Evaluation of the Mechanochemical Synthesis of ZnO Nanoparticles as a Potential Treatment Technology for Restaurant Wastewater Discharge Within Awka Capital City, Nigeria.

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DOI: https://doi.org/10.51584/IJRIAS.2025.100800103

Received: 07 August 2025; Accepted: 12 August 2025; Published: 18 September 2025

ABSTRACT

The investigation of the mechanochemical synthesis of ZnO nanoparticles as a potential treatment technology for restaurant wastewaster discharge within awka metropolis was conducted. The ZnO nanoparticle synthesized through mechanochemical synthesis had irregular shape with sizes from a few micrometers to tens of micrometers, indicating a powdered sample. The surface between the particles was rough and porous, where EDX analysis revealed the material's elemental composition, of Silicon (4. 58%), Aluminium (1. 80%), Iron (8. 10%), and others. The turbidity levels for untreated and treated wastewater were 377 mg/L and 52 mg/L, showing an 86% removal rate. The pH of untreated water was 8. 4, while treated water was 7. 11. Concentrations of sulphate, nitrate, and phosphate decreased significantly after treatment. Heavy metals concentration, including cadmium and lead, were reduced, while zinc level increased. The untreated water had a TDS value of 1274. 333 mg/L, while after treatment with zinc oxide, TDS levels dropped to 411. 3333 mg/L. The dissolved oxygen (DO) levels in untreated (22. 7667 mg/L) and treated samples (8. 6 mg/L) were higher than EPA's permissible limit of 4 mg/L. The untreated wastewater showed a high BOD concentration of 297 mg/L. COD of the untreated samples was 627. 6667 mg which decreased to 139. 6667 mg/L after treatment. Untreated waste water contained higher concentrations of PAHs, which reduced after treatment with zinc oxide. Zinc oxide nanoparticles showed a 66% removal rate of VOCs, with the highest concentrations associated with styrene and n-Propylbenzene. These compounds can be treated with zinc oxide nanoparticles, demonstrating their potential for treating VOCs before discharge into the environment. The study concluded that treatment with zinc oxide nanoparticles effectively improved the quality of wastewater by reducing harmful substances to acceptable levels, thus minimizing environmental and health risks.

Keywords: Nanoparticle, Zinc oxide, Pharmaceutical Wastewater, Mechanochemical Synthesis., Restaurants

INTRODUCTION

There is an increased interest in porous materials due to their unique properties, such as high surface area, enhanced catalytic properties, and biological applications. Various solvent-based approaches have already been used to synthesize porous materials. However, the use of large volumes of solvents, their toxicity, and time-consuming synthesis make this process less effective, at least in terms of principles of green chemistry (Abbas et al, 2019: Tang et al, 2014: Billik et al, 2009). Mechanochemical synthesis is one of the effective, eco-friendly alternatives to conventional synthesis. It adopts the efficient mixing of reactants using ball milling without or with a very small volume of solvents, gives smaller size nanoparticles (NPs) and larger surface area, and facilitates their functionalization, which is highly beneficial for antimicrobial applications (Robindra et al, 2023: Gopalan and Singhal 2000). A large variety of nanomaterials for different applications have already been synthesized by this method. This review emphasizes the comparison between the solvent-based and mechanochemical methods for the synthesis of mainly inorganic NPs for potential antimicrobial applications. However, some metal-organic framework NPs are briefly presented too (Jibril et al, 2019: Ding et al, 1997: Otis et al, 2021). Mechanochemistry, a branch of chemistry that involves the application of mechanical energy to induce chemical reactions, has garnered significant attention for its unique approach to chemical synthesis and materials processing (Cagnetta et al,2018: Szczęśniak,et al, 2020) . This review examined the fundamental principles of mechanochemistry, including the impact of mechanical forces on crystalline structures and the resultant chemical transformations. Recent advancements highlight the field's potential in reducing reliance on hazardous solvents, improving energy efficiency, and supporting sustainable practices(Wu and Deng 2017: galant et al, 2022). Mechanochemistry's applications extend to recycling and resource recovery, particularly in the context of valuable metals and materials, aligning with the principles of green chemistry and the circular economy. Mechanochemistry stands as a transformative and evolving area of research with significant implications for scientific progress and industrial applications, promising to drive innovation and sustainability in various sectors (Billik, et al, 2007). Mechanochemical synthesis of zinc oxide nanoparticles holds the prospect for treating waste effluents, nevertheless, there are gaps in the subsequent knowledge domains. Most precursor for Zinc nanoparticles in the literature were Zinc acetate, Zinc Sulphate, Zinc nitrate and ZnO. This work tends to use $Zncl_2$ as precursor for ZnO nanoparticle. In the synthesis of ZnO nanoparticle, the commonly oxygen sources are oxygen gas, oxalic acid, citric acid, NaOH and KOH (Taherizadeh et al, 2021: Taheran, et al, 2018). It wound involved the use air as oxygen source in order to reduce cost and alse create room for green nanoparticle. Limited number of articles on surface modification of ZnO nanoparticles to improve the adsorption capacity and selectivity toward the pharmaceutical contaminants. There are very limited 'peer to peer' reviews comparing the effectiveness of mechanochemically synthesized ZnO nanoparticles with other treatment technologies (biological. Restaurant waste, Chemical and physical methods) for restaurant waste treatment (Xiao et al, 2028). There is no article published on the application of zinc oxide nanoparticles on restaurant effluents to the best of my knowledge.

