Nigerian Research Journal of Chemical Sciences (ISSN: 2682-6054)
Volume 13, Issue 2, 2025

Physicochemical Analysis of Industrial Effluents Discharged into Water Bodies in Ibadan, Nigeria

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Accepted: August 11, 2025. Published Online: August 18, 2025

ABSTRACT

This study assessed the pollution levels of industrial wastewater from abattoir as well as dairy and detergent industries in Ibadan, Nigeria. Silver nanoparticles (AgNPs) were synthesised using palm kernel shells extract. The AgNPs were used for remediation of the wastewater samples. Wastewater and the receiving river samples were collected *via* grab sampling and analysed for physicochemical parameters using standard procedures. Results revealed that different colours observed in the wastewater samples before treatment changed to colourless after treatment with AgNPs for most of the wastewater samples. Odour equally changed from unpleasant and offensive before the treatment to pleasant after treatment with AgNPs. Conductivity of the water samples before treatment ranged between 252 and 3268 µmhos^{-1} cm but reduced to 109 and 1490 µmhos^{-1} cm after treatment. Sulphates, dissolved oxygen, biochemical oxygen demand, total solids, total suspended solids, and ammonia contents of the wastewater samples were significantly reduced after treatment with the AgNPs. Most parameters that were above the WHO permissible limits before treatment were below the threshold limits after treatment. Conclusively, sustainable AgNPs adsorptive materials are recommended for remediation of industrial wastewater and effluents.

Keywords: Industrial effluents, Silver nanoparticles, Wastewater treatment, Physicochemical properties

INTRODUCTION

Water is one of the most crucial natural resources for human survival [1, 2]. Water may be found everywhere, but safe and clean water is difficult to come by in many countries across the world, most especially in Sub-Sahara Africa. Water transports nutrition to important organs, regulates body temperature, and removes waste from internal organs. It is second only to air in importance and use [1].

Industrial effluents from abattoirs, detergent, and dairy industries in Ibadan, Nigeria, contaminate water bodies, introducing organic and inorganic pollutants [3]. These pollutants, originating from animal waste, chemical additives, and processing equipment, are critical components of physicochemical analysis, which assess effluent quality and treatment efficacy [4–6].

Physicochemical parameters, including pH, chloride, hardness, sulphate, nitrate, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Total Solids (TS), calcium hardness, magnesium hardness, total acidity, total alkalinity, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), oil and grease, ammonia, colour, odour, taste, temperature, turbidity, and conductivity, provide a comprehensive profile of effluents' contamination. Improper management of industrial wastewater poses substantial risks to both environmental quality and human health, necessitating stringent regulatory frameworks and effective treatment strategies [7]. The complexity in the composition of industrial wastewater necessitates the usage of advanced treatment technologies capable of removing specific contaminants to meet the regulatory discharge standards [8, 9]. Additionally, sustainable management practices aim to minimise the environmental footprint of industrial activities through water reuse and resource recovery [10]. The management of industrial wastewater in Nigeria is constrained by several factors, including inadequate infrastructure, limited access to clean water resources, and the prevalence of informal and small-scale industries operating without adequate regulatory oversight [9]. This situation has resulted in widespread pollution of water bodies, such as rivers, lakes, and coastal areas, affecting both urban and rural communities that rely on these water sources for their livelihoods [7].

Water pollution is a growing concern in the world's developing regions. As a problem, it is getting complex in the face of rapidly increasing human population, advancement in technologies, poor application of environmental laws governing human existence, and understanding of the trends and patterns of climatic change [11, 12]. The offensive odour of dairy industry wastewater is due to the formation of hydrogen sulphide that often creates a problem to nearby areas and affects the population health as well as aquatic life [13]. Dairy wastewater has nitrogenous compounds such as nitrate which are converted into nitrite that serves as ambient environment for development of methemoglobinemia [14]. Wastewater samples from dairy industry are rich in high BOD, COD, TDS, and CO_2 that create high organic load and also rich in calcium, magnesium, nitrogenous compounds and phosphorous [15]. The wastewater generated from different dairy industries varies in their characteristics mainly due to discontinuous manufacturing process and high production heterogeneity in the milk processing [13, 14].

Physicochemical treatment involves the use of physical and chemical processes to remove pollutants; wastewater treatment is crucial for protecting public health and the environment. Ogundiran and Fawole in 2014 assessed the impacts of industrial effluent discharges on the water quality of Asa River in Ilorin, Nigeria [16]. The study revealed that water from Asa River was polluted and not good for human consumption. Similarly, Okoyomon *et al*. in 2021 characterised physicochemical properties and heavy metal contents in industrial effluents and other river tributes in Ibadan, Nigeria [17]. It was reported in the study that improper treatment of effluents, by chemical and allied industries, before being discharged to the environment or water bodies may lead eventually to heavy metals' pollution in the study area. In the previous studies, there was no information on the treatment of industrial effluents and polluted water around the studied areas.

This study is novel because it reports synthesis and application of silver nanoparticles (synthesised using palm kernel shells extract), an economically and environmentally friendly approach, for treatment of physicochemical contaminants in abattoir, detergent, and dairy industrial effluents in Ibadan Metropolis. Unlike conventional methods such as chemical precipitation or membrane filtration, which are costly and often lead to secondary pollution (e.g. sludge generation). This method leverages on locally abundant agricultural waste to produce effective, sustainable nanoparticles without generating harmful by-products.

MATERIALS AND METHODS

Study Design

The study involves both field and experimental studies. Wastewater samples and samples from water bodies were obtained from dairy industry, abattoir and detergent industry in Ibadan, Nigeria.

Sampling and Preparation

Grab sampling technique was used to collect the various wastewater samples (main point) at the industries of interest, and river water samples at 100 m and 200 m away from the point of discharge of the effluents into the rivers. The maps showing the sampling areas are presented in Figures 1-3. The samples were collected in cleaned 1-litre plastic bottles and were immediately transported to the laboratory and kept in the refrigerator at 4ºC for further analysis. The palm kernel shells were collected from Federal Research Institute of Nigeria

(FRIN), Ibadan, Nigeria, and were milled into a powdery form using a well cleaned electric blender.

