Environmental sustainability of an ecosystem by biotemplated nano Titania

N. Saikumari¹*, S. Monish Dev², S. Avinaash Dev¹
¹Science and Humanities, RMK College of Engineering and Technology, Chennai, India
²Anna University, Chennai, India

A R T I C L E  I N F O

Article history:
Received 26 October 2020
Received in revised form 8 February 2021
Accepted 15 February 2021

Keywords:
Sustainability
Ecosystem
Pollution
Nano titania
Plant extract

A B S T R A C T

Environmental sustainability apart from spoken at different levels need to investigate the management of industrial activities in terms of eco friendliness. It is well known that an effluent from various industries becomes a major source of environmental degradation in particular water pollution. Thus water analysis report turns to be more significant, to determine the quality and standard of life maintained in a typical ecosystem. This study includes the analysis of physico-chemical factors of raw as well as treated water samples from Korattur Lake employing nano sized adsorbents like titania with tuned structural and morphological properties through organic plant extract. The XRD analysis, BET analysis, DRS-UV analysis, SEM and TEM analysis have been carried out and reported. The usual indicators of contamination level at a given source namely Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Chloride, Nitrate and Phosphate contents etc. were used to ascertain the efficiency of contaminants removal using tea leaf extract mediated nano titania. The reliability factor of the treatment process was found to be less than 1, revealed the effectiveness and reliability of nano material.

1. Introduction

Water is one of the indispensable resource that is available on the earth and is also one of the primary need of an individual at present. But due to various industrial, agricultural and domestic discharge of wastewater into different water sources resulted in water exploitation and pollution, therefore made the availability of fresh water a rare commodity now a days [1]. It is very important to know that industrial growth, human health, environmental enrichment, plant growth and sustainable development etc. are directly linked to quality of water, is the vital concern of the mankind today. It is worldwide concern that lack of pure and safe water supply lead to ill health affecting human kind especially in developing countries. Increasing population, urbanization, mining, other agricultural and industrial activities followed by their immediate impacts deteriorate the surface and subsurface, thus polluting water on surface. The different forms of metabolic and physiological activities and life cycle of aquatic animals are greatly influenced by the polluted water and thus the analysis on physiochemical characteristics of water is found to be highly essential [2-5]. River water is the chief water source meant for drinking, agriculture and engineering purpose both in rural and urban areas. The numerous chemicals used in the industries, pollutants [6] like heavy metals, dyes and suspended solids in the form effluents discharged into rivers, continue to generate wastewater having significant effect on flora and fauna. Hence it is mandatory to monitor and confirm the standard of the same by regular evaluation of their physical, chemical and biological parameters through water treatment processes prior to their discharge. In this regard heterogeneous photo catalysis using semiconductor metal oxides as catalysts proved to be highly dominating among different water treatment techniques in removing pollutants from water and air without leaving any secondary pollutants [7]. Titania in the nano size is one of the promising photo catalysts employed to the greater extents in the recent decades being cost effective, ease of
production, less toxic and photo stable with desired band gap. But its poor visible light absorption along with low surface area restricted its applications in larger scale [8] that could be overcome by the controlled synthesis of titania either by doping with metal and non-metal or coupling with other metal oxides [9]. To meet with this requirement bio template assisted sol-gel mediated nano titania is proved to be clean, safe, eco-friendly, cost effective and less toxic and yield titania with high superficial area, widespread pores and extensive morphologies [10]. In the present study water sample is taken from Korattur lake also known as Vembu Pasumai Thittu of Korattur, India. Korattur is a western suburb of Chennai and is bordered by Madhananguppatham in the north, Kolathur in the east, Patteravakkam/Ambattur in the west and Padi in the south. This area hosts the sprawling Korattur lake, whose area may vary anywhere between 600-990 acres today. The lake is located to the north of the Chennai–Arakkonam railway line; it is one of the largest lakes in the western part of the city. Korattur Aer is one of a chain of three water bodies, including the Ambattur Aer and the Madhavaram Aer, where surplus water from one is transported to another. The residents of Chennai have been benefiting from this source during the water scarcity but were found to be polluted by the continuous release of runoffs from the nearby domestic and commercial sources. The canals that connect this lake with other water bodies are vestiges of the once-prevailing agricultural practice in this area. There are two main canals – one running from the Ambattur lake that takes excess water and feeds the Korattur lake (located to the south); and the other running to Retteri lake, which drains excess water from Korattur lake (located to the north). The lake suffers from multiple issues ranging from sewage contamination to illegal encroachments, and the conditions have only deteriorated over the years due to noncompliance by the people and the civic agencies.

