Chemical synthesis, characterization and application of nanosized ZnO in the treatment of ciprofloxacin formulated aquaculture effluent: COD, kinetics and mechanism

Omolola Helen Aremu[1*], Cecilia Olufunke Akintayo[1], Olushola Sunday Ayanda[1]

[1] Department of Industrial Chemistry, Faculty of Science, Federal University Oye-Ekiti, Ekiti State, Nigeria

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ABSTRACT

Antibiotics are generally applied for the treatment of infections in humans and animals due to their economic value, easy accessibility, and potency. The use of veterinary pharmaceuticals such as antibiotics for the treatment of various infections in aquaculture cannot be overemphasized; the discharge of aquaculture effluent without necessary remediation techniques leads to the toxicity of the ecosystem. In this work, zinc oxide hexagonal-nanorods were synthesized via a precipitation method and calcined at $500^{0}C$ in a muffle furnace for the catalytic degradation of ciprofloxacin (CIP) formulated aquaculture effluent. The characterization of nano-sized ZnO (n-ZnO) was conducted using scanning electron microscopy-electron dispersive spectroscopy (SEM-EDS), transmission electron microscopy (TEM), x-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FTIR) and Brunauer, Emmett and Teller (BET) surface area determination. The SEM micrograph depicted both hexagonal and rod-like structures. The TEM micrograph subjected to ImageJ software showed an average particle size of 42.69 nm. The weight percent of the elements from the electron dispersive spectroscopy (EDS) followed the trend of Zn>O>C>Cl. The sharp peak of the Zn-O band was observed around 463.12 $cm^{-}1$. The results from XRD showed that pure n-ZnO was achieved at a temperature of $500^{0}C$ with a BET surface area of 8.3 m^{2}/g, pore volume of 0.072 cm^{3}/g, and pore size of 184.77 A^{0}. The percentage of chemical oxygen demand (COD) removal of CIP formulated aquaculture effluent followed the trend of 42.8%, 73.9%, and 94.8% for the ultrasound (US), US/n-ZnO, and US/n-ZnO/H_2O_2systems.The US/n-ZnO/H_2O_2system showed the highest removal efficiency of CIP from the aquaculture effluent. The kinetics best fit the pseudo-second order, while the mechanism of degradation followed the Langmuir-Hinshelwood model for the US/n-ZnO/H_2O_2system. Hence, the utilization of US/n-ZnO/$H_2O_2$for the degradation of CIP formulated aquaculture effluent has proven to be a sustainable system that is dependable, faster, less tedious, and does not

*Corresponding author: Tel: 08065784036
 E-mail: omololaaremu21@gmail.com

generate additional waste superior performance compared to individual materials. As such, findings from this study confirmed the performance and effectiveness of the Mg-(OH)$_2$-Ca-NPs nanocomposite on the removal of Mn from real river water. This will go a long way in curtailing the impacts of Mn in drinking water and further afield.

1. Introduction

The presence of pharmaceuticals as waste in the environment cannot be over-emphasized as novel technologies for the production of pharmaceuticals are increasing daily. The production rate of any pharmaceutical is directly proportional to its positive or negative effect on the environment [1]. Pharmaceuticals are known universally as evolving pollutants that are found to be unrestricted in the environment. They are released into the environment via wastewater treatment plants [1], sewage sludge [3], households, pharmaceutical industries, and veterinary hospitals [4]. They pose a great risk to water bodies and the environment at large [5]. Figure 1 shows the emergence of pharmaceuticals into the environment via wastewater treatment plants, sewage sludge, household, pharmaceutical industries, and veterinary hospitals.

Antibiotics are generally known as anti-bacterial drugs and are used to treat infections that are caused by the growth of bacteria in the cells of plants and animals. They are widely used in veterinary medicine, especially aquatic treatment, due to their economic value, easy accessibility, and potency in helping the living organisms in the aqua environment to grow under normal circumstances. Antibiotics are known to be complex in their structure; they contain organic compounds that cannot be broken down easily via conventional wastewater treatment, and this suggests their availability in the environment making the ecosystem unsafe for living organisms [3]. They are classified based on their chemical composition and system of operation in the body: fluoroquinolones, penicillin, tetracyclines, polypeptides, macrolides, aminoglycosides, and cephalosporins [6].
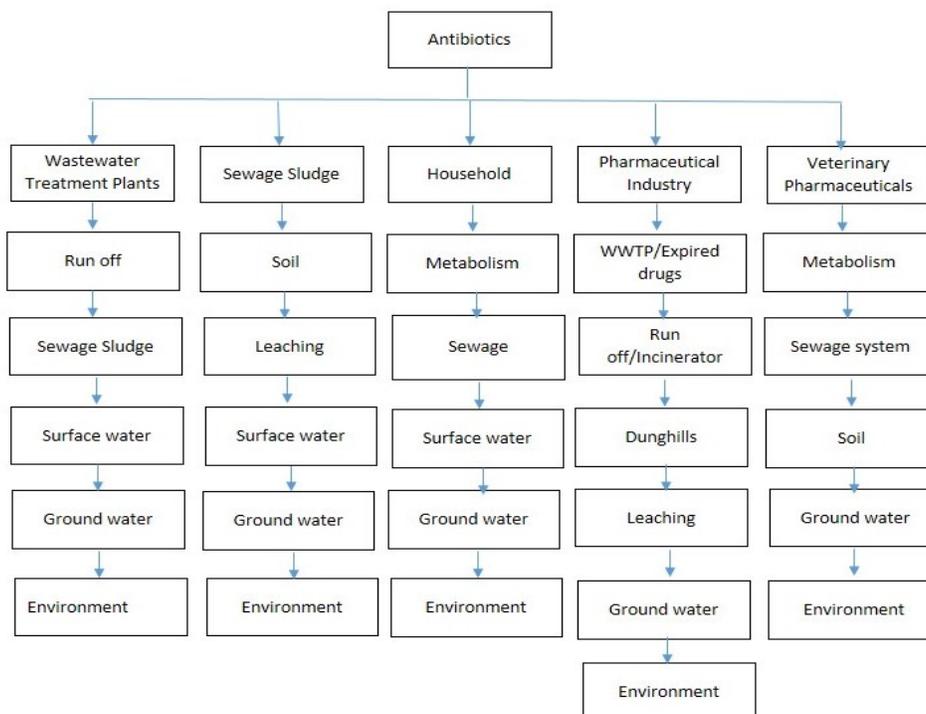
Fig. 1. The emergence of pharmaceuticals into the environment.