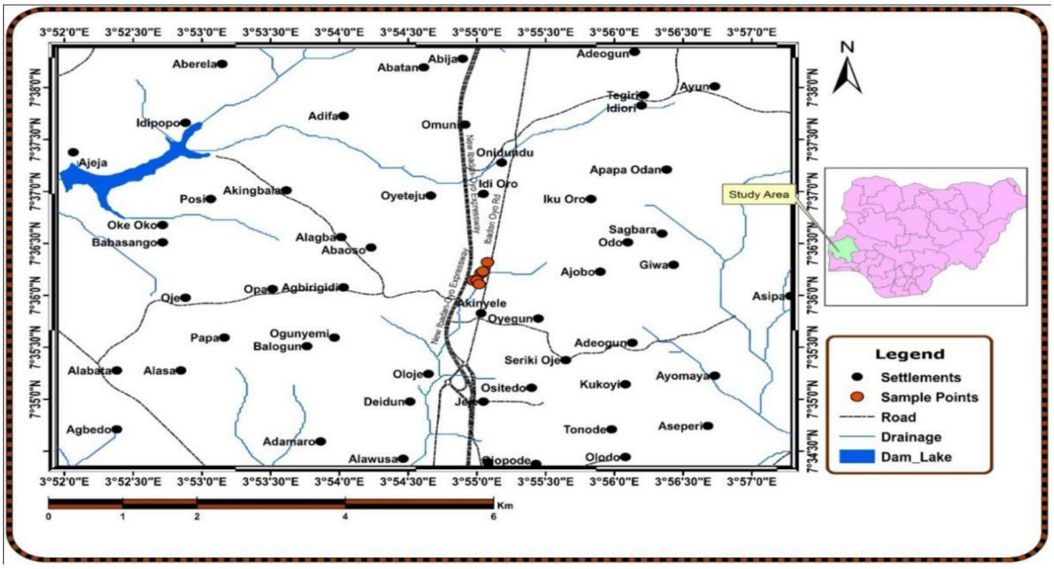

Figure 1: Map of Akinyele and environs showing Abattoir sampling points

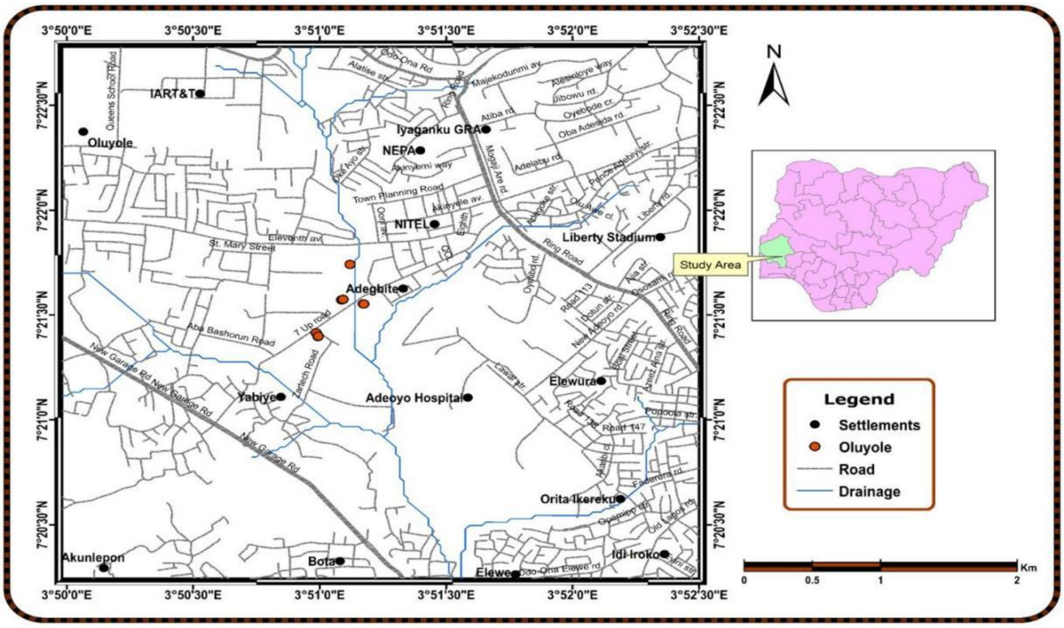

Figure 2: Map of Oluyole estate and environs showing detergent sampling points

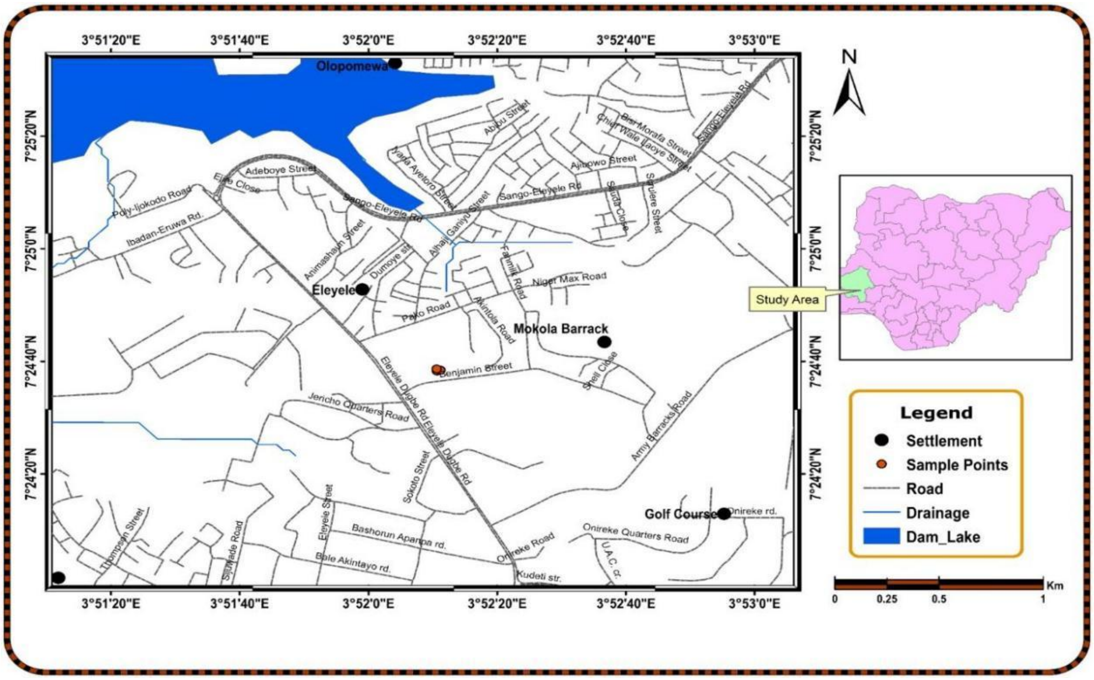

Figure 3: Map of Eleyele and environs showing dairy sampling points

Determination of Physicochemical Parameters

Chemical Oxygen Demand, Total Suspended Solids, Sulphate, Turbidity, Dissolve Oxygen, Temperature, pH, Total Solids, Total Dissolved Solids, Nitrate, Biochemical Oxygen Demand, Ammonia, Oil and Grease, Total Acidity, Total Alkalinity, Hardness, Calcium Hardness, Magnesium Hardness and Chloride were determined using the standard methods. Some of the methods are subsequently discussed.

The Chemical Oxygen Demand content of the samples was determined using the closed reflux colorimetric method (APHA Method 5220D) [4]. A 2 mL aliquot of each sample was added to a hach COD digestion vial (0–150 mg L^{-1} range) containing potassium dichromate and sulphuric acid [4]. The mixtures were digested at 150°C for 2 min a hach DRB200 reactor. After cooling, the absorbance was measured at 620 nm (high range) or 420 nm (low range) using a spectrophotometer.

The values of TSS were measured gravimetrically (APHA Method 2540D) [4]. A 100 – 250 mL of the sample (adjusted for high turbidity in all the samples) was filtered through a pre-weighed Whatman filters (1.2 µm). Filtrates were dried at 103–105°C for 1 h, cooled in a desiccator, and weighed using an analytical balance (0.1 mg precision). The values of TSS were calculated using Equation 1.

$$\text{TSS (mg } L^{-1}) = \frac{(\text{Final weight} - \text{Initial weight})}{volume\ filtered\ (L)} \text{x } 1000 \qquad (1)$$

The amounts of sulphates in the samples were quantified turbidimetrically (APHA Method 4500-SO_4^{2-} E). A 10 mL filtered sample was mixed with 1 mL conditioning reagent (glycerol, HCl, NaCl) and 0.1 g barium chloride to form $BaSO_4$ precipitate. After 5 min, turbidity was measured at 420 nm using a spectrophotometer [4]. Concentrations were derived from a sodium sulphate calibration curve (0–100 mg/L, RSD <4%). Samples were analysed to assess sulphate removal. The turbidity was measured nephelometrically (USEPA Method 180.1) using a (turbidimeter, Hach 2100Q), calibrated with formazin standards (0 – 800 NTU) [18].

The amounts of DO were measured using a specify meter, YSI 550A, calibrated in water-saturated air [18]. Samples were collected in 300 mL.

BOD bottles, and readings were recorded in mg/L (RSD <4%). Temperature values were measured using the YSI Pro30 temperature probe, recorded in °C with ±0.1°C precision while the pH values were measured using a Hanna HI9813, calibrated with pH 4, 7, and 10 buffers.

The amounts of the TS in the samples were determined gravimetrically (APHA Method 2540B). A 100 mL sample was evaporated in a pre-weighed dish at 103–105°C, cooled, and weighed [4]. The TS value was calculated using Equation 2.

$$\text{TS (mgL}^{-1}) = \frac{(\text{Final weight} - \text{Initial weight}) \text{ x } 1000}{volume\ \ (L)} \quad (2)$$

The values of TDS were measured (APHA Method 2540C) by filtering 100 mL through a 0.45 µm filter, evaporating the filtrate at 180°C, and weighing. The TDS values were evaluated using procedure similar to that of TS.

The concentrations of nitrate were quantified *via* cadmium reduction (APHA Method 4500-NO_3^- E) while the BOD values were measured (APHA Method 5210B) [4]. Samples were diluted with nutrient-enriched dilution water. The values of initial DO (DO_o) and final DO (after 5 days at 20°C) were measured using a meter, YSI 550A. The values of BOD were calculated using Equation 3.

$$\text{BOD (mg L}^{-1}) = \frac{(\text{DO}_0 - \text{DO}) - (\text{Blank correction})}{Dilution\ factor} \quad (3)$$

The ammonia contents of the samples were determined using the Nesslerization method (APHA Method 4500-NH_3 C) while the amounts of oil and grease were measured gravimetrically (APHA Method 5520B) [4]. A 500 mL acidified sample (pH < 2 with HCl) was extracted with 50 mL *n*-hexane in a separatory funnel, repeated thrice. The organic phase was evaporated at 70°C in a pre-weighed dish, cooled, and weighed. The values of oil and grease were calculated using Equation 4.

$$\text{Oil and grease (mg L}^{-1}) = \frac{\text{(Final weight} - \text{Initial weight) x 1000}}{volume\ \ (L)} \qquad (4)$$

Total acidity values were determined by titration (APHA Method 2310B) [4]. A 50 mL sample was titrated with 0.02 N NaOH to a pH 8.3 endpoint using phenolphthalein indicator [4]. Acidity value was calculated using Equation 5.

$$\text{Total acidity (mg L}^{-1}CaCO_3) = \frac{\text{(Volume of NaOH× Normality x 50,000}}{volume\ of\ sample\ \ (L)} \qquad (5)$$

Total alkalinity values were measured by titration (APHA Method 2320B) [4]. A 50 mL sample was titrated with 0.02 N H_2SO_4 to a pH 4.5 endpoint (using methyl orange indicator). Alkalinity value was calculated using Equation 6.

$$\text{Total alkalinity (mg L}^{-1}CaCO_3) = \frac{\text{(Volume of H}_2\text{SO}_4 \times \text{Normality x 50,000)}}{volume\ of\ sample\ \ (L)} \qquad (6)$$

The total hardness values of the samples were determined by using EDTA titration (APHA Method 2340C) [4]. A 50 mL sample was buffered to pH 10 with ammonia buffer and titrated with 0.01 M EDTA using Eriochrome Black T indicator until a colour change from red to blue. Hardness value was calculated using Equation 7.

$$\text{Hardness (mg L}^{-1}CaCO_3) = \frac{\text{(Volume of EDTA× Molarity x 100,000)}}{volume\ of\ sample\ \ (L)} \qquad (7)$$

Calcium hardness was measured by using EDTA titration (APHA Method 3500-Ca B). A 50 mL sample was adjusted to pH 12–13 with NaOH to precipitate magnesium, then titrated with 0.01 M EDTA using murexide indicator [4]. Calcium hardness was calculated as using Equation 8.

