PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 28 (2) 551-564 February 2024

Remediation of Brewery Wastewater Using Green Synthesized Nano-Particles

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ABSTRACT: The brewing industry consumes a large amount of water needed for brewing, rinsing, and cooling purposes, and therefore produces huge amount of effluents. Therefore, the objective of this paper was to evaluate the use of *Moringa oleiferra* (MO) powder and synthesized 1.0 and 2.0 g TiO_2NPs as green synthesized nano-particles for the remediation of brewery wastewater using standard methods. The raw wastewater sample characterization for pH, BOD, COD, Lead and coliform count were: 7.26, 935, 1045, 0.083 mg/L and 136 cfu/100 mL respectively. Results of the UV – Visible spectrophotometer showed the maximum wavelength of 275, 275, 278 and 282.50 nm for 5:20, 10:20, 15:20, 20:20 of MO and TiO_2 ratio respectively, while the FTIR results show the presence of oxygen surface complex groups such as hydroxyl and carbonyl. The SEM reveals a porous surface area accompanied by several wide opening pores of different sizes and shapes, while EDX shows the concentration of titanium, Sulphur and silicon in percent weight; 85.79, 2.96 and 1.46 % respectively. Results of the wastewater treated with 50 g defatted *M. oleiferra* revealed the removal efficiency of 47, 93.2, 56.2, 18, 31.3, 97, 76.1, 81 and 71% for Turbidity, COD, EC, Nitrate, Nitrite, BOD, TS, TDS and TSS respectively. Results of wastewater treated with 1.0 g of TiO_2 NPs showed the removal efficiency of 97.8, 94.64, 53.5, 34.2 and 35.1% for COD, BOD, EC, Nitrate and Nitrite respectively. That of 2.0 g of TiO_2 NPs showed the removal efficiency of 67, 58, and 87% for Cu, Pb, and Ag respectively. Conclusively, *M. oleiferra* and varying proportions of green synthesized TiO_2 NPs were effective in the remediation of the wastewater from brewery industry as it improves its physicochemical properties, but not so much for the heavy metal concentration.

DOI: https://dx.doi.org/10.4314/jasem.v28i2.28

Cite this paper as: OWOLABI, S. O; FADIPE, O. O; ADELEKE, J. T; ADELEKE, A. E; ONIFADE, A. P; ISOLA, O. E; SANGOREMI, A. A; BAMISAYE, F. D. (2024). Remediation of Brewery Wastewater Using Green Synthesized Nanoparticles. *J. Appl. Sci. Environ. Manage.* 28 (2) 551-564

Dates: Received: 10 December 2023; Revised: 19 January 2024; Accepted: 17 February 2024 Published: 28 February 2024

Keywords: Wastewater, *Moringa oleiferra*, Nano-particles, Titanium dioxide.

One of the major industries producing beers and malt in Nigeria is the brewery industry (Adeleke *et al.,* 2018). The production involves blending and fermentation of yeast-based maize, malt and sorghum grits, requiring large amount of water as the primary raw material (Wang and Agunwamber, 2010). Usually, the brewing industry produces a large amount of wastewater from manufacturing units (effluent by-products and non-production units (washing and cooling). The brewing process takes in large amount of water and up to 70% being discharged as wastewater (Valta *et al.,* 2014). Wastewater or sewage originates from domestic

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wastewaters, industrial wastes, animal wastes, rain runoff and groundwater infiltration (Samer, 2015). Generally, wastewater is the flow of used water from a neighborhood and it consists of 99.9% water by weight, where the remaining 0.1% is suspended or dissolved material (Gray, 2005). This solid material is a mixture of excrements, detergents, food leftovers, grease, oils, salts, plastics, heavy metals, sands and grits (Lin, 2007). The various types of wastewater include municipal wastewater, industrial wastewaters, mixtures of industrial/domestic wastewaters and agricultural wastewaters. Furthermore, typical agricultural industries include dairy processing industries, meat processing factories, juice and beverage industries, slaughterhouses, vegetable processing facilities, rendering plants and drainage water of irrigation systems (Russell, 2006). Consequent upon the primary treatment of wastewater, the wastewater still requires physical treatment because it still contains large amounts of dissolved and colloidal materials that must be removed before discharge (Samer *et al.,* 2014)..The type of industrial wastewater pollutants depend on the type of plant which produces those pollutants (WHO, 2018). Some Industrial wastewaters which contain toxic and corrosive gases and compounds can have devastating effects on sewage networks and biological treatment process, therefore pre-treatment process is necessary before discharging them to the municipal wastewater network. Brewery industries produce million liters of various types of beers each year such that the global beer production in 2011 was approximately 103 million liters (L) and this consumed about 50.9 billion gallons of water, which also corresponded to an average consumption of 23 L per person per year (Holdings, 2012; Fillaudeau *et al.,* 2006). Brewery wastewater is an agro-industrial waste generated in large quantities, whose treatment can be combined with energy production in the form of biogas rich in methane (CH_4) or hydrogen (H_2) (Mabel *et al.,* 2017).

Brewery industry is one of the largest users of water and characterized by high levels of organic pollutants, and requires higher attention for remediation before discharge to the environment (Werkneh *et al.,* 2019). Sugars, soluble starch, ethanol and total suspended solids that primarily come from the processing unit, are the main constituents of this form of waste water, according to Simate *et al.* (2011). It is estimated that, depending on the production technique and specific water use, 3 to 10 liters of waste effluent is produced in the production of 1 liters of beer. The brewing industry has therefore shown growing understanding of environmental conservation and the need for sustainable production processes for some time now (Driessen and Vereijken, 2003). Traditionally, the quantity of water needed to brew beer is several times the volume actually brewed. This large volume of water also adds to the amount of wastewater that is discharged from the industry after the manufacture of beer (Simate *et al.,* 2011). Consequently, the biggest challenge for developing countries is how to upgrade the industrial processes in the treatment of wastewater, which at times are based on outdated technology, within financial, institutional and legal constraints which leads to inadequate wastewater treatments and disposal (Hajira *et al.,* 2012). Studies have shown that when untreated wastewater is released into the environment, the environment becomes seriously polluted (Ahmed *et al.,* 2013; Anjum *et al.,* 2016). This can lead to the generation of foul odor and the storage pond, formed can become a breeding ground for disease vectors. A preliminary investigation of the study showed that the wastewater generated from the International Breweries Ilesha is usually retained in ponds. A reconnaissance survey and oral interview with residents around the study area revealed that the wastewater generated from this brewery is causing air pollution and creating unpleasant atmosphere especially in the evenings. So many methods have been used to treat brewery wastewater; however, treatment using green synthesized nano-particles has not been reported. Hence, the objective of this paper was to evaluate the use of *Moringa oleiferra* (MO) powder and synthesized 1.0 and 2.0 g TiO_2NPs as green synthesized nano-particles for the remediation of brewery wastewater using standard methods

MATERIALS AND METHODS

Study Location: The study location was International Breweries Plc South Western, Nigeria with coordinates: 7.625882^{o}N, 4.784449^{o}E. This location was chosen because the brewery is the biggest in Southwestern Nigeria and the production capacity of the plant is large enough to create an environmental nuisance.

