Photocatalytic Degradation of a Basic Dye Using Zinc Oxide Nanocatalyst

Chijioke-Okere O. Maureen^{1,a*}, Okorocho J. Nnaemeka^{2,b},
Anukam N. Basil^{1,c}, Oguzie E. Emeka^{1,d}

¹Department of Chemistry, Federal University of Technology Owerri, Nigeria

²Department of Pure and Industrial Chemistry, University of Calabar, Nigeria

^aoby.chijioke85@gmail.com, ^bemybeck@yahoo.com, ^cbobbykingz@yahoo.com,
^demekaoguzie@gmail.com

Keywords: Zinc oxide; Malachite green, Degradation; Photocatalyst; Kinetics

Abstract. The potential of calcinated and uncalcinated zinc oxide as an effective photocatalyst for the degradation of malachite green dye (MG) from aqueous medium using UV light has been identified. The photocatalysts were characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The SEM investigations of the calcinated ZnO revealed highly dispersed nanomaterials and the particles were of nanometer size in agreement with the XRD result. The uncalcinated zinc oxide, ZnO revealed some pronounced nanoparticles. The degradation of MG by the photocatalyst was found to be influenced by adsorbent loading and irradiating time. The optimum degradation was obtained at 0.5g catalyst loading of both calcinated and uncalcinated zinc oxide which is 98.48% and 96.31 % respectively at 150 minutes. The degradation kinetics conformed to the pseudo-first-order kinetic model. The present study showed that calcinated and uncalcinated zinc oxide ZnO can be effectively used as efficient photocatalyst for the degradation of Malachite green dyes from aqueous solutions and effluents.

Introduction

The pollution of water resources by dyes or dye-based effluent is already a worldwide problem which has resulted in the scarcity of clean and healthy water. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff being produced annually across the world today [1]. It is estimated that 10 – 15% of the dyes used are lost during the dyeing process and discharged with the effluent [2]. Most dyes are non-biodegradable, toxic in nature and can affect water aesthetically at as little concentration as 1 ppm [3,4] which poses environmental concern. Thus, the effective removal of dyes from aqueous systems becomes environmentally important. Several processes have been used over the past years for the removal of dyes from wastewater such as biological (aerobic and anaerobic), chemical precipitation, coagulation/ flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction and adsorption [5,6]. However, these techniques are non-destructive, since they only transfer the non- biodegradable matter into sludge, giving rise to a new type of pollution, which needs further treatment [7, 8]. Consequently, a more promising technology based on advanced oxidation processes (AOPs) has and is been studied extensively for decolourization and degradation of textile dyes. The heterogeneous photocatalytic oxidation process is a technique utilizing nanotechnology under thorough study now [9-11]. Nanoparticles are mostly used because of its large surface area and ease to produce. The most profound nanoparticle used is Titanium dioxide due to its high photocatalytic activity, low cost, non-toxicity and high stability in aqueous solution [12] and is also a whitening ingredient in toothpaste. Other metal oxides used for photocatalytic degradation includes ZnO, SnO₂ and ZnO₃ [13].

The photocatalytic decolorization of a dye is believed to take place according to the following mechanism: when a TiO₂ catalyst is exposed to UV radiation, electrons are promoted from the valence band to conduction band and an electron-hole pair is produced (equation 1) [14].

where e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases, h^+_{vb} can react easily with surface-bound H_2O to produce $OH^\bullet$ radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen (equations 2 and 3) [14].

This reaction prevents the combination of the electron and the hole which are produced in the first step. $OH^\bullet$ and $O_2^{\bullet-}$, can then react with the dye to form other species and are thus responsible for the decolorization of the dye (equations 4 - 7) [14-17].

This is considered to be very excellent means for treating coloured industrial effluent and for saving huge amounts of water, especially, in country like Nigeria which are experiencing shortage of clean water. The present work reports an investigation of photocatalytic degradation of Malachite green dye from simulated wastewater using calcinated and uncalcinated ZnO as photocatalysts with irradiation with UV-light at different times.