Ciprofloxacin is an antibiotic that is classified under the fluoroquinolone group. It is globally used as a curative measure against bacterial infections in humans and animals (aquatic or terrestrial). It shows a low dissolving ability in aqueous solution as a result of the presence of strong quinolone structures, which are highly toxic and need to be removed from aquaculture effluent before it is discharged into water bodies and the earth crust [7]. However, CIP is commonly overused as a supplement in fish feed to reduce infection, but it gets introduced into the water and causes drug poisoning, etc. This tends to affect the plants that grow within and the animals that depend on water for their livelihood [8]. Zhu et al. [9] reported that the traces of antibiotics found in the environment as a result of sewage sludge, pharmaceutical industries, hospitals, and wastewater treatment plants might escalate the resistance rate of bacteria to the drugs, which might negate the hygiene of the water. Boudriche et al. [10] explored the removal of ciprofloxacin from wastewater using UV/ H_2O_2. Their results showed that a 100% degradation of ciprofloxacin was achieved at 30 min with increasing H_2O_2 to 10 mg/L, as generating more hydroxyl radicals and enhancing the degradation rate of ciprofloxacin. De Bel et al. [11] investigated the effect of ultrasound on the degradation of ciprofloxacin at 520 kHz. Ciprofloxacin was degraded at a pH of 7 by 57% after 2 hr, implying that there was a formation of hydroxyl radicals from the reaction of wastewater with the pollutant. Samadi et al. [12] studied the removal of ciprofloxacin oxidation by magnetic Fe_3O_4/Multi walled carbon nanotube composite as a heterogeneous Fenton catalyst from synthetic wastewater. Their result showed that as the concentration of the catalyst increased, the heterogeneous Fenton process efficiency increased and led to a maximum removal of 94% of ciprofloxacin at 2g/L of magnetic Fe_3O_4/MWCNT composite. Balarak et al. [13] investigated the removal of ciprofloxacin from aquatic effluent using red mud and activated red mud by HCl. Their results showed that as the adsorbent dose was increased from 0.5 to 8g, the adsorption of ciprofloxacin increased from 25.4% to 61.7% for the red mud. This was a result of the increase in the number of active sites and the adsorbent dosage.

The activated red mud, as the dose of the adsorbent, increased from 0.5 to 8g, and ciprofloxacin removal was 98.29%. This higher percentage of removal suggested that the acid treatment of red mud led to an increase in the surface area and porosity, which is a factor for the maximum adsorption of antibiotics. Githinji et al. [14] evaluated the contribution of sorption in the removal of ciprofloxacin and amoxicillin in synthetic wastewater. This implies that at concentrations of 100 for ciprofloxacin, kinetics as a function of pH and time, the percentage of ciprofloxacin absorbed at the initial period was 2% and later increased respectively to 6.4%, 9.9%, 10.3%, 12.0%, and 14.9% with varying pH of 8.5, 7.5, 3.5, 6.6, and 5.5 after 24 hours. The basic structure and properties of ciprofloxacin are shown in Table 1.

Table 1. Properties of ciprofloxacin.
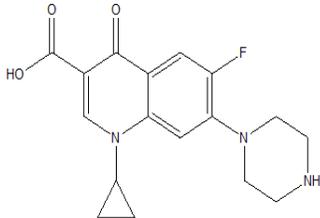
Structure	
Physical state	Solid
Class	Fluoroquinolone
Melting point	255-257^{0}C
Color	Light yellow
Boiling point	581.8 ± 50^{0}C
Molecular formulae	$C_{17}H_{18}FN_3O_3$
Molecular weight	331.34g/mol
Density	1.5 ± 0.1g/cm
Solubility	30000mg/L in water @ 20^{0}C
Synonyms	Ciprobay
λ_{max}	275nm

Several metal oxide nanoparticles, such as ZnO and TiO_2, have been extensively used in the remediation of antibiotics from different wastewater [15]. The small size, stress-free synthesis, non-toxicity [16],

the increased band gap of 3.37eV [17], the high binding energy of 60meV [18], photocatalytic ability [19], piezo and pyro-electric properties [20], and antibacterial properties [21] associated with zinc oxide nanoparticles have made researchers to explore its usability. ZnO nanoparticles have been synthesized in several ways, such as chemical vapor deposition, co-precipitation, ultrasound, sol-gel, and green synthesis [22]. Diverse techniques such as photocatalysis [23], sonocatalysis [24], nanofiltration [25], sonolysis [26], adsorption [27], etc., have been used in the remediation of antibiotics. Researchers have shown interest in the use of ultrasound to remediate pollutants in wastewater, including phenolsulfonphthalein [28], amoxicillin [29], N-acetyl-para-aminophenol [30], etc. Studies have shown that conventional treatments are not capable of remediating ciprofloxacin from the aquatic environment [31]. Therefore, this study employed ultrasound, one of the advanced oxidation processes (AOPs), to degrade ciprofloxacin. Acoustic cavitation is the mechanism involved in ultrasound as there is fast production, increase and breakdown of bubbles in liquid from sound waves producing sound energy in wastewater which is later transformed to heat energy in the chemical reaction. This invariably generates highly interactive chemical species such as OH^-, H^+ etc. Hydroxyl radicals are powerful oxidants, non-toxic, not corrosive to piece of equipment, possess a short lifespan, and do not generate additional waste. They attack the pollutants found in wastewater, minimize the particle size of the pollutants and mineralize to carbon(IV) oxide, water and less toxic compounds [28]. However, studies have shown that the utilization of AOPs alone often results to partial removal of pollutants [26,32] unlike the synergetic effect of AOPs and catalyst which gives a better degradation efficiency. According to the existing literatures, there is no existing work on the removal of ciprofloxacin formulated aquaculture effluent using ultrasound, ultrasound/n-ZnO and ultrasound/n-ZnO/ H_2O_2. However, the objective of this study is to synthesize and characterize a non-toxic zinc oxide hexagonal-nanorods calcined at 500^0C and to explore the extent of degradation of ciprofloxacin formulated aquaculture effluent with the use of ultrasound only, ultrasound/n-ZnO and

ultrasound/H_2O_2/n-ZnO with different operating parameters such as ultrasonic amplitude, concentration of ciprofloxacin, pH, concentration of H_2O_2 and nano-dosage. These parameters are essential as it determines the degradation process. Ultrasonic amplitude is the most important factor in terms of oxidation as it leads to the formation of cavitation bubbles that forms hot spots for the degradation of pollutants. Concentration determines the extent of pollutants that is available for degradation. pH alters the composition of pollutants in a solution. Nanodosage produces active sites that are capable of attacking the available pollutants.H_2O_2 are initiator of hydroxyl radicals which are responsible for the reduction of pollutant sizes and convert to CO_2 and H_2O. The ultrasonic reactor is comprised of an ultrasonic processor and an ultrasonic probe. The ultrasonic probe is inserted into the vacuum containing the wastewater which rotates depending on the amplitude with the generation of highly reactive radicals. Ultrasonic waves are produced alongside to form cavitation bubbles that collide with one another to form hot spots. As hot spots are formed, hydroxyl radicals that are capable of minimizing the sizes of pollutants are generated and this converts the pollutants to CO_2 and H_2O which are eco-friendly.

