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# Synthesis and Characterization of Zinc Oxide Nanoparticle for the Adsorptive Remediation of Petrochemical Effluents

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**ABSTRACT:** The zinc oxide nanoparticle was synthesized via precipitation method. It was characterized using SEM-EDX, FTIR and TEM for morphology, elemental, functional groups and internal structure respectively. The physicochemical behaviour of a refinery effluent was assessed. The untreated raw refinery effluent from the point of discharge contained very high concentrations of pollutants for all the parameters, ranging between, pH (6.52-6.82), Turbidity (10-12 NTU), conductivity (266-289µs/cm), COD (116-138 mg/l), BOD (14-18.5 mg/l), DO (7.5-15.6 mg/l), TDS (436-486 mg/l), TSS (127-133 mg/l), Oil and grease (14.8-16.3 mg/l), sulphate (113-125 mg/l) and chloride (240-280 mg/l). The effluent was treated with ZnO nanoparticle and reduced the pollutants to the normal permissible limit set by WHO, FEPA and NESREA standard for portable water. The treated effluent sample showed values ranging between, pH (6.55-6.6), Turbidity (4.2-4.5 NTU), conductivity (245-246 µs/cm), COD (39-40 mg/l), BOD (10 mg/l), DO (5.6-10.4 mg/l), TDS (151-183 mg/l), TSS (24-28 mg/l), Oil and grease (7.3-9.5 mg/l), sulphate (100 mg/l) and chloride (200 mg/l). The heavy metals profile that was investigated are Fe, Cu, Zn, Pb, Cd and Cr of which were found above the WHO and FEPA permissible limit, however, on the contact with the adsorbent therefore reduced the metals to the permissible limit. It can be ascertain that ZnO nanoparticle can be used as an effective adsorbent for the treatment of petrochemical effluent.

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**Keywords***:* physicochemical parameters, petrochemical effluent, ZnO, remediation.

Wastewaters released by crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals (Otokunefor and Obiukwu, 2005). Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous; leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al.,* 2001 and 2003). Various studies have shown positive correlation between pollutions from refineryeffluents and the health of aquatic organisms. Previous observations suggested a correlation between contamination of water and sediments with aromatic hydrocarbons from refinery effluents, and compromised fish health (Kuehn *et al.,* 1995). An earlier study by (Onwumere and Oladimeji, 1990) demonstrated the accumulation of heavy metals with accompanying histopathology in *Oreochromis niloticus* exposed to treated petroleum refinery effluent from the Nigerian National Petroleum Corporation, Kaduna. The waste water released from the refineries are characterized by the presence of large quantity of crude oil products, polycyclic and aromatic hydrocarbon, phenols, metal derivatives, surface active substances, sulfides, naphthalene acids and other chemicals (Otokunefor and Obiukwu, 2005). As a result of ineffectiveness of purification systems, wastewater may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al*, 2003; Aghalino and Eyinla,

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2009). Drinking contaminated water can cause various diseases such as typhoid fever, dysentery, cholera and other intestinal diseases (Adeyemi, 2004). According to Gore (1993), human beings are made up of water, in roughly the same percentage as water in the surface of the earth. Our tissues and membranes, brains, and hearts, our sweat and tears, all reflect the same recipe for life. Water is essential for the development and maintenance of the dynamics of every ramification of the society (United Nations Development Program, 2006).Water is indeed life and thus is the most important natural resource, without which life would be non-existent. Availability of safe and reliable source of water is an essential prerequisite for sustained development (Asonye *et al.*, 2007). Oil prospecting in Nigeria has brought with it untold hardship to the environment. Dwellers of oil producing areas generally suffer from scarcity of farm lands as their lands have been made unproductive due to constant oil spillages and waste dump. One of the most visible consequences of numerous oil spills had been the loss of mangrove trees. The mangrove was a source of both fuels for the indigenous people and a habitat for the area's biodiversity, but it is now unable to be sourced due to the oil toxicity of its habitat. Oil spills pose serious health risks to people when they consume contaminated seafoods (Bogardy, 2004; Onuoha, 2007). From several literatures search, it was revealed that no research work has reported the physico-chemical characterization and adsorption of physicochemical parameters using synthesized zinc oxide nanoparticle. Hence, the aim of this paper is to assess the physicochemical properties of petrochemical effluent and adsorptive nanoremediation of the effluent using zinc oxide nanoparticle.