$$\text{Calcium hardness (mg L}^{-1}\ CaCO_3) = \frac{\text{(Volume of EDTA× Molarity x 100,000)}}{volume\ of\ sample\ \ (L)} \qquad (8)$$

Magnesium hardness was calculated as the difference between total hardness and calcium hardness as depicted in Equation 9.

$$\text{Mg Hardness (mg L}^{-1}\ CaCO_3) = \text{Total Hardness} - \text{Calcium Hardness} \quad (9)$$

The chloride concentration was measured by using argentometric titration (APHA Method 4500-Cl^- B). A 50 mL sample was titrated with 0.0141 N silver nitrate ($AgNO_3$) using potassium chromate as an indicator until a reddish-brown endpoint [4]. The chloride value was calculated using Equation 10.

$$\text{Chloride (mg L}^{-1}) = \frac{(volume\ of\ AgNO_3 \times Normality \times 35{,}450)}{volume\ of\ sample\ (ml)} \quad (10)$$

Preparation of Extracts from Palm Kernel Shells

A 1.0 g of the milled shell was weighed and suspended in 10 mL of distilled water. The extract was obtained by heating in a water bath at 60°C for 1 h. The extract was then filtered using Whatman No. 1 filter paper and centrifuged at 4000 rpm for 20 min. The supernatant was collected and used for further processes.

Synthesis of Silver Nanoparticles (AgNPs)

The method used for the synthesis of AgNPs is similar to that of Aremu *et al*. [19]. The precursor for chemical synthesis was $AgNO_3$ while extract from palm kernel shells served as a capping agent. To synthesise the nanoparticles, 10 mL of the extract was added to 40 mL (1 mM) $AgNO_3$ solution in a reaction vessel for the reduction of silver ion to silver nanoparticles. The reaction was carried out at room temperature (30 ± 2°C) 2 h at 100 rpm. The formation of silver nanoparticles was monitored through visual observation of the change of colour and measurement of the absorbance spectrum of the reaction mixture using UV-Vis spectroscopy at 520 nm.

RESULTS AND DISCUSSION

Physicochemical Parameters before Treatment

A total of 23 parameters were tested for each water sample. These parameters cut across the physicochemical properties of water from abattoir, detergent and dairy industries. The parameters include colour, odour, taste, conductivity, turbidity, Chemical Oxygen Demand, Total Suspended Solids, sulphate, Dissolve Oxygen, temperature, pH, Total Solids, Total Dissolved Solids, nitrate, Biochemical Oxygen Demand, ammonia, oil and grease, total acidity, total alkalinity, hardness, calcium hardness, magnesium hardness and chloride.

Physiochemical Parameters of the Wastewater Samples Collected around the Abattoir

The results of the physicochemical parameters of wastewater from the abattoir are presented in Table 1. The colour of the wastewater sample ranged from dark red to deep wine and brownish from the main point to the upstream and the two downstream points. The dark colour can be ascribed to the deposit of animal blood, being a key part of abattoir waste, thus having a significant negative impact on aquatic bodies [20].

Table 1: Physicochemical Properties of Abattoir Wastewater and the Receiving River Water Samples

Physical Parameters	Main point	Upstream	Downstream 1	Downstream 2	WHO [21]
Colour	Dark red	Deep wine	Brownish	Dark red	15.00 TCU
Odour	Irritating	Pleasant	Unpleasant	Unpleasant	3.00 TON
Taste	ND	ND	ND	ND	
Temperature (°C)	$27.00^{a} \pm 0.01$	$25.30^{b} \pm 0.01$	$25.70^{a} \pm 0.03$	$25.30^{b} \pm 0.01$	25 – 30
Turbidity	$126.80^{a} \pm 5.13$	$14.40^{d} \pm 0.13$	$94.30^{b} \pm 0.05$	86.50 ± 1.07	5 – 50.00 NTU
Conductivity (µmhos^{-1} cm)	$3268.00^{a} \pm 20.14$	$252.00^{d} \pm 0.66$	$2470.00^{b} \pm 14.02$	2436.00 ± 4.13	150 – 1500.00
CHEMICAL PARAMETERS					
pH	$6.27^{d} \pm 0.13$	$6.97^{c} \pm 0.05$	$8.03^{a} \pm 0.06$	$7.92^{b} \pm 0.13$	6.50 – 8.50
Chloride (mg L^{-1})	$184.50^{a} \pm 6.02$	$87.90^{d} \pm 1.03$	$156.30^{b} \pm 2.01$	$138.70^{c} \pm 2.07$	250.00
Hardness (mg L^{-1})	$334.00^{a} \pm 4.05$	$112.00^{d} \pm 3.06$	$248.00^{b} \pm 2.13$	$224.00^{c} \pm 2.05$	100 – 500.00
Sulphate (mg L^{-1})	$248.63^{a} \pm 5.16$	$36.72^{d} \pm 0.03$	$192.52^{b} \pm 2.03$	$183.63^{c} \pm 3.14$	250.00
Nitrate (mg L^{-1})	$43.65^{a} \pm 1.03$	$4.38^{d} \pm 0.01$	$38.21^{b} \pm 1.03$	$31.17^{c} \pm 1.06$	50.00
Total suspended solids (mg L^{-1})	$971.50^{a} \pm 2.14$	$241.70^{d} \pm 0.51$	$872.40^{b} \pm 5.18$	$858.30^{c} \pm 3.06$	5-35.00
Total dissolve solids (mg L^{-1})	$413.80^{a} \pm 7.21$	$143.20^{d} \pm 4.06$	$398.70^{b} \pm 8.14$	$372.60^{c} \pm 2.07$	600.00
Total solids (mg L^{-1})	$1385.80^{a} \pm 12.08$	$384.90^{d} \pm 3.15$	$1271.20^{b} \pm 4.01$	$1230.90^{c} \pm 6.03$	1000.00
Calcium hardness (mg L^{-1})	$278.00^{a} \pm 3.17$	$83.00^{d} \pm 1.01$	$198.00^{b} \pm 1.05$	$180.00^{c} \pm 1.03$	50 – 200
Magnesium hardness (mg L^{-1})	$56.00^{a} \pm 2.03$	$29.00^{d} \pm 0.02$	$50.00^{b} \pm 1.13$	$44.00^{c} \pm 0.03$	10 – 50.00
Total acidity (mg L^{-1})	$6.80^{a} \pm 0.03$	$4.30^{d} \pm 0.02$	$5.80^{b} \pm 0.01$	$5.60^{c} \pm 0.02$	50.00

Total alkalinity (mg L^{-1})	140.00^{b} ± 0.01	98.00^{d} ± 2.06	160.00^{b} ± 0.13	160.00^{b} ± 3.15	20 – 200
DO (mg L^{-1})	3.20^{c} 0.01	6.80^{a} ± 0.03	3.80^{b} ± ^{b}0.01	3.80^{b} ± 0.01	4 – 8
BOD (mg L^{-1})	2.00^{c} ± 0.00	5.40^{a} ± 0.06	2.60^{b} ± 0.02	2.60^{b} ± 0.01	5.00
COD (mg L^{-1})	43.60^{d} ± 0.05	62.40^{a} ± 1.04	48.30^{c} ± 3.02	51.20^{b} ± 1.13	100
Oil and grease (mg L^{-1})	58.63^{a} ± 0.21	32.72^{d} ± 0.06	51.42^{c} ± 2.08	53.27^{b} ± 0.06	0.1
Ammonia (mg L^{-1})	16.71^{a} ± 0.13	1.06^{d} ± 0.01	10.31^{b} ± 0.01	10.68^{b} ± 0.03	1.5

The pH values ranged between 6.27 and 8.03 for all the samples. The values obtained are within the permissible limits of 6.5 – 8.5 sets by the WHO [21]. Similar results (pH 6.9 – 7.2) and (pH 6.66 – 7.78) were obtained by Kenechukwu *et al.* [6] and Terna *et al.* [20], respectively.

The wastewater samples were at ambient temperatures for all the samples, with values ranging from 25.3 to 25.7^{o}C. These values suggest that they are acceptable, as they lie within the permissible limits of 25 – 30^{o}C sets by the WHO. Ibimode *et al.* [22] reported similar results (23.5 – 23.7^{o}C) when they studied the impact of abattoir waste on water quality and public health around an abattoir in Jos Metropolis, Plateau State, Nigeria. According to the report, temperature is a crucial parameter as it affects the amount of dissolved oxygen which further affects the survival of microorganisms. In addition, high temperature enhances the growth of opportunistic pathogens such as *Pseudomonas aeruginosa.*

The result of turbidity showed that upstream had the least value (14.4 NTU), which is within the limits 5 – 50 NTU set by WHO [21].

Chloride in water is one of the water qualities' issues that could be ascribed to pollution from industrial or domestic activities. The values obtained in this study ranged from 87.9 to 156.3 mg L^{-1} at the upstream and downstream and 184.5 mg L^{-1} at the wastewater. The values obtained are within the permissible limit of 250 mg L^{-1} set by WHO [21]. Chloride in water above permissible level of 250 mg L^{-1} can bring about laxative effect in humans, change in taste of water and toxicity to aquatic life [23].