Fig. 1. Satellite view of Korattur Lake, Chennai with sampling stations.

A good part of greenery and natural vegetation was present in this lake, even till the last decade. Much natural vegetation once existed in the lake and its bund. Palmyrah, date palm, umbrella thorn trees dot the bund. Inside the lake, water hyacinth is to be seen. This apart, many aquatic vegetation, water lily and wetland rushes are present in the water body. The lake apart from reptiles and amphibians has a dwelling of common and rare birds like grey pelican, Asian open bill, grey heron, large egret, coot, purple swamp hen, common moorhen etc. Amphibians like green pond frog, skittering frog, Jerdon’s bullfrog, Indian bullfrog, Indian tree frog, Asian common toad, ornate narrow-mouthed frog, Microhyla rubra and Ramanella variegata occur here. All of these get very active during monsoon. The current work is an attempt to examine the technical feasibility of photo-catalytic effect of nano titania against the sample taken from Korattur lake at ambient conditions taking into account the different parameters like pH, catalyst dosage, light intensity and contact time on a pilot scale for further study. The nano titania catalyst was synthesized by simple, cheap one pot synthesis under sol-gel technique and characterized by XRD, BET, FTIR, DRS-UV, SEM and TEM analysis.

2. Materials and methods

2.1. Chemicals

Titanium tetraisopropoxide (TTIP, 99% pure) a precursor, Iso propanol (99% pure) and Acetic acid were collected from Sigma Aldrich. HCl and NaOH were obtained from Sigma Aldrich. A lemon tea extract used as a bio template was purchased from supermarket and washed repeatedly two to three times with double distilled water.

2.2. One pot synthesis of nano titania

In 100 ml beaker 60 ml of iso propanol was mixed with 9 ml of TTIP and 30 ml of 4% acetic acid and about 1 g of tea leaf extract. The mixture is subjected to continuous stirring for 1 h which was resulting in a homogeneous colloidal sol due to hydrolysis and condensation reactions. The suspension is left undisturbed for 10 h to get a gel, then dehydrated at 110°C for 4 h using oven. The dampness free powder obtained was calcined at 400°C for 4 h and stored and named as TNT.

2.3. Characterization of templated nano titania

The XRD pattern for the phase analysis were obtained using X-ray diffractometer with Cu Kα (λ=1.546A°) radiations in 2θ range from 20° to 80° with a scan rate of 2° per minute at room temperature in order to assess their crystallite size and structural properties. A Perkin-Elmer spectrometer using KBr pellet technique was used to study FT-IR. About 20 mg of the sample was made into a pellet along with special grade KBr using hydraulic press. The synthesized samples were subjected to scan within 4000-400 cm⁻¹. DRS-UV spectral analysis of the sample was carried out using Schimadzu UV 2450 with BaSO₄ as a standard. The band gap energy was calculated using Tauc equation (Tauc et al. 1966),
(ahu) n = const (hu – Eg)
Where, n= type of electronic transition, hu-photon energy, α-absorption co-efficient. The surface properties were analyzed using Quadrasorb Surface Analyzer. Scanning Electron Microscope (Quanta 200 ESEM) was used to study the morphology of the templated sample.

2.4. Treatment of sample water using green synthesized TNT

2.4.1. Sample collection

The raw water sample to be subjected for photo-catalytic degradation using templated nano catalyst TNT was collected from the selected point of Korattur Lake in 1 L plastic bottle which was sterilized and previously rinsed with the same. The basic overall characteristics were analyzed in Swasthi Enviro Solutions Private Limited, Chennai and showed in Table 1. It is noted that most of the parameters like nitrate, phosphate, calcium contents etc. were found to be within the permissible level of IS10500:2012. The other parameters likely to be treated were subjected to photo catalysis by a synthesized catalyst TNT under optimized conditions of pH, catalyst dosage, temperature etc.

