

GREEN SYNTHESIS OF TITANIUM OXIDE (TiO₂) NANOPARTICLES USING *Phyllanthus Niruri* AND ASSESSMENT OF ITS PHYSIOCHEMICAL PARAMETERS IN WASTEWATER TREATMENT

H. Yunusa ^{*1}, K. I. Omoniyi ^{*1}, S. E. Abechi¹, S. D. Sani², A. O. Ugwoke³ and N. Imam⁴

¹Department of Chemistry, Ahmadu Bello University, P.M.B. 06, Zaria, Nigeria.

²Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria

³Department of Chemistry, Nigeria Police Academy, Wudil, Kano State, Nigeria.

⁴Department of Chemistry, Federal University, Oye-Ekiti, Ekiti State, Nigeria.

***Correspondence authors: israelflourish@yahoo.com; 08036257789
faithyunusa8@gmail.com; 07067599881**

ABSTRACT

This study investigates the green synthesis of titanium oxide (TiO₂) nanoparticles, NPs and assessment of its physiochemical parameters in wastewater treatment. The methanol plant extract of *Phyllanthus niruri* was utilized for the biosynthesis of titanium oxide NPs. The preliminary phytochemical screening carried out on *Phyllanthus niruri* plant extract was conducted to identify the bioactive compounds such as alkaloids, flavonoids, tannins, saponins, terpenoids, anthraquinones, glycosides and steroids which may be responsible for stabilizing the nanoparticles synthesized. In the treatment of the industrial wastewater sample; the result indicated that the use of the synthesized titanium oxide nanoparticles led to percentage reduction of 67.21%, 58.96%, 91.19%, 75.56% and 94.67% for BOD, COD, turbidity, oil and grease and phosphate respectively, in the raw wastewater; and was more effective than the use of commercial titanium oxide NPs. The study indicates that synthesis of titanium oxide NPs using *Phyllanthus niruri* is a better alternative to chemical synthesis of NPs, the green synthesized material is eco-friendly and can serve as a treatment for industrial effluents.

Keywords: *Phyllanthus niruri*, biosynthesis, nanoparticles, wastewater, treatment

INTRODUCTION

One of the most significant and prevalent elements in the environment is water. Water is necessary for the existence and growth of all living things on earth. Currently, only earth is a planet with almost 70% water. But due to increased human population, industrialization, use of fertilizer in the agriculture and man-made activity it is highly polluted with different harmful pollutants [1]. Pollution of water represents a severe threat to the environment and human health. Nanotechnology offers the

potential for the development of alternative technologies for wastewater treatment. Nanotechnology involves the use of nanoscale materials that are generally between 1 and 100 nanometers in size [2].

Nanotechnology, like microtechnology, involves materials defined by a size scale, but unlike micromaterials, nanomaterials are capable of possessing remarkable properties that deviate dramatically from the bulk of the parent material. Nano-materials typically have a high reactivity

and degree of functionalization, large specific surface area, and size dependent properties, etc., which makes them suitable for applications like wastewater treatment, as well as for water purification [3]. Greener approaches for production of nano-materials are being adopted to minimize the use of unsafe reagents and maximize the efficiency of chemical processes [4].

Titanium oxide (TiO_2) is one of the most important chemically stable nanoparticles which has received the most attention as photo-catalyst and adsorbent in the removal of pollutants from wastewater [5]. Among the various kinds of nano-adsorbents, oxide-based nanomaterials such as Fe_3O_4 , TiO_2 and ZnO and their composites play important roles in water purification. This is due to their high surface area and super paramagnetism [5].

Miller *et al.* (2012) reported that titanium oxide generates reactive oxygen species when exposed to ultraviolet radiation; so nanoparticles of titanium oxide used in antibacterial coatings and wastewater disinfection have been investigated as an anti-cancer agent [6].