Hardness values obtained in all samples ranged from 112 ± 3.06 to 334 ± 4.05 mg L^{-1} in all samples, in the order upstream < downstream 2 < downstream 1 < wastewater. Hardness values are within the permissible limits (100 – 500 mg L^{-1}) sets by the WHO [21], in all samples. This result is the least among the values earlier reported [23, 24].

Sulphates concentration in the samples obtained from abattoir ranged from 36.72 ± 0.03 mg L^{-1} to 248.63 ± 5.16 mg L^{-1} in the same order as the hardness. The values obtained are within the permissible limit of WHO (250 mg L^{-1}) [21]. Adiele *et al.* [23] noted that animal matter may release sulphate into a water body, and the consumption of water containing sulphate may result in intestinal discomfort, diarrhoea, salty taste and consequently dehydration.

The concentrations of nitrates in the samples ranged between 4.38 ± 001 and 43.65 ± 1.03 mg L^{-1} with the upstream recording the least value and the same order recorded in hardness and sulphates is noticed for nitrates as well. The concentration of all nitrates obtained are below the WHO permissible limit of 50 mg L^{-1} [21], similar to the results obtained from previous studies [6, 23 – 25]. Several researchers have reported that high values of nitrate in water could cause excessive development of some aquatic plants and algae [6, 26], and could cause Blue-baby syndrome in children and pregnant women [6, 27].

The values of TSS ranged from 241.7 ± 0.51 to 858.3 ± 3.06 mg L^{-1} at the upstream and downstream samples. The wastewater contains elevated amount of TSS of 971.5 ± 2.14 mg L^{-1}. The results obtained for all the samples are above WHO permissible limits of 5 – 35 mg L^{-1} [21]. In the study of the effects of abattoir waste on water quality in Gwagwalada, Abuja [28], the TSS values reported were above the WHO acceptable limit [21]. In the study, a maximum value was recorded at the middle-stream, similar to the result of this present study. Tekenah *et al.* [26] reported that abattoir waste capable of increasing TS and TSS at point source include condemned meat, undigested ingest, animal waste, carcasses, and so on.

The DO values of the water samples (wastewater, upstream, and downstreams 1 and 2) ranged from 3.2 ± 0.01 to 6.8 ± 0.03 mg L^{-1}. The DO values are within the WHO permissible limits of 4 – 8 mg L^{-1} [21], with upstream having the highest DO value similar to the trend earlier reported [24], but with higher load. The levels of the DO indicate the degree of pollution by organic matter from the water body and in this study, DO values are below the threshold limits. The DO levels below 5.0 mg L^{-1} adversely affect aquatic biological life, while a concentration below 2.0 mg L^{-1} may lead to death for most fishes [6].

The BOD is a popular index used in water quality management and it shows the amount of oxygen needed for the biological decomposition of organic matter under aerobic condition. In this study, BOD values exhibited significant variations across the samples, with values ranging from 2.0 ± 0.0 to 5.4 ± 0.06 mg L^{-1}, with highest values in the upstream samples. These values lie within the permissible limit of WHO (5 mg L^{-1}) [21] except for upstream which is slightly above limit. The high BOD load observed at the upstream could be attributed to increase degradable organic waste load from the abattoir effluent discharged into the water body. According to the report published by Adiele *et al.* [23], water bodies with BOD concentrations between 1.0 and 2.0 mg L^{-1} were considered clean, 3.0 mg L^{-1} fairly clean, 5.0 mg L^{-1} doubtful and 10.0 mg L^{-1} definitely bad and polluted. The BOD concentrations in the abattoir wastewater may therefore reflect the level of organic pollution. This agreed with the observation by Adiele *et al.* [23] in their study on the effects of abattoir waste discharge on the quality of the Trans-Amadi Creek, Port-Harcourt, Rivers State, Nigeria.

The values for COD in the present study are within the range 43.6 ± 0.05 – 62.4 ± 1.04 mg L^{-1}. From the results, wastewater recorded the lowest concentration, followed by the downstream 1. The results are within the WHO permissible limits. This study agreed with that of Adiele *et al.* [23], where higher COD values was obtained at the upstream. According to different reports, high levels of COD suggest the presence of chemical oxidants in the effluents while low COD values suggest otherwise [6, 23]. A high COD value could likely cause nutrient fixation in the soil resulting to reduced rate of nutrient availability to plants. Chemical oxidants affect water treatment plants by causing rapid development of rust [23].

The values of oil and grease in all the samples range from 32.72 to 58.63 mg L^{-1}; these values are all above the permissible limit (0.1 mg L^{-1}) according to WHO [21]. This is obviously as a result of the nature of the industrial contaminants. According to Ndukwe *et al.* [24], excess oil and grease in water is capable of having adverse effects on aquatic biological lives and may lead to death of most aquatic organisms.

The ammonia values are in the order of 16.71 > 10.68 > 10.31 > 1.06 mg L^{-1} for wastewater, downstream 2, downstream 1 and upstream samples, respectively. All these results are above the permissible limit (1.5 mg L^{-1}) according to WHO [21] except the upstream sample (1.06 mg L^{-1}) which is within the permissible limit. Excess ammonia in the water sample can be attributed to a lot of untreated or poorly treated contaminants released into the water bodies. This is capable of bringing about laxative effect in human and change in taste of water and toxicity to aquatic lives [23].

Results of Physicochemical Parameters of the Detergent Wastewater and Water Samples from the Receiving River

Table 2 presents the result of the physicochemical properties of the detergent wastewater, the water samples from the upstream and downstream of the receiving river.

The samples were colourless at the upstream which is within the true colour unit (15.00 TCU) accepted by the WHO [21], however it was creamy at the wastewater, downstreams 1 and 2.

The odours of the upstream samples were pleasant, irritating at the wastewater and unpleasant at downstreams 1 and 2.

The pH values ranged from 6.98 ± 0.01 to 8.72 ± 0.08, all within WHO's limits (6.50 – 8.50) [21], with upstream recorded lowest value and wastewater recorded highest value. The samples' temperature values, between 25.2 ± 0.0 and 25.3 ± 0.01°C, are within WHO's limits (25 – 30°C) [21].

The turbidity upstream was 6.13 ± 0.02 NTU, within WHO's 5 – 50 NTU [21], but downstreams 1 and 2 have turbidity values ranging from 162.2 ± 0.03 to 162.3 ± 0.00 NTU and wastewater has 228.3 ± 3.05 NTU, all exceeded WHO limits [21].

The results of chloride concentrations obtained from detergent samples ranged from 65.20 to 209.86 mg L^{-1} for all the samples. The values are within the permissible limit of 250 mg L^{-1} sets by the WHO [21]. The chloride value of upstream sample remains the lowest (65.20 mg L^{-1}). Chloride in water above permissible level of 250 mg L^{-1} can bring about laxative effect in humans.

The hardness values obtained are in the order of 186.00 > 132.00 > 108.00 > 52.00 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. The wastewater sample recorded the highest hardness value (186.00 mg L^{-1}) while 52.00 mg L^{-1} (upstream) is the lowest. All the values are within the permissible limits set by WHO (100 – 500 mg L^{-1}) [21].

The sulphate concentrations in the samples obtained from detergent wastewater ranged between 21.48 and 158.63 mg L^{-1}, with the wastewater samples recorded the highest value (158.63 mg L^{-1}) while the sample from the upstream exhibited lowest value of 21.48 mg L^{-1}. All the values obtained are within the permissible limit of 250 mg L^{-1} set by the WHO [21].

The results of nitrates of the water samples from detergent industry follow the same trend as those of abattoir water samples, with values ranging between 3.24 and 13.48 mg L^{-1};

upstream has the least value and the wastewater has the highest value of nitrate. The concentrations of all nitrates obtained are below the WHO permissible limit of 50.00 mg L^{-1} [21].

The results of TSS obtained for all the samples are above WHO permissible limits of 5 – 35 mg L^{-1}. The values obtained are 108.46, 258.62 and 286.51 mg L^{-1} at the upstream, downstream 2 and downstream 1, respectively. This observation is similar to the trend of the abattoir samples. The wastewater sample contains elevated value of TSS (357.32 mg L^{-1}).

The results of TDS obtained are in the order of 163.41 > 136.42 > 124.56 > 67.31 mg L^{-1} for wastewater, downstream 1, downstream 2, and upstream, respectively.

