Photocatalysis Of Basic Black 2 (Janus Black) Dye Using Titanium Dioxide Doped With Zinc (Zn-TiO₂)

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ABSTRACT: Photo-catalysis of Basic Black 2 (Janus Black) dye was carried out to evaluate the Effect of Time, Metal load Concentration and Light source on the Photo-degradation of Basic Black 2 dye. The catalyst was synthesized by wet-impregnation of Zinc onto Titanium dioxide followed by calcinations at 500°C. The catalyst characterization results indicated that the synthesized TiO₂ powder had a pure two phases of Anatase and Rutile structures. The level of mineralization of Basic Black 2 dyes was monitored by taking the absorbance of the dye solution before and after irradiation with the light source at an interval of 20 minutes. The results obtained as shown in Figure 5 and 7 indicated that the efficiency of Photo-degradation of Basic Black 2 dye was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO₂ under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO₂ under UV light after irradiation for 80 Minutes respectively.

Keywords: Catalyst, Dye, Mineralization, Photo-catalysis, Titanium dioxide.

1. INTRODUCTION

Dyes are coloured organic compound that is used to impart colour to a substrate like Leather, Paper, Cloth, Plastics e.t.c and the imparted colour is reasonably wash-fast and lightfast, [1]. Azo dyes are the largest group of synthetic dyes used in leather and textile industries, [2], [3] which constitutes up to 70% of exclusively the known marketable dyes produced [4], [5]. The processing industries such as Leather and Textile industries are putting a severe burden on the environment through the release of heavily polluted wastewater, [6] and the exposures of these dyes to the environment generate coloration of natural water, toxicity, carcinogenicity and causes contamination and perturbation in aquatic life in eco-system, [2]. The treatment of colored waste water containing hazardous dyes is one of the rising needs of the present time and there is consequently great demand of technology to decolorize these extremely colored dyes waste water more efficiently, [7] and [8]. Traditional, chemical, physical and biological processes for treating textile dye wastewaters have difficulties such as high cost, energy waste and generating secondary pollution during the treatment process [9] and the treatment plant is ineffective in elimination of these dyes from the waste water [10], hence. Photo-catalysis seems as the most emerging destructive technology [11] and [12] this is because Titanium dioxide (TiO₂) has the greatest efficiency, productivity, the highest solubility, and lowest cost, [13] and [14]. The key advantage is its inherent destructive nature: it does not involve bulk transfer; it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) and may lead to whole mineralization of organic carbon into CO₂ and H₂O, [6]. The modification of these photo-catalysts facilitates to give better photo activity, [15]. Advance Oxidation Process (AOPs) have been established to degrade a wide variety of organic compound including dyes [16], Titanium dioxide, particularly in the anatase form, is a photo catalyst under ultraviolet (UV) light. It has been reported that Titanium dioxide, when doped with metal is also a photo catalyst under either visible or UV light, [17] and [18], improved degradation rates due to their improved band gap energy for using visible and solar radiation, reduces crystallize size, reduces band gap and control the surface property through increase in surface area, [19], [20], [21].

2. MATERIALS AND METHODS

Basic Black 2 (Janus Black) dyes, Oven, X-RD Machine, Centrifuge, FT-IR Spectrometer, UV/Vis-Spectrophotometer, Magnetic Stirrer (model 79-1), Analytical balance (model ES-B), UV-Fluorescence Analysis Cabinet, Muffle Furnace, Volumetric flasks, Magnetic Stirrer, Beakers, Measuring cylinder, Spatula, Syringe, Titanium dioxide (TiO₂), Zinc oxide (ZnO) and Distilled Water.

2.1 CATALYST PREPARATION

The Zn doped TiO₂ catalyst was synthesized based on the method of catalyst preparation described by [22]. Commercially available Titanium dioxide 14.81g support was weighed and dissolved in 100ml distilled water as per wet-impregnation method and 0.19g of Zinc Oxide was added to synthesize 1% Zinc in TiO₂ in total mass of 15g. The mixture was stirred at ambient temperature using...
mechanical stirrer for 1hr and the powder was separated by decantation. The powder was then dried in an oven at 150°C for 4hrs and calcined at 500°C. Similarly, 3% and 5% Zn-TiO₂ were synthesized by changing the amount of ZnO to 0.56g, 0.93g and TiO₂ to 14.44g and 14.07g to obtain samples of 3% and 5% Zn–TiO₂ in total mass of 15g respectively. The synthesized photo-catalyst was then characterized using XRD machine to determine the phases and the various minerals present.

2.2 PHOTODEGRADATION
The photo-catalysis was achieved by using UV/Visible analysis cabinet (Photo-reactor). 0.20g of Zn-TiO₂ catalyst was weighed into 100ml of 2x10⁻⁵mol.L⁻¹ of the dye in 200cm² beaker. The absorbance of the dye was measured at 620nm before irradiation and after every 20 minutes interval. In all the experiment, 0.20g of the catalyst was suspended in 100mls aqueous solution of 2x10⁻⁵mol.L⁻¹ of the dye concentration with constant stirring using a magnetic stirrer. The rate of Photo-degradation of the dye was assessed through decolourization level of the dye. After irradiation for every 20 minutes, 10mls of the solution was taking out of the reactor and centrifuged at a rate of 4000 rpm to remove the photo-catalyst and the absorbance was measured. The absorbance of the supernatant was estimated to determine the dye concentration after every 20 minutes and the used catalyst was use for FT-IR analysis after 80 minutes of irradiation.