Collection of Brewery Wastewater: Wastewater sample was collected in pre washed and pre sterilized 25 liters container. It was transported with ice- cubes support to the chemistry laboratory of Redeemer University Ede, where it was refrigerated to preserve the wastewater prior to analysis.

Preparation of *Moringa Oleiferra: M. oleiferra* pods were harvested from a plantation in Osogbo Local Government Area of Osun state. The harvested pods (Plate1) were sun-dried for 5days until a stable weight was obtained. The seeds were removed from the pod; air dried for 24 hours, ground into powder and kept in an air-tight container.

Plates 1: *Moringa oleiferra* Pods

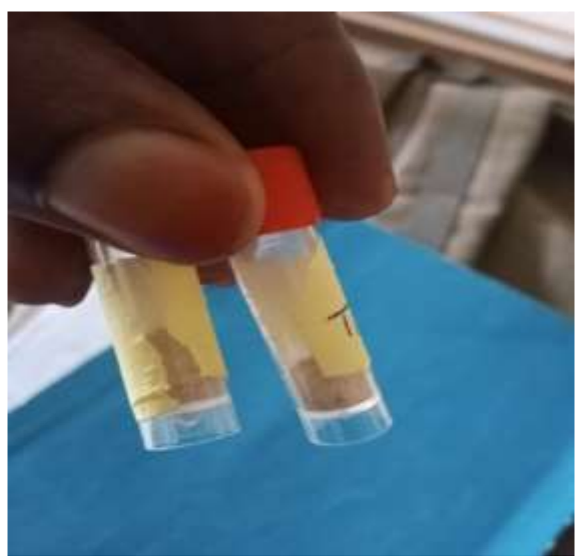
Defatting of moringa oleiferra powder: 250 mL of N-Hexane was poured into a flat bottom flask. A measured quantity of the blended moringa powder was poured into a white thimble and covered with a cotton wool to block any air opening. The white thimble was then placed in a siphon and a condenser was connected on the top. The flat bottom flask containing the N-Hexane was placed inside a heating mantle with a temperature probe beside it for temperature checks. The condenser was 4then placed on the set-up (flat bottom flask inside heating mantle and the white thimble on a siphon). The complete set-up (Plate 3) (flat bottom flask inside heating mantle and white thimble on condenser) was clamped with a retort stand for stability. The heating mantle was switched on and the temperature was set at 45-60 ^{0}C. The heating mantle and the water from the inlet of the condenser produced a Soxhlet extraction and the fat extracted was dropped into the flat bottom flask.

Plates 2: Complete set up of Soxhlet Extractor

Preparation of moringa oleiferra extract: 50g of defatted *moringa oleiferra* was weighed into a 500g beaker. 100 mL distilled water was added and steam bathed at 90^{0}C for 20minutes. This was cooled and filtered.

Plates 3: Stirring of the green synthesized titanium dioxide nano-particle

Preparation of synthesized titanium –dioxide: 10mL of moringa extract was measured into a beaker and Stirred for 15minutes before adding absolute ethanol and stirred for another 30minutes. 1 mL titanium (iv) butoxide (Plate 3) was added and agitated for 30minutes. The pH of the green synthesized nanoparticles was adjusted to7 by adding droplets of NaOH. This was then oven-dried for 1 hour, cooled and stored in a bottle as shown in pplate 3.



Plates 4: synthesized titanium –oxide

Analyses of the Raw Wastewater: The physicochemical and microbiological analyses were conducted on raw wastewater samples. The physicochemical parameters were pH, conductivity, temperature, odour, turbidity, dissolved oxygen, chemical oxygen demand, nitrate, nitrite, biochemical oxygen demand, total solids, total dissolved solids and total suspended solids. Heavy metals analyzed were copper, lead, silver, and titanium. The wastewater sample was also analyzed for total coliform.

Characterization of the Green Synthesized TiO_2 Nano-Particles: The green synthesized titanium dioxide nano-particles were also characterized using UV-Vis spectra analyses, Fourier transform infrared spectrometer, and Scanning Electron Microscope (SEM) and Energy dispersive X-ray (EDX) .spectrometer.

Chemical Parameters: The procedures for determination of all the chemical parameters are according to APHA, 1 998.

Determination of nitrate: 25 g phenol was dissolved in 150 mL concentrated H_2SO_4. 5 mLof fuming H_2SO_4 was added to this solution and stirred. The resulting solution was heated for 2 hours on water bath. The solution was allowed to cool before use. 100 mL wastewater sample was treated with 100 mL Ag_2SO_4 solution in order to remove interference by chloride. The silver sulphate solution was prepared by dissolving 4.4 g $AgSO_4$ in 1L distilled water. Nitrate stock solution was prepared by using 100 mg/L of nitrogen; this was done by dissolving 0.722 g anhydrous KNO_3 in 1L distilled water. This sample was neutralized to pH 7 with dilute NaOH and filtered. The wastewater sample was transferred to a beaker and evaporated to dryness. The residue was mixed with 2.0mL phenol disulfonic acid reagent using a glass rod to dissolve the solids. The resulting mixture was diluted with 20 mL distilled water and 6 mL concentrated ammonia was added until maximum colour of deep yellow was developed. The clear solution was transferred into a 50 mL volumetric flask and diluted to mark with distilled water.

Blank sample was prepared by measuring 100 mL of distilled water and following the procedures above. The working standards (0, 0.05, 1, 2, 4, 6, 10 mg/L NO_3^-) solutions were prepared by dilution of the stock and treated with appropriate reagents as for sample and used to prepare calibration graph for nitrate (R^2 = 0.987). Sample solution prepared above was measured at 410 nm wavelength and blank was read at the same wavelength with Spectrophotometer. Blank reading was subtracted from sample reading and result read from the graph. NO_3^- in the sample was recorded in mg/L.

Wastewater Treatment: 50 g of defatted moringa oleiferra powder, 1 g and 2 g of nano-particles were added to 100 mL of wastewater. The solutions were placed in the UV chamber for 50 minutes so as to have a photo catalytic reaction to activate the nanoparticles. The mixture was then stirred in UV chamber with rapid mix of (880 – 900) rpm for 10 minutes and slow mix of (140-150rpm) chemical and bacteriological analysis were repeated as previously conducted above. rpm for 40 minutes before allowing it to settle for 1 hour. The wastewater was then filtered and centrifuged to remove the suspended particles. The filtrate was removed and physicochemical properties were determined.

Determination of total dissolved solids: A portable TDS meter was dipped into a plastic container containing the wastewater water and the value read immediately. Replicate determinations were made to estimate precision.

