

Potential of Zinc Oxide Nanoparticles for Remediation of Oil-Contaminated Soil and Water

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Abstract

Long-term impact of oil spills on the environment and on the health and livelihood of people is one of the biggest concerns around the issue of environment in oil producing regions like the Niger Delta region of Nigeria, which has experienced oil spills for years and years; with years of impact on the environment and the health and livelihood of its inhabitants. In many cases, traditional remediation methods—like chemical oxidation using hydrogen peroxide—aren't effective enough, don't have to be intrusive, and aren't practical in resource-limited areas, where there is a need for simpler, sustainable and effective solutions that are readily available. In this work, the synthesis, characterization and photocatalytic application of zinc oxide (ZnO) nanoparticles for the remediation of oil-contaminated soil and water has been studied. Facile precipitation methodology was used for the synthesis of nanoparticles and its characterization was done by Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet-Visible (UV-Vis) spectroscopy, Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). FTIR spectrum revealed the presence of Zn-O stretching vibration at $\sim 535\text{ cm}^{-1}$ and sharp absorption peak at 367 nm which corresponds to the Band gap energy of 3.38 eV as revealed by the UV-Vis spectroscopy. SEM image showed good dispersion of the nanoparticles (20-50 nm in diameter) and XRD analysis showed hexagonal wurtzite crystal structure. The photocatalytic remediation experiments under UV exposure resulted in the reduction of total petroleum hydrocarbon (TPH) of 85.1% in water samples, and 76.9% in soil samples, much better than that of the conventional hydrogen peroxide treatment (65.0% for water samples and 68.3% for soil samples). The results revealed that the ZnO nanoparticles were very effective, eco-friendly and were also synthetically scalable which was better than the existing chemical oxidation methods. The current technologies have deficiencies in reducing the impact of hydrocarbons in sensitive area impacted by oil pollution, it is a scientific solution that is theoretically sound and practically viable.

Keywords: Zinc oxide nanoparticles, oil contamination, photocatalytic remediation, soil remediation, water treatment, hydrocarbon degradation.

1.0 Introduction

1.1 Background and Problem Statement

Oil spillage and associated contamination are a global issue due to their environmental impact, particularly in countries where oil exploration and extraction is the mainstay of their economy. Nigeria is one of the biggest crude oil producers in Africa and over decades the Niger Delta region has suffered from frequent oil spills that have made farmlands barren, contaminated water sources, and affected livelihoods of the people in these regions [8]. Even years after the spills, the groundwater in Ogoniland was still undrinkable, as reported by the United Nations Environment Programme (UNEP) [14].

Crude oil is made up of a complex mixture of hydrocarbons, such as alkanes, aromatics, resins, and asphaltenes. Of these compounds many are toxic, mutagenic and persistent in the environment [1]. Hydrocarbons that pollute a soil system also alter its physicochemical properties such as its pH, water holding capacity, porosity and affect the indigenous soil microbial community that play a role in the soil's nutrient cycling process [9]. Oil films in aquatic systems reduce oxygen exchange, reduce the penetration of the sun's rays and result in bioaccumulation within the aquatic biota [10].

Conventional technologies for remediation of oil contamination have been used such as bioremediation, soil washing, thermal desorption, and chemical oxidation. Each of these techniques has its own disadvantage. Bioremediation is ecological and is slow but sensitive to temperature, pH and nutrient levels [3]. Significant amount of secondary waste is generated from soil washing and the thermal desorption process is expensive and may lead to soil structure alteration [15]. Chemical oxidation, using a chemical oxidant such as hydrogen peroxide, is not selective and can produce undesirable side products [6]. This has led to researchers looking at novel solutions.

Nanotechnology is a promising technology for the remediation of the environment. Considering unique physicochemical properties of ZnO nanoparticles including high surface area to volume ratio, high photocatalytic activity, chemical stability and moderate toxicity, ZnO has been widely studied among different nanomaterials [13, 11]. ZnO is a wide band gap semiconductor and on the exposure of UV or solar radiation produces reactive oxygen species (ROS) as represented in Figure 1. The hydroxyl radicals and superoxide anions are the reactive

species which can oxidize and degrade complex hydrocarbon molecules to harmless products, such as carbon dioxide and water [4].

