



Effective Removal of Nitrobenzene under Visible Light by Coupled Grafted Cassava/ZnO in a Closed Photocatalytic Reaction Chamber

Hauwa Sidi Aliyu^{a*}, Ja'afar Yusuf^b, Musa Ibrahim Mohammed^c

^{a,b}*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.*

^b*Advance Materials and Nanotechnology Laboratory, Institute of Advance Technology
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*

^b*Department of Chemistry, Kaduna State University, Nigeria*

^c*Department of Chemistry, Bayero University Kano, Nigeria*

^a*Email: Email: hauwamee1@gmail.com*

^b*Email: yusufja39far@gmail.com*

^c*Email: musaimf@yahoo.com*

Abstract

Almost 95% oil of mirbane best known as Nitrobenzene is being used for the production of aniline precursor chemicals in pesticides, dyes, rubber and pharmaceuticals processing. Oil of mirbane is regarded highly toxic and easily absorbed through the skin with Threshold Limit Value 5 mg/m³. Recently, monitory of drinking water supply by some industries have identified the presence of this compound. The normal conventional methods are yet to achieve efficiently the complete degradation and removal of the nitrobenzene. This study aimed at characterizing and measuring the effective removal ability of this pollutant (oil of mirbane) through visible light photocatalysis by interacting with microwave prepared Coupled Grafted Cassava/ZnO nanocomposite material. Prepared nanocomposite powder was characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared (FT-IR) Spectroscope.

* Corresponding author.
E-mail address: hauwamee1@gmail.com

Optimal experimental conditions such as irradiation time, pollutant concentration and mass of catalyst (loading) were determined using the Closed Photocatalytic Reaction Chamber (CPRC) under visible light. Results obtained revealed the maximum catalyst and nitrobenzene concentration to be 1.0g and 30ppm respectively. The efficiency of Coupled Grafted Cassava/ZnO nanocomposite was found to be 86.7% after 120mins of photodegradation period which is higher as compared with the pure ZnO and the ordinary grafted cassava.

Keywords: Coupling, grafting nitrobenzene, Photocatalysis ZnO.

1. Introduction

Wastewater disposal by industrial activities is the major concern to both environment and drinking water due to existence of several amounts of toxic materials. Such pollutants, their physical appearance seems to be the most obnoxious, as human eyes can easily recognize it. It is now a well-established fact that the coloration of water is mainly caused by dyes, which are generally toxic, non-decomposable and stable. The stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures. Therefore, their removal methods are selected with a great deal of care and considerateness [1]. Before now, various technologies has been adopted for the removal of contaminants from industrial effluent includes, filtration, surface complexation, chemical precipitation, ion exchange, electrode position, membrane processing, flocculation etc. However, all these methods received some setbacks due to metal selectivity, low adsorption, and high consumption of chemicals and use of expensive equipment. According to previous literatures shows that different kinds of products have been used as adsorbent, these include peat [2, 3] and baggasse fly ash [4, 5]. Recently, biopolymers received much attention by the researchers due to the fact that is the most abundant and low-cost natural commercially available and non-toxic.

Generally, introducing inorganic nanoparticles (materials) into the matrix of a polymer can result in some changes in the behavioural properties of the polymer such as; nanostructure, improved moisture resistance, performance efficiency and also able to posses multi-functional features which is beyond what an ordinary normal polymer micro-composite material exhibits.

Nanocomposite materials can be regarded as a special group of materials that posse some unique properties which are potentially applicable in wide range of areas. [6-7]. The addition of inorganic nanosized particles into the matrix of a polymer material leads to the formation of a new composite material which tends to exhibit different characteristic properties that actually differs greatly from the actual starting material. Attaining of homogenous nanosized dispersion during synthetic procedure for the formation of the nanocomposite material can be very difficult, due to the agglomeration tendency of the nanoparticles. [3-5]. Therefore in order to avoid this nanoparticle agglomeration in polymer, the coupling of the inorganic material into the matrix of the polymer is usually accomplished by surface modification.

Grafting of polymer as surface modification of nanoparticle is known to effectively improve the

dispersive ability by ameliorating the polymer matrix, leading to enhancement of resulting composite properties.

