



PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE FROM TEXTILE EFFLUENTS WITH GREEN SYNTHESIZED UREA-DOPED ZINC OXIDE NANOPARTICLES AS PHOTOCATALYST.

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ABSTRACT

The consistent discharge of untreated effluents by industries into water bodies that serve as a source of water for human consumption has resulted in a break out of several lethal diseases especially among communities with proximity to these industries. One industry that contributes to water pollution Textile industry. Its effluents are known to contain organic pollutants like methylene blue, methyl red, etc. In the last five decades, several technologies have been developed but Advanced Oxidation Processes have proven more efficient in tackling the menace of organic pollutants. In this research study, organic compounds pollutant in textile wastewater was degraded through Photocatalysis with green synthesized urea-doped zinc oxide (GS Urea-doped ZnO) acting as photocatalyst. The photocatalyst (GS Urea-doped ZnO) was produced from Zinc Nitrate through wet impregnation method. Structural, morphological and optical properties of the synthesized GS Urea-doped ZnO were obtained by carrying out SEM-EDX, FTIR and XRD analysis. The effects of process parameters (Time, catalyst dosage, pH and initial concentration) on the rate of degradation was also studied. Preliminary studies on photocatalytic degradation revealed that GS Urea-doped ZnO yielded a higher percentage of photocatalytic degradation than pure ZnO and the latter was safe and environmentally friendly than the former. The optimum percentage degradation for the preliminary studies experiments was observed to be 75% and it was achieved with GS 5% Urea-ZnO, 150 minutes and at an initial concentration of 20mg/L. From the results obtained, it can be

established that green synthesized Urea-doped Zinc oxide nanoparticles can be used effectively in water treatment and environmental safety applications.

Keywords: *Photocatalysis, Photocatalyst, Tigernut oil, Trans-esterification, Biodiesel,*

INTRODUCTION

Water pollution is the discharge of untreated waste materials into several water bodies. It is one major challenge faced in the world today.

Seventy per cent of the universe is composed of water, and this makes water pollution a major threat to the ecosystem. Water pollution often results from the consistent discharge of untreated industrial/municipal waste into various water bodies. The toxicity of these untreated waste often makes the water unfit for human consumption. One of the industries that contribute to water pollution is the textile industry. The textile industry discharges untreated non-biodegradable dye into water bodies, and these dyes contain recalcitrant organic and inorganic compounds. Ingestion of these pollutants into the system of living organisms can result in various epidemics, cancerous and genetic diseases.

In recent years, various technologies have been used to combat water pollution caused by organic pollutants. However, advanced oxidation processes (AOPs) has been identified as the most economically viable option for treating industrial/municipal wastewater. Advanced Oxidation Processes (AOPs) are of six types and they include; radiation, photolysis and photo-catalysis, Sonolysis, electrochemical oxidation technologies, Fenton-based reactions, and ozone-based processes.

In recent years, Photocatalysis has been reported to exhibit high degradation of organic pollutants present in effluents from textile industries (Prabakaran 2019). Photocatalysis is defined as the occurrence of redox reaction with the help of a photocatalyst in the presence of visible light or ultraviolet light. However, the drawback for Photocatalysis has been the difference in bandgap energies between the photocatalytic material and visible light or ultraviolet light, and also the recombination of electrons in the valence band. In recent times, Photocatalysis has employed

various unique semiconductor metal oxide nanoparticles which include; TiO₂, ZnO, WO₃, In₂O₃ and SnO.