Experimental

Preparation of zinc oxide nanoparticles

60g of zinc oxide powder was weighed using electronic weighing balance. The weighed zinc oxide was put in a ceramic crucible, placed in a muffle furnace and calcinated for four (4) hours at 600°C . It was then cooled to room temperature, grinded in a mortar and labelled as calcinated zinc oxide (CZnO). The uncalcinated zinc oxide was labelled as UZnO. All materials were used as sourced without further purification.

Preparation of malachite green solution solution

Stock solution of malachite green dye solution was prepared by dissolving 1 g of commercially available malachite green dye (Fluka grade) in 1 L of distilled water to obtain a stock concentration of 1000 mg/L. Experimental dye solutions of desired concentrations were prepared by appropriate dilution of stock solution.

Adsorbent characterization

Surface morphology and texture of the adsorbent was analyzed using scanning electron microscope (SEM) (Model-PHENOM ProX). Prior to scanning, some quantity of the adsorbent was placed on a double adhesive sticker placed in a sputter machine for 5 sec; this gave the adsorbent a conductive property. Sample (adsorbent) stud was fixed on a charge reduction sample holder, and then was charged in the SEM machine. In addition X-ray diffraction of the calcinated ZnO was analyzed in determining the particle size using an Shimadzu XRD, model 6000 with a Cu target $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$). The measurements were made at room temperature.

Photocatalytic Degradation Experiment

Photocatalytic activities of the calcinated and uncalcinated ZnO photocatalysts were studied for degradation of Malachite green dye (MG). The experiment was carried out under ultraviolet illumination in a photoreactor. 0.25-1.5g weighed amount of the UZnO and CZnO photocatalyst powder was placed in a reactor containing 100 ml of aqueous solution of MG dye (50mg/L) and magnetically stirred for 5min. The mixture was then exposed to UV light. The UV lamp (Fozhao Light) with the definite power 15 W, 220 V and 60 Hz frequency was employed as UV source and positioned parallel to reactor. The distance between the top of reactor and light source was 10 cm. UV-Vis absorption spectra of samples were measured at regular intervals of 30 min to monitor the decolouration of MG. The resulting suspension was centrifuged at 3000 rpm for 5 minutes and filtered with Whatman 0.45µm Millipore filter paper to remove the catalyst particles before measuring the absorbance using UV-Vis spectrophotometer.

Percentage degradation of MG was calculated using the relation:

$$\% \text{ degradation} = [(A_0 - A_t)/A_0] \times 100 \quad (8)$$

where A_0 is absorbance of dye at initial stage, A_t is absorbance of dye at time “t”.

Results and Discussion

Adsorbent characterization

Scanning electron magnification, SEM imaging was carried out to show the surface morphology of ZnO photocatalyst. The SEM investigations of the calcinated ZnO (Fig.1) revealed highly dispersed nanomaterials and the particles were of nanometer size in agreement with the XRD result. But the uncalcinated ZnO image (Fig. 2) indicates dispersed nanomaterials but not as highly aggregated as the calcinated ZnO image. Furthermore, the X-ray diffraction, XRD characterization was performed to show the crystalline structure of the ZnO photocatalysts as well as obtain an estimate of the grain size distribution. The XRD pattern of the crystal surface of calcinated ZnO photocatalysts is shown in Fig. 3.

The size of ZnO nano is calculated using Scherrer's formula [15-17]:

$$D = 0.9 \lambda / \beta \cos \theta \quad (9)$$

where K =constant (0.9), λ =Radiation wavelength, β =FWHM (Full Width Half wave Maxima), θ =Bragg angle in degree and D =Particle Size.