ZnO considered as an inorganic material with multifunctional unique properties has recently drawn the attention of scientists due to its chemical stability, high photocatalytic activity, ability to absorb great portion of solar spectrum, thus, able to remove many organic pollutants in an aqueous solution under visible light irradiation. [8-10].

ZnO possesses high surface area capable of dispersing into the matrix of organic solvents just like other nanoparticles, therefore, it's of utmost importance to synthesize the nanocomposite coupled ZnO/polymer in order to avoid the nanoparticle agglomeration. The formation of nanocomposite can highly enhance dispersion stability of the ZnO in the polymer matrix and in turn increase the interfacial adhesion between the ZnO nanoparticle and the polymer.

Microwave-based synthetic route considered as one of the methods that is quick, energy saving, green and easy for production of nanoparticles in large scale, energy-efficient, low-cost, eco-friendly, hygienic, rapid and a novel route and also very convenient heating method that leads to high production yield within short reaction period, is used to obtain the nanosized coupled couple Grafted Cassava/ZnO (GC/ZnO) [11-13].

In this paper, the synthesis of nanocomposite coupled grafted cassava/ZnO as photocatalysts is achieved using the microwave-based synthetic route and its efficiency was tested by employing oil of mirbane as a model organic pollutant.

2. Experimental

2.1 Materials

Cassava starch was purchased locally around Malaysian market. Reagent grade acrylonitrile of 99.0% purity was supplied by Merck. Potassium persulphate (KPS) and sodium bisulphate (SBS) were also supplied by ChemPUR System. Other chemicals such as solvents, inorganic salts, acids, etc., were of analytical grade without further purification.

2.2 Gelatinization of cassava starch

To form cassava slurry different amount of cassava starch were mixed with 200 ml with deionized water in a 500 ml three necked round bottom flask. The reaction process was stirred at 250 rpm and heated to about 80°C for 1 hour under continuous purging of nitrogen gas in order to remove oxygen gas present.

2.3 Grafting of copolymer of cassava starch-co-acrylonitrile

The cassava slurry formed was cooled to about 45°C [7]. The acrylonitrile monomer was filtered through aluminium oxide to remove any impurities if presence, and then added to the reaction medium. To initiate the polymerization process, 2.09 g of sodium bisulphate (SBS) was added and then followed by 2.16 g of potassium per sulphate (KPS). The mixture was allowed to proceed for about 3 hours under continuous nitrogen purging and stirred at 250 rpm. The reaction was terminated by pouring the product suspension into 50 ml of methanol and left to precipitate for about 1 hour. The product was then filtered using Buchner and washed thoroughly with 50 ml methanol followed by 100ml deionized water to removed traces of unreacted monomer and initiator. The resulting product was dried in vacuum oven at 50°C until constant weight was obtained.

2.4 Coupling of grafted cassava with ZnO

5.2g each of Zn (CH₃OO)₂·2H₂O and the grafted co-polymer were dissolved separately into 80ml deionised water respectively under agitation forming two different solutions. Obtained solution 1 was mixed with dissolved 0.2g EDTA and was added into the solutions 1 in drop wise manner under agitation. The mixtures were then transferred into Teflon reaction vessels and were irradiated in the microwave oven for 30mins at 70°C and 120W. Sample were then removed from the microwave and allowed to cool down naturally. Precipitates formed were separated by microfiltration, washed several times with ethanol absolute and deionised water. The obtained crystallite sample was further dried in the oven for 6hrs at temperature of 50°C.

Obtained samples where further characterized using various solid state characterization techniques in other to confirm their purity, structure, morphology, elemental composition, energy band gap and their optical properties. Efficiency of synthesized sample was determined by employing oil of mirbane as model organic pollutant under visible light in a closed photocatalytic reaction chamber.