Table 2: Physicochemical Properties of Detergent Wastewater and the receiving River Water Samples

Physical Parameters	Main point	Upstream	Downstream 1	Downstream 2	WHO [21]
Colour	Cream	Colourless	Cream	Cream	15.00 TCU
Odour	Irritating	Pleasant	Unpleasant	Unpleasant	3.00 TON
Taste	ND	ND	ND	ND	
Temperature (^{o}C)	$25.20^{ab} \pm 0.01$	$25.60^{a} \pm 0.01$	$25.20^{b} \pm 0.00$	$25.30^{ab} \pm 0.01$	25-30
Turbidity	$228.30^{a} \pm 3.05$	$6.13^{d} \pm 0.02$	162.20 ± 0.03	$162.30^{c} \pm 0.00$	5-50.00 NTU
Conductivity (µmhos^{-1} cm)	$368.00^{a} \pm 1.03$	$137.00^{d} \pm 2.15$	254.00 ± 1.13	$242.00^{c} \pm 0.03$	150 – 1500.00
CHEMICAL PARAMETERS					
pH	$8.72^{a} \pm 0.08$	$6.98^{d} \pm 0.01$	$7.62^{c} \pm 0.01$	$7.76^{b} \pm 0.06$	6.50 – 8.50
Chloride (mg L^{-1})	$209.86^{a} \pm 3.16$	$65.20^{d} \pm 0.03$	$157.62^{b} \pm 1.03$	$129.03^{c} \pm 0.00$	250.00
Hardness (mg L^{-1})	$186.00^{a} \pm 0.09$	$52.00^{d} \pm 0.05$	$132.00^{b} \pm 0.02$	$108.00^{c} \pm 0.07$	100 – 500.00
Sulphate (mg L^{-1})	$158.63^{a} \pm 0.02$	$21.48^{d} \pm 0.01$	$121.43^{b} \pm 0.01$	$93.27^{c} \pm 0.05$	250.00
Nitrate (mg L^{-1})	$13.48^{a} \pm 0.03$	$3.24^{d} \pm 0.00$	$9.83^{b} \pm 0.01$	$7.41^{c} \pm 0.00$	50.00
Total suspended solids (mg L^{-1})	$357.32^{a} \pm 6.02$	$108.46^{d} \pm 1.03$	$286.51^{b} \pm 0.05$	$258.62^{c} \pm 1.06$	5-35.00
Total dissolve solids (mg L^{-1})	$163.41^{a} \pm 2.15$	$67.31^{d} \pm 0.21$	$136.42^{b} \pm 0.06$	$124.56^{c} \pm 0.13$	600.00
Total solids (mg L^{-1})	$520.73^{a} \pm 3.14$	$221.32^{d} \pm 2.03$	$409.88^{b} \pm 0.09$	$383.18^{c} \pm 0.41$	1000.00
Calcium hardness (mg L^{-1})	$134.00^{a} \pm 0.03$	$34.00^{d} \pm 0.05$	$83.00^{b} \pm 0.03$	$76.00^{c} \pm 0.00$	50 – 200
Magnesium	$48.00^{a} \pm$	$18.00^{d} \pm 0.01$	$49.00^{b} \pm 0.01$	$32.00^{c} \pm 0.01$	10 – 50.00

hardness (mg L^{-1})	0.01				
Total acidity (mg L^{-1})	8.62[a] ± 0.01	3.40[d] ± 0.02	6.40[c] ± 0.02	6.80[b] ± 0.00	50.00
Total alkalinity (mg L^{-1})	260.00[a] ± 1.04	82.00[d] ± 0.01	180.00[b] ± 0.02	160.00[c] ± 0.02	20 – 200
DO (mg L^{-1})	5.40[c] ± 0.03	6.80[a] ± 0.00	6.90[a] ± 0.01	6.20[b] ± 0.03	4 – 8
BOD (mg L^{-1})	3.20[c] ± 0.01	4.60[a] ± 0.00	4.60 ± 0.01	4.60 ± 0.01	5.00
COD (mg L^{-1})	64.36[c] ± 0.05	132.40[a] ± 0.13	87.60[b] ± 1.04	89.30[b] ± 0.05	100
Oil and grease (mg L^{-1})	10.54[a] ± 0.02	3.41[d] ± 0.01	8.56[b] ± 0.02	8.17[b] ± 0.02	0.1
Ammonia (mg L^{-1})	11.13[a] ± 0.02	2.09[d] ± 0.01	6.26[b] ± 0.01	5.64[c] ± 0.01	1.5

The wastewater sample has the highest TDS value of 163.41 mg L^{-1} while the upstream has the lowest value of 67.31 mg L^{-1}. All the values are within the permissible limit set by WHO (600 mg L^{-1}) [21]. The result of TDS obtained are in the order of 163.41 > 136.42 > 124.56 > 67.31 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. The wastewater sample has the highest TDS value of 163.41 mg L^{-1} while the upstream has the lowest value of 67.31 mg L^{-1}. All the values are within the permissible limit of WHO (600 mg L^{-1}) [21].

The results of TS obtained for all the samples are below WHO permissible limit of 1000 mg L^{-1} [21]. The values obtained are 520.73, 409.88, 383.18 and 221.32 mg L^{-1} for the wastewater, downstream 1, downstream 2 and upstream, respectively.

The results of calcium hardness obtained are in the order of 134.00 > 83.00 > 76.00 > 34.00 for wastewater, downstream 1, downstream 2, and upstream, respectively. The wastewater sample has the highest calcium hardness value of 134.00 mg L^{-1} while upstream sample has the lowest value of 34.00 mg L^{-1}. All the values are within the permissible limits set by WHO (50 – 200 mg L^{-1}) [21].

The results of magnesium hardness in the detergent samples range between 18.00 and 49.00 mg L^{-1} with the upstream recorded the least value of 18.00 mg L^{-1} and downstream 1 with the highest value of 49.00 mg L^{-1}. The results obtained are within the WHO permissible limits of 10 – 50 mg L^{-1} [21].

The results of total acidity obtained are in the order of 8.62 > 6.80 > 6.40 > 3.40 mg L^{-1} for wastewater, downstream 1, downstream 2, and upstream, respectively. The wastewater sample has the highest total acidity value of 8.62 mg L^{-1} while the upstream sample has the lowest values of 3.40 mg L^{-1}. All the values are within the permissible limit set by WHO (50 mg L^{-1}) [21].

Total alkalinity values obtained from the detergent samples ranged between 82.00 and 260.00 mg L^{-1}, with the wastewater sample has the highest value of 260.00 mg L^{-1} while the sample from the upstream has the lowest value of 82.00 mg L^{-1}. All the values obtained are also within the permissible limits of WHO (20 – 200 mg L^{-1}) except that of wastewater which is above the limits [21].

The values of DO from detergent wastewater samples are higher than those obtained at the abattoir samples. The DO values of the samples ranged from 5.40 to 6.90 mg L^{-1}, with the wastewater recorded the least value of 5.40 mg L^{-1} while the highest value of DO (6.90 mg L^{-1}) was obtained at the downstream 2. All the DO values are within the WHO permissible limits of 4 – 8 mg L^{-1}. This suggests that the degree of pollution by organic matter in this wastewater is higher than the one obtained from the abattoir samples.

The BOD values obtained from the samples show the variations from 3.2 to 4.6 mg L^{-1}, with least value obtained from the wastewater (3.20 mg L^{-1}) while the three other samples have the same average value of BOD (4.60 mg L^{-1}). All the BOD values are within the permissible limit of WHO (5 mg L^{-1}) [21].

The COD values lie between 64.36 and 132.40 mg L^{-1} for all the samples. Wastewater has the lowest value (64.36 mg L^{-1}) and others occur in the order of 87.60 < 89.30 < 132.40 mg L^{-1} for downstream 1, downstream 2, and upstream, respectively. The results obtained at the wastewater, downstreams 1and 2 are below the permissible limit of 100 mg L^{-1} sets by WHO [21] while the upstream sample has a value which is above the stated permissible limit.

Oil and grease values in all the samples range from 3.41 to 10.54 mg L^{-1} and are all above the permissible limit (0.1 mg L^{-1}) according to WHO [21]. According to Ndukwe *et al.* [24], excess oil and grease in water is capable of causing adverse effects on aquatic life which may lead to death of most aquatic organisms.

The ammonia values are in the order of 11.13 > 6.26 > 5.64 > 2.09 mg L^{-1} for wastewater, downstream 1, downstream 2, and upstream samples, respectively. All these values are above the permissible limit (1.5 mg L^{-1}) according to WHO [21]. Excess ammonia in the water sample can be attributed to a lot of untreated or poorly treated contaminants released into the water bodies. This is capable of bringing about laxative effect in human and change in taste of water and toxicity to aquatic life [23].

Results of Physicochemical Parameters of the Dairy Wastewater and the Water Samples from the Receiving River

Table 3 presents the results of the physicochemical properties of the dairy wastewater, and the samples from the upstream and downstreams of the receiving river. From the results, the colour of the wastewater, upstream, downstreams 1 and 2 varied from clear to cream. Similar result was obtained by Porwal *et al*. [29], the wastewater sample has an irritating odour, upstream has a pleasant odour while downstreams 1 and 2 have unpleasant odour.

The temperature of all the samples analysed, ranges between 25.30 and 25.60°C, are within the ambient values of 25 – 30°C set by the WHO [21]. Downstream 1 has the highest temperature value of 25.60°C, closely followed by the wastewater (25.40°C) while the least value was recorded in upstream and downstream 2 (25.30°C). Similar result of 25.40°C was obtained by Jana *et al*. [5].

The turbidity results of the water samples were less than the values obtained from abattoir and detergent samples. The upstream samples were the least turbid (9.07 NTU), followed by the downstream 2 having value of 47.9 NTU. The results obtained from the two samples are within the limits of 5 – 50 NTU sets by the WHO [21]. Samples from the downstream 1 and wastewater have high turbidity values of 64.70 and 87.20 NTU, respectively, which are above the permissible limits.