## MATERIALS AND METHODS

*Synthesis of zinc oxide nanoparticle*: Zinc oxide nanoparticle was synthesized in accordance with the reported method by Awodugba and Abdul-mojeed, (2013). Solution of zinc acetate dihydrate was prepared by dissolving 3 g of the salt in 100 ml deionized water and kept under stirring till the salt totally dissolved. Solution of sodium hydroxide was prepared by dissolving 6 g of the pellet in 100 ml of deionized water and kept under stirring till the salt totally dissolved. The solution of sodium hydroxide was added to the solution of zinc acetate dihydrate in drop wise. The precipitate was obtained and the pH of the resultant mixture was adjusted to 11 using 0.1M of HCl acid and NaOH. The solution was filtered using nano-filtered machine. The precipitate obtained was washed for three times using ethanol and oven dried at 80 °C for 6 hours. The equation of the reaction is shown below;

$$\mathrm{Zn(CH_3COO)_2 . 2H_2O + 2NaOH \rightarrow Zn(OH)_2 + 2CH_3COONa.H_2O}$$

$$\mathrm{Zn(OH)_2 \rightarrow ZnO + H_2O}$$

After the completion of the synthesized ZnO nanoparticle, it was characterized using Fourier Transform Infra-red Microscopy (FTIR) on Perkin Elmer Spectrum 100 FTIR spectrometer at wave numbers 4000-400 $cm^{-1}$, scanning electron microscopy (SEM) was done using LEO 1450 Scanning Electron Microscope (Tungsten filament, EHT 20.00kV) and Transmission Electron MicroscopeJEOL JEM 1400 model for (TEM).

*Sampling of Petrochemical Effluent*: The sampling of the petrochemical effluent was done according to the method reported by (Otokunefor and Obiukwu, 2005). The sample was collected once a month between June 2018 and February 2019. The effluent was collected at the point of discharge with a 2 litre plastic hydrobios water sampler and transferred to clean 2 litre polyethylene containers. The samples were transported inice chests and analyzed for pH, temperature and conductivity within an hour of collection. Other physicochemical parameters were analyzed later using refrigerated samples.

*Physicochemical Analysis Procedure*: An HACH conductivity/TDS meter (Loveland, CO 80539) was used for conductivity, mercury thermometer (0-110ºC) for temperature, An HACH pH meter and turbid meter was used for pH and turbidity determination. Dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solid (TS), total dissolved solid (TDS) and total suspended solid (TSS) were determined using the method reported by Amigun *et al.,* (2018).

*Heavy Metals Analysis*: About 100 ml of the effluent were digested using 10 ml triple acid mixture (5:1:1 - $HNO_3$:$HClO_4$:$H_2SO_4$) in a 250 ml conical flask placed in a fume cupboard and heated on a hot plate until the solution was reduced to 10 ml. Thereafter, it was allowed to cool and make up to a mark with distilled water, it was then filtered into a 50 ml standard flask labeled and made ready for further analysis (Amigun *et al.*, 2018). The concentrations of the heavy metals in the wastewater were determined using Atomic Absorption Spectrometer (Perkin, 210 VGP model).

*Adsorption procedure for physicochemical and heavy metals*: This was carried out using the method reported by Jimoh *et al.* (2013) with slight modifications. A 25 ml of petroleum effluent was measured in to 100 ml conical flask, about 0.1 g of the zinc oxide nanoparticle was added and shaken in a flask shaker machine for about 3 hours, the sample was filtered and filtrate was analyzed for physicochemical parameters. In the case of heavy metals, about 25 ml was taken from the already digested sample, about 0.1 g of the adsorbent was added, agitated on a flask shaker for 3 hours and the filtrate was analyzed using Atomic Absorption Spectrophotometer.

## RESULT AND DISCUSSION

*Spectroscopic Characterization of Zinc oxide Nanoparticle: Scanning Electron Microscopy-Electron Dispersive Spectroscopy (SEM-EDX)*: The morphology of the synthesized ZnO nanoparticle was investigated by scanning electron microscopy (SEM), as shown in Fig. 1. The SEM photograph shows that the powder was porous with spherical shape and smooth surfaces, homogenous and agglomerated.