3. Results and Discussion

3.1 Characterization of the Coupled Grafted Cassava/ZnO nanocomposites

Spectral images from the XRD analysis of both pure Microwave synthesized ZnO and Coupled Grafted Cassava/ZnO nanocomposites are illustrated in fig. 1. Series of characteristic peaks where observed as follows: (100), (002), (101), (102), (110), (103), (200), (112) and (201) which are all in accordance with the accordance with the International Centre for Diffraction Data hexagonal zincite structure of ZnO (Reference Code; 98-005-2842). No extra peaks of impurities were detected in Fig. 1a, indicating the high purity of the As-prepared ZnO nanocomposite with 99% and 1b with 91% purity for Coupled Grafted Cassava/ZnO nanocomposites crystalline phase evaluation, while extra peaks arising as a result of mainly carbon, hydrogen and oxygen in fig. 1b are as a result of the coupled polymer containing carbonyl stretching throughout its structure.

Images obtained from FESEM of the ZnO and Coupled Grafted Cassava/ZnO nanocomposites in fig. 1a&b revealed loose particle agglomeration with the size of the Coupled Grafted Cassava/ZnO being

considerably smaller than that of the ZnO nanopowder. This observation can be as a result of strong interfacial interaction between the surface of the ZnO semiconductor and the matrix of the copolymer.

TEM image of the Coupled Grafted Cassava/ZnO nanocomposite as shown in fig. 2b revealed rod-like nanostructure of the synthesized material having diameter in the nano range with average size less than

The hexagonal zincite nanocrystalline formation of the as-synthesized nanocomposites and effect of coupling was further confirmed by FT-IR spectral analysis. Fig. 3 indicated the spectrum of the MW-synthesized nanocomposites with absorption peaks at $\sim 3400\text{cm}^{-1}$ corresponding to O-H stretching of surface adsorbed water molecule.

EDX (Table1) obtained from the FESEM shows that the composition of the selected areas of the MW as-synthesized nanocomposites. Extra bands observed were confirmed to be due to equipment vibration and the spectra shows that all the observed peaks Zn $L_{\alpha 1,2}$ at 1.00keV, K α_1 at 8.60keV and K β_1 at 9.60keV are within the coupled loaded synthesized materials. This indicates that the coupling of polymer into the matrix of the ZnO semiconductor those not affect the structural and morphological properties of the actual ZnO material.

3.2 Photocatalytic Activity Measurement (Optimization)

3.2.1 Effect of different photocatalysts materials on PCA of Nitrobenzene

Effect of different Microwave synthesized photocatalysts ZnO, Grafted Cassava and Coupled Grafted Cassava/ZnO nanocomposites was shown in fig. 4. It was observed that coupling of a polymer into the matrix of a semiconductor has greatly influenced the photocatalytic activity of the new hybrid material as compared with uncoupled species i.e. pure ZnO and the ordinary grafted cassava (copolymer).

3.2.2 Effect dosage of photocatalyst on PCA

The photocatalytic degradation of various nitrobenzene concentrations 20ppm-100ppm, was studied Fig. 5. Percent photodegradation was observed to increase from 68.72% to 86.7% with increase in concentration of nitrobenzene from 20ppm to 50ppm and subsequently drops 58.52% at 100ppm. The sudden drop in %efficiency of removal could be due to the assumption that active sites of the photocatalyst and its intermediates tends be covered with the nitrobenzene at higher concentration leading to reduction in $e^- - h^+$ generation and consequently causes reduce efficiency of photodegradation. Another possible responsible factor for the decrease in photocatalytic activity can be as a result of the competition of photodegraded h^+ between H_2O molecules and adsorbed nitrobenzene [18].

3.2.3 Effect of mass loading of photocatalyst on PCA

In order to obtain the optimum catalyst loading and to avoid excessive loading of the catalyst, series

of experiments were conducted by varying the amount of the photocatalysts (0.25-1.0g/L) and the Percent of photodegraded nitrobenzene (% Deg) Versus Period of Irradiation was plotted in Fig. 6. The maximum Percentage (% Deg) was achieved at 1.0g/L at 50ppm. This observation may be attributed to the fact that by increasing amount of catalyst, the number of active sites also increases and subsequently leads to enhanced $\bullet\text{OH}$ radical production [30]. However, the number of absorbed nitrobenzene molecules was increased due to increase in the amount of photocatalyst particles leading to increased photodegradation percentage [31]. It was observed that when the amount of photocatalyst was increased beyond the optimum load, percent degradation was not increased but rather decreased. The decrease in degradation efficiency observed beyond optimum loading may be well attributed to the screening effect of the excess particles present in the solution of the photocatalyst as earlier discussed [4].