Table 3: Physicochemical Properties of Dairy Wastewater and the Water Samples from the Receiving River

Physical Parameters	Main point	Upstream	Downstream 1	Downstream 2	WHO [21]
Colour	Cream	Clear	Cream	Cream	15.00 TCU
Odour	Irritating	Pleasant	Unpleasant	Unpleasant	3.00 TON
Taste	ND	ND	ND	ND	
Temperature (°C)	$25.40^{c} \pm 0.00$	$25.30^{b} \pm 0.01$	$25.60^{a} \pm 0.01$	$25.30^{b} \pm 0.00$	25 – 30
Turbidity	$87.20^{a} \pm 0.01$	$9.70^{d} \pm 0.01$	$64.70^{b} \pm 0.02$	$47.90^{c} \pm 0.02$	5 – 50.00 NTU
Conductivity (µmhos^{-1} cm)	$3268.00^{a} \pm 11.03$	$252.00^{d} \pm 0.06$	$2467.00^{b} \pm 20.08$	$2054.00^{c} \pm 12.07$	150 – 1500.00
CHEMICAL PARAMETERS					
pH	$5.67^{c} \pm 0.03$	$6.98^{a} \pm 0.01$	$6.21^{b} \pm 0.02$	$6.27^{b} \pm 0.00$	6.50 – 8.50
Chloride (mg L^{-1})	$142.46^{a} \pm 0.03$	56.24 ± 0.03	$116.28^{b} \pm 0.05$	$97.28^{c} \pm 0.02$	250.00
Hardness (mg L^{-}	$292.00^{a} \pm$	$108.0^{d} \pm 0.02$	$258.00^{b} \pm$	$214.00^{c} \pm$	100 – 500.00

^{1})	0.01		0.33	0.31	
Sulphate (mg L^{-1})	176.43^{a} ± 0.06	41.72^{d} ± 0.01	128.46^{b} ± 0.61	132.74^{c} ± 0.06	250.00
Nitrate (mg L^{-1})	26.51^{a} ± 0.00	6.42^{d} ± 0.00	21.73^{b} ± 0.13	16.38^{c} ± 0.01	50.00
Total suspended solids (mg L^{-1})	1209.42^{a} ± 13.06	431.67 ^{d} ± 0.03	1032.43^{b} ± 6.08	956.25^{c} ± 6.07	5 – 35.00
Total dissolve solids (mg L^{-1})	312.09^{a} ± 4.13	131.42^{d} ± 0.02	274.68^{b} ± 3.01	268.47^{c} ± 1.06	600.00
Total solids (mg L^{-1})	1521.54^{a} ± 10.06	563.09^{d} ± 0.06	1307.11^{b} ± 10.03	1224.72^{c} ± 8.13	1000.00
Calcium Hardness (mg L^{-1})	198.00^{a} ± 0.00	79.00^{d} ± 0.01	168.00^{b} ± 0.21	142.00^{c} ± 2.07	50 – 200
Magnesium Hardness (mg L^{-1})	94.00^{a} ± 0.01	29.00^{d} ± 0.00	90.00^{b} ± 0.13	72.00^{c} ± 0.02	10 – 50.00
Total acidity (mg L^{-1})	9.70^{a} ± 0.02	5.30^{d} ± 0.02	8.60^{b} ± 0.01	7.20^{c} ± 0.01	50.00
Total Alkalinity (mg L^{-1})	180.00^{a} ± 0.02	86.00^{d} ± 0.01	140.00^{b} ± 0.00	120.00^{c} ± 0.00	20 – 200
DO (mg L^{-1})	3.60^{c} ± 0.00	7.60^{a} ± 0.00	4.80^{b} ± 0.02	4.80^{b} ± 0.01	4 – 8
BOD (mg L^{-1})	2.40^{c} ± 0.01	5.90^{a} ± 0.01	3.20^{b} ± 0.00	3.20^{b} ± 0.00	5.00
COD (mg L^{-1})	64.30$^{\mathbf{b}}$ ± 0.03	86.20^{a} ± 0.03	52.70^{c} ± 0.14	47.20^{d} ± 0.01	100
Oil and Grease (mg L^{-1})	86.36^{a} ± 0.13	13.63^{d} ± 0.00	62.38^{b} ± 0.33	54.47^{c} ± 0.02	0.1
Ammonia (mg L^{-1})	24.62^{a} ± 0.01	3.21^{d} ± 0.01	17.63^{b} ± 0.02	13.38^{c} ± 0.01	1.5

The conductivity results are in the order of 3268.00 > 2467.00 > 2054.00 > 252.00 µmhos^{-1} cm for wastewater, downstream 1, downstream 2 and upstream, respectively. All conductivity results of the samples are above the WHO permissible limits of 150 – 1500 µmhos^{-1} cm [21] except that of upstream which lies within the limits.

The pH values of the samples range from 5.67 and 6.98; wastewater has the least value while the highest value was obtained from the upstream water sample. The values obtained are within the permissible limits of 6.50 – 8.50 sets by the WHO [21]. Porwal *et al.* [29] reported pH values of 6.03 and 6.06 in their report on biodegradation of dairy effluents using microbial isolates. According to Bharati and Shinkar [30], dairy wastes are white and usually slightly alkaline and become acidic quite rapidly due to the fermentation of milk sugar to lactic acid. Similarly, Ritambhara *et al.* [31] reported that dairy wastewater has pH ranging from 4.6 to 11. They further stated that the pH decreases (becomes acidic) as a result of lactic acid fermentation caused by prolonged exposure to anaerobic conditions.

Chloride values obtained from the dairy industry samples are in the order 56.24 < 97.28 < 116.28 mg L^{-1} for upstream, downstream 2, and downstream 1, respectively while wastewater has the highest chloride concentrations (142.46 mg L^{-1}). All the values obtained in the samples are within the permissible limit of 250 mg L^{-1} sets by WHO [21]. Similar work conducted by Shivsharan *et al.* [32] reported average chlorides value of 151.23 mg L^{-1} which is higher than the result obtained in the present study.

Hardness values obtained range from 108.0 to 292.0 mg L^{-1}. The wastewater has the highest value of 292.0 mg L^{-1}; understandably upstream has the lowest value of 108.0 mg L^{-1}. All results obtained are within the permissible limits of 100 – 500 mg L^{-1} sets by WHO [21]. Sulphates' concentrations obtained from dairy samples are 41.72, 128.46, 132.74 and 176.43 mg L^{-1} at the upstream, downstream 1, downstream 2 and wastewater, respectively. All these values are within the permissible limit of WHO (250 mg L^{-1}) [21]. The study conducted by Nabbou *et al.* [33] reported average sulphates' value of 108.86 mg L^{-1}.

The concentrations of nitrates presents in the dairy water samples range from 6.42 to 26.51 mg L^{-1} and follow the same trend as those obtained in water samples from abattoir and detergent industry. The upstream has the least value of 6.42 mg L^{-1} and the wastewater has the highest value of 26.51 mg L^{-1}. The concentrations of nitrates obtained are below the WHO permissible limit of 50 mg L^{-1} [21]. Nabbou *et al.* [33] recorded similar results with average nitrates concentration of 7.34 mg L^{-1} in dairy wastewater studied.

The results of TSS obtained range from 431.67 to 1209.42 mg L^{-1}. The wastewater sample has the highest value of 1209.42 mg L^{-1} while the upstream has the lowest value of 431.67 mg L^{-1}. All the values obtained are above the WHO permissible limits of 5 – 35 mg L^{-1} [21]. The results of TSS obtained in this study are above the TSS values reported in similar studies carried out earlier [29, 33].

The results of TDS obtained are in the order of 312.09 > 274.68 > 268.47 > 131.42 mg L^{-1} for wastewater (main point), downstream 1, downstream 2, and upstream, respectively. The wastewater sample has the highest values of 312.09 mg L^{-1} while the upstream recorded the lowest value of 131.42 mg L^{-1}. All results obtained are within the permissible limit of WHO (600 mg L^{-1}) [21].

The values of Total Solids (TS) obtained are 1521.51, 1307.11, 1224.72 and 563.09 mg L^{-1} for the wastewater, downstream 1, downstream 2 and upstream, respectively. The results of TS for all the samples are above WHO permissible limit of 1000 mg L^{-1} [21] except for upstream with the value of 563.09 mg L^{-1}.

The results of calcium hardness obtained are in the order of 198.00 > 168.00 > 142.00 > 79.00 mg L^{-1} for wastewater, downstream 1, downstream 2, and upstream, respectively. The wastewater sample has the highest value of 198.00 mg L^{-1} while the upstream has the lowest value of 79.00 mg L^{-1}. All the values obtained are within the permissible limits set of WHO (50 – 200 mg L^{-1}) [21].

The values of magnesium hardness in the dairy samples range between 29.00 and 94.00 mg L^{-1}; water sample from upstream has the least value of 29.00 mg L^{-1} while wastewater has the highest value of 94.00 mg L^{-1}. The results obtained are above the WHO permissible limits of 10 – 50 mg L^{-1} [21] except for upstream which is within the limits.

The results of total acidity obtained are in the order of 9.70 > 8.60 > 7.20 > 5.30 mg L^{-1} for wastewater, downstream 1, downstream 2, and upstream, respectively. The wastewater sample has the highest value of 9.70 mg L^{-1} while the upstream sample recorded the lowest value of 5.30 mg L^{-1}. All the values are within the permissible limit of the WHO (50 mg L^{-1}) [21].

Total alkalinity results ranged between 86.00 and 180.00 mg L^{-1}; the wastewater sample recorded the highest value of 180.00 mg L^{-1} while the value from the upstream is the lowest (86.00 mg L^{-1}). All the values obtained are within the permissible limits of the WHO (20 – 200 mg L^{-1}) [21].

The values of DO obtained diary water samples ranged from 3.60 to 7.60 mg L^{-1}. The least value was obtained from the wastewater (3.60 mg L^{-1}) while the upstream has the highest values of 7.60 mg L^{-1}. The DO values are within the WHO permissible limits of 4.00 – 8.00 mg L^{-1} [21] but the degree of pollution at the upstream is higher than the other samples.

