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ENHANCED PHOTOCATALYTIC DEGRADATION OF 4-NITROPHENOL USING ACRYONITRILE MODIFIED POLYMER/ZnO NANOCOMPOSITE

Photodegradation of 4-Nitrophenol

Muhammed M. Ibrahim, Hauwa S. Aliyu and Sirajo B. Lawan

Abstract— Factors affecting the degradation efficiency of one of the major persistent organic waste water pollutant 4-nitrophenol such as light source, photocatalyst load, maximum concentration of 4-nitrophenol, pH and period of irradiation are the main focus concern in the present work. Results obtained revealed the maximum photocatalyst loading and pollutant concentration to be 0.75g and 100ppm respectively with a pseudo-first-order decomposition reaction kinetics. The efficiency of 1:2 acryonitrile modified polymer/ZnO nanocomposite was found to be 96.47% after 120mins of exposure period which is higher as compared with the pure ZnO and the ordinary grafted cassava with 91% TOC removal ability. Incorporating of 1:2 acryonitrile modified polymer/ZnO was also found to increase the surfaced area and pore volume of the ZnO matrix thus increasing its porosity and visible light absorption which is the reason for the increased degradation efficiency.

Keywords— microwave, Phenol, Photocatalysis, Polymer, ZnO.

I. Introduction

The aim of every industrialist is to optimize profit therefore for every industrial process taking cost effectiveness is very important. Thus, in trying to do so, the use of less expensive but environmentally more toxic chemical materials are being employed and at the end leads to the need for treatment before discharge into the water ways. It is believed that industries are the major sources of waste water pollutants and in order to maintain continues profit optimization an effectively cost efficient method is required for the degradation and absorption treatment of such waste water pollutants [1]. Photocatalysis has been considered as one of the most effective methods for the mineralization and degradation of such persistent pollutants. Though various semiconductor photo-catalysts have been used, ZnO nanomaterial has received much attention due to its chemical and thermal stability, non-toxicity, high catalytic efficiency and low cost [2]. Generally, introducing inorganic nanoparticle (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 [3]. Rapid recombination of excited electron with produced holes during photocatalysis limits the efficiency of the photocatalytic processes. Different methods have been developed in order to retard this electron-hole pair's recombination and also enhance efficiency of photocatalysis by coupling the photocatalyst with different materials such as metal, semiconductors, grapheme, polymer etc. Due to the uniqueness features of microwave irradiation synthetic method such as high reaction rate, rapid, energy saving, selective heating with increased output in synthetic organic chemistry have recently drawn the attention of scientist towards employing it as an effect tool [4&5] In the present work, we report the photocatalytic degradation efficiency of microwave synthesized 1:2 acryonitrile modified polymer/ZnO nanocomposite employing 4-nitrophenol as a model organic pollutant, with no further requirement for additional annealing treatment or addition of surfactants all of which save cost thus, making it suitable for industrial application.

II. Experimental

Material

All reagents used in the present study are of analytical grade. Cassava was purchased from local markets around Malaysia. Acryonitrile of analytical purity grade 99.0% and Zinc acetate dihydrate 99.9% were supplied by Merck. Potassium persulphate (KPS) and sodium bisulphate (SBS) where supplied by ChemPUR system, other inorganic salts, solvents and acids are also of analytical grade used without further purification.

Shimadzu UV-1650 PC UV-Vis spectrophotometer was used for the establishment of the correlation coefficient of the 4-NP calibration curve of 0.9999 and also to measure the percentage of initial concentration of 4-NP degraded per unit time using Eq. (1).

$$\text{Photodegradation } \% = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 = Initial concentration of nitrobenzene and C = concentration of 4-nitrophenol after time ***t*** of photo irradiation. All the photodegradation experiments for carried out in triplets.

Surface area and pore volume where determined using Brunauer-Emmet-Teller Thermo Finnegan Sorptomatic 1990 series analyzer applying static method with nitrogen gas as analysis gas at out gas temperature of 250^0C.