2. Materials and methods

2.2. Reagents and chemicals

Ciprofloxacin, zinc chloride, sodium hydroxide and hydrogen peroxide were supplied by Sigma Aldrich. A 50mg/L CIP solution was prepared by dissolving a certain quantity of CIP in 1000mL of deionized water with pH value <8. The solution was filled up to the mark. Working solutions were prepared for subsequent solutions. A PHS-3C pH meter was used and the simulated ciprofloxacin wastewater was regulated by the addition of 0.05M H_2SO_4 or 0.05M NaOH solutions.

2.3. Synthesis of n-ZnO

A 20 g of $ZnCl_2$ was weighed and added to 100 mL of de-ionized water dissolved in a 250mL beaker, stirred continuously for 20 min with a magnetic stirrer at a temperature of 90 °C. The $ZnCl_2$ solution was allowed to cool down. A 0.2M NaOH solution was prepared and titrated against 50mL of the zinc

chloride solution. A milky white solution was obtained. The n–ZnO was separated from the liquid phase with a vacuum pump. The n–ZnO was washed thrice with deionized water. The filtered sample was dried in an oven at 75 $^{\circ}$C for 24 hr. This was then calcined at 500 $^{\circ}$C in a muffle furnace for 2 hr and crushed with agar mortar and pestle. The reactions and schematic representation for the synthesis of zinc oxide hexagonal-nanorods is shown in Eq. (1 and 2) and Figure 2.

$$ZnCl_2 + NaOH \rightarrow Zn(OH)_2 + NaCl \qquad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (2)$$
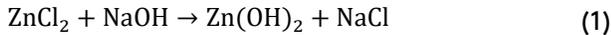
2.4. Characterization of n-ZnO

A scanning electron microscope (SEM; Phenon type Model: Pro X) and transmission electron microscope (TEM; Tecnai G^2 20) at 100nm were used for the morphological study of the synthesized n-ZnO. The crystallinity and phase identification were examined via XRD (Siemens D8 Advance Bruker) with CuK∞ radiation. The elemental composition of the n-ZnO was quantitatively determined by EDS. The infrared spectrum of the synthesized n-ZnO was investigated with FTIR (Perkin Elmer Spectrum Two ^{TM} Spectrometer). The BET surface area was examined by a Tristar 3000 analyzer with N$_2$ adsorption at -196 $^{\circ}$C. The pore volume and pore were obtained by the Barrette-Joyner-Halenda (BJH) method, with the adsorption data as a function of p/p$^{\circ}$.

2.5. Degradation of CIP

The degradation of CIP was done with ultrasound only, ultrasound/n-ZnO and a combined ultrasonic/n-ZnO/H$_2$O$_2$ system. At the end of each time of degradation, samples were taken from the ultrasonic reactor for analysis with a UV-visible spectrophotometer at a wavelength of 275nm.

2.5.1. Ultrasound only

2.5.1.1. Effect of amplitude and sonication time on the degradation of CIP

A 50mL of 50 mg/L of CIP aqueous solution was placed in a 100ml beaker and sonicated at varying times (20-60 min) using 20, 40, 60, 80, and 100 % ultrasonic amplitudes and a frequency of 20 kHz. The filtrates from the degradation process were monitored with a UV/Visible spectrophotometer at a wavelength of 275 nm.

2.5.1.2. Effect of pH and sonication time on the degradation of CIP

The effect of varying pH (2-10) was investigated at sonication times of 20-60 min, 60% amplitude, and a frequency of 20 kHz. The filtrate from the degradation process was monitored with a UV/Visible spectrophotometer at a wavelength of 275 nm.
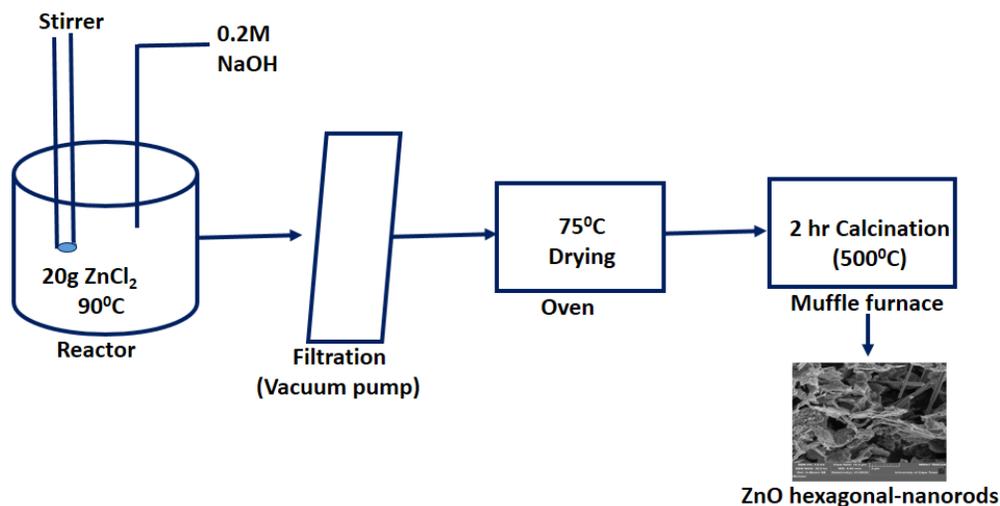
Fig.2. Schematic representation for the synthesis of ZnO hexagonal-nanorods.

2.5.2. Ultrasound/n-ZnO

2.5.2.1. Effect of nanodosage and sonication time on the degradation of CIP

The effect of varying nanodosage of (0.02-0.1g) was investigated using US/n-ZnO at sonication times of (20-60 min), 60% ultrasonic amplitude, and a frequency of 20 kHz. The CIP solution was filtered, and the filtrate was analyzed with a UV/Visible spectrophotometer at a wavelength of 275 nm.