Among these ZnO showed superior properties because of its absorption range within the visible region, high photo-stability, good sensor abilities, light-emitting diodes and solar light harvesting. The photocatalytic performance of ZnO was not effective for the degradation of organic dyes due to an extensive bandgap (3.37eV) and the recombination of electron-hole pairs. In the past decade, researchers have synthesized ZnO from parent compounds such as; Zinc Nitrate, zinc sulphate, etc and various morphologies such as nanoparticles, nanorods, nanobelts, nanoarrows, nanoplates, nanotubes, nanowires, nanoflowers, nanospheres etc. were obtained. Also, functionalized ZnO nanoparticles have proven to have distinctive properties which include biocompatibility, a non-toxic nature, high stability and good photo-catalytic potential. Doping and introduction of impurities in ZnO nanoparticles have rendered them more active over a wide range of wavelengths (UV region to visible region) by reducing the bandgap energy. ZnO nanoparticles have been modified with different dopants consisting of nitrogen and sulphur atoms for enhancing the photocatalytic oxidation of organic dyes under UV light irradiation. Nitrogen-doped ZnO nanoparticles in the form of nanorods and nanowires have been used for water splitting applications.

In the last decade, nitrogen doping on ZnO nanoparticles has been synthesized using various methods such as thermal evaporation, pyrolysis and thermal nitridation with ammonia as a nitrogen source precursor. However, these methods demonstrated major disadvantage like higher temperature demands, hence these materials cannot be used in photocatalytic applications. Hydrothermal methods have exhibited better advantages such as simple processes, lower temperature demands, eco-friendliness and better time control.

Industrial activities of the textile industries have had adverse effects on the environment and it has immensely affected aquatic life, human activities, soil deterioration etc. Among the organic pollutants from textile industries, Methylene blue (MB) dye is a major compound that causes a serious problem. It is a cationic dye consisting of a conjugated aromatic moiety, which makes it favourable for photocatalytic activities because of easily

identified as cation and colour change. It is relatively easy to identify intermediate products during photocatalytic degradation. The identification of intermediates is in turn important for understanding the degradation mechanism on the aromatic group and methyl functionalized group on the benzene ring. Hence, MB degradation processes are crucial for noting whether complete mineralization occurs during Photocatalysis.

MATERIALS AND METHODOLOGY

Material and Equipment

The entire chemicals to be used in this study will be analytical grade (98-99.5%). They include Zinc Nitrate, Urea, Sodium Hydroxide, Deionized water. The equipment used are pH meter, weighing balance, beakers and conical flask, oven, stirrer, Furnace, Separatory funnel, UV Spectrophotometer.

Methodology

Photocatalyst Preparation

Sourcing of Paw-Paw & Extraction of Leaf Extract

Fresh paw-paw leaves were locally sourced and trees within the surrounding. It was then washed with distil water, dried for seven days and milled to obtain a powder form of it.

Phytochemical Test for paw-paw leaf liquid extract

Fifty grams of powdery form of paw-paw leaf was weighed using an electric weighing balance, it was soaked in 100ml of distilled water and then heated at 100oC for sixty minutes. Upon conclusion of the boiling process, the mixture was filtered and the liquid extract was obtained. Phytochemical process was then conducted on the liquid extract using the following procedures;

Total Phenol Determination

Singleton et al., (1999) method was used to determine total phenol content of aqueous extract of Datura metel seed. 0.01g of the crude extract was dissolved in 10mL of distilled water, and 0.5mL was oxidized by 2.5mL of 10% Folin-Ciocalteu's reagent which was then neutralized by 2mL of 7.5%

sodium carbonate. The reaction mixture was incubated at 45°C for 40 minutes. Absorbance was read at 765 nm using double beam Shimadzu UV spectrophotometer, UV-1800. Standard garlic acid was used to prepare the calibration curve.

Total Flavonoids Determination

Total flavonoid content of the aqueous extract of *Datura metel* seed was determined using the method of (Chang et al., 2002). 0.5 ml of the extract was added to a test tube containing 1.5 ml of absolute methanol, 0.1 ml of 10% aluminum chloride, 0.1 ml of 1M sodium acetate and 2.8 ml of distilled water and incubated at ambient temperature for 30 minutes. The absorbance was read at 415 nm with double beam Shimadzu UV-spectrophotometer, UV-1800. Standard quercetin was used to prepare the calibration curve.