Method

1:2 acryonitrile modified Polymer/ZnO nanocomposite was prepared by dissolving zinc acetate dihydrate and microwave dried 1:2 acryonitrile modified cassava powder in to 100ml deionised water under vigorous agitation for 20mins and transferred into Teflon Reaction vessels. The agitated solution was further irradiated in the microwave oven for 30mins at 60^0C and 100W. Irradiated mixture was allowed to cool naturally to room temperature and filtered through micro filters; the filtrate was washed several times with ethanol followed with deionised water. The obtained sample was further dried in the oven for 12hrs at temperature of 50^0C resulting in the formation of a yellowish crystalline nanopowder, which was further characterized and applied in the degradation 4-nitrophenol (4-NP) through dispersion method under Philips lamp (23watt) as visible light source in a closed photocatalytic reaction chamber equipped with air pump continuous dispersion homogeneity of the system.

Photodegradation procedure

As reported in our previous work [6]. Different concentration of the pollutant was made to obtain the absorption wavelength of the pollutant and to establish a calibration curve with linear correlation of R^2=0.9998. At specific time intervals of 15mins sample aliquot was withdrawn from bulk solution up to 120mins, and filtered through 0.45µm PTFE filters. Concentration of Nitrobenzene was determined by measuring the absorption intensity at its maximum absorbance wavelength of λmax=405nm using UV-Visible spectrophotometer (Shimadzu, UV-1650 pc) with 1cm path length spectrometric quartz cell, and calculated from the calibration curve. The photodegradation percentage of the pollutant in the waste water was calculated using eqn.1.

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III. Results and Discussions

BET analysis revealed the surface areas and pore volume of the microwave as-synthesized (fig.7) ZnO and (fig.8) 1:2 acryonitrile modified polymer/ZnO nanocomposites to be: $4.562m^2/g$ & 0.006cc/g for ZnO; $54.7485m^2/g$ & 0.994cc/g for AMP/ZnO. It can be observed the immobilizing modified polymer into the matrix of the ZnO semiconductor has increases both its surface area and pore volume as shown in fig.1&2. This observation might be as a result of the porosity of the material which is the measure of the empty spaces in a material expressed as a fraction of the volume of empty area over the total volume, between 0 and 1, or between 0 and 100% as percentage. Porosity is a term frequently used almost interchangeably with absorption. A material with high porosity is expected to have high absorption since a highly porous material may have a large number of pores which can facilitate absorption ability of the material. This is similar with the present study.

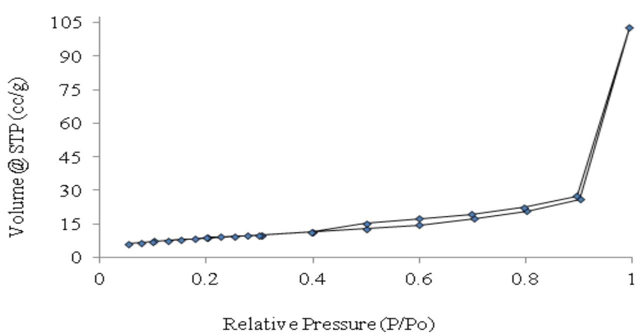

Figure 1: BHJ desorption pore size distribution for mesoporous surfaces of the synthesized ZnO nanocomposite

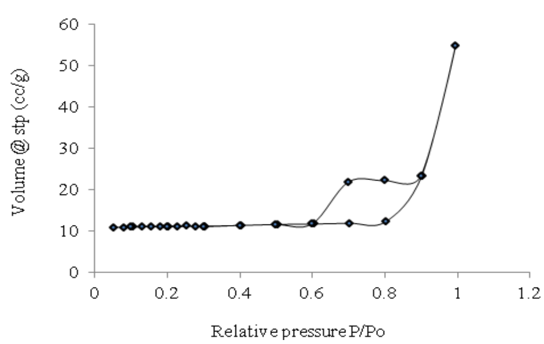

Figure 2: BHJ desorption pore size distribution for mesoporous surfaces of the synthesized ZnO & AMP/ZnO nanocomposites

Photocatalytic Measurement

Catalyst loading Effect

The effect of catalyst loading was investigated within the mass range of 0.25g-1.25g at 100ppm concentration of 4-nitrophenol (Fig. 3). There was an appreciable increase the percentage removal of the 4-NP from 0.25g l^{-1} until 0.75g l^{-1} during the photocatalytic period of 120min. This observation could well be as a result of increasingly availability of reactive sites on the surface of the photocatalyst. Removal rate was found to decrease by increasing catalyst load above 0.75g l^{-1} as a result of scattering of light by the excess catalyst nanoparticle thus, leads to insufficient utilization of the light. Hence 0.75g l^{-1} can be regarded as the optimum catalyst load for this study which is far less as compared with previous reports [7& 8].