This study aimed at meeting the quest for eco-friendly approach to reducing the contamination in wastewater is in line with the shared blueprint on SDG by using biosynthesized titanium oxide nanoparticles to reduce some physiochemical parameters of health concern in an industrial wastewater.

MATERIALS AND METHOD

Collection and preparation of *Phyllanthus niruri* leaf extract

A 20 g amount of fresh *Phyllanthus niruri* leaves were collected from a garden at Sabon-Gari Local Government Area, Kaduna State, Nigeria. The sample (*Phyllanthus niruri*) which belongs to the family of *Phyllanthaceae* was identified and authenticated by a botanist at the herbarium unit of the Biological Sciences of Faculty of Life Sciences of Ahmadu Bello University, Zaria, Kaduna State with voucher number ABU0716.

The *Phyllanthus niruri* leaves were well-washed with water to remove the dust particles from their surface. The leaves were further rinsed with the deionized water, followed by the drying process at room temperature. The leaves were kept at room temperature for 15 days and transferred to the grinder to crush into a fine powder. The powdered sample 2.00 g was carefully weighed using an analytical balance and mixed with 100 cm^3 of methanol to obtain the hydro-alcoholic crude extract using an Erlenmeyer flask at room temperature. After 72 hours, the filtrate was separated from the mash by using a filter paper (Whatman No. 1). The obtained filtrate was stored for further analysis.

Collection of wastewater sample

The wastewater sample was collected from Sunseed Nigeria Limited, located at old Jos Road Dekace village Zaria, Kaduna State. The

wastewater was collected in January 2022 at about 10:00 a.m. in a 2000 cm³ sample bottle and stored at 4°C for further analyses.

Quality assurance

All reagents used are of analytical grade, including distilled water. All the glassware, and sample bottles were washed with liquid soap, rinsed with distilled water, soaked in 10% HNO₃ for 24 hours and rinsed thoroughly with distilled water and thereafter dried.

Green Synthesis of TiO₂-NPs

Green synthesis of the TiO₂ nanoparticles was achieved by following the method of Kalaifarasi *et al.* (2013) with some modifications [7]. A 0.99 g amount of Titanium oxide was weighed and mixed with 250 cm³ of distilled water. To the mixture, 25 cm³ of the prepared extract of *Phyllanthus niruri* was added. After that, the mixture was stirred for four hours using a magnetic stirrer while stirring sodium hydroxide (1M) was added dropwise to adjust the pH to 7 and to increase the yield of titanium oxide nanoparticles, a colour change from light green to white was noted. The solution was then filtered using Whatman No 1 filter paper to separate the nano-sized particles from the suspension, the powder obtained was dried by using a hot air oven and stored for further analysis.

Phytochemical Screening of the Crude Plant Extracts

The hydro-alcoholic crude extract was subjected to phytochemical analysis to screen it for the presence of secondary metabolites, such as alkaloids, saponins, flavonoid, terpenoids, steroids, tannins, anthraquinones and glycosides. The phytochemical screening was carried out using standard procedure [8].

Determination of physiochemical parameters of the wastewater

The physiochemical parameters determined in the wastewater before and after treatment with the synthesized TiO₂ NPS and then pure commercial TiO₂ were: pH, temperature, and turbidity, dissolve oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), electrical conductivity (EC), nitrate and phosphate. This was carried out using standard procedure [9].

RESULTS AND DISCUSSION

Qualitative phytochemical screening

The preliminary phytochemical screening carried out on the *Phyllanthus niruri* plant extract (Table 1) showed that the plant extract contains alkaloids, tannins, anthraquinones, glycosides, flavonoids, steroids and terpenoids compounds, which are in agreement with the work of Adebisi *et al.* (2021) [10] carried out on the plant extract.

Table 1: Quantitative phytochemical constituent of the methanolic extract of *Phyllanthus niruri*

Constituents	Qualitative Analysis
Alkaloid	+
Flavonoid	+
Tannins	+
Saponins	+
Terpenoids	+
Anthraquinones	+
Glycoside	+
Steroids	+

(+) = positive

The plant derivatives contained various bioactive compounds which can be responsible for capping and stabilizing agents of the titanium oxide nanoparticle from agglomeration.