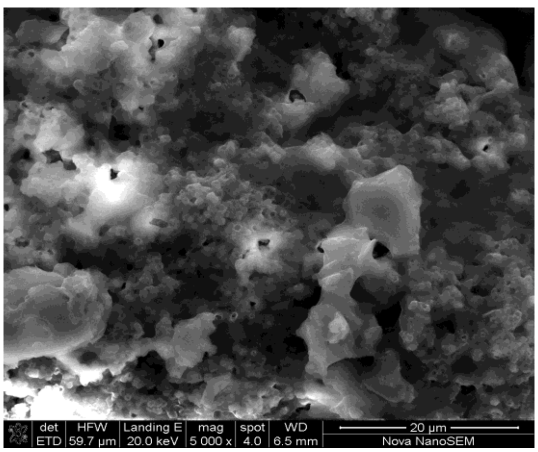


**Fig. 1**: SEM image of ZnO nanoparticle

The Fig. 2 shows the EDX spectrum of ZnO nanoparticle. EDX spectrum shows predominant peaks which are identified as zinc and oxygen (Table 1). Hence, it has been shown that pure ZnO nanoparticles in this study can be prepared by precipitation method. The present result is in line with reported ZnO nanoparticle prepared by Swatil and Raut, (2012).

*Transmission Electron Microscopy*: Physical characterization of nanoparticles is commonly characterized using transmission electron microscope (TEM). The shape, pattern and actual particle size was obtained which is normally explained by TEM. ZnO synthesized from the present study showed a homogenous shape that seem to be near hexagonal or nanosphere at 50 nm (Fig. 3).

*Fourier Transform Infrared Spectroscopy (FTIR):* FTIR spectrum studies shown in fig. 4 gives information regarding the chemical bonding between Zn and O. The spectrum showed a broad peak around 3454.87 $cm^{-1}$ corresponding to O-H stretching, the peak at 1636.82 $cm^{-1}$ corresponding to C=O while the peak at 452.61 $cm^{-1}$ corresponding to Zn-O bend. The FTIR results support the synthesized ZnO nanoparticle.

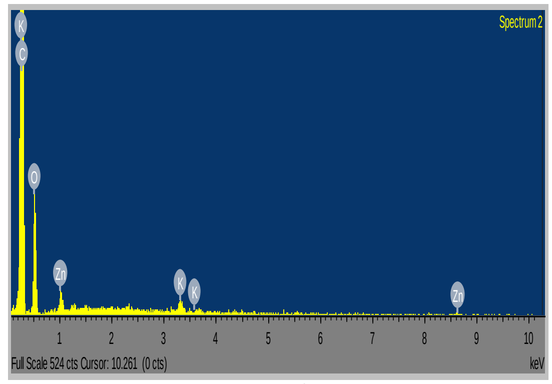


**Fig. 2:** EDX spectrum of ZnO nanoparticle

**Table 1:** EDX weight % of elements present in ZnO nanoparticle

| S/N | Elements | Weight (%) |
|---|---|---|
| 1 | Zinc | 71.91 |
| 2 | Oxygen | 20.85 |
| 3 | Carbon | 4.2 |
| 4 | Potassium | 3.04 |

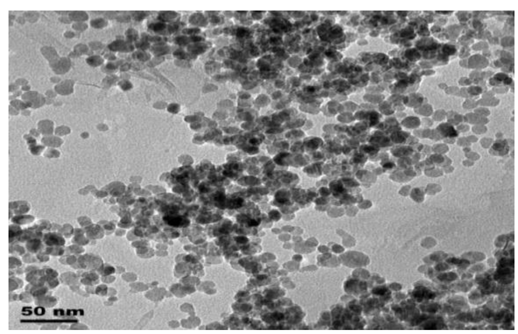


**Fig. 3:** TEM image of ZnO nanoparticle

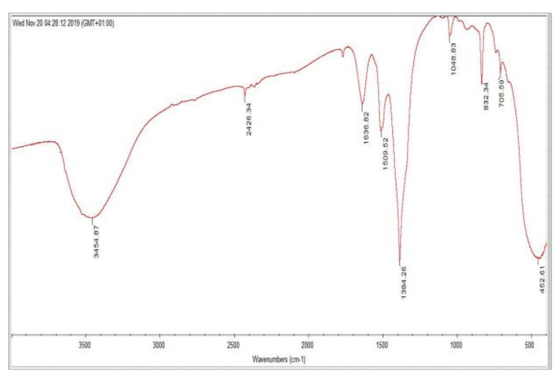


**Fig. 4:** FTIR spectrum of ZnO nanoparticle

*Physicochemical Analysis of Petrochemical Effluent Result:* The experimental data on physicochemical properties of water samples collected from Kaduna petroleum refinery industry is presented in Tables 2 and 3.