Table 1. Physico-chemical parameters of the sample from Korattur Lake.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>COD-chemical oxygen demand</td>
<td>mg/L</td>
<td>185</td>
</tr>
<tr>
<td>2</td>
<td>BOD-biological oxygen demand</td>
<td>mg/L</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>DO-dissolved oxygen</td>
<td>mg/L</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>5</td>
<td>TDS-total dissolved solids</td>
<td>mg/L</td>
<td>7000</td>
</tr>
<tr>
<td>6</td>
<td>EC-electrical conductivity</td>
<td>µS/cm</td>
<td>8500</td>
</tr>
<tr>
<td>7</td>
<td>chloride content (Cl)</td>
<td>mg/L</td>
<td>520</td>
</tr>
</tbody>
</table>

2.4.2. Photo-catalytic treatment of sample water

To evaluate the efficacy of synthesized nano catalyst TNT towards the degradation of pollutants in sample water taken from Korattur Lake, 500 ml of the sample without any alterations was transferred to 2 L wide mouthed petri dish made of borosilicate glass and exposed to direct sunlight. HCl and NaOH were used to adjust the pH of the sample water containing pollutants. The HTC make Digital Lux meter (model LX-101A) has been used to determine the intensity of sunlight in the month of April and May from 12 noon to 2 pm and was found to be 1.25x10^5. Before subjecting the suspension mixture to solar irradiation the experiment was carried out in the dark to equilibrate the adsorption of pollutants on the surface of TNT. The degradation of pollutants in the wastewater was followed by regular withdrawal of samples at regular intervals from the dish and the variation in its concentration was monitored by Lambda 35, Perkin Elmer a spectrophotometer at wavelength 590 nm.

3. Results and discussion

3.1. Characteristics of green synthesized and calcined TNT

Figure 2 shows the XRD pattern of templated titania TNT calcined at 400°C, in which the peaks originated from (100), (004), (105), (301), (105), and (116) planes that of pure anatase phase were in fine agreement with JCPDS 21-1272 (the standard pattern of anatase phase) confirmed the formation of phase pure anatase titania [11]. The crystallite size was calculated with respect to (101) plane (θ=25.1°) with highest intensity using Debye Scherrer formula \( D = \frac{K\lambda}{\beta \cos \theta} \). The average crystallite size of TNT catalyst was calculated to be 12.4 nm.

![XRD pattern of Calcined TNT](image)

Figure 3 gives the FT-IR spectrum of raw template (3a), as synthesized (3b) and calcined (3c) TNT catalysts. FT-IR spectrum of fresh leaf extract has shown the peaks corresponding to stretching vibrations of poly phenols, carboxylic acid, poly saccharide, amino acid etc. at 1623, 1025, 1394 and 1025 cm\(^{-1}\)[12] and the peaks due to O-H, symmetric and asymmetric stretching vibrations of CH2, CH, C=O etc. at 3369, 2924, 2866, 1750 respectively [13]. In as synthesized TNT (curve b) and calcined TNT (curve c), peaks due to the presence of –OH and other functional groups were shifted to lower number showing the weak hydrogen bond interaction between hydroxyl hydrogen and oxygen of titania on the surface [30]. The absence of respective peaks of an organic leaf extract in the case of calcined TNT (curve c) clearly indicated the removal of template from the catalyst and the broad absorption band at 400-750 cm\(^{-1}\) established the formation of Ti-O-Ti linage characteristic as that of titania [15].
Figure 3. FTIR spectrum of a) tea leaf template b) as-synthesized TNT c) Calcined TNT

Figure 4 shows the N₂ adsorption-desorption isotherm of TNT sample, the specific surface area was observed to be 105 m²/g. The isotherms match with the type III adsorption pattern confirming capillary condensation of the particles on the surface of nano titania. The results of surface analysis are in good agreement with the report that reduced crystallite surface would enhance the photo-catalytic activity of a catalyst [16]. From BJH analysis, the average pore size of the catalyst TNT is 9.21 nm. Thus a template has played a critical role in tuning surface area and pore size distribution uniformly to support the overall photo-catalytic wastewater treatment.