MATERIALS AND METHODS.

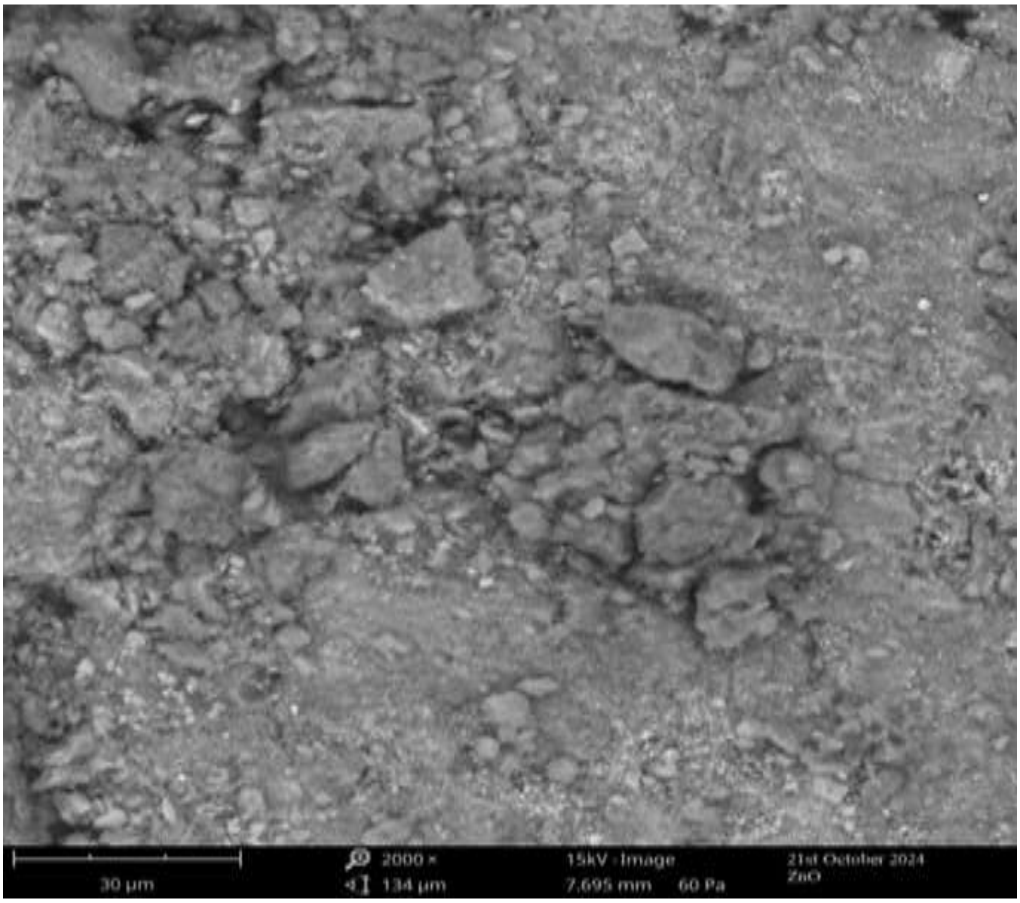
The waste water samples were collected from five different restaurants in Awka, Anambra state (5 star, Crunches, Nourisha, Stanel and Ofiaku Kitchen). The sampling points (5 locations) in the restaurant's Wastewater stream and outlets were first identified within each restaurant. Grab sampler in the form of syringe was used to suck the wastewater into a plastic container (water bottle) these collection bottles were washed with distilled water to avoid contamination and were labeled appropriately. The starting materials were anhydrous $ZnCl_2$ granules (Merck,99.5%), Na_2CO_3 powder (Merck,99%) and NaCl (Merck,99%). All the starting materials were dried in air. The NaCl was used as an inert diluent and added to the starting powders. The mixture of starting powders was milled in a ball mill with zirconia balls of 10mm in diameter and 250 rpm . The precursor was calcined at 400°C in air in a porcelain crucible for 0.5h to prepare the ZnO nanoparticles. Since the mechanochemically formed $ZnCO_3$ nanoparticles were isolated in the NaCl matrix, sintering of the ZnO powder did not occur during heat treatment. Removal of the salt by-product was carried out by washing the powder with de-ionized water. The washed powder was dried in a spray drier. Powder characterization was carried out using XRD (Cu-Kα radiation), SEM. American Public Health Association, APHA standard method was used in the evaluation of the physiochemical parameters of the pharmaceutical wastewater. Identification of the bacterial isolates was accomplished by the observation of colonial characteristics, Gram reaction and biochemical tests (Chessbrough, 1984). The characterization of the isolates were performed, by employing Gram staining reaction, Catalase test, Citrate test, Sugar fermentation test, Coagulase test, Motility test, Indole test, Methyl Red and Voges proskauer test as described by (Bergey's Manuel of Determinative Bacteriology, 1994).

RESULTS AND DISCUSSION.

The image on fig 1 shows the SEM analysis of the synthesized zinc oxide nano particles. SEM analysis was done to determine the morphological composition and crystal structure of materials. The EDX analysis was carried out to determine the elemental composition of the synthesized nanoparticles .