Theory indicates that ZnO nanoparticles have great potential to be used as an oil contaminant remediation agent for oil soil and water; however, very few studies have been conducted on the use of these nanoparticles for the remediation of oil spills in sub-Saharan Africa where the majority of oil spills occur and remediation infrastructure is not available [2]. Hence, the study went ahead and studied the potentiality of the ZnO nanoparticles for remediation of oil contaminated soil and water under controlled laboratory experiments. The aims were synthesis and characterization of the ZnO nanoparticles for use in the environment, simulation of oil contamination in both soil and water samples, application of the nanoparticles to the contaminated soil and water samples, monitoring of the degradation of hydrocarbons, a comparison of the remediation efficiency with traditional techniques and an evaluation of environmental consequences.

2.0 Materials and Methods

2.1 Synthesis of ZnO Nanoparticles

The precipitation method was selected as the method for the synthesis of zinc oxide nanoparticles because it was simple, inexpensive and could be employed to produce nanoparticles on a laboratory scale. The zinc precursor used was zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and precipitating agent used was sodium hydroxide, NaOH.

Zinc acetate dihydrate was dissolved in 100 ml of distilled water to prepare a 0.1 M solution of zinc acetate dihydrate which was stirred continuously at 60°C and sodium hydroxide was dissolved in 100 ml of distilled water to prepare a 0.2M solution of sodium hydroxide. A certain amount of NaOH solution was added to the zinc acetate solution, stirring was then done. A white precipitation of zinc hydroxide was immediately formed and this was slowly transformed into zinc oxide nanoparticles by further heating. The reaction was stirred for 2 hrs at 60-70°C. The precipitate was filtered on Whatman filter paper, washed several times with distilled water and ethanol and dried. The washed precipitate was dried in an oven at 80°C for 12 hours then calcined in a muffle furnace at 400°C for 2 hours to get pure ZnO nanoparticles.

2.2 Characterisation Techniques

Shimadzu IRTracer-100 spectrometer was used for Fourier Transform InfraRed Spectroscopy. The KBr pellet method was used, which involved grinding 1-2 mg of ZnO nanopowder with 100 mg of dry KBr powder and then forming it into a transparent KBr pellet. This spectrum was obtained between 4000 cm^{-1} and 600 cm^{-1} .

Shimadzu UV-1800 spectrophotometer was used for the UV-Vis Spectroscopy. The particles of ZnO were dispersed in distilled water and sonicated for 5 minutes. Quarts cuvettes with a path length of 1 cm were used and blank reference distilled water was used.

A field emission scanning electron microscope, Hitachi S-4800, was used for scanning electron microscopy. Dry nanopowder of ZnO was glued with conductive adhesive tape on an aluminium stub and the surface was covered with 5-10 nm of platinum in order to avoid charging up from the surface. The microphotographs were taken from 10,000× to 100,000×.

The X-ray Diffraction analysis was performed on a PANalytical X'Pert Pro diffractometer, where the Cu K α radiation has been used. The dried ZnO nanopowder was placed in a sample holder, a glass tube, and scanned over 2θ range of 20° to 80° with a step size of 0.02° and a scan speed of 2° per minute.

2.3 Preparation of Oil-Contaminated Samples

Samples from uncontaminated soils (far land) were taken at the 0–15 cm depth. Soil was air-dried for 48-hours, sieved through 2 mm mesh to remove soil particles and then contaminated with crude oil (Bonny Light) at 5% w/w concentration. The oil was thoroughly mixed into soil, and left outdoors for natural weathering for 7 days.

Crude oil sample was prepared by mixing distilled water and crude oil at 1% v/v in water samples. The mixture was stirred for 15 – 30 minutes to create a semi-stable oil in water emulsion, and allowed to stabilise for 1 hour before the remediation experiments were begun.

2.4 Remediation Experiments

The water samples for water remediation were contaminated with 500 mL and the ZnO nanoparticles were added to the water samples at 10 mg/L, 30 mg/L and 50 mg/L concentrations. Samples were exposed in the direct sunlight for 6 h and aliquots were collected after 0, 2, 4 and 6 h. Residual concentration of TTHCs was measured by means of UV-Vis absorbance spectroscopy at 272 nm.

The soil remediation was carried out by adding 1%, 3% and 5% (w/w) concentration of ZnO nanoparticles in contaminated soil samples. The treated soils were then placed into a natural light and ambient temperature, then stirred daily and kept at a constant moisture level by adding 10 mL distilled water every 2 days, for a 14 day

incubation period. Subsamples were collected at days 0, 7 and 14 for the gravimetric extraction method of total petroleum hydrocarbon analysis.