2.5.3. Ultrasound/n-ZnO/H₂O₂

2.5.3.1. Effect of initial concentration of CIP and sonication time on the degradation of CIP

The effect of the initial concentration of CIP (50-3.125 mg/L) was examined with the synergetic effect of US/n-ZnO/H₂O₂. 0.08g of n-ZnO and 5 mL of 1% H_2O_2 were added to 50mL of each of the varying concentrations, sonicated at varying sonication times (20-60 min), 40% ultrasonic amplitude, and a frequency of 20 KHz. The CIP solution was filtered, and the filtrate was analyzed with a UV/Visible spectrophotometer at a wavelength of 275 nm. The percentage degradation of CIP was calculated using Eq. (3).

$$\% \text{ Degradation} = \frac{C1P_0 - CIP_f}{C1P_0} \times 100 \tag{3}$$

where CIP_0 and CIP_f are the initial and final concentrations of CIP, respectively.

2.5.4. Analysis of ciprofloxacin formulated aquaculture effluent

The sample of wastewater from the aquaculture was obtained from the Federal University Oye Ekiti farm at Ikole Ekiti, Ekiti State, stored in plastic sampling bottles, and transferred to the laboratory. Then, a specific amount of ciprofloxacin was dissolved in the wastewater. The degradation process was monitored using a chemical oxygen demand (COD) analyzer. The optimum conditions, such as the best sonication time, best amplitude, best nanodosage, and best H₂O₂ concentration were tested on the effluent. The percentage degradation was achieved using Eq. (4).

$$\%COD = \frac{COD_0 - COD_f}{COD_0} \times 100 \tag{4}$$

Where COD_0 and COD_f are the initial and final COD values, respectively

3. Results and discussions

3.1. Characterization

The SEM with a magnification of 20.0kx, scaled at 2μm, and TEM micrographs shot at 100nm of the calcined n-ZnO at 500 ^{0}C are shown in Figures 3a and 3c, respectively. It was observed that the nanoparticle depicted a hexagonal and rod-like structure with high homogeneity, which was similar to the report of [33]. The EDS spectrum of the synthesized n-ZnO is presented in Figure 3b. The percentage elemental composition of n-ZnO by EDS was in the proportion 17.93±4.9wt% C, 21.65±7.2wt% O, 1.27±0.4wt% Cl, and 59.15±11.3wt% Zn. The result showed that more Zn was obtained with a decrease in Cl at a high calcination temperature. The Cl present was a result of the zinc chloride used in the synthesis of n-sized ZnO. The particle size distribution of n-ZnO shown in Figure 3d was determined by subjecting the TEM micrographs to ImageJ software to measure the diameter of particles. The results showed that the average particle size was 42.69nm. This result is similar to the report of [34], who reported that the particle size of n-ZnO was in the range of 10-40nm. The N₂ adsorption-desorption isotherm and BJH pore size distribution of n-ZnO are shown in Figures 3e and 3f. The value of the BET surface area was 8.3 m²/g, which was in the mesoporous range [35]. This is in consonant with the study of [36], with a BET surface area of 8 m²/g for n-ZnO. The BJH pore size and pore volume were184.77 A° and 0.072 cm³/g, respectively. The plot shows a slit-shape, which is a Type IV isotherm, and the hysteresis loops as Type H3, which is in line with the IUPAC arrangement [37]. The X-ray diffractograms presented in Figure 3g show the hexagonal structure of n-ZnO due to its total crystallinity with the highest peak at (101) plane, which corresponds to the previous study of [38]. The FTIR spectrum of n-ZnO in Figure 3h shows only one absorption peak at 463.12 cm^{-1}, which is associated with the characteristic vibration mode of Zn-O bonding. The disappearance of other absorption peaks indicated that the high purity of ZnO was synthesized at 500 $^{\circ}$C. This result is similar to those observed by [39-42].
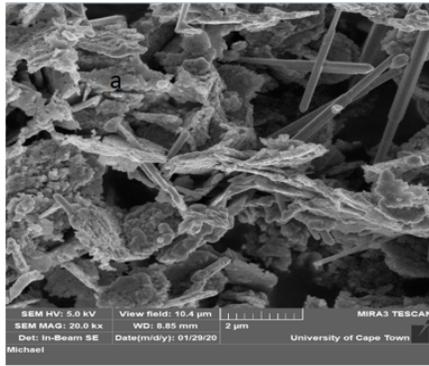
Fig (a): SEM
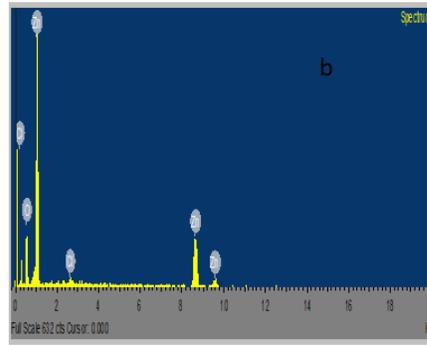
Fig (b): EDS
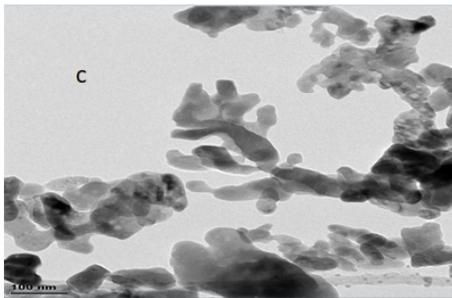
Fig (c): TEM micrographs
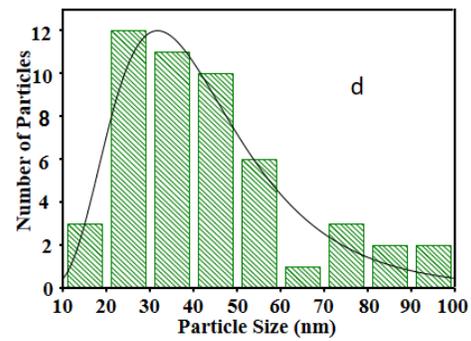
Fig (d): Particle size distribution
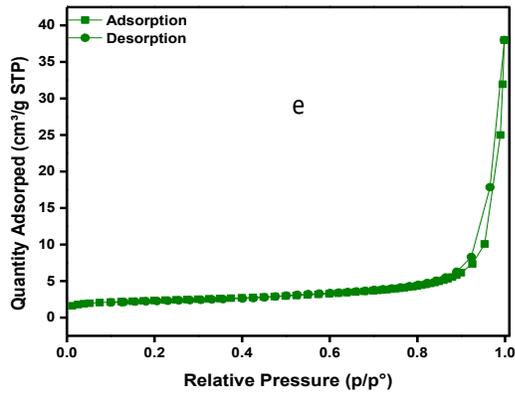
Fig (e): N_2 adsorption-desorption isotherm
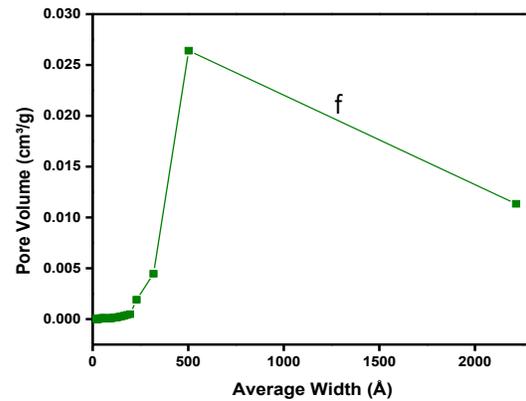
Fig (f): BJH pore size distribution
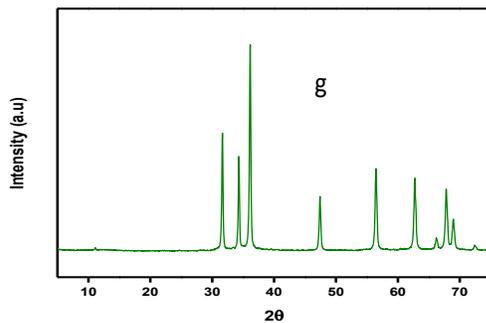
Fig (g): XRD
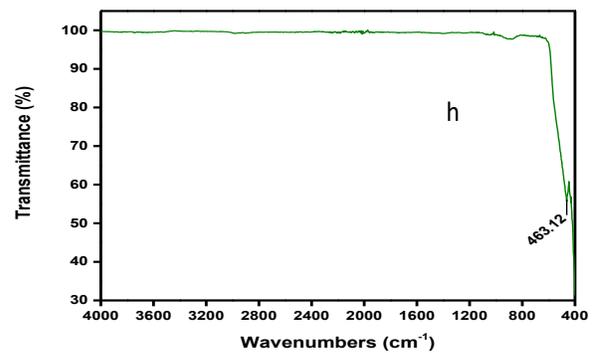
Fig (h): FTIR spectrum