A DRS-UV Visible spectrum (Figure 5a) clearly has shown a bathochromic shift i.e. the shifting of absorption band to visible region corresponding to appearance of absorption edge at 424 nm. Also the band gap energy was found to be 2.83 eV, from the Tauc plot (Figure 5 b). The above facts clearly illustrated the fine-tuning of TNT to act as a active photo catalyst in the visible UV region and could be employed as a water treatment agent successfully.

Figure 6a shows the results of SEM analysis of calcined TNT. The finely dispersed nano particles with moderate agglomeration and irregularities in the image of TNT confirmed the presence of widespread particles that would increase the adherence and interaction of the pollutant molecules in the sample water with the titania catalyst [17]. EDS analysis of TNT (Figure 6b) pattern clearly indicated the presence of only Ti and O and the non-existence of other elements, thus confirmed the purity and complete elimination of an leaf extract during the calcination of TNT at 400°C.

Figure 4. a) N₂ adsorption-desorption b) Pore size distribution analysis of calcined TNT.

Figure 5. a) DRS-UV and b) Tauc plot of calcined TNT.
Figure 7a gives the TEM image, the uniform distribution of nano particles in calcined TNT. The crystallite size of the nano particles were ranging from 12.2 - 14.6 nm, and holds good with the average crystallite size of TNT reported in XRD analysis. The presence of particles of lowered agglomeration and indefinite shape showed the impact of biotemplate during the synthesis on the grain growth and morphology of TNT, a catalyst. Highly resolved lattice fringes and well defined ring pattern of SAED image (Figure 7b) that were of typical anatase phase clearly substantiated the purity and crystallinity of synthesized and calcined nano catalyst TNT [18].

3.2. Removal efficiency of water parameters by green synthesized and calcined TNT

To study the photo-catalytic efficiency performance of the synthesized nano catalyst TNT, the physico chemical properties of raw (Table 1) and treated wastewater sample were compared and analyzed. From the data given in Table 1, the values of various parameters recorded clearly recommended the requisite of water treatment of the sample as some values reported were higher than the permissible level as per water pollution control board, Tamilnadu, due to discharge of nearby industrial and domestic effluents. The reduction efficiency of the catalyst synthesized and used in this study, namely TNT was given by the equation

\[
\text{Removal efficiency} = \frac{\text{A} - \text{A'}}{\text{A}} \times 100
\]

Where \(\text{A}\) = Concentration of wastewater before treatment and \(\text{A}'\) = Concentration of wastewater after treatment.

3.2.1. Chemical oxygen demand-COD, biological oxygen demand-BOD, and dissolved oxygen-DO.

COD is the quantity of oxygen required to oxidise an organic matter present in the water which is responsible for the contamination, and was determined titrimetric method using a powerful oxidizing substance. It is usually more than the value of BOD as few organic pollutants which are resistant to biological oxidation could undergo oxidation chemically. COD calculations are made quickly whereas BOD estimation used to take minimum 5 days [19]. Th COD of raw sample was 124 mg/L while 93.8 % reduction of the same parameter after the photocatalytic treatment was realized. BOD is the sum of oxygen required for oxidizing organic pollutants microbially, is used as a standard test to examine the efficiency of the treatment method adopted and the level of toxicity in the effluent. BOD is directly associated with DO, higher is a BOD level, greater is the reduction of available oxygen which lead to more deaths of aquatic organisms [20]. The photo-catalytic treatment using TNT brought about 84.9 % reduction of BOD with respect to the reported value of raw sample as 80 mg/L. The value of BOD/COD wastewater is used as an index, which is designed to estimate the presence as well as the nature of biodegradable chemical impurities in the wastewater in turn applied to predict the suitable water treatment techniques [21]. DO- Dissolved Oxygen is one of the vital parameter of water parameters and is served as a tool to study the condition of an ecosystem [22]. The amount of dissolved oxygen in water is partially dependent of different activities occurring in it physically, chemically and biologically. The dissolved oxygen content in water would be directly proportional to pressure and is inverse to temperature and salinity as reported by the scientists [23]. Prior to the photo-catalytic treatment, the amount of dissolved oxygen was about 4.1 mg/L, and after the
treatment it was increased to 7.7 mg/L and nearly 86 \% efficacy has been realized. Dissolved Oxygen content in water varies inverse to BOD/COD as reported [24]. During the visible light photo catalysis, the various organic pollutants were decomposed effectively when they come into contact with TNT catalyst’s surface as shown in Figure 8 [25].