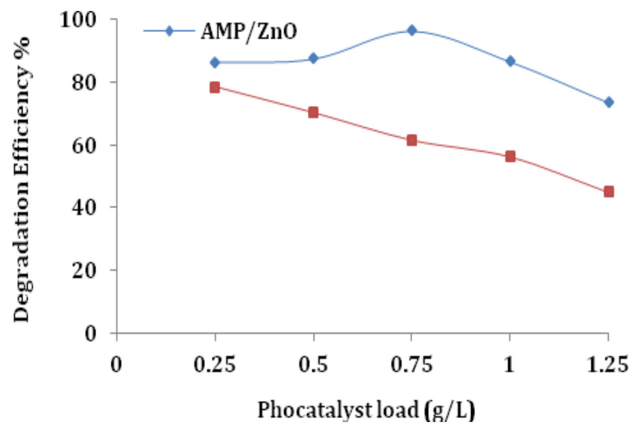

Figure 3: Influence of catalysts loading at constant Concentration 100ppm and pH=7.28

4-Nitrophenol Concentration Effect

One of the guaranteed factors to qualify the effectiveness transformation of any pollutant by a catalyst is the substrate level (concentration). In the present study, the 4-NP concentration effect was studied within a wide range of varying concentrations 10 to 300ppm in the presence of 0.75g l^{-1} Removal efficiency of the catalyst under visible light was found to increase concurrently with increase in 4-NP concentration up to a certain level because the substrate occupies most of the catalyst active sites decomposing subsequently. 100ppm was found to exhibit the highest 4-NP removal efficiency and thus, regarded as the optimum concentration for this study since increase in concentration beyond 100ppm, the removal efficiency was found to decrease as observed in (Fig. 4). This is basically because as the optimum concentration is exceeded; there will be increase in the amount of unabsorbed 4-NP on the surface of the photocatalyst thus, results in the decrease in photonic efficiency.

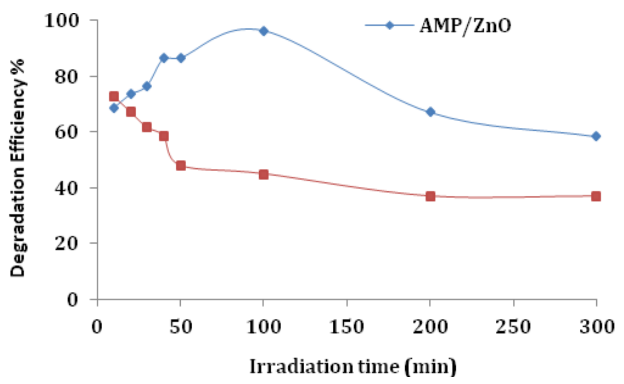

Figure 4: Influence of concentration on Degradation efficiency under visible light: Catalyst Concentration= 0.75g l^{-1}; pH=7.28; Initial Conc. =100ppm

Kinetics of Photodecomposition process

Among the major facets in photocatalysis is the study of output of the photo process [8]. In the present study, the decomposition 4-NP by the MW-synthesized 1:2 AMP/ZnO nanoparticle was observed to be consistent with the pseudo-first-order reaction kinetics Eq. 2 which is in agreement with earlier work reported [2].

$$r = \frac{-dc}{dt} = KrKC = K_0 C \qquad (2)$$

C_t and C_o are the final and initial concentrations at time t and t=0, k and k_0 is defined as pseudo-first-order rate constant that is expressed in min $^{-1}$. Upon rearrangement and integrating equation (1), a typical pseudo-first-order equation can be obtained as follows:

$$C = C_0 e^{-k_0 t} \qquad (3)$$

$$In\frac{C_0}{C} = K_r Kt = K_0 t \qquad (4)$$

The plot of the variations of In(C/C_0) as function of time is shown in Fig.3 and the k_0 value according to the straight line is calculated as 0.9875. The observed quality of the linear fitting in Fig. 5 may be attributed to the slow rate of 4-NP decomposition at a shorter adsorption period (0-45mins) which could be as a result in the formation of intermediate species with active sites serving as the rate limiting role for the analysis. This can best be supported by previous reported work of [8] revealing that during the first hour of an irradiation period there is absence of CO_2 evolution by degrading DCP with particles of TiO_2.