Determination of biological oxygen demand (BOD_5): The wastewater sample was incubated for 5 days in the dark, using the bottle incubation method. The reduction in dissolved oxygen concentration during the incubation period yielded a measure of the biological oxygen demand.

$$BOD = D1 - D5 \qquad (1)$$

Where; D_1 = initial DO of the wastewater sample; D_5 = final DO of the sample after 5 days incubation (APHA, 1998).

Determination of chemical oxygen demand (COD): 10 mL of the wastewater samples was pipetted into a conical flask.5 mL of potassium dichromate ($K_2Cr_2O_7$) and 15 mL of concentrated H_2SO_4 were added and diluted with 40 mL of distilled water. Then 7 drops of phenanthroline ferrous sulphate indicator was added. This results into an effervescent that made the flask hot. The mixture was therefore left to cool, during which the mixture changed to light blue green colour. The procedure was repeated for the blank. The COD (mg/L) was calculated as in equation 2.

$$COD(mgO_2 / L) = \frac{(A-B)xmx8000}{V_s} \qquad (2)$$

Where; A = ml of ferrous ammonium sulphate (FAS) used for blank; B = ml of FAS used for sample; M =

molarity of FAS; V_s = volume of sample used (ml); 8000 = milliequivalent weight of oxygen x 1000 ml/L

Determination of dissolved oxygen: This was observed using the Winkler's titration. 20 mL of waste water sample was pipetted into a conical flask. 1 mL of potassium fluoride was added into it as well as 2 mL of manganous sulphate. 2 mL of alkaline iodide acid and concentrated H_2S0_4 were added to the mixture. Titration was done with sodium thiosulphate (NaS_20_3) until a clear solution was obtained. Then 5 mL of freshly prepared indicator was added. It was observed that the colour changed to blue-black. Titration was then repeated with the sodium thiosulphate to get a colourless solution. DO (mg/l) was calculated as in equation 3.

$$DO(mg / L) = \frac{8x100xN}{Vxv} \quad \text{……... (3)}$$

Where; V = volume of sample taken (ml); v = volume of used titrant (ml); N = Normality of titrant; 8 = constant, since 1 ml of0.025 N sodium thiosulphate solution is equivalent to 0.2 mg oxygen

Heavy metals analysis: 5 mL of concentrated nitric acid was added to 250 mL water sample in a beaker, and stirred. This was heated on a hot plate till the volume was reduced to about 20 mL. This was diluted to 50 mL with deionized water and transferred to a labeled sample bottle. Stock solutions were prepared by dissolving specific amount of salts in 1L flask and made up to 1000 mL. Serial dilution was then made from the stock ready for instrumental analysis. The final concentration was then determined in ppm using Atomic Adsorption Spectrophotometer (AAS).

Biological Analysis: The microbiological analysis was performed using most probable number (MPN) of counting coliform. 9 mL of distilled water was added to 6 different test tubes. 3.8 g of Eosine Methylene Blue (EMB) agar was measured into 100 mL distilled water. Both test tubes and EMB solution were placed into autoclave for sterilization for 45 minutes. After the cultured sample was sterilized, 1mL of properly mixed wastewater sample was added to the first test tube with 9 mL of sterilized distilled water to make 10^{-1} dilution and then shaken properly. Exertly 1 mL from properly mixed 10^{-1} dilution was taken and added to the second test tube (10^{-2} dilution). The same process was repeated for the remaining test tubes, taking 1 mL from the previous test tube and added it to the next 9 mL diluents. The final dilution for the bacterial/ cells was then taken to be 10^{-6} dilution. 1 mL of sample was taken from each of the test tubes and poured into plates mixed with EMB Agar and cover, afterward kept inside incubator for 72 hours and finally counted the E. coli using colony counter.

RESULTS AND DISCUSSION

The UV-vis spectra analysis: The UV- Vis spectra shows that the absorbance peak of the *Moringa oleiferra* mediated with TiO_2NPs were all within UV (200 to 400) wavelength band. The peak increases with increase in concentration of the moringa extract in the NPs. This implies that the photo-catalytic ability of the green synthesized TiO_2NPs is very high and hence it could be used as a photo-catalyst for wastewater remediation. The UV-Vis spectra measurement was obtained for raw Titanium dioxide (TiO_2), raw moringa extract, and four various concentrations (5:20 for A, 10:20for B, 15:20 for C and 20:20 for Do for moringa extract to TiO_2 respectively. The results are presented in Figures 1 - 4. Figure 1 showed wavelength at which there was maximum absorbance (275nm), Figure 2 showed wavelength at which there was maximum absorbance (275nm), Figure 3 showed wavelength at which there was maximum absorbance (278nm) and Figure 4 showed wavelength at which there was maximum absorbance (282.50nm). All these values fall within the range of 275- 285 nm for anatase structure, while 285- 320 nm was the range for rutile structure in titanium dioxide nanoparticles (Lewis, 2007).

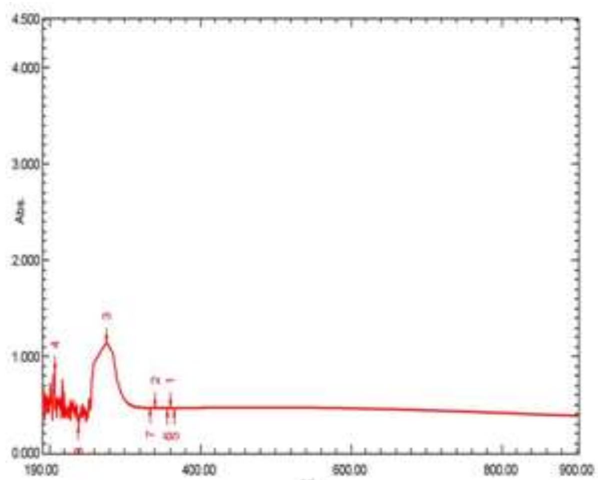


Fig 1: The UV-vis spectra of Moringa Extract Combined with TiO_2 (05:20)

Energy Dispersive X- ray spectroscopy (EDX) Analysis: Analysis spectral of the green synthesized TiO_2 NPs were shown in Table 1 and Figure 10 respectively. Table 1 revealed the chemical composition (qualitative and Quantitave) and graphical representation of the green synthesized TiO_2 NPs. The elemental composition of the TiO_2 NPs showed very high atomic prominence of titanium and a few other elements such as sulphur, silicon, potassium, silver, aluminum, niobium, phosphorus, chlorine, yttrium, vanadium, calcium, magnesium, sodium, iron and copper.