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

Fig. 1: Scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) analysis of synthesized nanoparticles



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	10.35	4.58
13	Al	Aluminium	6.97	1.80
26	Fe	Iron	6.43	8.01
20	Ca	Calcium	2.78	3.40
12	C	Carbon	33.85	24.24
11	Na	Sodium	6.36	5.96
30	Zn	Zinc	41.18	30.88
16	S	Sulfur	10.61	10.60
17	Cl	Chlorine	0.52	0.57
15	P	Phosphorus	5.58	5.55
19	K	Potassium	5.36	4.47

The particles appear to be irregularly shaped and range in size from a few micrometers to tens of micrometers. Some particles seem to have more rounded shape, while others are more angular. These characteristics shows that the particles analyzed is powdered sample as irregular shapes and sizes of the particles are consistent with a powdered material. The surface between the particles is not smooth but has a somewhat porous or rough appearance. There are small cervices and indentations visible. The uneven surface is due to the coating process

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

or the underlying materials texture. This shows the surface of a material coated with zinc oxide. The variation in shapes and sizes reflects different crystal growth habits.

The EDX analysis shows elemental composition of the analyzed material. The element and weight composition identified in the sample include Silicon (4.58%), Aluminium (1.80%), Iron (8.10%), Calcium (3.40%), Carbon (24.24%), Sodium (5.96%), Zinc (30.88), Sulfur (10.60%), Chlorine (0.57%), Phosphorus (5.55), Potassium (4.47%). From the analysis, it can be noted that the sample contains high percentage of zinc.

The infrared spectra of the synthesized zinc oxide was measured from 400 to 4000 cm-1 to determine the functional group present in the sample. fig 4.1.2 shows the FTIR spectra obtained.

Table 2: FTIR analysis of synthesized zinc oxide nanoparticle.

Peak	Peak sharp	Peak intensity	Bond	Compound
762.049	Strong	Broad	C-H bending	1,2,3-trisubstituted alkene
1228.409	Medium	Broad	C-O stretching	Alkyl aryl ether
1435.423	Strong	Sharp	C-H bending	Alkane
1622.39	Strong	Sharp	C=O stretching	δ-lactam
1841.337	Strong	Sharp	C=O stretching	Anhydride
1933.084	Weak	Broad	C-H bending	Aromatic compound
2455.438	Strong	Sharp	P-H stretching	Phosphine
2695.343	Medium	Sharp	C-H stretching	Aldehyde
2810.917	Medium	Sharp	N-H stretching	Amine salt
2997.26	Medium	Sharp	C-H stretching	Alkane
3149.652	Medium	Broad	O-H stretching	carboxylic acid
3395.721	Medium	Sharp	N-H stretching	aliphatic primary amine
3512.543	Medium	Sharp	O-H stretching	Alcohol

The FTIR analysis of the synthesized zinc oxide nanoparticles is shown in table 2. Different peaks were observed indicating the presence of different functional group in the nanoparticles. Absorption peak for O-H stretching was observed at 3512.543 cm^{-1} indicating the presence of alcohol. Peak for N-H stretching was observed at 3395.721 cm^{-1} indicating the presence of aliphatic primary amine with overtones at 2810.917 cm^{-1}. O-H stretching of carboxylic acid was identified at 3149 cm^{-1}. Absorption peak corresponding to C-H stretching of alkane was found at about 2997cm^{-1} with overtone at about 1435 cm^{-1}. The presence of aromatic compound was found at about 19933 cm^{-1}. The presence of carbonyl functional group was found at about 1622 cm^{-1} and 1841 cm^{-1}.

Table3: Physiochemical Analysis of Untreated/Treated Restaurant Wastewater Discharge

	Untreated sample	Treated sample	% Removal
Turbidity NTU	377.0000 ± 0.000	52.3333 ± 0.5774	86.1185
pH	8.4000 ± 0.000	7.1100 ± 0.000	15.3571
TDS (mg/L)	1274.333 ± 1.1547	411.3333 ± 1.1547	67.7217
Conductivity usm/cm	215.3333 ± 1.5275	58.0000 ± 0.0000	73.0650
Chloride (mg/L)	170.6667 ± 7.2342	34.6667 ± 2.5166	79.6875

DO (mg/L)	22.7667 ± 0.0577	8.6000 ± 0.0000	62.2255
BOD (mg/L)	297.0000 ± 8.7178	25.6333 ± 1.2014	91.3693
Sulphate (mg/L)	159.7300 ± 0.0400	7.0967 ± 0.0306	95.5571
Phosphate (mg/L)	85.2533 ± 0.0390	2.3167 ± 0.0306	97.2826
Phenol mg/L	0.5870 ± 0.1053	0.4080 ± 0.3727	30.4940
Nitrate (mg/L)	320.0433 ± 12.5164	0.1990 ± 0.0114	99.9378
TSS (mg/L)	13.0533 ± 0.5499	1.1333 ± 0.0814	91.3179
COD mg/L	627.6667 ± 8.3865	139.6667 ± 5.8595	77.7483

The turbidity values for the untreated and treated waste water were analyzed. The result of this study indicated that the level of turbidity was 377.0000±0.000 mg/L and 52.3333±0.5774 mg/L for the untreated and treated waste discharge respectively (Table 3). There was a percentage removal of 86.1185 %. The mean turbidity between the samples were statistically different at $p<0.05$. turbidity id a measure of cloudiness of fluids owing to the availability of suspended particles, it gives an insight of the state of water quality, high turbidity increases the percentage of contamination which will invariably constitute to water borne diseases (Owatude et al., 2020).