Total Alkaloid Determination

Total alkaloid of the crude extract was determined using method of Oloyed, (2005). Using this, 0.5 g of the crude extract was weighed and dissolved in 5 ml of mixture of 96% ethanol:20% H₂SO₄ (1:1) and then filtered. 1 ml of the filtrate was then added to a test tube containing 5 ml of 60% H₂SO₄ and allowed to stand for 5 minutes. Thereafter, 5 ml of 0.5% formaldehyde was added and allowed to stand at room temperature for 3 hours. The absorbance was read at wavelength of 565 nm. Vincristine extinction coefficient (E₂₉₆, ethanol{ETOH}= 15136 M⁻¹cm⁻¹) was used as reference alkaloid.

Determination of Tannins

Tannin content of the crude extract was determined using the method of (AOAC, 1984). 0.2 g of the crude extract was weighed into a 50 ml beaker and 20 ml of 50% methanol was added to it and covered with para film and heated in water bath at 80°C for 1 hour. The reaction mixture was shaken thoroughly to ensure uniformity. The extract was then filtered into a 100 ml volumetric flask, and 20 ml of distilled water, 2.5 ml of Folin-Denis' reagent, and 10 ml of sodium carbonate were added and mixed properly. The reaction mixture was then allowed to stand for 20 minutes at room

temperature for the development of bluish-green coloration. The absorbance was taken at 760nm using double beam shimadzu UV-spectrophotometer, UV-1800. Standard tannic acid was used to prepare the calibration curve.

Determination of Saponins

Saponins content of the crude extract was determined using the method of (Oloye, 2005). 0.5g of the crude extract was weighed and dissolved in 20ml of 1N HCl and boiled in water bath at 80°C for 4 hours. The reaction mixture was cooled and filtered. 50ml of petroleum ether was added and the ether layer was collected and evaporated to dryness. Thereafter, 5ml of acetone-ethanol (1:1), 6ml of ferrous sulphate and 2ml of concentrated sulphuric acid were added and allowed to stand for 10 minutes. The absorbance was taken at 490nm. Standard Saponins was used to prepare the calibration curve.

Preparation of Pure Zinc oxide (ZnO)

Twenty grams of Zinc nitrate heptahydrate was weighed using the electric weighing balance and was poured into a flat bottom flask containing 30ml of deionized water and the mixture was then stirred thoroughly at 50rpm for 60min. Upon the conclusion of stirring, drops of 4M of sodium hydroxide (NaOH) was intermittently added to the mixture to precipitate zinc oxide and at pH 12, it was observed that formation of precipitates ceased to happen.

Thirty milliliters of deionized water was added to the resulting mixture, it was allowed to settle for thirty minutes and the liquid at the top layer of the flat bottom flask was decanted. The washing process was repeated three times. The mixture containing the precipitate and minute amount of liquid was dried in the oven at 100°C for six hours and the dried solid zinc oxide was crushed using an agate mortar so as to increase its surface area. The weight of the dried zinc oxide was taken and it was observed to be 10grams. The resulting solid particles (pure zinc oxide) were calcined at 350°C for two hours in a furnace.

Preparation of Green synthesized ZnO nanoparticles (G.S ZnO)

Fifty grams of powdery form of paw-paw leaf was weighed using an electric weighing balance, it was soaked in 500ml of distilled water and then heated at 100oC for sixty minute. Upon conclusion of the boiling procedure, the mixture was filtered and the liquid extract was obtained.

Twenty grams of Zinc nitrate heptahydrate was weighed using the electric weighing balance and was poured into a flat bottom flask containing 30ml of deionized water and 30ml of liquid paw-paw leaf extract and the result mixture was then stirred thoroughly at 50rpm for 60min. Upon the conclusion of stirring, drops of 4M of sodium hydroxide (NaOH) was intermittently added to the mixture to precipitate zinc oxide and at pH 12, it was observed that formation of precipitates ceased to happen.