Table 1. Particle size of ZnO nanoparticle

Nanoparticles	2Theta	Beta Value
CZnO	25.4362	0.20800

Figure 1. SEM image of calcined Zinc Oxide at 1000×

Figure 2. SEM image of uncalcined Zinc Oxide at 1000×

Figure 3. X- ray diffraction spectra of calcinated Zinc oxide (CZnO)

Effect of Catalyst dosage or loading

Fig. 4 represents effect of catalyst dosage or loading on the degradation of MG by calcinated ZnO (CZnO) and uncalcinated ZnO (UZnO). The percentage degradation increased from 94.31 % to 95.74 % for calcinated ZnO and from 92.71 to 94.52 % for uncalcinated ZnO as the dosage increased from 0.25 to 0.5g but it decreased to 83.24 % for CZnO and 87.02% for UZnO as the catalyst dosage further increased to 1.5g for 120 minutes. The effect of increase in percentage degradation of MG as dosage increased from 0.25-0.5g, is probably due to more catalyst active sites and higher adsorption area were available for the generation of active radicals to degrade the dye [18]. Further increase in catalyst loading from 0.2-1.5g led to decrease in photo degradation. This is due to light scattering effect and increase in the particle aggregation [19]. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering [20]. A similar trend has been reported in the literature [21-23].

Figure 4. Effect of catalyst loading on the degradation of MG by CZnO and UZnO

Effect of Irradiating Time

The effect of irradiating time on the percentage degradation of MG by 0.5g calcinated and uncalcinated ZnO is shown in Fig. 5. It was observed that the percentage degradation of MG increased from 89.67 to 98.48% for CZnO and from 81.90 to 96.31% from UZnO as the irradiating time increased from 30minutes to 150minutes. This shows that the UV degradation of Malachite green is directly proportional to the time of irradiation.

Figure 5. Effect of Irradiating Time on the percentage degradation of MG by CZnO and UZnO

Dye Degradation Kinetics

A Langmuir-Hinshelwood approach was selected to calculate the degradation rates of each of the solutions. This approach states that

$$r = dC/dt = k\theta = -kKC / 1 + KC \quad (10)$$

where r =Degradation rate, K =Degradation rate constant, θ =Occupation coverage of adsorption sites, K =Adsorption equilibrium constant $K = k_{ads}/k_{des}$, C_t = equilibrium concentration (after adsorption), t = time.

Since at low concentrations $kC \ll 1$, the term KC can be assumed to be negligible, therefore reducing the model to:

$$\ln C_t / C_0 = -k_{app} * t \quad (11)$$

or

$$\ln C_0 / C_t = k_{app} * t \quad (12)$$

This integrated reaction rate equation follows the first-order kinetics, where C_0 and C_t is the initial concentration of the dye solution and concentration at any time respectively. The apparent rate constant k_{app} contains both the degradation rate constant k and the adsorption equilibrium constant K .

Figure 6. Pseudo First order kinetic plot for UV degradation of MG by CZnO and UZnO

Fig. 6 shows the pseudo-first-order kinetics for the degradation of MG by calcinated and uncalcinated ZnO. The pseudo-first-order rate constant (k_1) and correlation coefficient determined from the model are presented in Table 2. It is observed from Fig.6 that the relationship between $\ln C_0 / C_t$ against t is linear with R^2 values above 0.95 for both the calcinated and the uncalcinated ZnO. Therefore, the kinetic law of degradation of the MG dye is of first-order kinetics with respect to the concentration of the dye.

Table 2. Pseudo-first order kinetic model parameters for MG degradation

ZnO	$k(g.mg.min^{-1})$	R^2
Calcinated	0.0182	0.958
Uncalcinated	0.0169	0.95

Conclusion

The potential of calcinated and uncalcinated zinc oxide as effective photocatalyst for the degradation of malachite green dye from aqueous medium using UV light has been identified. The degradation of MG by both photocatalyst was found to be influenced by adsorbent loading and irradiating time. The optimum degradation was obtained at 0.5g loading of both calcinated and uncalcinated photocatalyst. The percentage degradation increased continuously with increase in irradiating time. The kinetic studies revealed that the degradation of MG by calcinated and uncalcinated zinc oxide, ZnO was adequately represented by the pseudo-first-order kinetic model. SEM and XRD characterization of the photocatalysts showed there were more pronounced nanoparticles/crystals in the calcinated zinc oxide, ZnO than in the uncalcinated zinc oxide. The present study showed that calcinated and uncalcinated zinc oxide, ZnO can be effectively used as efficient photocatalyst for the degradation of Malachite green dyes from aqueous solutions and effluents.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