The pH of a solution refers to its hydrogen ion activity and is expressed as the logarithm of the reciprocal of the hydrogen ion activity at a given temperature. The pH of the untreated water sample was 8.4, this indicated that the effluents is slightly alkaline. The pH of the treated sample was 7.11±0.000, indicating that the treated sample was neutral with a % removal of 15.3571%. The high pH value could be as a result of the constituents added together in making the finished product. Discharge of wastewater with extremely high pH is injurious to the environment (Nirgude et al., 2013).

Total dissolve solids (TDS): TDS values for the untreated and treated water sample was 1274.333 ± 1.1547 mg/L and 411.3333 ± 1.1547 mg/L with a % removal of 67.7217 %. Water may be adjudged based on the level of TDS: for drinking purpose (500 mg/L); for irrigation (about 2,000 mg/L), not suitable for drinking and irrigation purposes (> 3000 mg/L) (ICMR, 1975). TDS is a function of all the dissolved matters such as dissolved ions of resins, organic/inorganic solvents, surfactants, etc. (Uwidia and Ukulu 2013).

Electrical Conductivity: The ability of water to convey electrical charge is measured by determining it electrical conductivity. It is proportional to its dissolved mineral matter content (Acharya et al., 2008). The source of conductivity may be an abundance of dissolved salts due to addition of table salt in food materials, actual salt present in pure water, and other mineral discharges. The conductivity values are found to be 215.3333 ± 1.5275 µs/cm for the untreated water sample and 58.0000 ± 0.0000 µs/cm for the treated water sample with a % removal of 73.0650%. The values of conductivity in food waste water is high as a result of high salt content in food. Chloride content: The chloride content in the untreated waste water sample was 170.6667 ± 7.2342 mg/l, and that of the treated waste water sample was 34.6667 ± 2.5166 mg/l with a % removal of 79.6875 %. High chloride content is an indication of unsafe water as it may threaten the sustainability of ecosystem and thus pose a risk to the survival of many species, their growth and reproduction (Imo et al., 2017). The levels of DO, BOD, and COD in this study for the untreated were 22.7667 ± 0.0577 mg/L, 297.0000 ± 8.7178 mg/L, and 627.6667 ± 8.3865 mg/L and for the treated sample were 8.6000 ± 0.0000mg/L, 25.6333 ± 1.2014 mg/L and 139.6667 ± 5.8595 mg/L. DO is a measure of pollution degree and decomposition of organic matters, and self-purification capacity of water body. BOD is the rate at which oxygen is used by microorganisms for the aerobic degradation of dissolved organic matters in a period of 5 days (Lokhande et al 2011). COD test is useful in pinpointing toxic condition and presence of biological resistant substances (Chaurasia and Tiwari 2011).

Sulphate, Nitrate, and Phosphate. The concentrations of sulphate, nitrate, and phosphate in untreated water sample 159.7300 ± 0.0400 mg/L, 320.0433 ± 12.5164 mg/L and 85.2533 ± 0.0390 mg/L respectively. The concentration of sulphate, Nitrate and Phosphate in the treated sample were 7.0967 ± 0.0306 mg/L, 0.1990 ± 0.0114 mg/L and 2.3167 ± 0.0306 mg/L respectively refer Table 4.2. High concentration of sulphate, nitrate, and phosphate was observed at the untreated water samples but was reduced in the treated waste effluent with a

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

percentage removal at 95.5571% for sulphate, 99.9378% for nitrate and 97.2826% for phosphate with zinc oxide. High amounts of sulphate impart bitter taste to water (Bodhaditya 2008). Nitrate is a major ingredient of farm fertilizers and is necessary for plant uptake and is essential for plant growth (Neal et al.,2008). However, if algae grow too wildly, oxygen levels will be reduced and fish will die. Phosphates are mostly from fertilizers, pesticides, industry, and cleaning compounds. Phosphates enhance the growth of plankton and water plants that serve as food for fish and aquatic life which results in increase of fish population that improves the quality of aquatic life. If excess phosphate is present, it may result in eutrophication. Many fish and aquatic organisms may not survive (APHA 2005).

Table 4: Heavy metal analysis of untreated and treated restaurant effluent by zinc oxide nanoparticles.

metals	Untreated	Treated	% Removal
Cd (mg/L)	0.4690 ± 0.0197	0.0077 ± 0.0050	1.6347
Cr (mg/L)	0.2190 ± 0.0340	0.1050 ± 0.0062	47.9452
Cu (mg/L)	0.9150 ± 0.5560	0.8717 ± 0.1150	95.2641
Pb (mg/L)	0.8663 ± 0.0145	0.2948 ± 0.0033	34.0285
Hg (mg/L)	0.0587 ± 0.0067	0.0020 ± 0.0026	3.4091
Zn (mg/L)	0.2920 ± 0.0078	1.5318 ± 0.1690	524.5890
Ni (mg/L)	0.0133 ± 0.0047	0.0013 ± 0.0006	10.0000
As (mg/L)	0.0067 ± 0.0025	0.0000 ± 0.0000	0.0000
Fe (mg/L)	1.9587 ± 0.1366	0.5798 ± 0.1266	29.6035