**Table 2:** The mean±SD concentration of physicochemical characteristics of petrochemical effluent before and after adsorption process (dry season) and comparison with standard permissible limit

| Physicochemical parameters | Raw value before adsorption | Raw value after adsorption | Standard limits (WHO) | Standard limits (FEPA) | Standard limits (NESREA) |
|---|---|---|---|---|---|
| pH | 6.82±0.001 | 6.6±0.001 | 6.5-8.5 | 6.5-8.5 | 6-9 |
| Temperature ($^0$C) | 35±0.1 | 30±0.1 | 30 | 30 | 40 |
| Turbidity (NTU) | 12±1.3 | 4.2±0.6 | 5 | 5 | 10 |
| Conductivity (µs/cm) | 289±0.19 | 245±0.19 | 250 | 240 | NS |
| COD (mg/l) | 138±0.11 | 40±0.11 | 40 | 40 | 40 |
| BOD (mg/l) | 18.5±0.8 | 10.3±0.8 | 10 | 10 | 50 |
| DO (mg/l) | 15.6±0.5 | 10.4±0.2 | 10 | 10 | 5 |
| TDS (mg/l) | 486±2.26 | 183±2.26 | 250 | 200 | NS |
| TSS (mg/l) | 133±5.34 | 28±5.16 | 30 | 30 | NS |
| Oil and grease (mg/l) | 16.3±1.42 | 7.3±1.93 | 10 | 10 | 10 |
| Nitrates (mg/l) | 0.46±0.01 | 0.19±0.01 | 50 | 44 | 20 |
| Sulphates (mg/l) | 125±1.23 | 100±0.82 | 100 | NS | NS |
| Chlorides (mg/l) | 280±4.10 | 197±4.10 | 200 | NS | NS |

**Table 3:** The mean±SD concentration of physicochemical characteristics of petrochemical effluent before and after adsorption process (rainy season) and comparison with standard permissible limit

| Physicochemical parameters | Raw value before adsorption | Raw value after adsorption | Standard limits (WHO) | Standard limits (FEPA) | Standard limits (NESREA) |
|---|---|---|---|---|---|
| pH | 6.52±0.011 | 6.55±0.011 | 6.5-8.5 | 6.5-8.5 | 6-9 |
| Temperature ($^0$C) | 32±0.1 | 30±0.1 | 30 | 30 | 40 |
| Turbidity (NTU) | 10±1.12 | 4.5±0.1 | 5 | 5 | 10 |
| Conductivity (µs/cm) | 266±0.13 | 246±0.19 | 250 | 240 | NS |
| COD (mg/l) | 116±0.02 | 39±0.11 | 40 | 40 | 40 |
| BOD (mg/l) | 14±0.2 | 10±0.1 | 10 | 10 | 50 |
| DO (mg/l) | 7.5±0.5 | 5.6±0.2 | 10 | 10 | 5 |
| TDS (mg/l) | 436±2.35 | 151±1.112 | 250 | 200 | NS |
| TSS (mg/l) | 127±4.31 | 24±5.05 | 30 | 30 | NS |
| Oil and grease (mg/l) | 14.8±1.32 | 9.5±1.92 | 10 | 10 | 10 |
| Nitrates (mg/l) | 1.83±0.01 | 1.19±0.01 | 50 | 44 | 20 |
| Sulphates (mg/l) | 113±2.23 | 100±0.41 | 100 | NS | NS |
| Chlorides (mg/l) | 240±2.21 | 194±6.11 | 200 | NS | NS |

NB: WHO= World Health Organization, NESREA= National Environmental Standards Regulatory and Enforcement Agency, FEPA=Federal Environmental Protection Agency, NS= Not specify. The analysis are conducted in triplicate and the results were expressed as mean± standard deviation

The physicochemical parameters of the effluents investigated during dry and raining seasons before and after adsorption are presented in Table 2 and 3. The pH values of these industrial effluents range from 6.52 to 6.82 before adsorption and 6.55 to 6.6 after adsorption, which are within permissible limit of portable water (FEPA, 1991 and WHO, 1983). The pH value is an important index of acidity or alkalinity and the concentration of hydrogen ion in ground water. It has also beenreported that the toxicity of heavy metals in water also acquired at particular pH, which is crucialsignificance in deciding the quality of waste water effluent (Amigun*et al.*, 2018).