Thirty milliliters of deionized water was added to the resulting mixture, it was allowed to settle for thirty minutes and the liquid at the top layer of the flat bottom flask was decanted. The washing process was repeated three times. The mixture containing the precipitate and minute amount of liquid was dried in the oven at 100oC for six hours and the dried solid zinc oxide was crushed using an agate mortar so as to increase its surface area. The weight of the dried zinc oxide was taken and observed to be 10grams. The solid particles (green synthesized zinc oxide) were calcined at 350oC for two hours in a furnace.

Doping of Green synthesized ZnO nanoparticles with Nitrogen from Urea

Ten grams of G.S ZnO and 1gram of urea were separately measured and poured into a round bottom flask containing 30ml of deionized water. The mixture was stirred rigorously at 80rpm for six hours and allowed to settle for 30minute. The liquid at the top layer was decanted and the mixture (thick slurry) remaining in the flat bottom flask was dried in the oven at 100oC for six hours. The resulting solid particles (Green synthesized nitrogen doped zinc oxide) were calcined at 350oC for two hours in a furnace. The process was repeated with 0.2gram and 2grams of urea.

Preliminary studies on degradation of Methylene Blue solution

The preliminary degradation of Methylene blue solution was carried out using various processes and the following parameters were kept constant;

pH of the solution, initial concentration of Methylene blue solution (20mg/L), catalyst dosage (0.5g/L) and time (150minutes).

Preparation of Methylene Blue Calibration Curve

The calibration curve on the ultra-violet spectrophotometer (UV-Vis Spec) was obtained by preparing various concentrations (20mg/L, 40mg/L, 60mg/L, 80mg/L and 100mg/L) of Methylene blue solutions and a wavelength of 663nm was used to calibrate the solution on the UV-Vis Spec.

Photolysis on Methylene blue solution

Hundred milliliters of 20mg/L of Methylene blue solution was placed in a round bottom flask and exposed to sunlight rays for sixty minutes. The concentration of the solution was measured hereafter using the UV-Spec and 1.1% degradation efficiency was observed.

Adsorption on Methylene blue solution

0.05g of the 5% green synthesized nitrogen doped zinc oxide (5% G.S N-ZnO) photocatalyst was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was stirred at 50rpm in the absence of sunlight rays for sixty minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for 10minutes so as to separate the photocatalyst. The concentration of the clear liquid sample solution after centrifugation was measured using the UV-Spec and 26.72%% degradation efficiency was observed.

Photodegradation of Methylene blue solution using pure ZnO

0.05g pure zinc oxide was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was first stirred at 50rpm for 30minutes in the absence of sunlight to attain absorption-desorption equilibrium, before it was exposed to sunlight rays and stirred at 50rpm for 150minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for 10minutes so as to separate the photocatalyst. The concentration of the

clear liquid sample solution after centrifugation was measured using the UV-Spec and 53.45% degradation efficiency was observed.

Photodegradation of Methylene blue solution using GS ZnO

0.05g green synthesized zinc oxide (G.S N-ZnO) photocatalyst was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was first stirred at 50rpm for 30minutes in the absence of sunlight to attain absorption-desorption equilibrium, before it was exposed to sunlight rays and stirred at 50rpm for 150minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for 10minutes so as to separate the photocatalyst. The concentration of the clear liquid sample solution after centrifugation was measured using the UV-Spec and 56.25% degradation efficiency was observed.

Photodegradation of Methylene blue solution using 5% GS N-ZnO

0.05g of the 5% green synthesized nitrogen doped zinc oxide (5% G.S N-ZnO) photocatalyst was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was first stirred at 50rpm for 30minutes in the absence of sunlight to attain absorption-desorption equilibrium before it was exposed to sunlight rays, and stirred at 50rpm for 150minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for 10minutes so as to separate the photocatalyst. The concentration of the clear liquid sample solution after centrifugation was measured using the UV-Spec and 72.6% degradation efficiency was observed.