The concentrations of the metals in the untreated sample include Cd (0.4690 ± 0.0197 mg/L), Cr (0.2190 ± 0.0340 mg/L), Cu (0.9150 ± 0.5560 mg/L), Pb (0.8663 ± 0.0145 mg/L), Hg (0.0587 ± 0.0067 mg/L), Zn (0.2920 ± 0.0078 mg/L), Ni (0.0133 ± 0.0047 mg/L), As (0.0067 ± 0.0025 mg/L) and Fe (1.9587 ± 0.1366 mg/L) (Table 4). The treated waste water had metal concentration of Cd (0.0077 ± 0.0050 mg/l), Cr (0.1050 ± 0.0062 mg/L), Cu (0.8717 ± 0.1150 mg/L), Pb (0.2948 ± 0.0033 mg/L), Hg (0.0020 ± 0.0026 mg/L), Zn (1.5318 ± 0.1690 mg/L), Ni (0.0013 ± 0.0006 mg/L), As (0.0000 ± 0.0000 mg/L) and Fe (0.5798 ± 0.1266 mg/L. All the heavy metal reduced upon treatment with zinc oxide nanoparticles except zinc which increased which could be attributed with the zinc nanoparticle leaching out into the sample. copper had the highest % removal of about 95% followed by Cr >Pb>Fe>Ni>Hg>Cd>AS. Heavy metals are inorganic elements that are very toxic in relatively higher amounts (Egborge 1994). High concentration of Cd will inhibit the bio-uptake of P and K by plants (Matsuo et al., 1995). The implication is that such effluent if discharged into the environment untreated poses a great risk to humans and animals altogether.

Table 5: Physiochemical parameters compared with standard for effluent discharge to the environment.

	Untreated sample	Treated sample	Permissible limit by CPCB (mg/L)	EPA standard (2002)
Turbidity NTU	377.0000	52.3333	-	-
pH	8.4000	7.1100	5.5-9.0	5 – 9
TDS (mg/L)	1274.333	411.3333	2100	-
Conductivity usm/cm	215.3333	58.0000	-	-
Chloride (mg/L)	170.6667	34.6667	1.000	750
DO (mg/L)	22.7667	8.6000	-	4

BOD (mg/L)	297.0000	25.6333	30.00	40
Sulphate (mg/L)	159.7300	7.0967	2.0	750
Phosphate (mg/L)	85.2533	2.3167	10	10
Phenol mg/L	0.5870	0.4080	1.0	0.5
Nitrate (mg/L)	320.0433	0.1990	10	10
TSS (mg/L)	13.0533	1.1333	<100	45
COD mg/L	627.6667	139.6667	250	120

The pH concentrations in the water samples were within the acceptable range (5-9) specified by CPCB and EPA (Table 5). The TDS values for the untreated water sample (1274.333 mg/L) was above the permissible limit (2100 mg/L) specified by CPCB but after treatment with zinc oxide, the levels of TDS (411.3333 mg/L) was lower than the CPCB standard. The chloride concentration for both samples (untreated and treated), were above the acceptable limit specified by CPCB but was lower than the acceptable limit by EPA. The DO in the untreated water sample (22.7667 mg/L) and treated water sample (8.6 mg/L) were higher than the permissible limit by EPA. 4 mg/L is the standard for keeping aquatic lives, concentration below 2 mg/L poses hazard to aquatic life in general and could cause death of vulnerable fishes (Chapman 1997). The BOD concentration in the untreated waste water (297 mg/L) was higher than the permissible limit by CPCB (30 mg/L) and EPA (40 mg/L) for discharge of water into the environment. Treatment with zinc oxide causes a reduction in the BOD concentration to the permissible limit as indicated in table 4.2.3. The COD concentration in the untreated water (627.6667 mg/L) was higher than the specified limit by EPA(150 mg/L) and CPCB (250 mg/L) for discharge of effluent into the environment. This reduces upon treatment with zinc oxide to permissible range (139.6667 mg/L). The high BOD and COD concentrations observed in the waste water might be due to use of chemicals in food processing.

The levels of sulphate in the samples, were within the acceptable limit of EPA standard for discharge of effluents into the environment. This was not same for the acceptable limit by CPCB standard as the concentration of sulphate for both samples were above the permissible limit for discharge of waste water into the environment as shown in table 4.2.3. Phosphate and nitrate concentration in the untreated waste effluent were above the permissible level by CPCB (10 mg/L) and EPA (10 mg/L). The treated water shows reduction the concentration of Phosphate and nitrate below the permissible limit by CPCB and EPA. Phenol concentration in both samples was within the acceptable limit for discharge of effluent into the environment specified by CPCB and EPA.

Table 6: Comparison of the physiochemical parameters with previous work on discharge of food processing industries.