To compare, the conventional treatment was done on soil and water samples with 5% hydrogen peroxide solution. The contaminated samples at which no treatment was given were used as controls. The remediation efficiency was determined by applying Equation (1):

$$\text{Efficiency(\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

where C_0 is the initial total petroleum hydrocarbon concentration and C_t is the concentration after treatment time t .

3.0 Results and Discussion

3.1 Characterisation of ZnO Nanoparticles

3.1.1 FTIR Spectroscopy

The FTIR spectrum of the synthesised nanoparticles of ZnO is presented in the Figure 2. A strong absorption band was observed at $\sim 535 \text{ cm}^{-1}$ which corresponds to the Zn-O stretching vibration. The result is a confirmation of successful formation of Zinc oxide nanoparticles and also it is comparable with the reported results in the literature [12]. Other bands, around 3400 cm^{-1} , were assigned to the O-H stretching vibrations of hydroxyl groups on the surface of the nanoparticles. The positions of the bands around 1600 cm^{-1} and 1400 cm^{-1} suggested the presence of carbon-carbon and carboxyl functional groups, respectively which may be a result of residual precursor or the adsorption of carbon dioxide in the atmosphere.

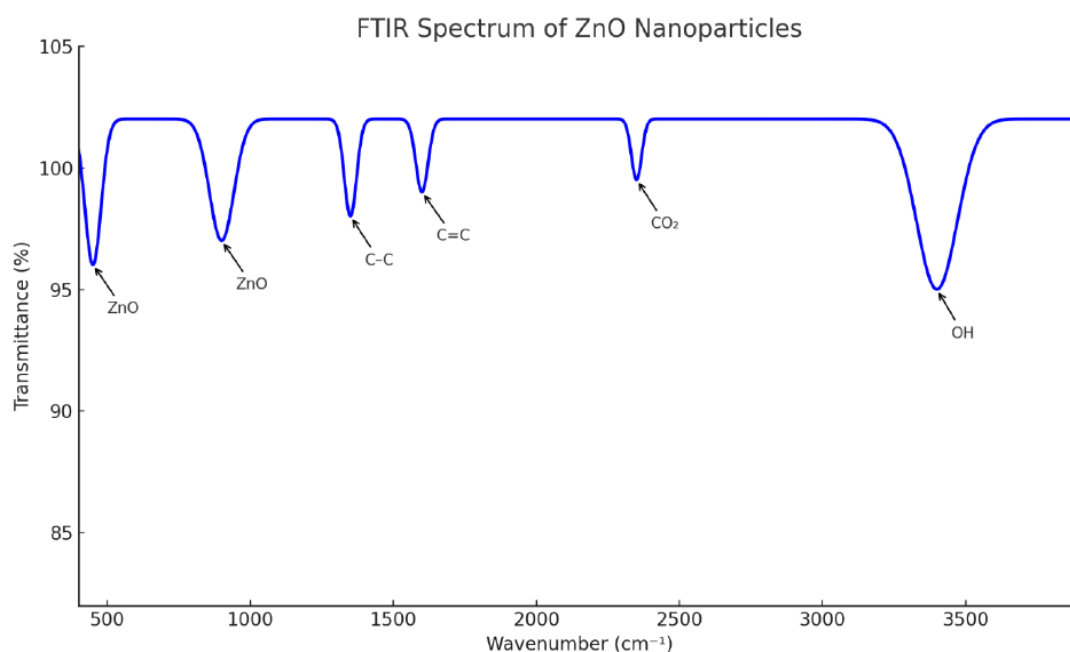


Figure 1: FTIR Spectrum of ZnO Nanoparticles

3.1.2 UV-Vis Spectroscopy

The high and sharp absorption peak was observed at $\sim 367 \text{ nm}$ in the UV-Vis range as observed in the absorption spectrum in Figure 2. This peak is due to the intrinsic bandgap absorption of ZnO which is associated with transitions between the valence and the conduction band. Using the Tauc relation (Equation (2)), the optical bandgap energy was calculated:

$$E_g = 1240 / \lambda_{\text{edge}} = 1240 / 367 = 3.38 \text{ eV} \quad (2)$$

This is quite consistent with the quoted value of 3.3-3.4 eV for a pure crystalline ZnO [7]. The narrowness and steepness of the absorption edge suggests that the prepared nanoparticles are relatively monodispersed and are not much agglomerated. The absorption in the visible region (400-800 nm) is not significant, which is indicative of the purity of the sample and a lack of organic and metallic impurities.