Igwemmar *et al.* (2013) reported that biochemical reactions of aquatic organisms are temperature dependent. Increase in temperature of water body will promote chemical reactions in the water. Effects, such as bad odour and taste will result due to non solubility of gases such as oxygen. The temperatures obtained were between 32 to 35$^o$C which are above the permissible limit of WHO and FEPA, but within the permissible limit of NESREA. After adsorption, the temperature fell within the permissible limit of WHO (30$^o$C). The higher temperature obtained from the raining season might be due to the climatic condition, because temperature values are known to be dependent on the climatic condition at a particular geographical area and period.Turbidity is due to the presence of colloidal particles arising from clay and silt during rainfall, or from discharges of sewage and industrial wastes. The turbidity of the petroleum effluent obtained was between 10 to 12 (NTU) which are above permissible limit of WHO and FEPA, but after adsorption, the turbidity of the samples were ranged from 4.2 to 4.5, which are within the permissible limit of portable water.Conductivity measures the ionic content of the water and it is linked directly to total dissolved solids. The conductivity of the samples ranged between (266 – 289 µs/cm) which is above the permissible limit of WHO and FEPA and it can be attributed to due to high dissolved inorganic minerals. After adsorption process the conductivity obtained was between (245-246 µs/cm) which is within the permissible limit of portable water.The Chemical Oxygen Demand (COD) determination is a measure of the oxygen corresponding to the portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant (Amigun *et al.,* 2018). COD is one of the common measures of organic pollutant material in water. Its function is similar to BOD; they both measure the amount of organic compounds in water. The COD values obtained were between 116 to 138 mg/l which is above the permissible limit of WHO, FEPA and NESREA. After the adsorption process, the value fell within the permissible limit of 39 to 40 mg/l. The biological oxygen demand (BOD) is the rate of removal of oxygen by microorganisms in aerobic degradation of the dissolved organic matter in water over a 5-days period.

Its function is similar to COD; they both measure the amount of organic compounds in water. BOD values obtained were between 14 to 18.5 mg/l which is above the permissible limit. After adsorption, BOD of 10 mg/l was obtained which is within the permissible limit of WHO and FEPA.The dissolved oxygen concentrations (DO) obtained were (7.5-15.6 mg/L) which is higher than the treated DO after adsorption (5.6-10.4 mg/L), these treated values are within the permissible limit of WHO and FEPA. The lower value of treated effluent could be attributed to the presence of degradable organic matter by aerobic microbes. Uzoekwe and Oghosanine (2011) also reported that, it may be partly due to the displacement of dissolved oxygen by dissolved solids within the effluent. Total dissolved solids (TDS) content in water is a measure of salinity in the water body. A large number of salts are found dissolved in natural waters, the common ones are chlorides, carbonates, sulphates, and nitrates of calcium, magnesium, sodium and manganese. Water can be classified based on the concentration of TDS (Wilcox 1995), desirable for drinking (up to 500 mg/l), permissible for drinking (up to 1000 mg/l), useful for irrigation (up to 2000 mg/l), not useful for drinking and irrigation (above 3000 mg/l). In the present study, the wastewater has TDS value of 436 to 486 mg/l. Based on the above classification, it was observed that industrial wastewater effluents is above the permissible limit of WHO, FEPA and NESREA.

The value obtained after treatment with nanoparticle adsorbent is 151 to 183 mg/l which is within the permissible limit. Total suspended solids (TSS) are the dry weight of suspended particles that are not dissolved in a sample of water. The values obtained for TSS before adsorption was 127 to 133 mg/l, which is higher than the permissible limit. After the treatment of the effluent with ZnO nanoparticle, the value fell within the permissible limit of 24-28 mg/l. In the present investigation, the average oil and grease content varies between (14.8 -16.3 mg/l), which is above the WHO permissible limit of (10 mg/l). The concentration fell between (7.3 – 9.5 mg/l) which is moderately between the permissible limit. It is essential to note that oil which forms a surface film on the river can coat plants and animals reducing oxygenation from the atmosphere.