	Untreated sample	Jingxi et al., 2020	Jingxi et al., 2020
Turbidity NTU	377.0000	36.22	34.34
pH	8.4000	10.20	9.30
TDS (mg/L)	1274.333	370.44	255.23
Conductivity usm/cm	215.3333	1335.21	1340.32
Chloride (mg/L)	170.6667	-	-
DO (mg/L)	22.7667	8.40	6.45
BOD (mg/L)	297.0000	160.15	150.25
Sulphate (mg/L)	159.7300	115.35	85.25
Phosphate (mg/L)	85.2533	12.75	10.50

Phenol mg/L	0.5870	-	-
Nitrate (mg/L)	320.0433	30.30	25.15
TSS (mg/L)	13.0533	310.25	210.30
COD mg/L	627.6667	210.30	195.15

The pH value obtained for the untreated waste water was lower than those obtained by Jingxi et al., 2020 (9.30 and 10.20). The turbidity of the restaurant waste water (377 NTU) was higher than that obtained by jingxi et al.2020 for waste water from restaurant at different point (36.22 and 34.4 NTU). The conductivity obtained for the untreated waste water was lower than those obtained by jingxi et al.2020 (Table 6). The sulphate, phosphate, nitrate, DO, BOD and COD values were higher those obtained by jingxi et al.2020 (table 4.2.3). The concentration of total soluble solids (13.0533 mg/L) was lower than those reported by jingxi et al.2020.

Table 7: Comparison of the metal concentration with standard for discharge of effluent into the environment.

Metal	Untreated	Treated	CPCB	WHO
Cd	0.4690	0.0077	2.00	0.01
Cr	0.2190	0.105	2.00	0.50
Cu	0.9150	0.872	3.00	0.01
Pb	0.8663	0.29	0.10	0.10
Hg	0.0587	0.0020	0.01	0.0005
Zn	0.2920	1.53	5.00	0.20
Ni	0.0133	0.0013	3.00	0.10
As	0.4690	0.0077	0.20	0.05
Fe	0.2190	0.1050	3.00	1.00

From the result (Table 7), it was observed that the concentration of cadmium (0.4690 mg/L) in the untreated water sample was lower than the CPCB standard (2.00 mg/L) but higher than 0.01 mg/L of WHO standard but when treated with zinc oxide, it was within the specified standard of both CPCB and WHO. The chromium concentration of both samples were within the acceptable limit by CPCB and WHO for discharge of effluent into the environment. Copper concentration in the untreated (0.915 mg/L) and treated (0.872 mg/L) waste water sample was above the acceptable limit by CPCB (3 mg/L) and WHO (0.01 mg/L). Lead concentration in the treated and untreated samples were higher than the acceptable limit by CPCB and WHO. The untreated samples showed higher concentration of mercury than the acceptable limit of 0.01 mg/L by CPCB and 0.0005 mg/L by WHO standard. Zn concentration for the untreated sample was within the CPCB snd WHO standard for discharge of effluents into the environment. The treated samples showed higher concentrations of zinc above the CPCB and WHO standards. This can be attributed to the zinc ions from the nanoparticles in the higher concentration in the sample which shows that water is danger for aquatic life. Zn plays a biochemical role in the life processes of all aquatic plants and animals; therefore, it is essential in the aquatic environment in trace amounts. Zinc is used in a number of alloys including brass and bronze, batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals, but at elevated levels, it is toxic to some species of aquatic life (Chaurasia and Tiwari 2011). Nickel concentration in the samples were within the acceptable limit specified by CPCB and WHO standard. Arsenic concentration for the untreated waste water was above the CPCB and WHO (table 4.3.1). The treated waste water had concentration of arsenic below the CPCB and WHO standard for discharge of effluents into environment. Iron concentration were found to be below the acceptable limit by CPCB and WHO. Although, iron is one of the essential elements in human nutrition, however, its presence at elevated concentration in aquatic ecosystems poses serious pollution and health problems (De, 1994). Vomiting, cardiovascular collapse, and diarrhea have been reported due to deficiency of iron, while it may lead to failure of blood clotting. According to the WHO guideline value, maximum contaminant levels of 1 mg/L (water) for

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

Fe are acceptable. Above 1 mg/L might lead to pollution of the aquatic environment. The untreated samples had higher concentrations of heavy metals above the acceptable limit. The implication is that such effluent if discharged into the environment untreated poses a great risk to humans and animals altogether. Similar report was made by Siyanbola et al. (2011) whereby the concentrations of Pb, Cr, Cd, and Fe in some effluents were away from the standards stipulated by FEPA (FEPA 1991).

Table 8: Contamination Factor for Heavy metal

Metals (mg/L)	Contamination factor for Untreated effluents		Contamination factor for Treated effluents	
	CPCB	**WHO**	**CPCB**	**WHO**
Cd	0.2345	46.9000	0.0038	0.7667
Cr	2.1900	0.4380	1.0500	0.2100
Cu	0.3050	91.5000	0.2906	87.1667
Pb	8.6633	8.6633	2.9480	2.9480
Hg	5.8667	117.3333	0.2000	4.0000
Zn	0.0584	1.4600	0.3064	7.6590
Ni	0.0044	0.1333	0.0004	0.0133
As	0.0333	0.1333	0.0000	0.0000
Fe	0.6529	19.5867	0.1933	5.7983

$$CF = \frac{\text{Metal concentration in sample}}{\text{Background or reference value}}$$

CF<1: No contamination, CF =1-3:moderate contamination, CF=3-6: significant contamination CF>6: severe contamination. CF compared between CPCB standard and WHO standard for discharbe of effluents into the environment.