Photodegradation of Methylene blue solution using 10% GS N-ZnO

0.05g of the 10% green synthesized nitrogen doped zinc oxide (10% G.S N-ZnO) photocatalyst was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was first stirred at 50rpm for 30minutes in the absence of sunlight to attain absorption-desorption equilibrium, before it was exposed to sunlight rays and stirred at 50rpm for 150minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for

10minutes so as to separate the photocatalyst. The concentration of the clear liquid sample solution after centrifugation was measured using the UV-Spec and 63.3% degradation efficiency was observed.

Photodegradation of Methylene blue solution using 10% GS N-ZnO

0.05g of the 2% green synthesized nitrogen doped zinc oxide (2% G.S N-ZnO) photocatalyst was weighed on an electric weighing balance and poured into a flat bottom flask containing 100ml of 20mg/L of Methylene blue solution. The solution was first stirred at 50rpm for 30minutes in the absence of sunlight to attain absorption-desorption equilibrium, before it was exposed to sunlight rays and stirred at 50rpm for 150minutes. 10ml of the solution was taken from the solution and centrifuged at 1000rpm for 10minutes so as to separate the photocatalyst. The concentration of the clear liquid sample solution after centrifugation was measured using the UV-Spec and 63.3% degradation efficiency was observed.

Upon the conclusion of the preliminary studies, it was affirmed that 5% G.S N-ZnO gave the optimum degradation efficiency. It was then used as the catalyst when various parameters such as pH, catalyst dosage and time were varied during the photocatalytic process.

Variation of solution pH, Time & Initial concentration during Photocatalysis

Parameters to be varied; pH, Catalyst dosage, Initial concentration, Time
Catalyst dosage

Constant parameters; pH of the solution, Initial concentration (15mg/L),

Note; Adsorption-desorption equilibrium is to be carried out for 30min in dark phase before photocatalytic degradation. Each run is to be carried out for 120.

Run number	Catalyst dosage (mg/400ml)	Initial Conc (mg/400ml)	pH of the solution
1st	100	6	7
2nd	75	6	7
3rd	50	6	7

Initial Concentration;

Constant parameters; pH of the solution, Catalyst dosage (250mg/L or 100mg/400ml),

Note; Adsorption-desorption equilibrium is to be carried out for 30min in dark phase before photocatalytic degradation. Each run is to be carried out for 120.

Run number	Catalyst dosage (mg/400ml)	Initial (mg/400ml)	Conc pH of the solution
1st	100	8	7
2nd	100	4	7
3rd	100	2	7

pH of the solution;

Constant parameters; Initial concentration (15mg/L or 6mg/400ml), Catalyst dosage (250mg/L or 100mg/400ml),

Note; Adsorption-desorption equilibrium is to be carried out for 30min in dark phase before photocatalytic degradation. Each run is to be carried out for 90min & samples are to be withdrawn intermittently every 10min for UV-Spec absorbance test.

Run number	Catalyst dosage (mg/400ml)	Initial (mg/400ml)	Conc pH of the solution
1st	100	6	3
2nd	100	6	5
3rd	100	6	9
4th	100	6	11

Characterization of Pure ZnO, G.S ZnO, G.S N-doped ZnO photocatalyst
Pure zinc oxide, green synthesized zinc oxide and green synthesized urea doped zinc oxide was collated and sent to South Africa for Fourier Transform Infrared x-ray, X-ray Diffraction and Scanning electron microscopy-electron analysis.