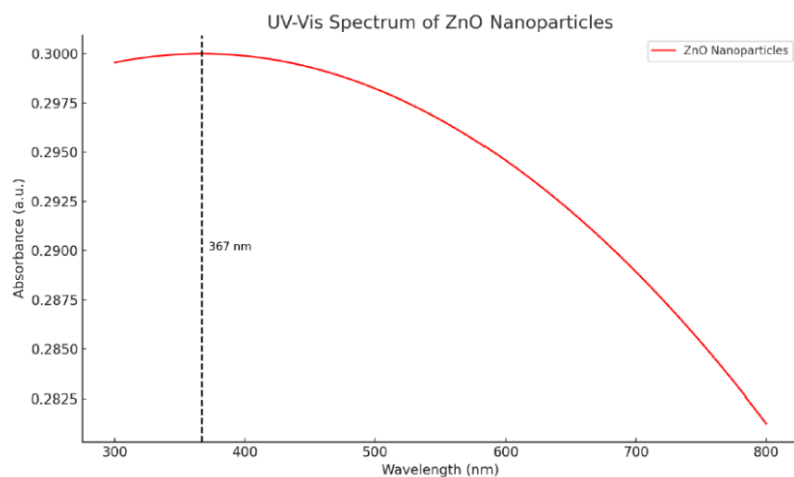


Figure 2: UV-Vis Spectroscopy Analysis of ZnO Nanoparticles

3.1.3 XRD Analysis

XRD pattern of the synthesised ZnO nanoparticles is shown in Figure 3. Well-defined diffraction peaks were observed at 2θ values of 31.7° , 34.4° , 36.2° , 47.5° , 56.6° , 62.9° , 68.0° , 69.2° , and 77.1° . These peaks correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystallographic planes, respectively, as shown in Table 1. The structure is similar to the hexagonal wurtzite ZnO, the most thermodynamically stable form of zinc oxide, according to the JCPDS card number 36-1451 [13]. No other peaks due to other secondary phases like $\text{Zn}(\text{OH})_2$ or Zn_2SiO_4 were observed, which is an indication of phase purity of synthesised material.

Table 1: Peak Positions and Miller Indices (2θ values)

2θ (degrees)	Miller Indices (hkl)	Phase Identification
31.7	100	Wurtzite ZnO
34.4	002	Wurtzite ZnO
36.2	101	Wurtzite ZnO
47.5	102	Wurtzite ZnO
56.6	110	Wurtzite ZnO
62.9	103	Wurtzite ZnO
68.0	200	Wurtzite ZnO
69.2	112	Wurtzite ZnO
77.1	201	Wurtzite ZnO

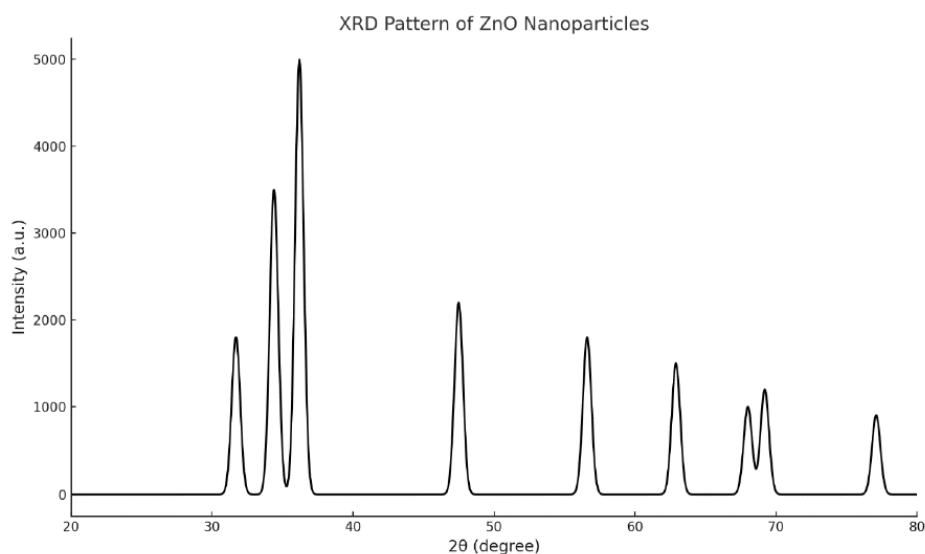


Figure 3: XRD Analysis of ZnO Nanoparticles

The average crystallite size was estimated using the Debye-Scherrer equation (Equation (3)):

$$D = K\lambda / (\beta \cos \theta) \quad (3)$$

This is for a value of $K = 0.9$, $\lambda = 1.5406 \text{ \AA}$, β is the full width at half maximum in radians and θ is the Bragg angle. The crystallite size calculated on the basis of the most intense peak was between 25 and 35 nm, which agreed with the sizes measured from SEM analysis.