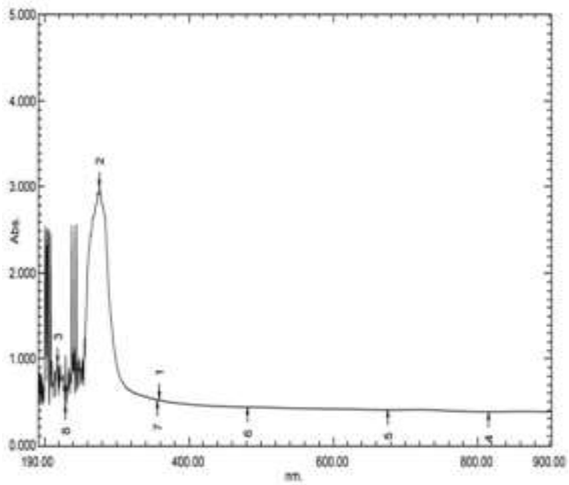


Fig 2: The UV-vis spectra of Moringa Extract Combined with TiO_2 (10:20)

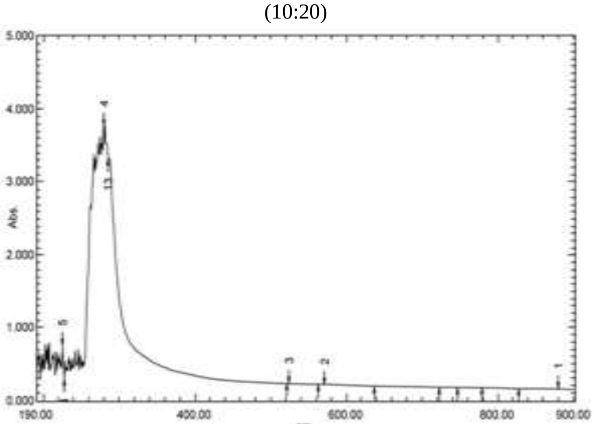


Fig 3: The UV-vis spectra of Moringa Extract Combined with TiO_2 (15:20)

Fourier transform infrared spectroscopy (FTIR): The results of the FTIR were presented in Figures (5 - 8). The various peaks observed represented the main absorption bands. These were due to O-H and C-C bending of the hydroxyl and carbonyl group at range of 1400.00 – 1500 cm^{-1} and 1500 0 -1700 cm^{-1} respectively (Coates, 2000; Ezema and Nwankwo, 2010; Onawumi *et al*., 2021) and O-H out of plane bending of the hydroxyl group at range of 500 - 700 cm^{-1} (Coates, 2000) O-H stretching of hydroxyl group at 3311.39 cm^{-1} (Nakamoto, 1997); Ti-O stretching of TiO_2 at 400.00cm^{-1} and 518.87cm^{-1} (Coates, 2000; Ezema and Nwankwo, 2010). The presence of OH, C=O, C=C, C-H, C-H, Ti-O-Ti, vibrations are indicative of polyphenol and terpenoid responsible for reduction and capping of TiO_2 NPs. This enhanced the removal of toxic pollutants from wastewater.

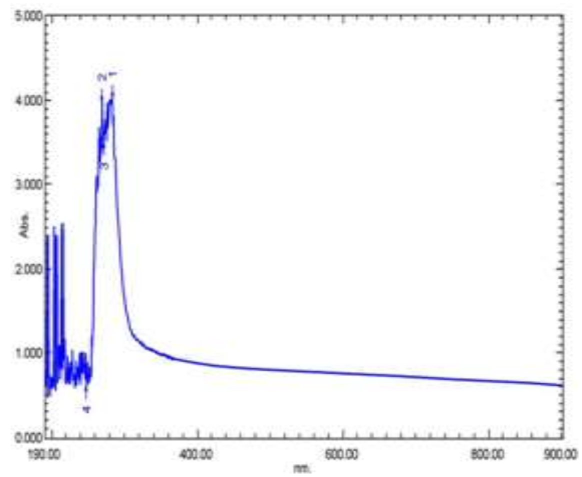


Fig 4: The UV-vis spectra of Moringa Extract Combined with TiO_2 (20:20)

Scanning electron microscope analysis: Morphological analysis of TiO_2 NPs was shown in Figure 9. It showed that TiO_2 NPs was highly porous crystalline nanoparticles with average particle size of 8.3*10^4 nm. The porosity and the crystalline nature of the green synthesized NPs made it suitable for the remediation of the industrial effluents. The SEM micrograph also revealed that the green synthesized TiO_2 have hexagonal shaped nanorods with granula10 nm – 25 nm nano-sized

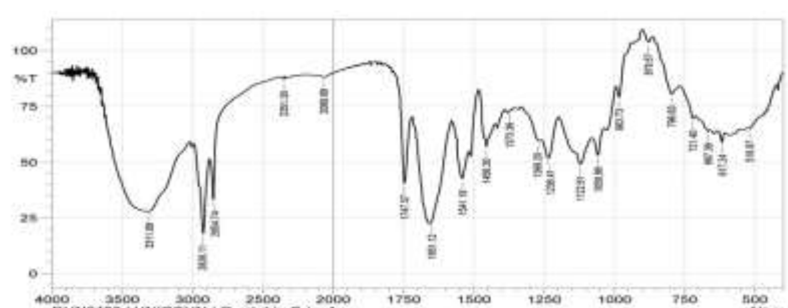


Fig 5: Fourier Transform Infrared Spectroscopy (FTIR) of Moringa combined with Titanium dioxide (5:20)

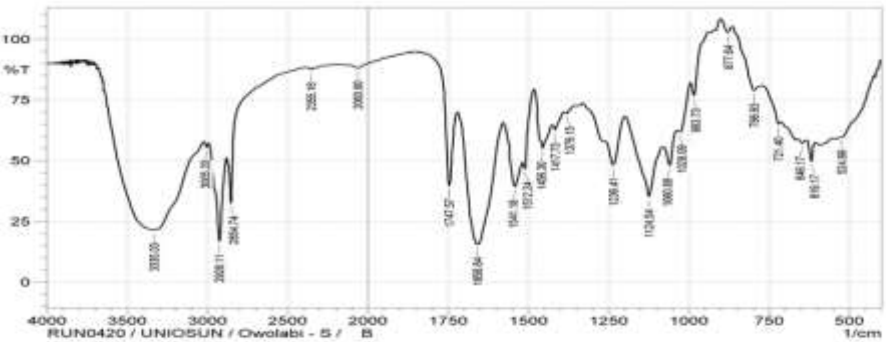


Fig 6: Fourier Transform Infrared Spectroscopy (FTIR) of Moringa combined with Titanium dioxide (10:20)