- [1] T. Robinson et al., Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, *Bioresource Technology*. 77(3) (2001) 247-275.
- [2] A. Ezgi, B. Mufit, Y. Mustafa, Removal efficiency of a calyx [4] arene-based polymer for water-soluble carcinogenic direct azo dyes and aromatic amines, *Journal of Hazardous Materials*. 162 (2008) 960-966.
- [3] M. Mehra, T.R. Sharma, Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO_2 , *Advances in Applied Science Research*. 3(2) (2012) 849-853.
- [4] E. Fosso-Kankeu et al., Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes, *Journal of Industrial and Engineering Chemistry*. 22 (2015) 171-178.
- [5] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, *Bioresource technology*. 97(9) (2006) 1062-1070.
- [6] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste management*. 27(9) (2006) 1-8.
- [7] I. Arslan et al., $\text{H}_2\text{O}_2/\text{UV-C}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-C}$ versus $\text{TiO}_2/\text{UV-A}$ treatment for reactive dye wastewater, *Journal of Environmental Engineering*. 126(10) (2000) 903.
- [8] N. Stock et al., Combinative sonolysis and photocatalysis for textile dye degradation, *Environmental Science & Technology*. 34(9) (2000) 1747.
- [9] A. Ahmad et al., Recent advances in new generation dye removal technologies: Novel search for approaches to reprocess wastewater, *RSC. Adv.* 5(39) (2015) 30801–30818.
- [10] F. Meng et al., Localized fluorescent complexation enables rapid monitoring of airborne nanoparticles, *Environmental Science: Nano*. 1(4) (2014) 358–366.
- [11] F. Meng, V.M. Ugaz, Instantaneous physico-chemical analysis of suspension-based Nanomaterials, *Sci. Rep.* 5 (2015) 9896.
- [12] C. Hu, Y. Wang, Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastewater, *Chemosphere*. 39 (1999) 2107-2115.

-
- [13] N. Deneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst for TiO₂, *Journal of Photochemistry and Photobiology*. 162 (2004) 317-322.
- [14] J. Jeni, S. Kanmani, Solar nanophotocatalytic decolorisation of reactive dyes using titanium dioxide, *Iran J. Environ. Health. Sci. Eng.* 8(1) (2011).
- [15] M.T. Aghareed, S.H. Dina, Synthesis of TiO₂ nanoparticles and their photocatalytic activity for methylene blue, *American Journal of Nanomaterials*. 3(2) (2015) 57-63.
- [16] J.A. Abbas, H.K. Salih, H.H. Falah, Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide, *E-Journal of Chemistry*. 5(2) (2008) 219-223.
- [17] P.S. Jon, D.F. Ollis, Integration of chemical and biological oxidation processes for water treatment: Review and recommendations, *Environmental Progress*. 14(2) (1995) 88-103.
- [18] S. Mioara, Z. Carmen, Advanced oxidation processes for decolorization of aqueous solution containing acid red G azo dye, *Central European Journal of Chemistry*. 2(4) (2004) 573-588.
- [19] R. Chhotu, K.P. Ravi, S. Varinder, Photocatalytic degradation of textile dye by using titanium dioxide nanocatalyst, *International Journal of Theoretical & Applied Sciences*. 4(2) (2012) 82-88.
- [20] B. Priti, S. Dhiraj, Photodegradation of commercial dye, procion blue herd from real textile wastewater using nanocatalysts, *Desalination*. 267 (2011) 244-249.
- [21] N. Elaziouti, J. Laoued, A. Bekka, ZnO-assisted photocatalytic degradation of congo red and benzopurpurine 4B in aqueous solution, *J. Chem. Eng. Process Technol.* 2 (2011) 1-9.
- [22] I.K. Konstantinou, T.A. Albanis, TiO₂-Assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review, *Applied Catalysis B-Environmental*. 49(1) (2004) 1-14.
- [23] S.K. Kansal, M. Singh, D. Sud, Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts, *Journal of Hazardous Materials*. 141(3) (2007) 581-590.