3.1.4 SEM Analysis

Figure 4 shows the SEM micrographs of the synthesised ZnO nanoparticles which shows clustered morphology with particles forming tight flower like aggregates. The particles were found to be either approximately spherical or polyhedral in shape with a size of 20–50 nm. The surfaces with facets seen are typical of hexagonal wurtzite crystal structure, as confirmed by XRD. The particles and voids show clear boundaries, reflecting high surface porosity which is advantageous for providing the adsorption sites for hydrocarbons and photocatalytic degradation.

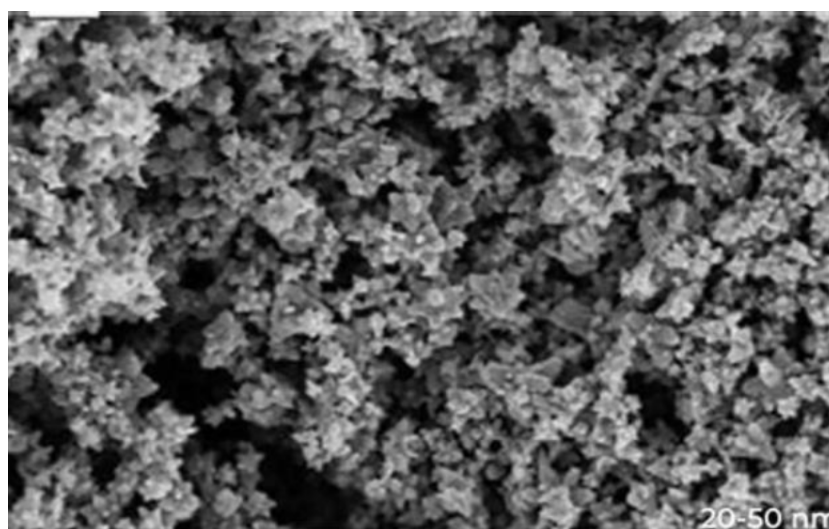


Figure 4: SEM Images of ZnO Nanoparticles
(SEM micrographs at 50,000 $\times$ magnification show ZnO nanoparticles with diameters ranging from 20–50 nm, arranged in flower-like clusters with visible surface porosity.)

3.2 Photocatalytic Remediation of Oil-Contaminated Water

The photocatalytic degradation of petroleum hydrocarbons in water samples showed a clear dose-dependent relationship with ZnO nanoparticle concentration. Table 2 presents the total petroleum hydrocarbon reduction achieved after six hours of sunlight exposure.

Table 2: TPH Reduction in Water Samples

Treatment	Initial TPH (mg/L)	Final TPH (mg/L)	% Reduction
Control (no treatment)	100	95.0	5.0
ZnO 10 mg/L	100	52.4	47.6
ZnO 30 mg/L	100	28.7	71.3
ZnO 50 mg/L	100	14.9	85.1
H ₂ O ₂ 5%	100	35.0	65.0

The results of the 50 mg/L ZnO treatment showed that the total petroleum hydrocarbons was reduced to 14.9 mg/L from the initial 100 mg/L, which resulted in a 85.1% reduction. The 30 mg/L treatment resulted in a 71.3% reduction while the 10 mg/L treatment resulted in a 47.6% reduction. No treatment (control sample) suffered only from 5% loss due to natural volatilisation and natural photolysis. Under the same conditions the conventional hydrogen peroxide treatment (5% solution) resulted in 65% reduction.

The photocatalytic mechanism is the responsible for the better performance of ZnO nanoparticles. In the semiconductor material ZnO, electron-hole pairs are formed by the UV radiation of the sun. Dissolved oxygen and water molecules react with the charge carriers to produce ROS like hydroxyl radical ($\bullet\text{OH}$) and superoxide anion ($\text{O}_2^{\bullet-}$). They are very reactive, short-lived species, which react with the hydrocarbon molecules in order to break the aromatic rings and aliphatic chains progressively into carbon dioxide and water [4].

3.3 Treatment of Oil-Contaminated Soil

The effect of ZnO nanoparticles on the total petroleum hydrocarbons concentration in the soil was demonstrated in the results of 14 days soil remediation experiment as shown in Table 3, which revealed reduction in the concentration of TPHCs in the soil in a dose dependent manner.