Fig.3. SEM (a), EDS (b), TEM micrographs (c), Particle size distribution (d), N_2 adsorption-desorption isotherm (e), BJH pore size distribution (f), XRD (g) and FTIR spectrum (h) of n-ZnO calcined at 500^0C.

3.2. CIP degradation with ultrasound only

3.2.1. Effect of amplitude and sonication time on the degradation of CIP

Ultrasonic amplitude is a parameter that needs to be considered in remediating pollutants with ultrasound. An increase in ultrasonic amplitude usually results in increased reactions, thereby producing more hydroxyl radicals via the cavitation mechanism [43]. Ultrasonic amplitudes of 20%, 40%, 60%, 80%, and 100% were varied in the degradation process. The initial concentration of ciprofloxacin was 50 mg/L, with percentage degradations of 31%, 34%, 36.4%, 41.6%, and 46% within 20-60 min sonication time. Figure 8 shows that 46% degradation of ciprofloxacin was achieved at 60% ultrasonic amplitude within 60 min sonication time. Ultrasound alone may not achieve higher degradation of pollutants due to the presence of the quinolone group, which is not easily degradable [29,44]. The degradation plot of the effect of amplitude and time is shown in Figure 4.

3.2.2. Effect of pH and sonication time on the degradation of CIP

The pH of solutions is known to have a great impact on the degradation rate of pollutants in wastewater [45]. The influence of pH on the removal of ciprofloxacin was examined. The pH values ranged from 2-10 and were verified with 50 mg/L of ciprofloxacin at a sonication time between 20-60 min. The results showed that an increase in pH decreased the degradation rate of ciprofloxacin; the degradation was more promising in the acidic environment than the alkaline one [46]. The maximum degradation values were 56.9%, 61.4%, 64.3%, 66.5%, and 68.8% within a 20-60 min sonication time. The best percentage degradation of 68.8% was achieved at pH 2 (acidic medium), and a 60% amplitude within a 60 min sonication time. This is similar to the work reported by [47]. At low pH, more protons were likely to be available, which improved the electrostatic attraction within the reaction process [48]. The degradation chart is shown in Figure 5.
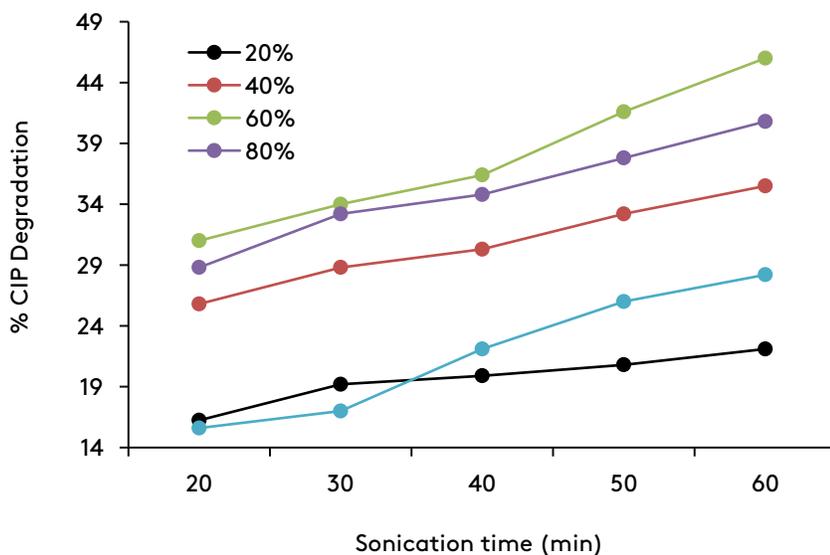
Fig. 4. Effect of amplitude and sonication time on the degradation of CIP. Experimental condition: Concentration of CIP= 50 mg/L; Volume of CIP = 50mL; Sonication time= 20-60 min; Ultrasonic frequency = 20 kHz.
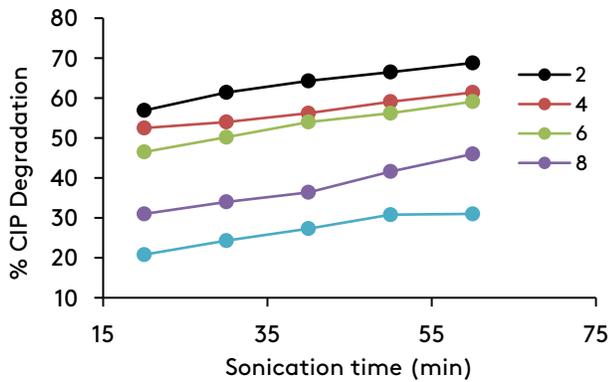
Fig. 5. Effect of pH and sonication time on the degradation of CIP. Experimental condition: Concentration of CIP= 50 mg/L; Sonication time= 20-60 min; Volume of CIP = 50mL; Ultrasonic amplitude = 60 %; Ultrasonic frequency = 20 kHz.