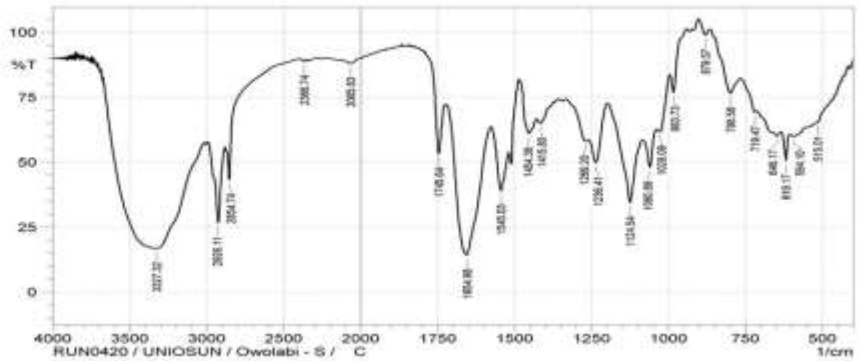


Fig 7: Fourier Transform Infrared Spectroscopy (FTIR) of Moringa combined with Titanium dioxide (15:20)

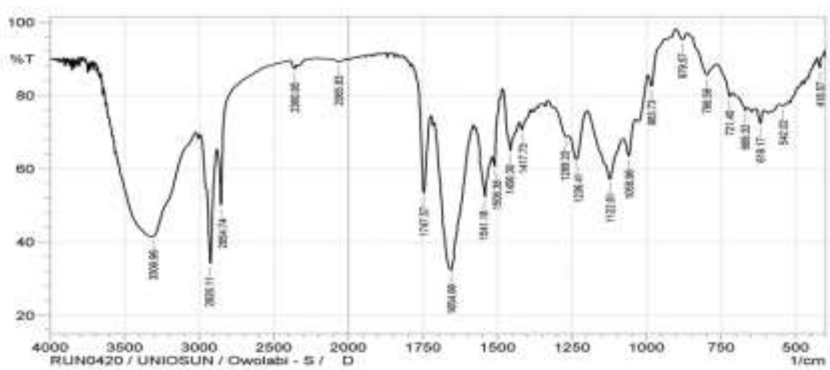


Fig 8: Fourier Transform Infrared Spectroscopy (FTIR) of Moringa combined with Titanium dioxide (20:20)

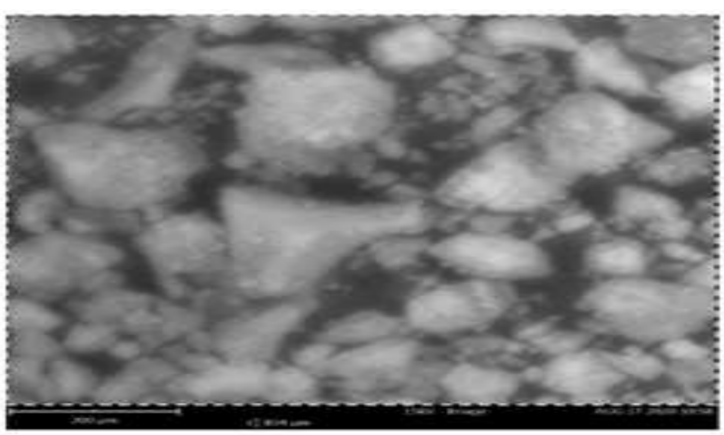


Fig 9: Scanning Electron Microscope (SEM, ZEISS-EVO 18 Research) for Green Synthesized TiO_2

Table 1: Elemental composition of green synthesized TiO_2 NPs

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Ti	Titanium	82.43	85.78
S	Sulfur	4.25	2.96
Si	Silicon	2.39	1.46
K	Potassium	1.71	1.46
Ag	Silver	0.61	1.43
Al	Aluminum	2.10	1.23
Nb	Niobium	0.50	1.01
P	Phosphorus	1.43	0.96
Cl	Chlorine	0.92	0.71
Y	Yttrium	0.36	0.70
V	Vanadium	0.58	0.64
Ca	Calcium	0.70	0.61
Mg	Magnesium	1.13	0.60
Na	Sodium	0.89	0.44
Fe	Iron	0.00	0.00
Cu	Copper	0.00	0.00

FOV: 834 µm, Mode: 15kV - Image, Detector: BSD Full, Time: AUG 17 2020 10:58

Treatment with 50 g Moringa oleiferra: When 50 g of the *M. oleiferra* was added to 100 mL of the wastewater, the percentage reduction of the physicochemical parameters were in the order of 47%, 93.2%, 56.2%, 18%, 31.3%, 97%, 76.1%, 81%, and 71% for turbidity, COD, EC, Nitrate, Nitrite, BOD, TS, TDS, and TSS respectively. This reduction in physicochemical characteristics of the wastewater was in agreement with the report of Mangale *et al.* (2012).

This implied that *M. oleiferra* was very effective in the removal of organic pollution and muddy or unclear state of wastewater from brewery industries. However, there was an increase in acidity level of the wastewater (pH 7.26 to 5.44). This was in agreement with the findings of Mustapha *et al.* (2019) where the analyzed pH values of wastewater obtained from a tannery in Niger State was 5.94. This acidity level reported in this study implied that if this water is released into the environment untreated, aquatic organisms such as fishes and zooplanktons are at risk of death.

There was a slight increase in the concentrations of all heavy metals in the wastewater. This may be attributed to the presence of heavy metals constituents in *M. oleiferra* plant thus, suggesting that the *M. oleiferra* might not be useful in the removal of heavy metals in wastewater or industrial effluent.

Also, there was a reduction in the amount of dissolved oxygen from 4.8 mg/L to 2.03 mg/L in wastewater and this might be responsible for the objectionable taste recorded in the water sample.

Treatment of raw brewery wastewater with 1.0gTiO_2NPs: When 1.0 g TiO_2NPs was added to the 100 mL of the raw brewery wastewater, the treatment reduced the turbidity slightly from 47% to 46% (Figure 11). The dissolved oxygen in the water increased to 29.5mg/L (Figure 19). The increased in dissolved oxygen was due to aeration of the wastewater for complete mixing of the TiO_2NPs. The study revealed that the heavy metals concentrations were also reduced by the addition of 1.0g TiO_2NPs as effective adsorbent. This finding was similar to the report of (Adesoji and Jayeoba, 2015) where the values of heavy metals inherent in the wastewater obtained from a pharmaceutical industry showed drastic reduction of heavy metals and higher values of dissolved oxygen.

The COD BOD_5, electrical conductivity, nitrate and nitrite were reduced by 97.8%, 94.64%, 53.5%, 34.2% and 35.1% (Figures 12 – 14.) respectively. Furthermore, 1.0gTiO_2NPs caused the TS, TDS and TSS of 100mL of the brewery wastewater to reduce by 94.5%, 93.3% and 95.9% respectively (Figures 15 – 17). The addition of the 1.0 gTiO_2NPs into wastewater affected the pH of the wastewater. The pH value dropped from 7.26 to 6.94 (Figure 18). These results showed that the addition of 1.0g TiO_2NPs has significant remediation effect on the physical and chemical properties of brewery wastewater.