RESULTS AND DISCUSSION OF RESULTS

3.1.1 Phytochemical Analysis Report

Table 3.1: Results for Phytochemical test of paw-paw leaf liquid extract

Phytochemical mg/100g

Sample	Phenols	Flavonoids	Tannins	Saponins	Alkaloids
Pawpaw	447.64	47.96	14.99	164.22	26.47

Table 3.2; Preliminary results for degradation of Methylene blue solutions

S/N	Type of process	Initial concentration (mg/L)	Time (Min)	Final concentration (mg/L)	Percentage degradation (%)
1	Photolysis	20	60	19.780	1.1
2	Adsorption	20	60	14.657	26.72
3	Pure ZnO	20	150	9.310	53.45
4	GS ZnO	20	150	8.750	56.25
4	5% GS N-ZnO	20	150	5.480	72.6
5	10% GS N-ZnO	20	150	7.340	63.3
6	2% GS N-ZnO	20	150	7.220	63.9

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From Table 3.2 above, it can be observed that percentage degradation of doped green synthesized zinc oxide photocatalyst was greater than pure or green synthesized zinc oxide. The doping of the ZnO photocatalyst with Urea (Nitrogen) provided enough stability and active pores/sites for Photocatalysis process to take place and this in turn resulted to high degradation of organic pollutants in the textile wastewater.

It can also be observed that doping of GS ZnO with Urea (nitrogen) greater than 5% w/w resulted to a decline in the rate of photocatalytic degradation and this provides enough convictions that the 5% w/w ratio is the optimum doping ratio and should be adopted when carrying out future studies related to production of green synthesized urea doped zinc oxide photocatalyst.

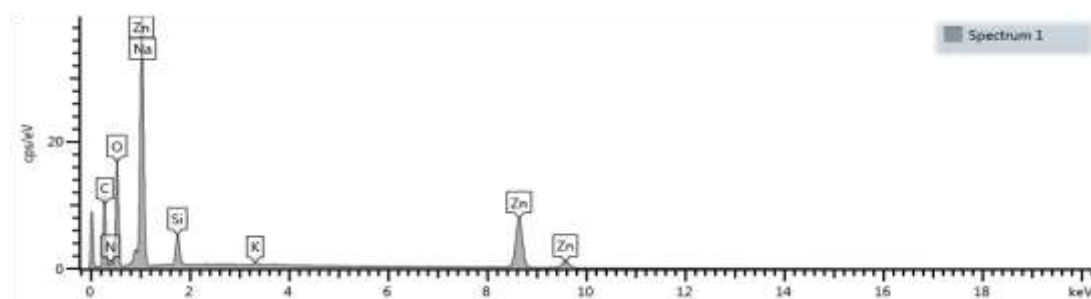


Figure 1.0: EDS plot of Cps/eV vs elemental composition of the green synthesized urea-doped ZnO