From table 8, it could be observed that according CPCB standard, there was no contamination (CF<1) of cadmium, copper, zinc, Nickel, Arsenic, iron and severe contaminations (CF>**6)** of lead and mercury. According to WHO standard, the was severe contaminations (CF>6**)** of Cd, Cu, Pb, Hg and Fe. There was no contamination (CF<1) of Cr, Ni and As. There was moderate contamination by (CF=1-3) of zinc. Upon treatment with zinc oxide, there was no contamination by Cd, Cu, Hg, Zn, Ni, As and Fe according to CPCB standard. Lead concentration reduced from severe contamination to moderate contamination. There was no contamination by Cd, Cr, Ni and As per WHO standard. The level of Hg and Fe reduced from severe contamination to significant contamination (3-6). Copper concentration was severe after treatment according WHO standard.

Table 9; Geo-Accumulation index of heavy metal in restaurant wastewater effluent.

	Untreated CPCB	Untreated WHO	Treated CPCB	Treated WHO
Cd (mg/L)	0.0471	9.4122	0.0008	0.1539
Cr (mg/L)	0.4395	0.0879	0.2107	0.0421
Cu (mg/L)	0.0612	18.3628	0.0583	17.4932
Pb (mg/L)	1.7386	1.7386	0.5916	0.5916
Hg (mg/L)	1.1774	23.5472	0.0401	0.8027
Zn (mg/L)	0.0117	0.2930	0.0615	1.5371

Ni (mg/L)	0.0009	0.0268	0.0001	0.0027
As (mg/L)	0.0067	0.0268	0.0000	0.0000
Fe (mg/L)	0.1310	3.9308	0.0388	1.1636

IGEO= log2 $\frac{\text{concentration of heavy metal}}{\text{1.5 background or reference value}}$

igeo ≤ 0: unpolluted. 0 < igeo ≤ 1: unpolluted to moderately polluted. 1 < igeo ≤ 2: Moderately polluted, 2 < igeo ≤ 3 moderately to heavily polluted, 3 < ige o≤ 4: Heavily polluted, 4 < igeo ≤ 5: Heavily to extremely polluted, igeo > 5: Extremely polluted**.**

The result obtained in this study (Table 9) showed that according by the specification by CPCB standard, the geo-accumulation of the heavy metals indicated that the waste water was in a rane of unpolluted to moderately polluted (0 < igeo ≤ 1) for Cd, Cr, Cu, Zn, Ni, As, and Fe. The waste water was moderately polluted with by Pb and Hg (1 < igeo ≤ 2) which after treatment, the geo-accumulation index of the heavy metals in the waste water was unpolluted to moderately polluted per CPCB standard. This was different when considering WHO standard. The result shows that the waste water was extremely polluted with Cd, Cu and Hg (igeo > 5), moderately polluted by Pb and not polluted by Cr, Zn, Ni and As. Upon treatment with zinc oxide, the waste water was not polluted with the analyzed heavy metals except Cu which extremely polluted the sample and Zn which moderately polluted treated waste water.

Table 10: Potential Ecological Risk Index (PERI) for Heavy Metal

	Untreated sample		Treated Sample	
	ERF CPCB	**ERF WHO**	**ERF CPCB**	**ERF WHO**
Cd	3.5917	23.9445	0.1983	1.3223
Cr	6.7085	0.0447	10.8658	0.0724
Cu	2.3357	23.3573	7.5170	75.1696
Pb	66.3450	2.2115	76.2677	2.5423
Hg	359.4221	239.6147	10.3484	6.8989
Zn	0.0894	0.0745	1.5852	1.3210
Ni	0.0340	0.0340	0.0115	0.0115
As	0.5105	0.0681	0.0000	0.0000
Fe	5.0000	5.0000	5.0000	5.0000
PERI	444.0370	294.3494	111.7939	92.3380

ERF (Ecological Risk Factor) = Erichment fator x Toxic response factor

Enrichment Factor = $(\frac{\text{metal concentration in sample}}{\text{Background value}})/(\frac{\text{Fe concentration in sample}}{\text{Background Fe}})$

PERI = ∑ (ERF values of each metal). Toxic response factor (TRF) values: Cd=30, Cr=2, Cu=5, Pb=5, Hg=40, Zn=1, Ni=5, As=10.

The potential ecological risk index is shown in table 10. The result indicated that the untreated waste water according to CPCB standard has a very high ecological risk (PERI ≤ 320) but reduces upon treatment with zinc oxide to considerable ecological risk (80 ≤ PERI < 160). The untreated waste water had a potential ecological risk index of 294.3494 mg/L per WHO standard indicating High ecological risk (160 ≤ PERI < 320) and reduces

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

upon treatment to considerable ecological risk.

