_3\)/TiO\(_2\) and 7.5% LaNiO\(_3\)/TiO\(_2\), (C) Reusability and Stability of 2.5%LaNiO\(_3\)/TiO\(_2\) catalyst, (D) XRD patterns of 2.5% LaNiO\(_3\)/TiO\(_2\) before and after the photocatalytic reaction in 4-CP degradation under visible light.

**Fig. 9** The schematic diagram of electron transfer in 2.5% LaNiO\(_3\)/TiO\(_2\) under visible light irradiation.
Fig. 1

Fig. 2

Fig. 3

Fig. 4
Fig. 7

Absorbance

Wavelength (nm)

0 min

180 min

\[\text{In} \, C_0 / C \]

\[\text{Photodegradation} \% \]

\[\text{COD} \% \]

4-CP Conversion (%)
Table 1

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<tr>
<th>Element</th>
<th>LaNiO₃</th>
<th>TiO₂</th>
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<td>Weight (%)</td>
<td>Atom (%)</td>
<td>Weight (%)</td>
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<td>100</td>
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Table 2

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<th>Absolute Electronegativity (X)</th>
<th>Estimated energy band gap Eg (eV)</th>
<th>Calculated Conduction band edge (eV)</th>
<th>Calculated Valence band edge (eV)</th>
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<tr>
<td>TiO₂</td>
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<td>2.18</td>
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