Physicochemical parameters

Tables 2 and 3 show the analysis of variants of the physicochemical parameters before and after treatment with both synthesized and commercial titanium oxide nanoparticles.

The pH of the wastewater during treatment is essential for the removal of organic compounds and heavy metals. In this study, the pH values before and after treatment were reported to be

within the WHO acceptable limit. A shift in the pH of surface water may cause highly mobile aquatic organisms to migrate to safer environments, while those that are sedentary may be killed [11]. At lower pH, metals tend to solubilize and are more reactive, therefore, it is preferable to discharge these effluents at alkaline pH.

Table 2: Effect of the synthesized titanium oxide nanoparticles on the physiochemical parameters of the effluent before and after treatment

Parameter	Concentration of untreated effluent	Concentration of treated effluent with synthesized TiO ₂	% Reduction	WHO Limit
pH	6.45± 0.01 ^a	6.71±0.03 ^a	4.03	6-9
Temperature (°C)	30.03±0.05 ^a	27.34±0.14 ^a	8.96	20-40
Dissolve Oxygen (DO) mg/l	216.67±5.77 ^a	106.89±7.78 ^b	50.67	4-5
Biological Oxygen Demand (BOD) mg/l	82±2.0 ^a	26.89±2.71 ^b	67.21	60
Total Dissolved Solid (TDS) mg/l	120.02±15.41 ^a	99.73±3.16 ^b	16.91	1500
Chemical Oxygen Demand (COD) mg/l	706.67±5.77 ^a	290±36.06 ^b	58.96	40

Electrical conductivity (EC) $\mu\text{S/cm}$	280.02 $\pm$ 0.1 ^a	197.45 $\pm$ 10.39 ^b	29.55	500
Turbidity (NTU)	48.83 $\pm$ 0.15 ^a	4.3 $\pm$ 0.89 ^b	91.19	5.82
Oil and Grease	272.33 $\pm$ 2.08 ^a	66.56 $\pm$ 40.56 ^b	75.56	-
Nitrate	26.93 $\pm$ 0.21 ^a	15.77 $\pm$ 5.01 ^b	41.44	45
Phosphate	5.07 $\pm$ 0.05 ^a	0.27 $\pm$ 0.20 ^b	94.67	5

* The result is presented as mean $\pm$ standard deviation, mean values of before and after treatment having different superscripts are significantly different at $p < 0.05$.

Temperature values of the effluent obtained from this study before and after treatment were within the range of the WHO acceptable limits of 20-40°C respectively [12].

Turbidity value measured in this study was higher than the WHO acceptable limits of 5 NTU. After treatment with synthesized titanium oxide nanoparticles, the turbidity of the industrial wastewater effluent was significantly reduced. The turbidity measurement recorded a value of 4.3 NTU, indicating a substantial decrease in the suspended particle content. This reduction corresponds to a percentage reduction of 91.19%

compared to the initial turbidity level, while after treatment with commercial TiO_2 the amount increased by 298.66 NTU. The remarkable decrease in turbidity can be attributed to adsorption and flocculation properties of TiO_2 NPs. The nanoparticles interact with suspended particles in the wastewater, promoting their aggregation and settling. The synthesized nanoparticles, combined with the natural properties of *Phyllanthus niruri*, enhance the effectiveness of the treatment process, resulting in the substantial reduction of turbidity.