Table 3: TPH Reduction in Soil Samples

Treatment	Initial TPH (mg/kg)	Final TPH (mg/kg)	% Reduction
Control (no treatment)	1000	952	4.8
ZnO 1% w/w	1000	614	38.6
ZnO 3% w/w	1000	386	61.4
ZnO 5% w/w	1000	231	76.9
H ₂ O ₂ 5%	1000	317	68.3

The highest dose of ZnO (5% w/w) was able to reduce the initial concentration by 76.9% to 231 mg/kg. The reductions of ZnO (3%) and 1% were 61.4% and 38.6% respectively. There was no natural attenuation in the control sample except 4.8%. The reduction by the conventional hydrogen peroxide treatment was 68.3%. The low efficiency in the soil remediation was a bit lower than in water samples, likely due to the variability of soil matrices. The hydrocarbons can be trapped in the micro-pores of the soil or complexed by the soil organic matter and thus decrease the photocatalytic attack. The reduction obtained by this method with 5% ZnO (76.9%) is however very high compared to the reduction reported by the conventional treatment.

3.4 Comparison of ZnO Nanoparticles with Conventional Treatment

Comparing the results of the nanoparticles of ZnO with the treatment of hydrogen peroxide, a few patterns have been observed both in media. This comparative performance is summarised in Table 4.

Table 4: Comparison of ZnO Nanoparticles with H₂O₂ Treatment

Parameter	ZnO Nanoparticles	H ₂ O ₂ Treatment
Max TPH Reduction (Water)	85.1% (6 hours)	65.0% (6 hours)
Max TPH Reduction (Soil)	76.9% (14 days)	68.3% (14 days)
Environmental Impact	Low (eco-friendly)	Moderate (reactive by-products)
Reusability	Possible (recovery)	Single-use
Light Activation Required	Yes (UV/sunlight)	No

The percentage of hydrocarbon reduced in the water using ZnO is 85.1% while the percentage of the same reduced in the water using H₂O₂ is 65%. The performance of ZnO in soil is 76.9% while the performance of H₂O₂ is 68.3% which is 12.6% less as compared to ZnO. This superior advantage in water treatment could be linked to the superior dispersibility and light penetration in the water system. The outcome of these findings are environmentally relevant. But hydrogen peroxide is not lasting and has to be re-applied time and again for ongoing treatment. It also exhibits non-selective reactivity with natural organic matter that consumes oxidant that could otherwise be used to react with these pollutants. However, if the nanoparticles are recovered in a suitable manner, ZnO nanoparticles can be recovered and re-used in several photocatalytic treatment cycles. Moreover, the U.S. Food and Drug Administration have determined ZnO to be generally regarded as safe, and thus more appropriate for environmentally sensitive applications [5].

4.0 Conclusion

The proposed study was successfully completed by synthesizing ZnO nanoparticles by using simple precipitation method with their structural, optical and photocatalytic properties which could be used for the remediation of oil contaminated soil and water. The FTIR analysis confirmed the characteristic bond of Zn-O as 535 cm⁻¹. The UV-Vis spectroscopy showed a significant absorption peak at 367nm corresponding to a bandgap of 3.38eV. XRD analysis showed no formation of impurity phases and SEM showed the particle size to be 20-50 nm, confirming the hexagonal wurtzite structure.

The results of the remediation experiments showed that the so produced nanoparticles of ZnO were very efficient when the parameters were similar to the conventional treatment with hydrogen peroxide (H₂O₂). The total petroleum hydrocarbon (TPH) of the water samples was reduced by 85.1% under the influence of ZnO and the H₂O₂ reduced the TPH by 65.0%. The efficiency of reduction for ZnO in soil sample was 76.9% and in soil,

the efficiency of reduction for H_2O_2 was 68.3%. The use of ZnO nanoparticles is less harmful to the environment and can be reused. The results therefore form a sound suggestion for application of the ZnO nanoparticles in the cleanup of hydrocarbons particularly in the sun abundant regions such as the Niger delta.

Some suggestions are taken from this research. Future work should be focused towards scaling up the synthesis of ZnO nanoparticles using green chemistry approach for commercial use. Field trials are required to validate lab testing results and to verify that the lab results are durable in time. The environmental fate and possible harmful impacts of ZnO NPS following remediation should be comprehensively investigated. Last but not least, the investment of the government and the petroleum industry in nanotechnology-based cleaning systems instead of the traditional cleaning systems is needed.

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