3. RESULTS AND DISCUSSION
3.1 XRD patterns of Zn-TiO₂

The major minerals contained in 1% Zn-TiO₂ as confirm by the various peaks against corresponding 2Theta Bragg’s angle were Zn, Rutile and Anatase, and the major minerals contained in 3% Zn-TiO₂ as confirm by the various peaks against corresponding 2Theta Bragg’s angle were: Anatase, Zinc, Baité and Cadmoselite while the major minerals contained in 5% Zn-TiO₂ as confirmed by the various peaks against corresponding 2Theta Bragg’s angle was Anatase as indicated in Figure 1, 2 and Figure 3 respectively.

3.2 PHOTODEGRADATION

![Diagram 1: Photo-reactor](image1)

![Figure 1: XRD pattern for 1% Zn-TiO₂](image2)

![Figure 2: XRD pattern for 3% Zn-TiO₂](image3)

![Figure 3: XRD Pattern for 5% Zn-TiO₂](image4)

![Figure4: Rate of Photo-degradation of Basic black 2 dye using 1% Zn-TiO₂, 3% Zn-TiO₂ and 5% Zn-TiO₂ under visible light Irradiation.](image5)
of photo excited species which in turn improves the photocatalytic activity. The rate of Photo-degradation of the dye was in the following order for both visible and UV irradiation: 1% Zn-TiO₂ > 3% Zn-TiO₂ > 5% Zn-TiO₂.

3.2.2 Effect of Light source on the Photo-catalysis of Basic black 2
100ml of 2.0 × 10⁻⁵ mol.L⁻¹ of Basic black 2 (Janus Black) dye was used to evaluate the effect of Light source on the Photo-degradation of Basic black 2 dye. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO₂ under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO₂ under UV light after irradiation for 80 Minutes respectively. The percentage Photo-degradation under visible light gives better activity compared to UV light irradiation. The higher activity of the modified catalyst might be attributed to the Zn which was used as the doping element which assists in narrowing the band gap of Titanium. However, the higher activity might also be ascribed to higher surface area and small particle size of the modified catalyst. The percentage of photo-degradation of the dye was in the following order for both visible and UV irradiation: 1% Zn-TiO₂ > 3% Zn-TiO₂ > 5% Zn-TiO₂.

3.2.3 Effect of Metal loading on the Photo-catalysis of Basic black 2 dyes
100ml of 2.0 × 10⁻⁵ mol.L⁻¹ of Basic black 2 (Janus Black) dye was used to measure the effect of metal concentration on the Photo-degradation of Basic Black 2 dye. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO₂ under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO₂ under UV light after irradiation for 80 Minutes respectively. However, reduction in the rate of degradation was in the following order: 1% Zn-TiO₂ > 3% Zn-TiO₂ > 5% Zn-TiO₂ in both Visible and UV light. Conversely, the reduction in the Photo-degradation of Basic black 2 using 3% and 5% Zn-TiO₂ could be owing to higher metal concentration which leads to the deactivation of active molecules by collision with ground state molecules, thus dominating the reaction.

3.3 RESULTS FOR THE FT-IR ANALYSIS OF THE USED Zn-TiO₂

From the result of the FT-IR spectra of used 1% Zn-TiO₂ shown in Figure 8, a vibration was observed at
1435.09 cm\(^{-1}\) which is assign to O-H due to hydroxyl or alcohol group broken from Basic Black 2 dye. Also 1633.76 cm\(^{-1}\) is observed due to \(\equiv\text{CH}_2\) broken down during the photo-catalytic reaction. The 2285.72 cm\(^{-1}\) is for \(-\text{N}=\text{C}=\text{O}, -\text{N}-\text{C}=\text{N}\) or \(-\text{N}_2\) which is the azide group and at 3435.34 cm\(^{-1}\) \(-\text{N}-\text{H}\) is a primary amine formed as intermediate during irradiation.

73.61% using 1%, 3% and 5% Zn-TiO\(_2\) under UV light after irradiation for 80 Minutes respectively and the FT-IR analysis results indicated that the Basic black 2 dye was mineralized by the Photo-catalyst. The degradation efficiency in the visible light seems to be more efficient compare to that of the UV light which could possibly be as a result of Zinc doped in Titanium dioxide which reduces the band gap of the Titanium and enhances its efficiency in the visible light. The results of this study clearly indicate that organic dyes in the tannery and textile waste can be efficiently degraded in the presence of Photo-catalyst.

**CONCLUSIONS**

Photo-catalytic degradation of Basic Black 2 dye was carried out using TiO\(_2\) modified with 1%, 3% and 5% Zn-TiO\(_2\) respectively as Photo-catalyst. From the results shown in Figure 5 and 7 the percentage photo-degradation was 99.92%, 95.94% and 74.46% using 1%, 3% and 5% Zn-TiO\(_2\) under Visible light and 98.22%, 97.46% and 73.61% using 1%, 3% and 5% Zn-TiO\(_2\) under UV light respectively as Photo-catalyst.

**ACKNOWLEDGEMENT**

The authors wish to express their heartfelt gratitude to Almighty God for the success of the research and also to Staff of the Department of Petrochemical, National Institute for Chemical Technology (NARICT), and also to the Department of Research and Development NILEST, Zaria where the research was conducted.

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