Table 11: Microbial analysis of Restaurant waste water

	No. of Bacterial colonies on plate (cfuml-[1])	Total Bacterial Count (cfuml-[1])	E.coli (cfuml-[1])	Total Fungal Count (CFU/ml)
BEFORE	**8.2 X 10^4**	**5.9 X 10^9**	**18**	**7.7 X 10^3**
AFTER	**35.0**	**3.0 x10^2**	**12**	**12 X 10^0**

From the result (Table 11), a total of 5.9 X 10^9 cfuml^{-1} bacterial, 8.2 X 10^4 cfuml^{-1} bacterial colony, 18 cfuml^{-1} E. coli, and 7.7 X 10^3 cfuml^{-1} fungal count were identified in the untreated water samples (Table 10). Treatment with zinc oxide, a total of 3.0 x10^2 cfuml^{-1} bacterial count, 35 cfuml^{-1} bacterial colony, 12 cfuml^{-1} E. coli and 12 X 10^0 cfuml^{-1} fungal count was identified. There was a decrease in the total number of microorganisms found in the samples after treatment with zinc oxide.

Table 12: Poly Aromatic Hydrocarbon (PAH)

PAH	**Untreated (mg/L)**	**Treated (mg/L)**	**% Removal**
Naphthalene	3.8341	0.1561	95.9286
Acenaphthene	1.7744	5.8254	69.5403
Fluorene	18.2963	0.4655	97.4558
Phenanthrene	12.1496	7.1183	41.4112
Anthracene	32.3179	0.5576	98.2746
Fluoranthene	10.4689	0.3892	96.2823
Acenaphthylene	1.6029	1.0576	34.0196
Pyrene	5.8944	0.1316	97.7674
Benzo(a) anthracene	11.3748	1.0439	90.8227
Chrysene	9.6763	1.8268	81.1209
Benzo (b) anthracene	6.2144	0.8593	86.1724
Benzo (b) fluoranthene	15.7278	0.3351	97.8694
Benzo (k) fluoranthene	6.6340	0.3563	94.6292
Benzo (a) pyrene	2.1988	1.8081	17.7688
Dibenzo (a, h) anthracene	11.0499	0.0976	99.1167
Benzo (g, h, i) perylene	13.8220	7.5177	45.6106
Indeno (1, 2, 3) pyrene	5.4326	1.4250	73.7695

The result (Table 12) showed that the untreated waste water contains higher concentrations of PAHs which reduces after treatment with zinc oxide. Higher percentage removal was observed in Dibenzo (a, h) anthracene (99.1167 %), Anthracene (98.2746 %) Pyrene (97.7674 %), fluorene (97.4558%), Fluoranthene (96.2823% Naphthalene **(**95.9286%), Benzo (k) fluoranthene (94.6292 %), Benzo(a) anthracene (90.8227 %), Benzo (b) anthracene (86.1724 %), Chrysene (81.1209 %), Indeno (1, 2, 3) pyrene (73.7695 %). Other had lower % removal.

The restaurant waste water samples were analyzed for the presence of VOCs using Gas Chromatography couped

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume X Issue VIII August 2025

with flame ionization detector. This proof to be an effective tool for determination of compounds. It was identified that the sample contains different concentrations of VOCs which upon treatment with zinc oxide reduces to a considerable amount.

Tabel 13: Volatile Organic Carbon (VOC) analysis of untreated Restaurant waste water. Organic Carbon (VOC) analysis of Restaurant waste water.

VOC	Untreated (mg/L)	Treated (mg/L)	% Removal
Benzene	1.11247	0.2519	77.3567
Toulene	0.17690	0.0013	99.2651
o-Xylene	7.2779	2.7674	61.9752
Styrene	31.8001	0.0000	100.000
Chloroform	9.4054	0.6468	93.1231
Chlorobenzene	1.3051	0.000	100.000
1,2,4-Trichlorobenzene	12.1821	4.0339	66.8867
Isopropylbenzene	4.2767	0.2239	94.7647
n-Propyllbenzene	16.8976	5.6805	66.3828
p-Isopropyltoluene	2.0777	1.03724	50.0775
n-Butylbenzene	1.2273	0.00	100.000
Carbontetrachloride	1.0492	1.043139	0.57768
Trichloroethlene	5.3930	2.99765	44.4159

From the result (Table 13), it was shown that the highest concentration of VOC identified was styrene (31.8001 mg/L), n-Propyllbenzene (16.8976 mg/L) and the lowest concentration identified was Toluene (0.1769 mg/L) in the untreated sample. These were removed by zinc oxide after treatment by at least 66 % removal. This shows that zinc oxide nanoparticles can be employed in the treatment of VOC containing compounds before discharge into the environment as they have significant adverse effects on human health. The health effects include both non-carcinogenic (sensory, irritation, allergic, and respiratory) and carcinogenic effects due to the high toxicity of VOCs (Fisher et al., 2017). The carcinogenic effects, on the other hand, are much more severe, with VOCs such as benzene and formaldehyde having considerably high lifetime cancer risk (Pandey and Yadav 2018).

CONCLUSION

The analysis of wastewater treatment reveals several critical findings regarding the characteristics and composition of both untreated and treated water samples. The particles examined are irregularly shaped and range from a few micrometers to tens of micrometers, indicating a powdered material with a rough surface. Elemental analysis through EDX shows a significant presence of various elements, particularly zinc, among others such as silicon, aluminum, and iron. Overall, the findings underscore the effectiveness of zinc oxide nanoparticles in treating wastewater, improving water quality, and mitigating health risks associated with untreated wastewater. The study emphasizes the importance of continued monitoring and treatment of wastewater to protect both human health and the environment.

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