The Biological Oxygen Demand results showed variations from 2.40 to 5.90 mg L^{-1}, with least values obtained from the wastewater (2.40 mg L^{-1}) and highest at the upstream (5.90 mg L^{-1}). All the values obtained were within the permissible limit of WHO (5 mg L^{-1}) [21] except for upstream which is relatively above the limit.

The Chemical Oxygen Demand values of dairy industry water samples are below what were obtained in the detergent industry. The values lie within 47.20 and 86.20 mg L^{-1}. The least values were recorded at the downstream 2 (47.20 mg L^{-1}) while the upstream has the highest values of 86.20 mg L^{-1}. The results obtained are below the permissible limit of 100 mg L^{-1} sets by the WHO [21].

Oil and grease values range from 13.63 to 86.36 mg L^{-1}. The wastewater has the highest value of 86.36 mg L^{-1} while the upstream has the lowest value (13.63 mg L^{-1}). All values are above the permissible limit (0.1 mg L^{-1}) according to WHO [21].

The ammonia values are in the order of 24.62 > 17.63 > 13.38 > 3.21 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. All these values are above the permissible limit (1.5 mg L^{-1}) according to WHO [21]. Excess ammonia in the water sample is attributed to untreated or poorly treated contaminants released into the water bodies.

Physicochemical Parameters of Water Samples after Treatment

The results of the physicochemical parameters of wastewater samples from abattoir as well as detergent and dairy industries after treatment with AgNPs are presented in Tables 4 to 6. The results showed great impact of the AgNPs in the treatment of the contaminated water samples.

The colour of the wastewater samples changed from dark red and deep wine to colourless and light brown at the main point.

The pH of the water samples after treatment still maintains the trend of water samples before treatment. Some parameters such as temperature, pH, calcium and magnesium hardness, acidity, alkalinity, DO, BOD, COD, oil and grease and ammonia remain unchanged after treatment of the water samples with AgNPs. The abattoir turbidity values were reduced in the order of 52.33 > 34.30 > 23.50 > 6.4 NTU for wastewater, downstream 1, downstream 2 and upstream, respectively, which are within the limits 5 – 50 NTU of WHO [21] except for the wastewater sample which is still slightly above the limits with the difference of 2.33 NTU. Similar results were observed for water samples from detergent and dairy industries.

Table 4: Physicochemical Properties of Abattoir Industrial Wastewater and the Receiving River Water Samples after Treatment

Physical Parameters	Main point	Upstream	Downstream 1	Downstream 2	WHO [21]
Colour	Light Brown	Clear	Clear	Clear	15.00 TCU
Odour	Pleasant	Pleasant	Pleasant	Pleasant	3.00 TON
Taste	ND	ND	ND	ND	
Temperature (^{o}C)	257.00^{a} ± 0.01	25.30^{b} ± 0.01	25.70^{a} ± 0.03	25.30^{b} ± 0.01	25 – 30
Turbidity	52.33^{a} ± 1.13	6.40^{d} ±	34.30^{b} ± 0.05	23.50 ± 1.07	5 – 50.00

		0.13			NTU
Conductivity (µmhos^{-1} cm)	1258^{a} ± 20.14	109^{d} ± 0.66	1042.00^{b} ± 6.02	9490.00 ± 4.13	150-1500.00
CHEMICAL PARAMETERS					
pH	6.27^{d} ± 0.13	6.97^{c} ± 0.05	8.03^{a}±0.06	7.92^{b} ± 0.13	6.50 – 8.50
Chloride (mg L^{-1})	229.50^{a} ± 6.02	86.9^{d} ± 1.03	107.3^{b} ±2.01	86.7^{c} ± 2.07	250.00
Hardness (mg L^{-1})	214^{a} ± 4.05	86.0^{d} ± 3.06	128.0^{b} ± 2.13	106^{c} ± 2.05	100 – 500.00
Sulphate (mg L^{-1})	169.31^{a} ± 5.16	21.64^{d} ± 0.03	134.52^{b} ± 2.03	112.63^{c} ±3.14	250.00
Nitrate (mg L^{-1})	16.52^{a} ± 1.03	4.38^{d} ± 0.01	7.12^{b} ± 1.03	5.16^{c} ± 1.06	50.00
Total Suspended Solids (mg L^{-1})	532.5^{a} ± 2.14	241.7^{d} ± 0.51	433.4^{b} ± 5.18	408.3^{c} ± 3.06	5 – 35.00
Total Dissolve Solids (mg L^{-1})	308.8^{a} ± 7.21	143.2^{d} ± 4.06	162.7^{b} ± 8.14	116.6^{c} ± 2.07	600.00
Total Solids (mg L^{-1})	897.8^{a} ± 12.08	384.90^{d} ± 3.15	593.2^{b} ± 4.01	524.9^{c} ± 6.03	1000.00
Calcium Hardness (mg L^{-1})	278.0^{a}±3.17	83.0^{d} ±1.01	198.0^{b} ±1.05	180^{c} ±1.03	50 – 200
Magnesium Hardness (mg L^{-1})	56.0^{a}±2.03	29.00^{d} ± 0.02	50.0^{b} ± 1.13	44.0^{c} ± 0.03	10 – 50.00
Total Acidity (mg L^{-1})	6.8^{a} ± 0.03	4.3^{d} ± 0.02	5.8^{b} ± 0.01	5.6^{c} ± 0.02	50.00
Total Alkalinity (mg L^{-1})	140.0^{b} ± 0.01	98.0^{d} ± 2.06	160.0^{b} ± 0.13	160^{b} ± 3.15	20-200
DO (mg L^{-1})	3.2^{c} ± 0.01	6.8^{a} ± 0.03	3.8^{b} ± 0.01	3.8^{b} ± 0.01	4 – 8
BOD (mg L^{-1})	2.0^{c} ± 0.00	5.4^{a} ± 0.06	2.6^{b} ± 0.02	2.6^{b} ± 0.01	5.00
COD (mg L^{-1})	43.6^{d} ± 0.05	62.4^{a} ± 1.04	48.3^{c} ± 3.02	51.2^{b} ± 1.13	100
Oil and Grease (mg L^{-1})	58.63^{a} ± 0.21	32.72^{d} ±0.06	5.142^{c} ±2.08	53.27^{b} ± 0.06	0.1
Ammonia (mg L^{-1})	16.71^{a} ± 0.13	1.06^{d} ± 0.01	10.31^{b} ±0.01	10.68^{b} ± 0.03	1.5

Table 5: Physicochemical Properties of Detergent Industrial Wastewater and the Receiving River Water Samples after Treatment

Physical Parameters	Main point	Upstream	Down Stream 1	Down Stream 2	WHO (2022)
Colour	Colourless	Colourless	Colourless	Colourless	15.00 TCU
Odour	Pleasant	Pleasant	Pleasant	Pleasant	3.00 TON
Taste	ND	ND	ND	ND	

Temperature (ºC)	25.2 [a] ± 0.01	25.6 [a] ± 0.01	25.2 [b] ± 0.00	25.3 [a b] ± 0.01	25 – 30
Turbidity	56.3 [a] ± 3.05	2.16 [d] ± 0.02	37.02± 0.03	28.3 [c] ± 0.00	5 – 50.00 NTU
Conductivity (µmhos cm^{-1})	178 [a] ± 1.03	137 [d] ± 2.15	142 ± 1.13	126 [c] ± 0.03	150 – 1500.00
CHEMICAL PARAMETERS					
pH	7.72 [a]±0.08	6.98 [d] ±0.01	7.62 [c] ±0.01	7.76 [b] ±0.06	6.50 – 8.50
Chloride (mg L^{-1})	139.54 [a] ± 3.16	65.2 [d] ± 0.03	92.63 [b] ± 1.03	87.03 [c] ±0.00	250.00
Hardness (mg L^{-1})	92.0 [a] ± 0.09	52.0 [d] ± 0.05	86.0 [b] ± 0.02	78.0 [c] ± 0.07	100-500.00
Sulphate (mg L^{-1})	106.73[a] ± 0.02	16.48 [d] ± 0.01	87.43 [b] ± 0.01	63.27 [c] ± 0.05	250.00
Nitrate (mg L^{-1})	8.48 [a]±0.03	3.24 [d] ± 0.00	6.86 [b] ± 0.01	5.42 [c] ± 0.00	50.00
Total Suspended Solids (mg L^{-1})	142.32 [a] ± 6.02	84.46 [d] ± 1.03	120.51 [b] ± 0.05	106.61 [c] ± 1.06	5 – 35.00
Total Dissolve Solids (mg L^{-1})	86.41 [a] ± 2.15	52.31 [d] ±0.21	86.42 [b] ±0.06	74.56 [c] ± 0.13	600.00
Total Solids (mg L^{-1})	248.73 [a] ± 3.14	136.32 [d] ±2.03	206.88 [b] ±0.09	183.18 [c] ± 0.14	1000.00
Calcium Hardness (mg L^{-1})	134 [a] ± 0.03	34.0 [d] ±0.05	83 [b] ±0.03	76 [c] ± 0.00	50 – 200
Magnesium Hardness (mg L^{-1})	48.0 [a] ± 0.01	18.0 [d] ± 0.01	49.0 [b] ± 0.01	32.0 [c] ± 0.01	10 – 50.00
Total Acidity (mg L^{-1})	8.62 [a]± 0.01	3.4 [d] ± 0.02	6.4 [c] ± 0.02	6.8 [b] ± 0.00	50.00
Total Alkalinity (mg L^{-1})	260.0 [a] ± 1.04	82.0 [d] ± 0.01	180.0 [b] ±0.02	160 [c] ± 0.02	20 – 200
DO (mg L^{-1})	5.4 [c] ±0.03	6.8 [a]±0.00	6.9 [a]±0.01	6.2 [b] ±0.03	4 – 8
BOD (mg L^{-1})	3.2 [c] ± 0.01	4.6 [a] ± 0.00	4.6±0.01	4.6 ± 0.01	5.00
COD (mg L^{-1})	64.36 [c] ±0.05	132.4[a] ± 0.13	87.6 [b] ±1.04	89.3 [b] ± 0.05	100
Oil and Grease (mg L^{-1})	10.54 [a]± 0.02	3.41 [d] ± 0.01	8.56 [b] ± 0.02	8.17 [b] ± 0.02	0.1
Ammonia (mg L^{-1})	11.13 [a]± 0.02	2.09 [d] ± 0.01	6.26 [b] ± 0.01	5.64 [c] ± 0.01	1.5