Fig. 6. Effect of nanodosage and sonication time on the degradation of CIP. Experimental condition: Concentration of CIP= 50 mg/L; Sonication time= 20-60 min; Volume of CIP = 50mL; Ultrasonic amplitude = 60 %; Ultrasonic frequency = 20 kHz.

3.3. Ultrasound/n-ZnO

3.3.1. Effect of nanodosage and sonication time on the degradation of CIP

Figure 6 shows the effect of n-ZnO dosage (0.02-0.1g) with ultrasound in the remediation of 50 mg/L of CIP. The results showed that as nanodosage increased from 0.02-0.06g, the rate of degradation increased from 57.7%-77% within a 60 min sonication time and 60% ultrasonic amplitude [49]. This was a result of the excitation of the orbital electrons, which led to the formation of positive charges on the pore surface that reacted with hydroxyl radicals to aid degradation. This is in consonance with the work done by [50]. It was also observed that as n-ZnO increased to 0.08g, there was a decrease in the rate of degradation of CIP from 68.8%-45.1% within 60 min. This implied that excess n-ZnO might cause saturation of the active sites that promote degradation. The maximum percentage degradation of 77% was achieved at 0.06g n-ZnO, and a 60% amplitude within a 60 min sonication time. However, increasing the degradation time above 60 min might further increase the degradation of CIP. A 0.06g n-ZnO was kept constant for further experiments. The plot of the effect of nanodosage and sonication time on the degradation of CIP is shown in Figure 6.
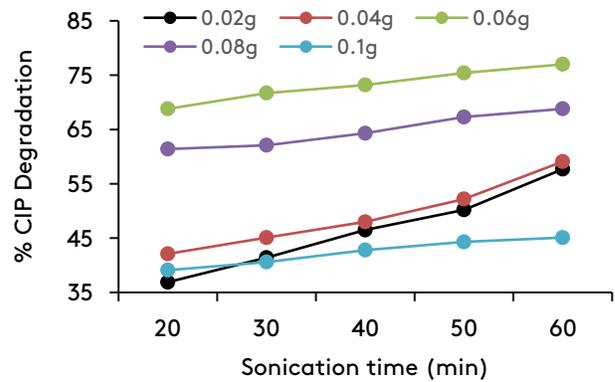
3.4.1. Effect of initial concentration of CIP and sonication time on the degradation of CIP

The effect of the initial concentration of CIP (3.125 mg/L-50 mg/L) was examined with the synergetic effect of US/n-ZnO/H_2O_2. The results in Figure 7 show that the degradation of CIP increased with a decrease in the initial concentration of CIP. The maximum percentage degradation achieved was 98.6% within 60 min of sonication time. As the concentration decreased, the degradation rate of CIP followed the trend of 84.3%, 88%, 90.2%, 91.7%, and 94% within a 20-60 min sonication time. This implied that as the concentration of CIP increased, there was a reduction in the shear stress generated by ultrasonic waves with increasing CIP concentration. In addition, at a reduced concentration of CIP, more radicals were generated for reactions with the molecules of CIP, which may lead to an increased degradation rate [26,51]. The plot of the effect of the initial concentration of CIP and time is shown in Figure 7. In the same vein, the experimental data of the synergetic effect of US/n-ZnO/H_2O_2 system were subjected to the pseudo-second-order kinetic model. The plot 1/ (CIP_t) versus t is presented in Figure8.
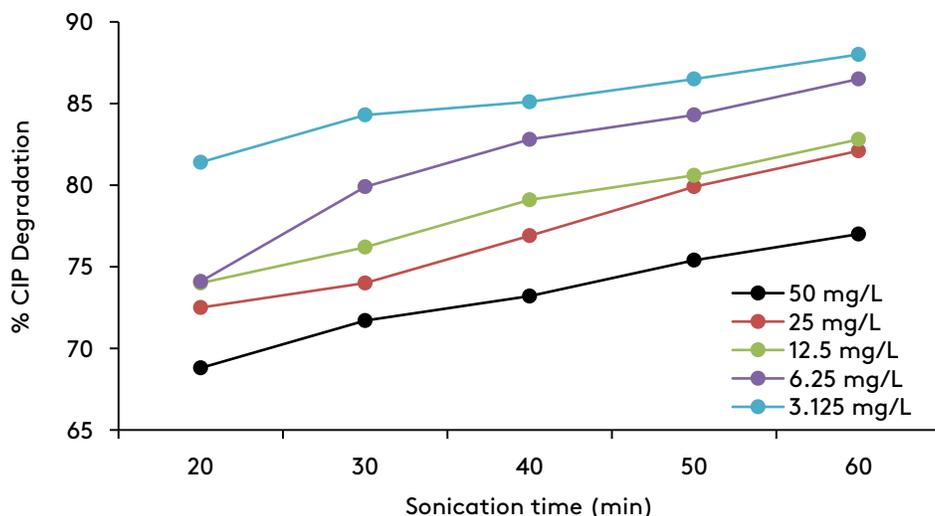
Fig. 7. Effect of initial concentration of CIP. Experimental condition: Volume of CIP = 50mL; Ultrasonic frequency = 20 kHz; Sonication time= 20-60 min; Ultrasonic amplitude = 40 %; Nanodosage =0.08g of n-ZnO; Concentration of H_2O_2 = 5 mL of 1% H_2O_2.
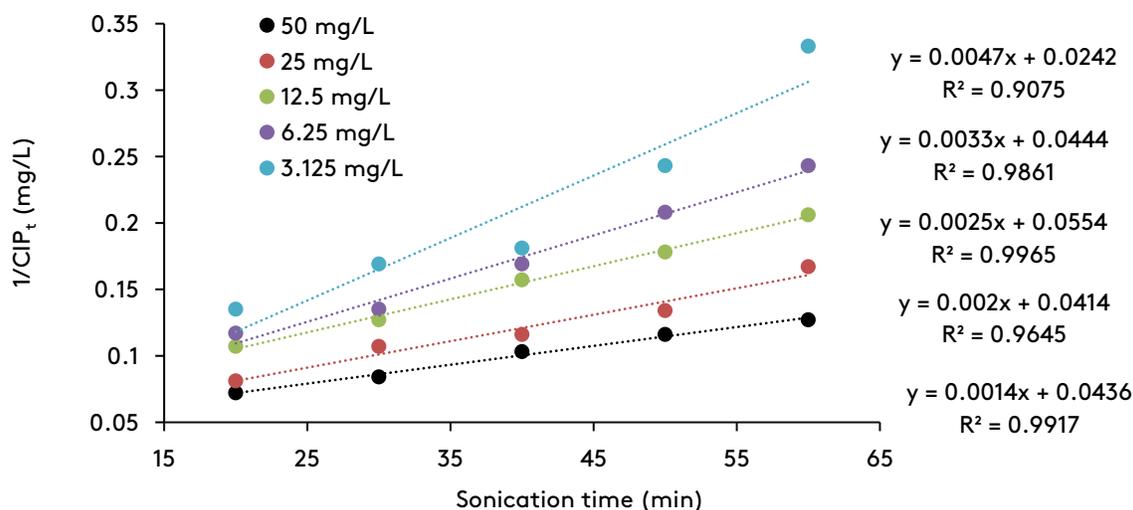
Fig. 8. Plot of 1/ (CIP_t) and sonication time for pseudo-second- order kinetic model.