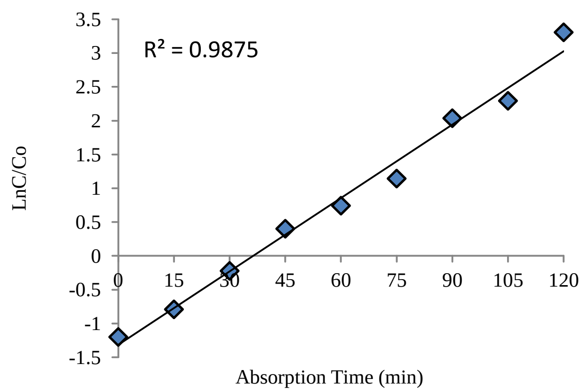

Figure 5: Pseudo-first-order Kinetics in the medium Degradation. Condition: Catalyst=0.75gl^{-1}; pH=7.28; Initial 4-NP Concentration = 100ppm

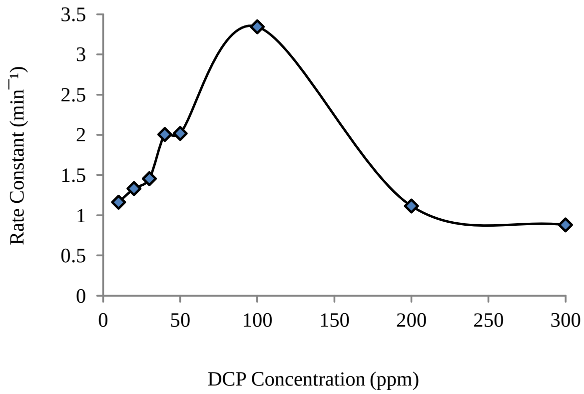

Figure 6: Rate constant based on the Pseudo-first-order Kinetics for the degradation of 4-NP by MW-synthesized 1:2 AMP/ZnO nanocomposite

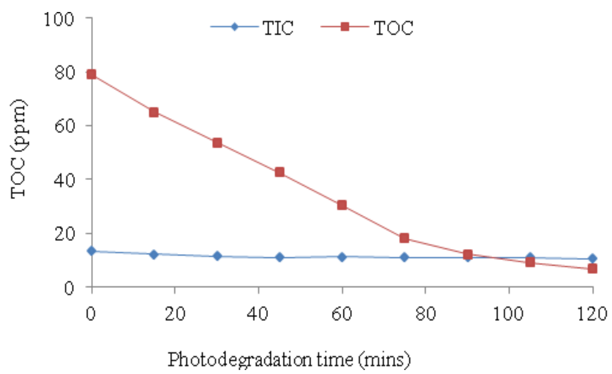

Figure 7: The amount of TOC and TIC during 4-NP photo-degradation under visible light irradiation. Reaction condition; Conc. =100ppm, pH 7.28, @ 120mins

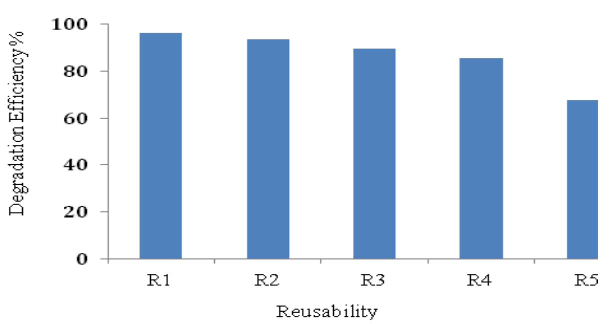

Figure 8: Reusability of the 1:2 acryonitrile modified polymer/ZnO nanocomposite

IV. Conclusion

In the present work, the degradation of 4-nitrophenol by microwave synthesized 1:2 acryonitrile modified Polymer/ZnO nanocomposite under visible light was reported. With an appreciable visible-light photodegradation activity 96.47% and total organic carbon removal of 91% achieved after 2hrs at 100ppm, 0.75g l^{-1} and pH 7.28 as the recommended optimum conditions respectively for the process.

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Image

[Degradation of 4-Nitrophenol Using Acryonitrile Modified Polymer/ZnO.]