Treatment of raw brewery wastewater with 2.0g TiO_2NPs: When the raw wastewater was treated with 2.0g TiO_2NPs in 100mL, the amount of the physicochemical parameters decreased further indicating that the green synthesized titanium dioxide nano-particles had great effect on the brewery effluent (Figure 11-24). More so, the concentration of titanium increased reasonably. The results obtained showed that the concentrations of Ti, Cu, Ag and Pb reduced by 40.1%, 33.3%, 40% and 21.7% respectively (Figures 20-23). This agreed with the report of Chen *et al.* (2016) on the treatment of brewery wastewater using ordinary nano-particles. The turbidity of the brewery wastewater was reduced by 49%. Similarly, the COD, BOD_5, electrical conductivity, nitrate and nitrites reduced by 96%, 98%, 61%, 35.5%, and 43.3 %. This was in agreement with Simate *et al.* (2011). (Figure 12 – 14). The acidity of the raw brewery wastewater was slightly increased from pH of 7.26 to 6.00 and dissolved oxygen reduced by 11.5%. The biological characteristic of the wastewater (total coliform) was reduced to 12 cfu/100 mL (Figure 24). These results showed that the addition of 2.0g TiO_2NPs has significant effect on the physical, chemical and biological properties of brewery wastewater.

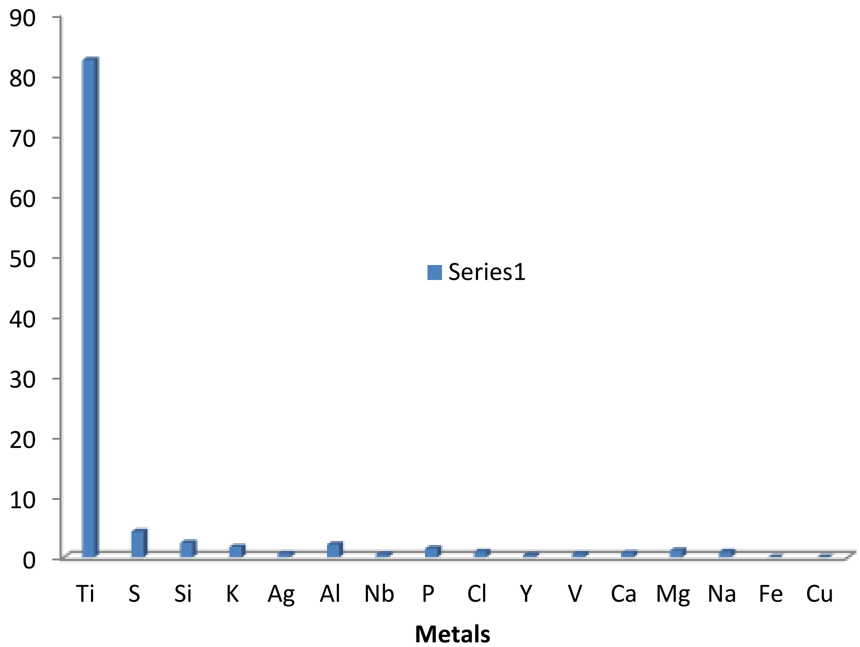


Fig 10: The energy dispersive spectroscopy spectrum of green synthesized titanium dioxide nanoparticles TiO_2 NPs.

Table 2: Quality Parameters of the Untreated and Treated Brewery Waste Water

S/N	*PARAMETERS*	*Untreated Brewery Wastewater*	*50g moringa/ 100ml BWW*	*1.0g TiO_2 NPs/100 ml BWW*	*2g TiO NPs/ 100ml BWW*	*FEPA STANDARD*	*NAFDAC*	*IESIPIE STANDARD*
				Physicochemical Properties				
1	pH value	7.26 602	5.44	6.94	6.00	6 – 9	6.5- 8.5	5.5 – 9
2	Cond.		263.5	280	233.5		1000us/cm	200-3000
3	Odour	OBJ	UOBJ	UOBJ	OBJ	UOBJ	UOBJ	UOBJ
4	Temp (^{0} C)	27.1	27.3	25.1	24.7	Less than 40^{0}C	Ambient	40
5	Turbidity	208	110.7	112.4	106	20 – 3000	Not turbid	200
6	DO	4.8	2.03	29.5	4.25			
7	COD	1045	71.3	56	43.7	80		120-400
8	Nitrate	15.2	12.5	10	9.81	20	10	
9	Nitrite	13.4	9.2	8.7	7.6		0.1	
10	BOD_5	935	30.9	20.2	18.2	50		20-60
11	TS	530	126.3	29	25.8			
12	TDS	284	54	19	17.8	2000	500	3000- 5000
13	K	6.660	4.98	3.99	3.99		3.99	
14	TSS	246	72.3	10	8	30	50-150	50-150

OBJ = Objectionable; UOBJ = Unobjectionable; COD = Chemical oxygen demand; DO = Dissolved oxygen; Temp = Temperature; Cond. = Conductivity

Table 2: Quality Parameters of the Untreated and Treated Brewery Waste Water (Cont'd)

S/N	*Parameters*	*Untreated Brewery Wastewater*	*50g moringa/ 100ml BWW*	*1.0g TiO_2 NPs/100ml BWW*	*2g TiO NPs/ 100ml BWW*	*FEPA STANDARD*	*NAFDAC*	*IESIPIE STANDARD*
				Heavy metal properties(mg/L)				
15	Cu	0.012	0.032	0.008	0.008	Less than 1	1	2
16	Ag	0.015	0.023	0.009	0.009	0.1		
17	Ti	0.005	0.014	0.053	0.052			
18	Pb	0.083	0.122	0.094	0.065	0.05	0.01	0.2
Biological Properties (cfu)								
19	Coliform Count	136		12	12			

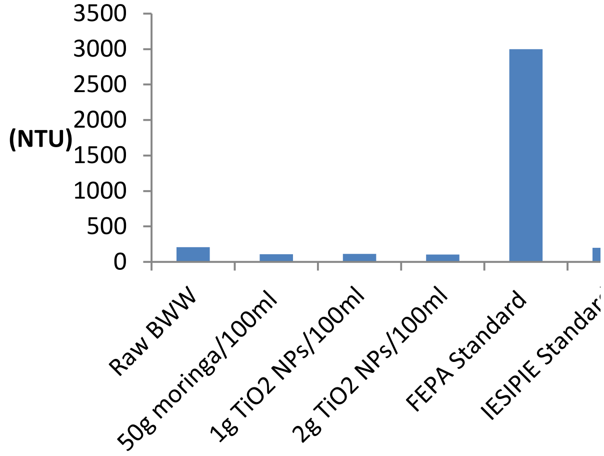


Fig 11: Turbidity concentrations of raw and treated wastewater compared with standards