3.3 Figures and Tables

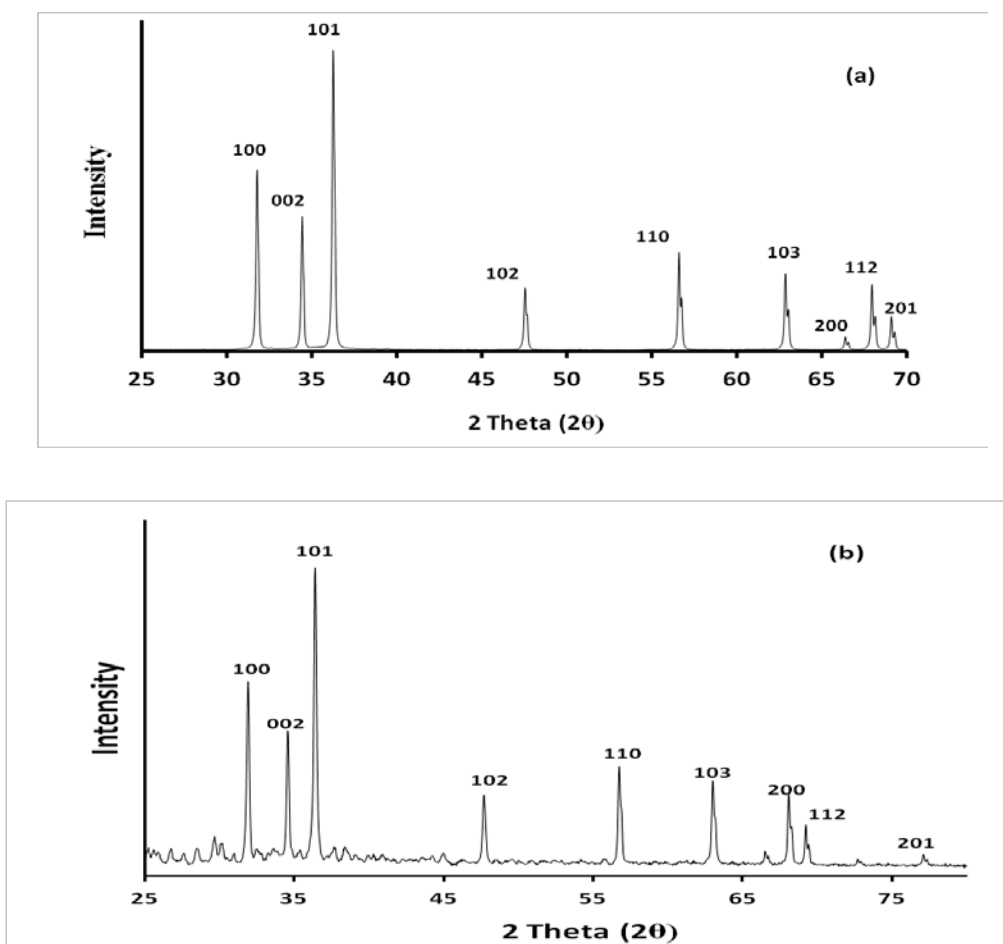


Figure 1: XRD Images of MW-Synthesized (a) ZnO, (b) Coupled Grafted Cassava/ZnO Nanocomposite