The synergetic effect of US/n-ZnO/H_2O_2 system proved to be more effective when compared with US/n-ZnO and US only. It could be deduced that the synergetic effect of US/n-ZnO/H_2O_2 system advanced the removal of CIP in aqueous solution as a result of

(1) The availability of more active sites of n-ZnO
(2) The removal efficiency of ultrasound
(3) The generation of more hydroxyl radicals through the decomposition of H_2O_2

The mechanism of degradation of CIP was examined by applying the Langmuir-Hinshelwood (L-H) model presented in Equation (5).

$$\frac{1}{K_{obs}} = \frac{1}{K_c K_{LH}} + \frac{1}{K_c} CIP_O \qquad (5)$$

where K_{obs} is the rate constant (min^{-1}), K_c is the surface reaction rate constant (mg/(Lmin)), and K_{LH} is the L-H adsorption equilibrium constant (L/mg). The plot of L-H kinetic and the R^2 value is shown in Figure9 with the respective values of 1.002×10^{-1} (mg/ (L min)) and 4.291×10^{-2} (L/mg) for K_c and K_{LH}. K_c and K_{LH}.
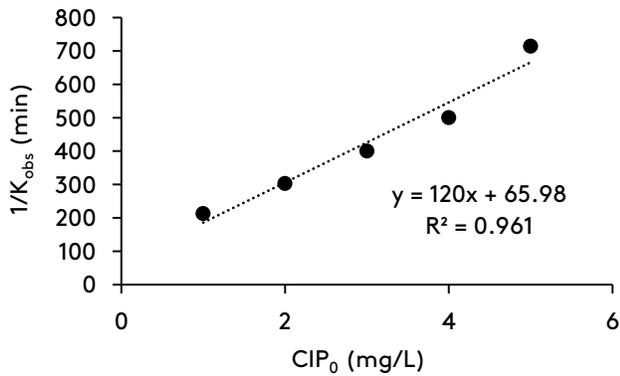
Fig. 9. Plot of Langmuir-Hinshelwood kinetics.

3.4.4.1. Proposed mechanism of reactions

From the available data, it was proposed that adsorption and oxidation took place concurrently in the removal of CIP by the US/n-ZnO/H_2O_2 system. The proposed mechanism of reaction is as follows.

US only

The production of cavitation bubbles via acoustic cavitation mechanism by ultrasound through sound waves, which enhanced the generation of *OH, *H, and HO_2* radicals in Equations (6-8).

$$H_2O+))) \rightarrow OH^* + H^* \tag{6}$$

$$H_2O + H^* \rightarrow OH^* + H_2 \tag{7}$$

$$O_2 + H^* \rightarrow HO_2^* \tag{8}$$

US/n-ZnO/H_2O_2

The availability of the active sites of n-ZnO with the combination of ultrasound produced an electron hole pair in the conduction and valence bands where oxidation took place at the surface of the n-ZnO to generate highly reactive OH* at the valence

band. The electrons at the conduction band led to a reduction in the reaction to yield HO_2*, *OH, and $O^*_2^-$. The available *OH collided with the CIP molecules to mineralize to H_2O and CO_2 andis presented in Eq. (9).

$$CIP + OH^* \rightarrow (OH)CIP^* \rightarrow CO_2 + H_2O \tag{9}$$
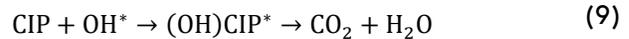
3.5. Degradation of ciprofloxacin formulated aquaculture effluent using US/n-ZnO/ H_2O_2

Different operating parameters, such as best nanodosage (0.08g), best sonication time (60 min), best H_2O_2 concentration (5 mL of 1% H_2O_2) and best amplitude (40%), were subjected for the degradation of CIP in aquaculture effluent. The COD removal percentage for CIP was 42.8%, 73.9%, and 94.8% for US only, US/n-ZnO, and US/n-ZnO/ H_2O_2 systems, respectively. Figure 10 shows the degradation efficiency of CIP removal in aquaculture effluent using COD. Table 2 shows the existing literature on the degradation of pollutants using different ultrasonic systems.