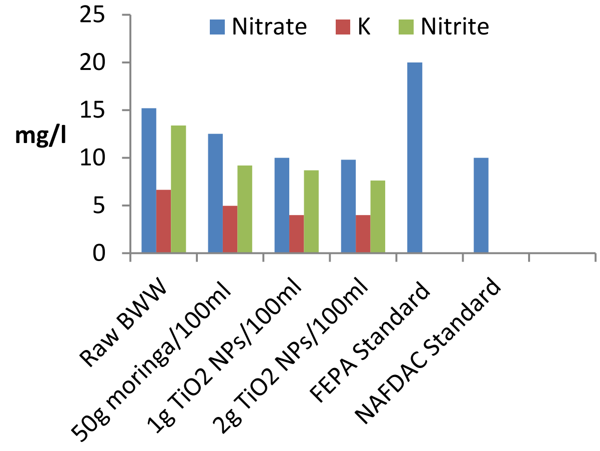


Fig 14: Nitrate, Potassium and Nitrite concentrations of raw and treated wastewater compared with standards

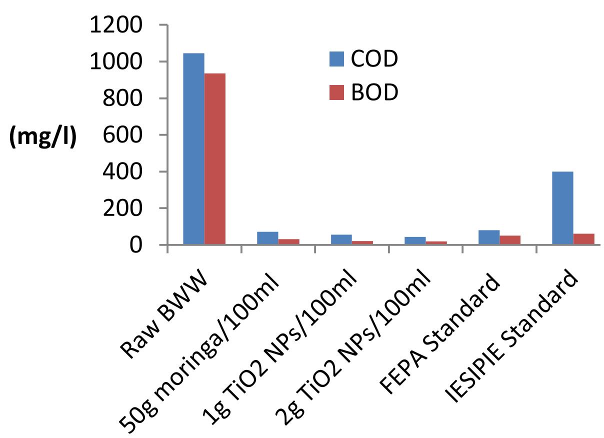


Fig 12: COD and BOD_5 concentrations of raw and treated wastewater compared with standards

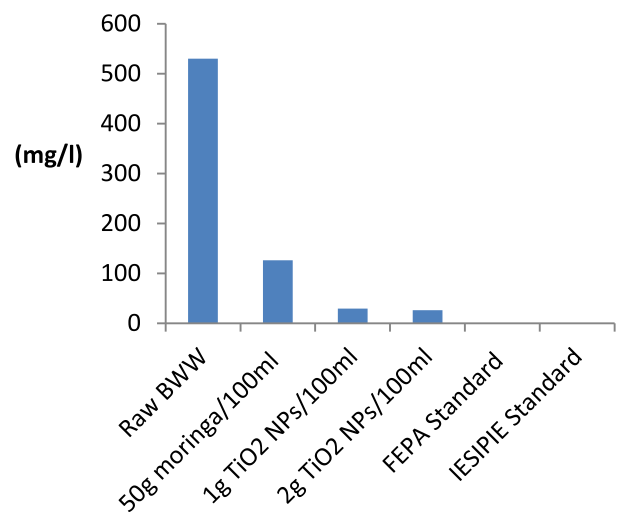


Fig 15: Total Solids concentrations of raw and treated wastewater compared with standards

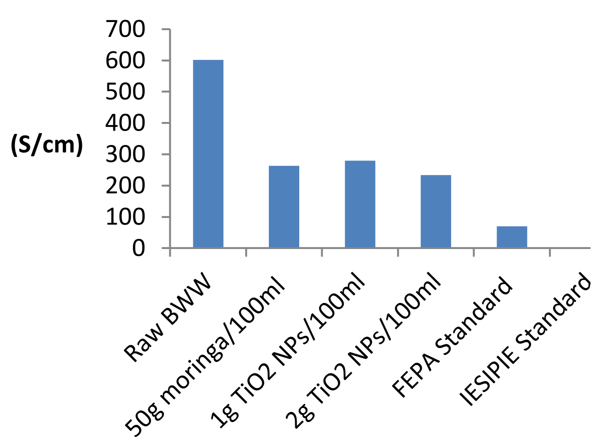


Fig 13: Electrical Conductivity concentrations of raw and treated wastewater compared with standards

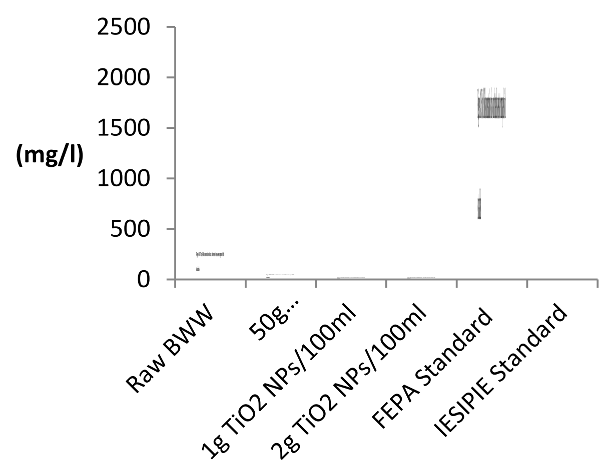


Fig 16: Total Dissolved concentrations of raw and treated wastewater compared with standards

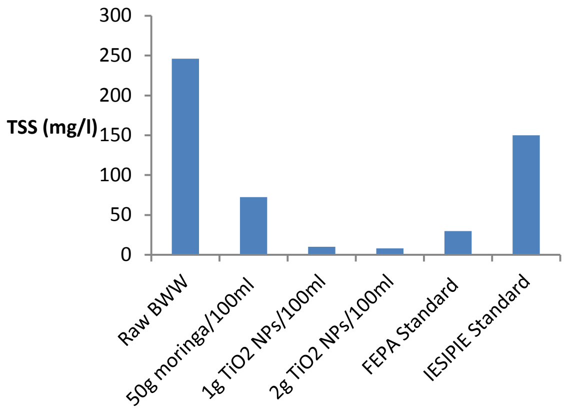


Fig 17: Total Suspended Solids concentrations of raw and treated wastewater compared with standards