![Graph showing removal efficiency of TNT on COD, BOD and DO contents.](image)

**Fig. 8.** Removal efficiency of TNT on COD, BOD and DO contents.

3.2.2. **Reduction of TDS-total dissolved solids, EC-electrical conductivity and Chloride content in wastewater**

TDS is a estimation of dissolution of chemical substances, inorganic and organic impurities in water [26]. Though there is no particular standard to have TDS in water, it should not go beyond 1500 mg/L for irrigative purposes and domestic uses. Excess TDS in water may lead to hard scaling in boilers, pipes and other household appliances [20]. Photo-catalytic treatment of wastewater using a nano catalyst TNT has shown 74.9 \% reduction efficiency and thus the water became free from suspended solids. This reduced concentration of TDS could control the dehydration of aquatic animals [20]. Water sample of particular electrical conductivity(EC) varies directly to total dissolved solids content or in other words it is the measure of dissolved solid impurities [27]. Higher value of EC is also the indication of richness of inorganic contents in the wastewater because of chemicals like additives, thinners and pigments in the form of effluents from industries. It is highly necessary to treat water with high EC content as it could easily cause imbalance for aquatic organisms by reducing the dissolved oxygen content [28]. By using TNT the decrease in EC was reported around 74.2 \% at the end of photo-catalytic treatment under solar irradiation. The chloride content in any water source should not exceed 350 mg/L as per WHO recommendation [29] as it would threaten the sustainability of food resources in an ecosystem in turn that might pose a high danger to living species, their growth and also reproduction [30]. Bio-accumulation and the tenacity of chloride in wastewater in high concentration may be due to the presence of chlorinated resins, chemical compounds like PVC, alkyl benzyl ammonium chloride etc. in the effluents of industries nearby. About 89 \% of reduction efficiency has been shown by TNT over the adsorption of chloride impurities. Thus the overall reduction of TDS, EC and chloride content as shown in Figure 9 directly meant to conserve aquatic organisms and water quality, substantiate the photo-catalytic efficiency of TNT in producing OH\(^{-}\) and O\(^2\) to decompose organic pollutants in wastewater into CO\(_2\) and H\(_2\)O [31].

![Graph showing removal efficiency of TNT on TDS, EC and Cl\(^-\) contents.](image)

**Fig. 9.** Removal efficiency of TNT on TDS, EC and Cl\(^-\) contents.

4. **Conclusions**

This present work involved green synthesis of nano titania and has brought out the importance of sustainability of local ecosystem to maintain high level bio-diversity. It also aimed to establish the photo-catalytic activity of nano titania TNT, produced by simple sol-gel mediated one pot synthesis to eliminate the organic toxins present in the effluent from industries. The various data obtained during the removal of contaminants used to interpret the photo stability of the synthesized catalyst as well as adsorption behavior of impurities on TNT surface. Thus, mesoporous phase pure titania catalyst with high surface area (105 m\(^2\)/g), moderate porosity along with bathochromic shift showed its maximum efficiency in the removal of pollutants from wastewater drawn from well-known key ecosystem. Thus, the role of biotemplate in shifting absorption edge of synthesized and calcined TNT to 424 nm was quite evident through its photo-catalytic reduction and the removal efficiencies under solar irradiation compared to commercially available Titania as discussed in earlier studies. This study highlighted the significance of continuous monitoring and conservation of nearby key water bodies to enable sustainable development of present eco-system and the possibility of reclamation of the same from degradation. This performance could be extended to large scale and employed as a better tool in the field of pollution abatement on profitable scale.
Acknowledgements

Dr. Saikumari N thanks the Management, RMK Group of Institutions, Chennai for their moral support to carry out the analysis and complete this work successfully.

References