The film of oil that floats over the water body affects the transmission of light through the water body there by disturbing the process of photosynthesis in the aquatic plants (Lokhande *et al.,* 2011). Sulphates cause water hardening and therefore high levels are not recommended. The presence of $Na_2SO_4$ and $MgSO_4$ in drinking water beyond the prescribed limit may cause cathartic action. Sulphate may undergo transformations to hydrogen sulphide depending largely upon the redox potential of water. This is also an important anion imparting hardness to the water. The $SO_4$ ion concentration in the present studied water sample was found between 113 to 125 mg/l, which exceeds the WHO permissible limit. After treatment the value fell within the permissible limit of 100 mg/l.

**Table 4:** The mean±SD concentration of heavy metals of petrochemical effluent before and after adsorption process (dry season) and comparison with standard permissible limit

| Physicochemical parameters | Raw value before adsorption | Raw value after adsorption | Standard limits (WHO) | Standard limits (FEPA) | Standard limits (NESREA) |
|---|---|---|---|---|---|
| Iron (Fe) | 1.270±0.1 | 0.99±0.11 | 20 | 20 | 1 |
| Copper (Cu) | 0.841±0.12 | 0.32±0.14 | 1.0 | 2.0 | 1 |
| Zinc (Zn) | 0.482±0.25 | 0.281±0.12 | 1.0 | 1.0 | <1 |
| Lead (Pb) | 0.386±0.2 | 0.013±0.01 | 0.01 | 0.001 | <1 |
| Cadmium (Cd) | 0.233±0.1 | 0.0014±0.01 | 0.003 | 0.005 | <1 |
| Chromium (Cr) | 0.310±0.5 | 0.08±0.01 | 0.1 | 0.05 | <1 |

**Table 5**: The mean±SD concentration of heavy metals of petrochemical effluent before and after adsorption process (rainy season) and comparison with standard permissible limit

| Physicochemical parameters | Raw value before adsorption | Raw value after adsorption | Standard limits (WHO) | Standard limits (FEPA) | Standard limits (NESREA) |
|---|---|---|---|---|---|
| Iron (Fe) | 1.120±0.1 | 0.28±0.11 | 20 | 20 | 1 |
| Copper (Cu) | 0.321±0.12 | 0.220±0.14 | 1.0 | 2.0 | 1 |
| Zinc (Zn) | 0.589±0.25 | 0.151±0.12 | 1.0 | 1.0 | <1 |
| Lead (Pb) | 0.213±0.2 | 0.001±0.01 | 0.01 | 0.001 | <1 |
| Cadmium (Cd) | 0.131±0.1 | 0.011±0.01 | 0.003 | 0.005 | <1 |
| Chromium (Cr) | 0.240±0.5 | 0.031±0.01 | 0.1 | 0.05 | <1 |

*NB: WHO= World Health Organization, NESREA= National Environmental Standards Regulatory and Enforcement Agency, FEPA=Federal Environmental Protection Agency, NS= Not specify. The analysis are conducted in triplicate and the results were expressed as mean± standard deviation*

The presence of chloride in natural water can be attributed to the salt deposits, discharge of effluents from chemical industries, sewage discharges etc. Each of these sources may cause the local contamination of both surface and ground water. Chloride content in the petrochemical effluent studied was found between 240 to 280 mg/l. This level of chloride content is above the permissible limit of WHO standards (200 mg/l). After adsorption process the values fell within the acceptable limit set by WHO.

*Heavy metals analysis results:* The experimental data on heavy metal analysis of water samples collected from Kaduna petroleum refinery is presented in Tables 4 and 5.

Heavy metal concentration in raw untreated petrochemical effluent samples was experimented to range from 0.213 to 1.270 mg/l, with most of these metals above the permissible limit such as Pb, Cd and Cr. However, Fe, Cu and Zn were found to be within the permissible limit by WHO and FEPA. After adsorption using ZnO nanoparticle, all the effluent samples fell within the permissible limit of WHO, FEPA and NESREA, ranging from 0.001 to 0.99 mg/l.

*Conclusion:*The results obtained in this research shows that most of the parameters are not within the standard specifications. Such effluent should not be discharged into the nearby water body or soil without treatment. They are unfit for irrigation and probably consumption. The high level pollution of the industrial effluents causes environmental problems which will affect plant, animal and human life.

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