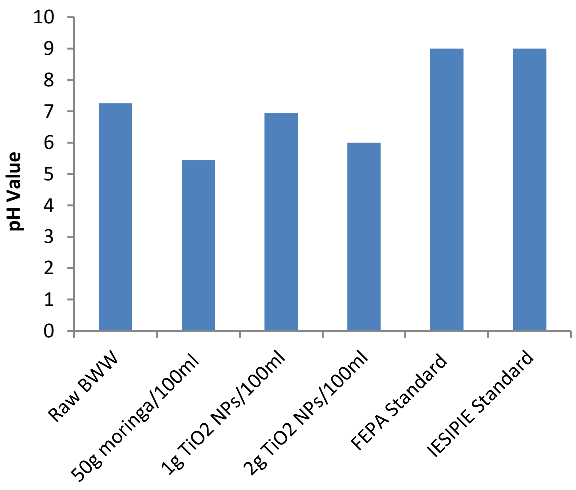


Fig. 18: pH values of the raw and treated wastewater compared with standards

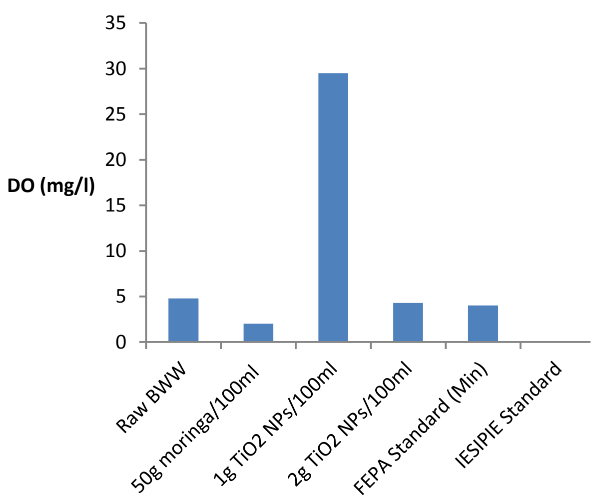


Fig 19: Dissolved Oxygen concentrations of raw and treated wastewater compared with standard

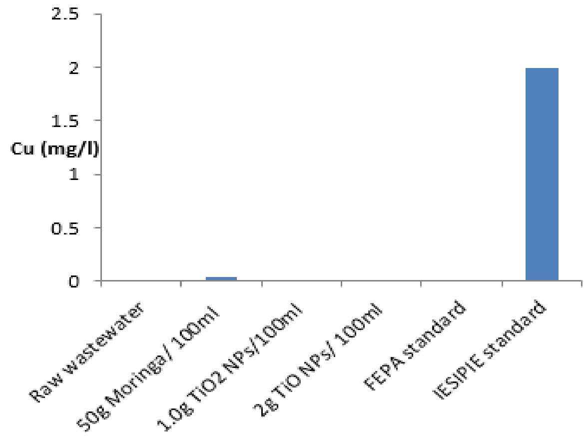


Fig 20: Copper concentrations of raw and treated wastewater compared with standards

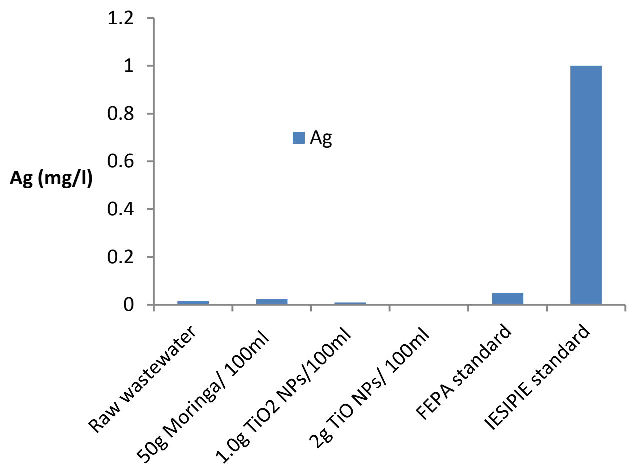


Fig 21: Silver concentrations of raw and treated wastewater compared with standards

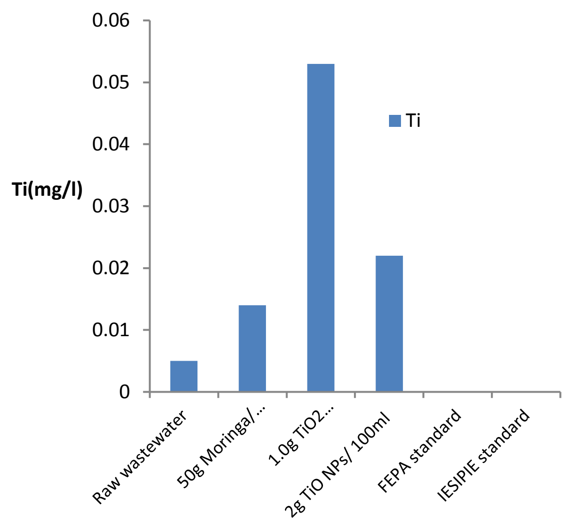


Fig 22: Titanium concentrations of raw and treated wastewater compared with standards

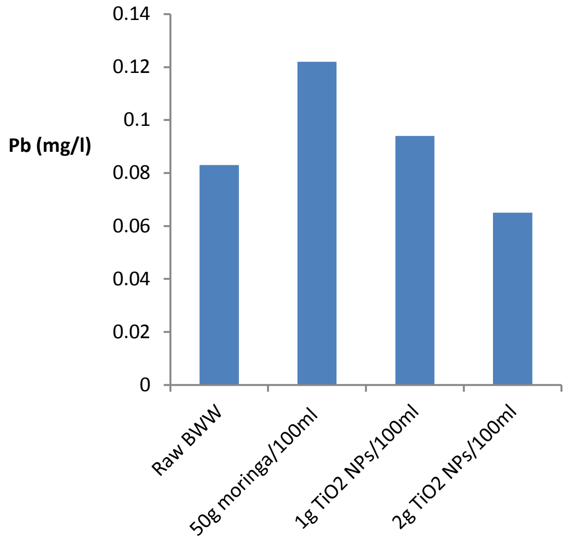


Fig 23: Lead concentrations of raw and treated wastewater compared with standards

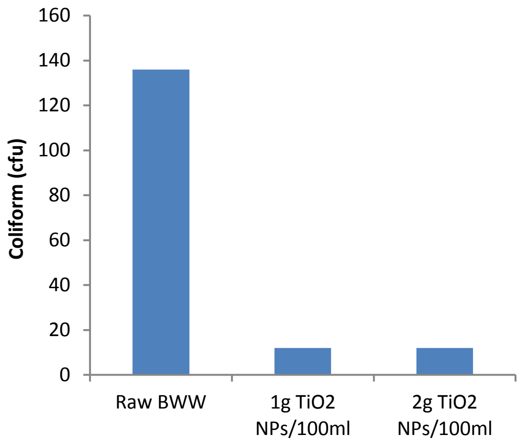


Fig 24: Total coliform of raw and treated wastewater compared with standards

Conclusions: The characteristics of the raw brewery wastewater obtained from a Brewery industry in South Western part of Nigeria showed that the raw wastewater was polluted since the physicochemical and biological parameters analysed were all above FEPA and IESIPIE standards. Treatment of the wastewater using the green synthesized nano-particles (TiO_2NPs) showed a considerable reduction in physicochemical and biological parameters. FTIR results show the functional groups Ti-O, C-C, C-H, O-H present in the nanoparticles were responsible for the removal of pollutants in the wastewater. SEM results confirm that the nano particles were highly crystalline with active sites to adsorb pollutants. Overall, the synthesized nano-particles were efficient in the removal of toxic pollutants in brewery wastewater, thus safeguarding the health of man and restoring the environment from further pollution.

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