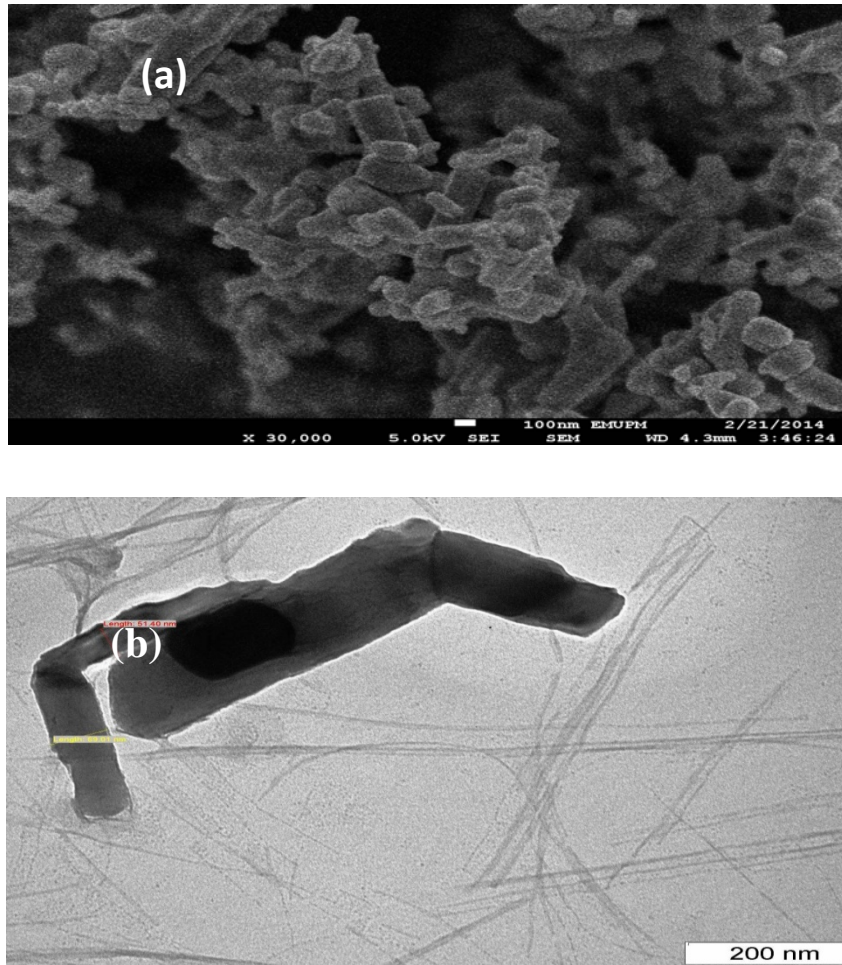
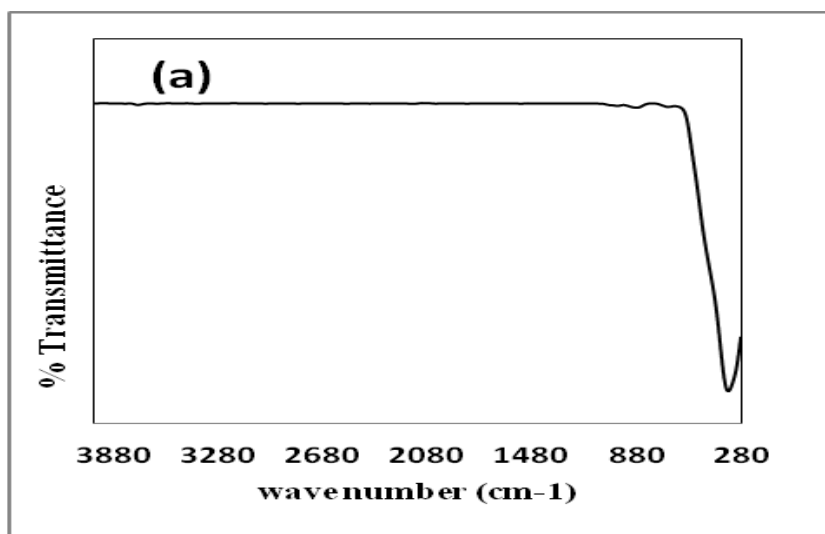


Figure 2: FESEM (a) and TEM (b) Images of Synthesized Coupled Grafted Cassava/ZnO Nanocomposite