3.6. Reusability tests of nano-sized ZnO

The reusability tests of nano-sized ZnO were carried out by subjecting the n-ZnO under the operating parameters using the US/n-ZnO/H_2O_2 system repeatedly five times. At the end of each experiment, the n-ZnO was filtered, washed with de-ionized water thrice, and dried in an oven at 75 °C for 24 hr. The results in Figure 11 show that the n-ZnO used throughout the experiment was a stable catalyst, which could be a result of the renewal of the n-ZnO surface via ultrasonic commotion during the experiment [55]. Figure 12 shows the degradation of CIP before and after treatment.
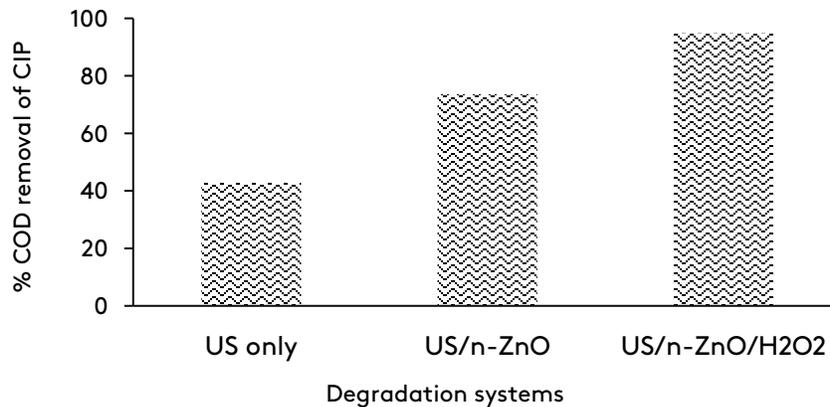
Fig. 10. Degradation efficiency by COD removal of CIP from aquaculture effluent using US only, US/n-ZnO and US/n-ZnO/ H_2O_2 systems.
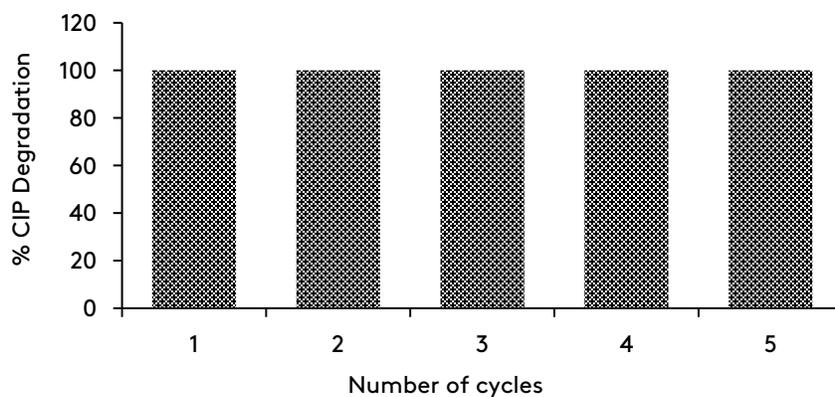
Fig. 11. Reusability test of nano-sized ZnO.

Table 2. Existing literatures on the degradation of pollutants using different ultrasonic systems.

Nanoparticles	Wastewater	Degradation Efficiency	Ultrasonic systems	References
Zinc oxide nanoparticles	Blue Cat. 41 dye	73%	US- H_2O_2-n-ZnO	[52]
Graphene oxide /Zinc oxide	Azo dye	99.4%	US-Graphene oxide Zinc oxide	[53]
Zinc oxide	Amoxicillin aquaculture effluent	98.9%	US/n-ZnO/ H_2O_2	[26]
Nano-Fe	Aqueous phenolsulfonphthalein	96.5%	US/n-Fe/ H_2O_2	[28]
Nano-Fe	Aqueous carbamazepine	90%	US/n-Fe^O/ H_2O_2	[54]
Nano-TiO$_2$	N-acetyl-para-aminophenol	99.5%	US/n-TiO$_2$	[30]
Nano-sized ZnO	Ciprofloxacin formulated aquaculture effluent	94.8%	US/n-ZnO/ H_2O_2	Present study
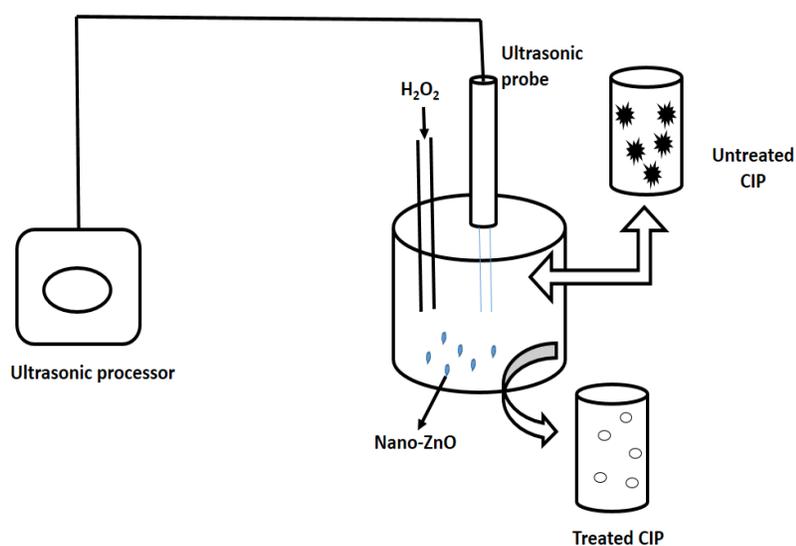
Fig. 12. Schematic representation of the before and after treatment of CIP formulated aquaculture effluent.

3.7. Future prospects, opportunities, and challenges of the study

Fish farming is a lucrative business in Nigeria as a result of the decrease in the consumption of red meat. Most fish farmers tend to protect their fish from infection by administering antibiotics, such as ciprofloxacin, into the fish pond without proper dosage. The discharge of ciprofloxacin contained in aquaculture effluent into the environment can lead to environmental pollution. It can affect the plants that grow within and the animals whose source of livelihood depends on water. The effluent can best be treated using the combined ultrasound/n-ZnO/H_2O_2 system before being discharged into the environment. Ultrasound is one of the advanced oxidation processes that generate hydroxyl radicals. Hydroxyl radicals are powerful oxidants since they do not generate additional waste, are non-toxic, not corrosive to pieces of equipment, and have a very short lifetime. The synthesis of nano-sized ZnO is challenging since a large quantity cannot be achieved. In addition, the procedure used in this work is less tedious, cost effective, and can be used to degrade large quantities of ciprofloxacin from aquaculture effluent. Hence, it gives economic value to environmental toxicologist and water management agencies.

4. Conclusions

In this work, a small sized, non-toxic, and cost-effective n-ZnO was synthesized via the precipitation method and calcined at a temperature of 500^0C, which depicted a good crystallinity for the degradation of CIP formulated aquaculture effluent. It was characterized using SEM-EDS, TEM, XRD, BET, and FTIR. Antibiotic formulated aquaculture effluent, such as ciprofloxacin, at a percentage of 94.8 was best degraded via the US/n-ZnO/H_2O_2 system. Other treatment techniques, such as US only and US/n-ZnO, showed lower degradation efficiency. The results of the experiment under the operating parameters from the degradation rate of CIP in aquaculture effluent followed the trend of US/n-ZnO/H_2O_2 > US/n-ZnO> US only. Oftentimes, the release of untreated aquaculture effluent led to the spread of harmful compounds that were non-biodegradable. Conclusively, the synergetic effect of ultrasound, which is one of the advance oxidation processes (AOPs), proved to be a reliable technique for degrading CIP in aquaculture effluent.

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