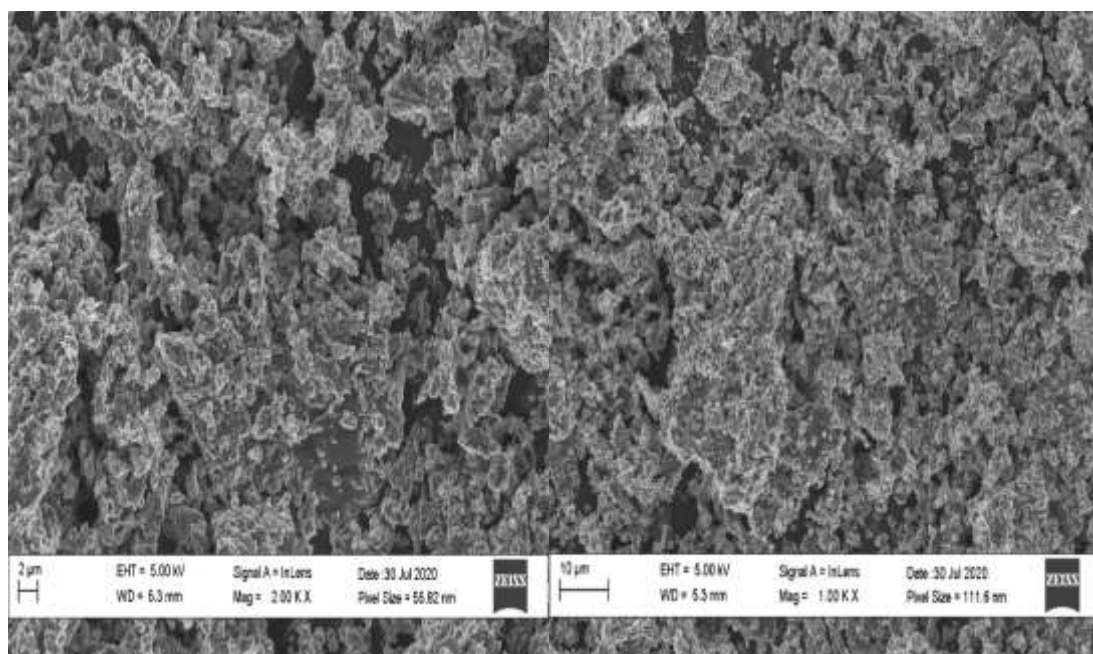
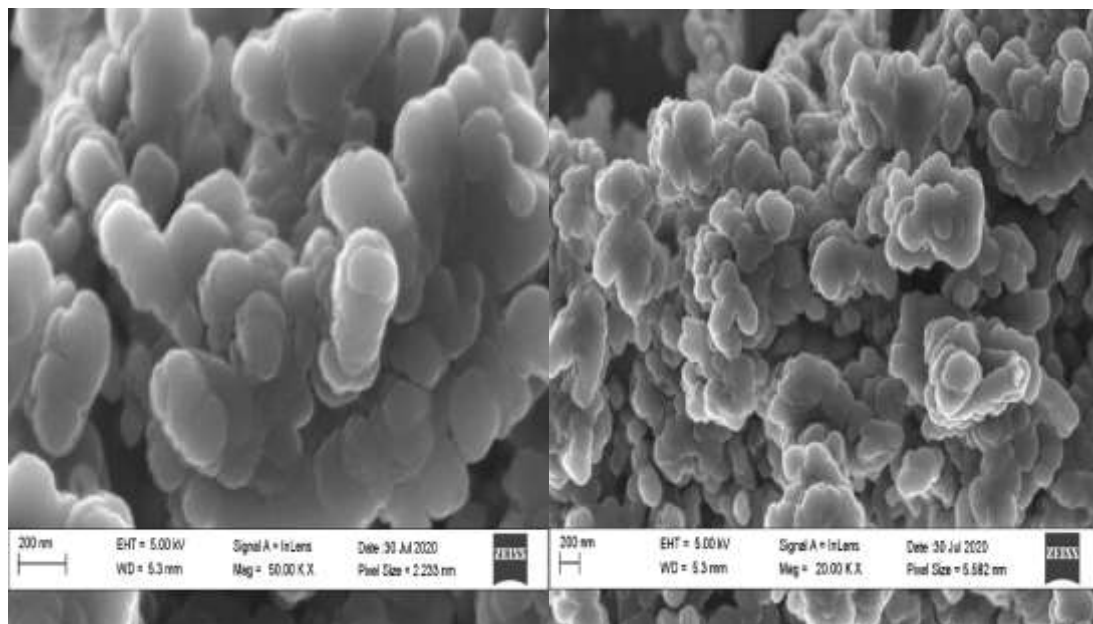


Figure 2.0: SEM images of green synthesized urea-doped ZnO at different magnifications

Scanning electron microscope (SEM) has been reported to be one of the notable leading techniques for the determination of the topographical

study of prepared samples. It is known for providing vital facts about the shape of synthesized samples. The SEM micrograph at different magnifications confirmed that ZnO nanoparticles were formed. The SEM micrograph of the green synthesized urea doped zinc oxide reveals loosed structure of uniformly distributed particles with increased surface area. The nanoparticles were spherical and granular in nature. In addition, the nanoparticles were inclined to aggregation due to the surface-to-volume ratio which is typical with green synthesized nanoparticles as suggested in many literatures. This is because green synthesized nanoparticles possess higher surface area. Remarkably, greater amount of the zinc oxide nanoparticles doped with urea (nitrogen) were identical in dimension.