Table 3: Effect of the commercial titanium oxide nanoparticles on the physiochemical parameters of the effluent before and after treatment

Parameters	Concentration of untreated effluent	Concentration of treated effluent with commercial TiO_2	% Reduction	WHO Limit
pH	6.45 $\pm$ 0.01 ^a	9.93 $\pm$ 0.07 ^a	53.95	6-9
Temperature (°C)	30.03 $\pm$ 0.05 ^a	28.04 $\pm$ 0.15 ^a	3.74	20-40
Dissolve Oxygen (DO) mg/l	216.67 $\pm$ 5.77 ^a	109.56 $\pm$ 3.65 ^b	49.43	4-5
Biological Oxygen Demand (BOD) mg/l	82 $\pm$ 2.0 ^a	36.55 $\pm$ 10.12 ^b	55.43	60
Total Dissolved Solid (TDS) mg/l	120.02 $\pm$ 15.41 ^a	116.66 $\pm$ 65.55 ^b	2.70	1500
Chemical Oxygen Demand (COD) mg/l	706.67 $\pm$ 5.77 ^a	384.22 $\pm$ 203.42 ^b	45.63	40
Electrical conductivity (EC) $\mu\text{S/cm}$	280.02 $\pm$ 0.1 ^a	231.92 $\pm$ 7.67 ^b	17.18	500

Turbidity (NTU)	48.83±0.15 ^a	298.66±217.88 ^b	511	5.82
Oil and Grease	272.33±2.08 ^a	179.89±46.41 ^b	33.94	-
Nitrate	26.93±0.21 ^a	16.66±1.52 ^a	38.14	45
Phosphate	5.07±0.05 ^a	1.08±0.80 ^b	78.60	5

* The result is presented as mean ± standard deviation, mean values of before and after treatment having different superscripts are significantly different at $p < 0.05$.

The result showed that the synthesized TiO_2 was more effective in the treatment of turbidity in effluent wastewater than the commercial TiO_2 nanoparticles.

According to Nwaichi and Wegwu (2010) [13], extremely high turbidity concentrations in wastewater effluent may portend serious environmental damage.

Electrical conductivity (EC) is the measure of water ability to conduct electric current is related to the amount of dissolved minerals in water, but it does not give an indication of which element is present; but higher value of EC is a good indicator of the presence of contaminants such as sodium, potassium and chloride [14]. Hence, results from this study indicate that the initial EC of the wastewater effluent was measured to be 280.02 $\mu\text{S}/\text{cm}$. After treatment with the synthesized titanium oxide nanoparticles, the concentration reduced from 280.02 to 197.45 $\mu\text{S}/\text{cm}$, this corresponds to a percentage reduction of 29.55 %, while that of the commercial TiO_2 NPs also decreased from 280.02 to 231.92 $\mu\text{S}/\text{cm}$, resulting in a percentage reduction of 17.18%. The treatment with synthesized TiO_2 NPs reduced the electrical conductivity of the wastewater effluent more effectively. Both treatment methods produced effluent concentrations below the WHO standard of 500

S/cm for wastewater electrical conductivity. The low level of conductivity observed in this present work is an indication that the wastewater contains very low level of inorganic ions [15].

The Total Dissolved Solids (TDS) values obtained from this study were acceptable in relation to the tolerable range of WHO acceptable limit of 1500 mg/l. The initial concentration was reduced by 16.91% and 2.70% after treatment with synthesized and commercial TiO_2 nanoparticles. Total dissolved solid in water is a measure of all dissolved substance in the water [16]. Water is said to be unpalatable and may begin to loss its commercial and domestic worth when TDS level exceeds 1500 mg/l. High concentration of TDS in water is said to be responsible for excessive scaling in water pipes, boilers, heaters and household appliances and can also result in dehydration of aquatic animals [17].

Oil and grease are highly viscous gelatinous lubricants that float on water due to their low density, the presence of high level of oil and grease in water bodies can be reduced productively in water [18]. The oil and grease value obtained from this study were higher than Federal Ministry of Environment (FME) and Department of Water Affairs (DWA) acceptable limits of 0.1mg/l and 2.5mg/l respectively (FEM,

2011; DWA, 2019). Although World Health Organization (WHO) do not have standard for oil and grease. There was statistically significant difference before and after treatment with both synthesized and commercial TiO₂ nanoparticles. High oil and grease concentration in effluent discharged into water bodies contribute to the death of aquatic animals. Oil and grease on the surface of water prevents the penetration of sunlight necessary for photosynthetic activities of aquatic flora and consequently reducing oxygen concentration in the water body [18].