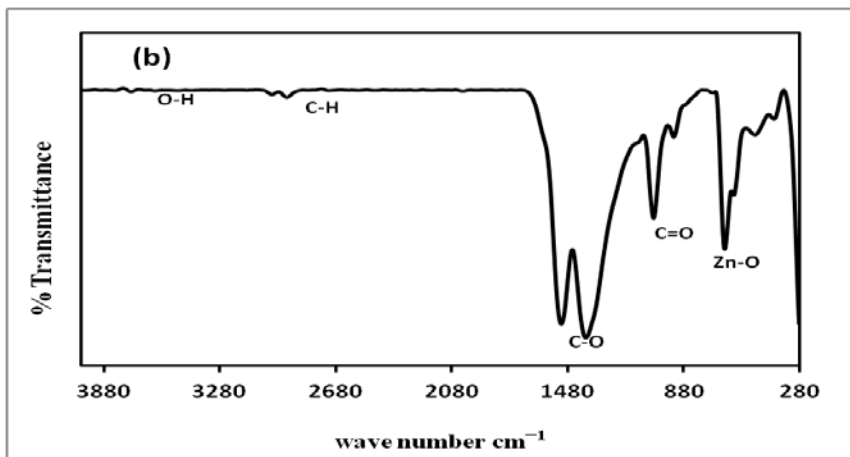


Figure 3: FT-IR spectra of MW synthesized (a) ZnO and (b) Coupled Grafted Cassava/ZnO Nanocomposite

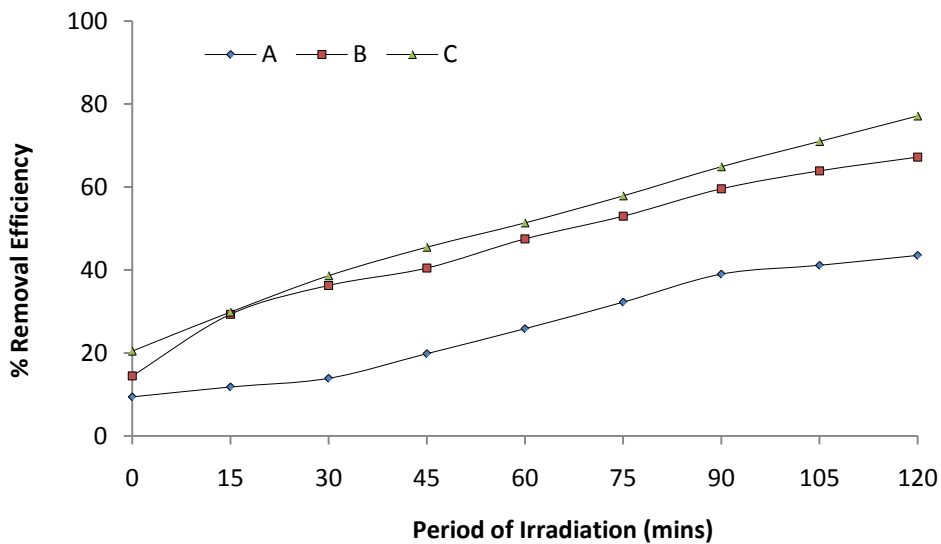


Figure 4: Effect of Different photocatalysts (A=Grafted Cassava, B=ZnO and C= Coupled Grafted Cassava/ZnO) loading on PCA of Nitrobenzene. Reaction Conditions: Concentration =50ppm, pH 6.93 and 1.0g/L