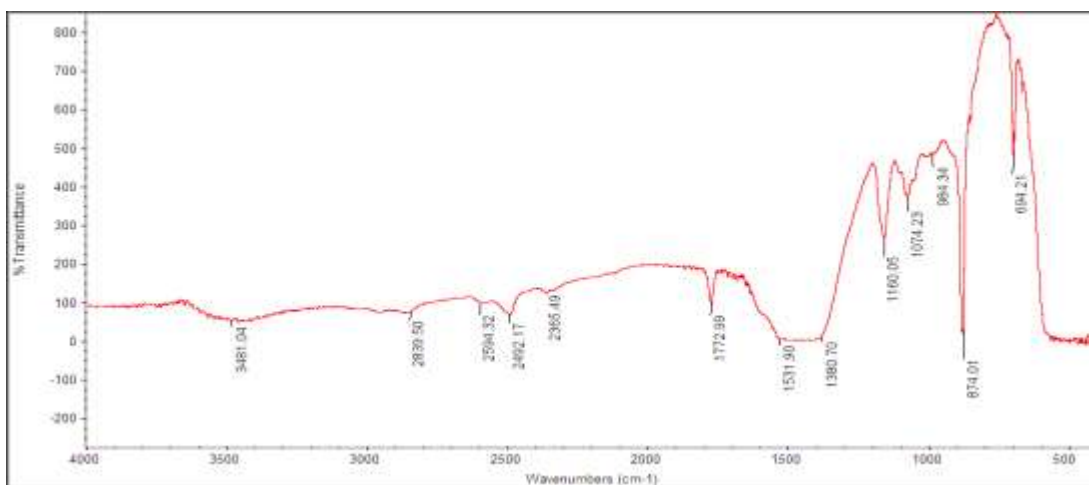


Figure 3.0: FTIR results for green synthesized urea-doped ZnO

The green synthesized zinc oxide nanoparticles doped with urea was characterized by FTIR. The FTIR spectrum revealed functional groups in all the samples investigated. These functional groups were revealed in the scan range of 4000–500 cm⁻¹. The spectrum showed peaks at 3481.04, 2839.50, 2594.32, 2492.17, 2365.49, 1772.99, 1531.90, 1380.70, 1160.05, 1064.23, 984.34 and 694.21 cm⁻¹ respectively. The obtained peak at 2492.17 cm⁻¹ and 2365.49 cm⁻¹ represents C=O of carbon dioxide. The peak at 1772.99 cm⁻¹ represents C-H bending of aromatic compounds. The observed peak at 1531.90 cm⁻¹ reveals the N-H bending and the peak at 1380.70 cm⁻¹ is assigned to symmetric vibration of C=O. The bandwidth of 1500 – 600 cm⁻¹ shows the fingerprint region of zinc oxide

nanoparticles. Emphatically, the introduction of urea (nitrogen) as dopant led to some modifications during synthesis. (Rajendran et al., 2017).

CONCLUSION

In this study, green synthesized urea doped zinc oxide nanoparticle was successfully developed via wet impregnation method. The photocatalyst produced was characterized by FTIR and SEM-EDX. The morphology of the photocatalyst at different magnifications confirmed that ZnO nanoparticles were formed. Revealing also loosed structure of uniformly distributed particles with increased surface area. Whereas the EDX confirms the elemental presence of Zn and O, the FTIR spectrum suggests the existence of functional groups typical of zinc oxide nanoparticle. The produced photocatalyst was successfully used to degrade methylene blue dye in synthetic textile effluents. The rate of photocatalytic degradation of methylene blue dye wastewater was higher with green synthesized urea-doped zinc oxide than pure zinc oxide, and the optimum percentage degradation was observed to be 72.6% at a process time and Initial concentration of 150 minutes and 20mg/L respectively.

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