Table 6: Physicochemical Properties of Dairy Industrial Wastewater and the Receiving River Water Samples after Treatment

Physical Parameters	Main point	Upstream	Downstream 1	Downstream 2	WHO [21]
Colour	Clear	Clear	Clear	Clear	15.00 TCU
Odour	Irritating	Pleasant	Unpleasant	Unpleasant	3.00 TON
Taste	ND	ND	ND	ND	
Temperature (ºC)	25.4 [c] ± 0.00	25.3 [b] ± 0.01	25.6 [a] ± 0.01	25.3 [b] ± 0.01	25 – 30
Turbidity	26.2 [a] ± 0.01	4.7 [d] ± 0.01	17.7 [b] ± 0.02	9.7 [c] ± 0.02	5 – 50.00

					NTU
Conductivity (μmhos cm^{-1})	1128 ^{a} ± 11.03	214 ^{d} ± 0.06	1072 ^{b} ± 12.08	954 ^{c} ± 7.07	150 – 1500.00
CHEMICAL PARAMETERS					
pH	6.87^{c} ± 0.03	6.98 ^{d} ± 0.01	6.21 ^{b} ± 0.02	6.27 ^{b} ± 0.00	6.50 – 8.50
Chloride (mg L^{-1})	142.46^{a} ± 0.03	56.24 ±0.03	116.28 ^{b} ± 0.05	97.28 ^{c} ± 0.02	250.00
Hardness (mg L^{-1})	292.0 ^{a} ± 0.01	108.0 ^{d} ± 0.02	258.0 ^{b} ± 0.33	214.0 ^{c} ± 0.31	100 – 500.00
Sulphate (mg L^{-1})	86.46 ^{a} ± 0.06	32.72 ^{d} ±0.01	67.46 ^{b} ± 0.61	52.74 ^{c} ± 0.06	250.00
Nitrate (mg L^{-1})	8.51 ^{a} ± 0.00	3.42 ^{d} ± 0.00	6.73 ^{b} ± 0.13	4.38 ^{c} ± 0.01	50.00
Total Suspended Solids (mg L^{-1})	809.42 ^{a} ± 13.46	240.67 ^{d} ±0.03	562.43 ^{b} ± 6.08	356.25 ^{c} ± 6.07	5 – 35.00
Total Dissolved Solids (mg L^{-1})	122.09 ^{a} ± 4.13	51.42 ^{d} ± 0.02	130.68 ^{b} ± 3.01	110.47 ^{c} ± 1.06	600.00
Total Solids (mg L^{-1})	931.54^{a} ± 10.46	291.09 ^{d} ± 0.06	692.11 ^{b} ± 0.03	466.72 ^{c} ± 8.13	1000.00
Calcium Hardness (mg L^{-1})	198 ^{a} ± 0.00	79.0 ^{d} ± 0.01	168 ^{b} ± 0.21	142.0 ^{c} ± 2.07	50 – 200
Magnesium Hardness (mg L^{-1})	94.0 ^{a} ± 0.01	29.0 ^{d} ± 0.00	90.0 ^{b} ± 0.13	72.0 ^{c} ± 0.02	10 – 50.00
Total Acidity (mg L^{-1})	9.7^{a} ± 0.02	5.3 ^{d} ± 0.02	8.6 ^{b} ± 0.01	7.2 ^{c} ± 0.01	50.00
Total Alkalinity (mg L^{-1})	180.0^{a}± 0.02	86.0 ^{d} ± 0.01	140.0 ^{b} ± 0.00	120 ^{c} ± 0.00	20 – 200
DO (mg L^{-1})	3.6 ^{c} ± 0.00	7.6 ^{a}± 0.00	4.8 ^{b} ± 0.02	4.8 ^{b} ± 0.01	4 – 8
BOD (mg L^{-1})	2.4 ^{c} ± 0.01	5.9 ^{a}± 0.01	3.2 ^{b} ± 0.00	3.2 ^{b} ± 0.00	5.00
COD (mg L^{-1})	64.3 ^{b} ±0.03	86.2 ^{a}± 0.03	52.7 ^{c} ± 0.14	47.2 ^{d} ± 0.01	100
Oil and Grease (mg L^{-1})	86.36 ^{a} ± 0.13	13.63 ^{d} ± 0.00	62.38 ^{b} ±0.33	54.47 ^{c} ± 0.02	0.1
Ammonia (mg L^{-1})	24.62 ^{a} ± 0.01	3.21 ^{d} ± 0.01	17.63 ^{b} ± 0.02	13.38 ^{c} ± 0.01	1.5

The chloride values obtained from abattoir after treatment noticeably reduced compared to the result gotten before the treatments. The results ranged from 86.90 to 129.50 mg L^{-1} for all the samples. The values obtained are within the permissible limit of 250 mg L^{-1} sets by the WHO [21]. Similar results were gotten for the water samples from detergent and dairy industries.

Hardness values obtained in all samples from abattoir water reduced in the order of 86.00 < 106.00 < 128.00 < 214.00 mg L^{-1} for upstream, downstream 2, downstream 1 and wastewater, respectively. The values lie within the permissible limits of 100 – 500 mg L^{-1} of the WHO [21]. In all the samples analysed, significant improvements were achieved when compared with the initial results before water treatments. Similar results were equally obtained for the water samples from detergent and dairy industries.

The sulphate concentrations in the abattoir samples reduced in values in the order of 169.31 > 134.52 > 112.63 > 21.64 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. Significant decreases in sulphates' levels were observed when compared to the samples before treatments. The values obtained lie within the permissible limit of WHO (250 mg L^{-1}) [21]. Water samples from detergent and dairy industries equally followed the same trends.

The amounts of nitrates in the abattoir water samples reduced significantly in values in the order of 16.52 > 7.12 > 5.16 > 4.38 mg L^{-1} for Wastewater, downstream 1, downstream 2 and upstream, respectively. The concentrations of all nitrates obtained are below the WHO permissible limit of 50 mg L^{-1} [21]. Several researchers have reported that high values of nitrates in water could cause excessive development of some aquatic plants and algae [26]. Similar results were equally obtained for detergent and dairy industrial water samples.

The values of TSS in abattoir water samples after treatment were reduced, and are 532.50, 433.40, 408.30 and 241.70 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. The results obtained are still above WHO permissible limits of 5 – 35 mg L^{-1} after treatment but had a significant decrease in all samples compared to the results before treatment. The results obtained for detergent and dairy industries water samples are similar to the results of abattoir water samples after treatment.

The TDS results obtained after water treatment reduced in values in the order of 308.80 > 162.70 > 143.20 > 116.60 mg L^{-1} for wastewater, downstream 1, upstream, and downstream 2, respectively. The wastewater sample has the highest TDS value as observed in the initial results of the samples before treatments. All samples after treatment showed significant decrease in values, specifically the wastewater, downstreams 1 and 2 samples. All the values lie within the permissible limit sets by the WHO (600 mg L^{-1}) [21]. Similar results were obtained for the water samples from detergent and dairy industries.

The TS values of abattoir water samples for all the samples, after treatment, reduced in values and lie within WHO permissible limit of 1000 mg L^{-1} [21]. The values obtained are 897.80, 593.20, 524.90 and 384.90 mg L^{-1} for wastewater, downstream 1, downstream 2 and upstream, respectively. Significant decreases in values are observed compared to the samples before treatment. Similar results were recorded for water samples from detergent and dairy industries.

CONCLUSION

This study assessed the physicochemical characteristics of wastewater samples from abattoir, dairy and detergent industries as well as water samples from the wastewater receiving rivers in Ibadan metropolis, Nigeria. Silver nanoparticles (AgNPs) were synthesised and used for the treatment of the contaminated water samples. The physicochemical characteristics of water samples before treatment and after treatment with AgNPs were compared. The results obtained revealed that most of the values of the physicochemical parameters of the water samples (before treatment) were above the WHO threshold limits; especially all the industrial wastewater samples whereas these values decreased considerably as the water bodies flowed. The most contaminated wastewater was the abattoir, followed by dairy, and then detergent (the least contaminated) effluents. These results corroborate previous studies on Nigerian industrial effluents. After the treatment of water samples with the adsorbent (AgNPs), the values of the physicochemical properties of treated water samples reduced significantly; some of these values are within WHO limits. The study showed that AgNPs are potential adsorptive materials for the treatment of industrial effluents and polluted water. Future research should explore seasonal variations and long-term physicochemical trends of water supplies in Ibadan.

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