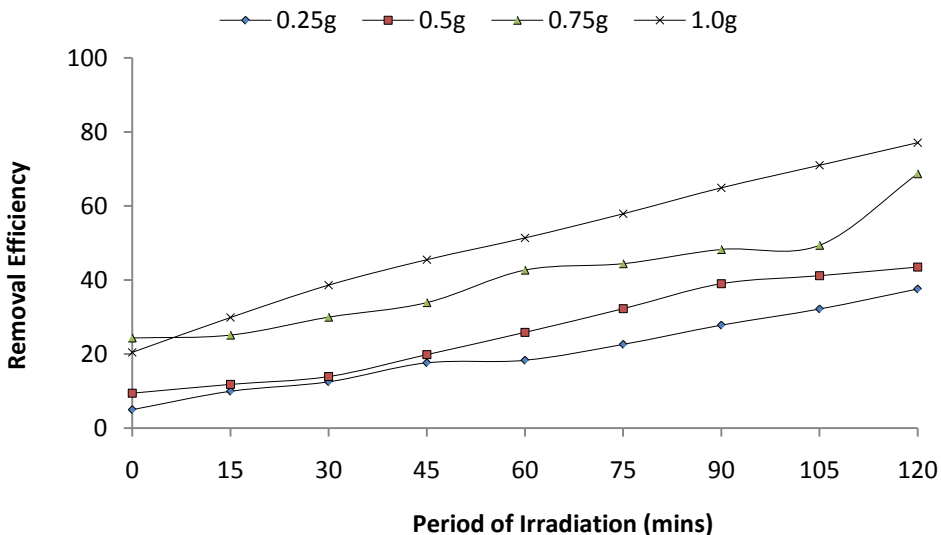


Figure 5: Effect of Coupled Grafted Cassava/ZnO Nanocomposite photocatalyst loading on photodegradation efficiency of Nitrobenzene under visible-light. Reaction condition; 50ppm and pH=6.93, for the period of 120mins

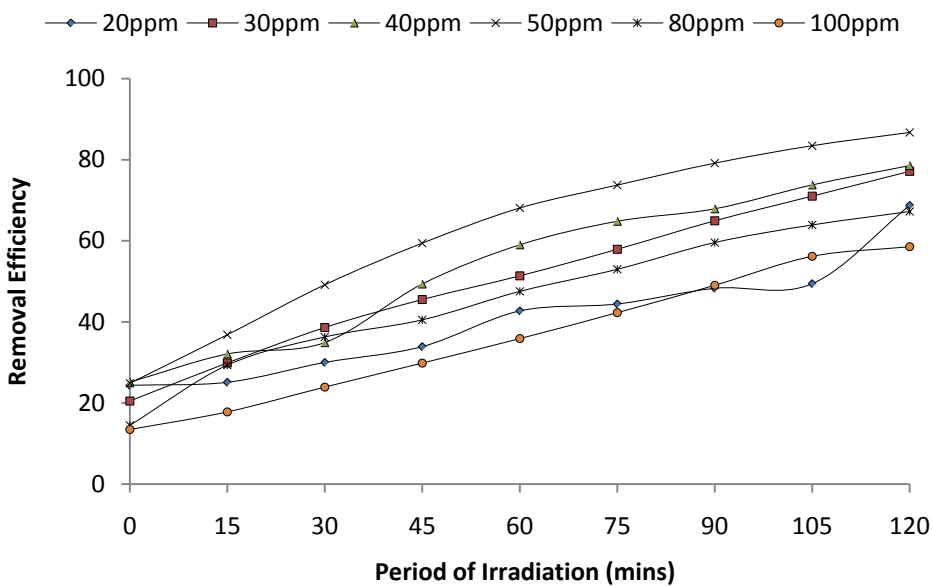


Figure 6: Effect of concentration Nitrobenzene under visible light on photodegradation efficiency. Reaction condition: Photocatalyst concentration= 1.0g/L, pH=6.93, Irradiation time =120mins.

Table1: Elemental Composition (EDX) of the Coupled Grafted Cassava/ZnO Nanocomposite

Spectrum	In stats.	C	O	F	Cu	Zn	Total
Spectrum 1	Yes	22.45	21.11	2.40	1.95	52.09	100.00
Spectrum 2	Yes	18.89	34.78	3.75	1.92	40.65	100.00
Spectrum 3	Yes	15.77	26.71	1.93	2.53	53.05	100.00
Mean		19.04	27.53	2.70	2.13	48.60	100.00
Std. deviation		3.34	6.87	0.94	0.34	6.90	
Max.		22.45	34.78	3.75	2.53	53.05	
Min.		15.77	21.11	1.93	1.92	40.65	

4. Conclusion

The synthesis of Coupled grafted Cassava/ZnO nanocomposite material was successfully carried out at a low and facial condition in the microwave oven milestone microwave laboratory system (Ethos plus II S/N 125899). With an appreciable visible-light photodegradation activity 86.7% achieved after 2hrs over an organic pollutant (Nitrobenzene) as compared to uncoupled ZnO achieving 67.21% and ordinary grafted Cassava copolymer with only 43.52%. Different characterization techniques used such as XRD, FESEM, TEM and FT-IR, confirmed the phase purity, morphology, molecule vibration, and elemental composition of the MW as-synthesized Coupled grafted Cassava/ZnO nanocomposite.

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