Dissolve Oxygen (DO) is essential for the survival of aquatic life, and thus it serves as an important indicator of ecosystem condition. The dissolve oxygen levels measured in this study are 50.67 % and 49.43 % which above the WHO acceptable limit of 4-5 mg/l for effluent the discharge. After treatment with both synthesized and commercial titanium oxide nanoparticles, the concentration dropped by 50.67% and 49.43% respectively. There was a significant difference in the dissolved oxygen level in both the treated and untreated wastewater samples. However, treatment with the synthesized TiO₂ NPs resulted to a slightly higher percentage reduction compared to the commercial TiO₂ NPs which may be due to the reduction of some organic compounds by the nanoparticles. The dissolved oxygen levels in water are partly dependent on the chemical, physical and biochemical activities occurring in the water. Dissolved oxygen concentrations are directly dependent on oxygen

generation through photosynthesis and consumption by living organisms especially bacteria [15].

Since, biochemical Oxygen Demand (BOD) is the amount of oxygen utilized by microbial organisms to decompose organic compounds in water. From the result the value obtained for BOD was above the WHO acceptable limit of 60 mg/l for effluent discharge before treatment. However, after treatment with both the synthesized TiO₂ NPs and commercial TiO₂ there was a significant reduction in BOD level compared to the initial concentration of 82 mg/L. So, the synthesized TiO₂ NPs demonstrated a higher efficiency in BOD reduction, with the final concentration of 26.89 mg/L (67.21% reduction), compared to commercial TiO₂ NPs, which resulted to having a final concentration of 36.55 mg/L (55.43 % reduction). The significance differenced in the levels shown in the synthesized TiO₂ NPs can be attributed to the unique properties of the synthesized TiO₂ NPS, mediated with *Phyllanthus niruri*. These nanoparticles are likely to exhibit enhanced catalytic activity, leading to increased degradation of organic compounds responsible for BOD. The higher the BOD concentration, the more oxygen is depleted in a water bodies.

Chemical Oxygen Demand (COD) is the measure of oxygen equivalent of the organic content of the sample that is susceptible to oxidation by a strong chemical oxidant. It is an evaluation used to

measure the level of water contamination by organic matter [19].

From this study the initial concentration of COD before treatment greatly exceeded the WHO acceptable limit of 40 mg/l for effluent discharge. However, after treatment with synthesized TiO₂ NPs, the COD concentration in the wastewater effluent was reduced to 290 mg/L (58.96 % reduction), this indicates a significant improvement in the wastewater quality, bringing it closer to the WHO standard of 40 mg/L while the commercial TiO₂ NPs also demonstrated a considerable reduction in COD, but it was found to be less effective compared to the synthesized TiO₂ NPs, which resulted in a higher reduction of COD concentration. These findings indicate that the synthesized TiO₂ NPS holds significant promise as an effective method for reducing COD in wastewater effluent. As high BOD and COD imply that more oxygen is required which means lesser oxygen will be available to oxygen demanding species to utilize and thus signifies low water quality.

Nitrates are the end products of the aerobic decomposition of organic nitrogenous matter [20]. The nitrate concentration of the effluent before and after treatment was reported to be within the WHO and FME acceptable limits of 45 mg/l and 40 mg/l for effluent discharge. There was a statistically significant difference before and after treatment (Table 2).

Phosphate is an essential nutrient for plants [17]. From this study, the result shows the

concentration of the effluent before and after treatment met the WHO acceptable limit of 5 mg/l for effluent discharge. Therefore, biosynthesized TiO₂ NPs can serve as an effective bio-reductant and low-cost alternative for the treatment of industrial wastewater.

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