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Editorial Comment

It is a great pressure for the editorial board of the Nigerian Journal of Materials Science and Engineering (NJMSE) to present Volume 10 Number 1 of the journal for 2020 for the world research and development community.

The Materials Science and Technology Society of Nigeria (MSN), as a professional learned body, has made the publication of this research journal to be of very good quality and high standard comparable to any in her class. Our major thrust is to disseminate materials science and engineering and allied research activities from Nigeria, Africa and the world over. We are slowly and gradually impacting on the research community work with this specialised journal from a reputable learned and professional body in Nigeria. We are presently not insisting on number but we very much believe, with the thoroughness of our approach to the review and assessment process, we are convinced that with our resolve to publish quarterly, the board is convinced that more researcher would take advantage of this.

As a journal whose policy is to maintain the standard best practices and in addition to help young researchers to advance in the art and science of scientific findings dissemination, had faced tremendous challenges which were expected. It is heart-warming that we can look back and be glad to see the society publishing the 10th volume. These volumes and the previous ones would be available for FREE downloading on our society website (www.msn.ng) through a link prior to the specialised journal website to be available soon. Arrangements are in advanced stages for the hosting of this journal by reputable international online submission system are being worked on.

Volume 10 (2020) Number 1 consists of eight (8) high standard articles covering different specialised areas of materials research. It is our hope that this humble effort, presently by voluntary efforts of senior members of the Society, at disseminating research findings as put together in this volume which have contributed to the body of knowledge, would have enriched the information base and complemented Materials Research efforts from around the world.

We appreciate all our reviewers and associate editors involved for their prompt action on the manuscripts and cooperation as we look forward to submission of manuscripts which can be forwarded as detailed below.

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NJMSE is introduced to publish research findings on current topical issues of interest to both public and private sectors. The scope of the Journal focuses on experimental, empirical and theoretical research in Materials Science and Engineering. Findings from multidisciplinary research covering diverse areas of interest with potential impact on the public and private sectors of both the national and international communities will be priorities of the journal. Our major focus is the use of Materials Science and Engineering principles to solve basic problems peculiar to African and the developing world while contributing to knowledge on the global scale.

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Comparative Activity of Undoped TiO_2 and 5% N-TiO_2 for Photocatalytic Degradation of Indigo Carmine Dye

[*]**Oyegbami** Victoria Bola,, **Odebunmi** Ezekiel Oluyemi, [1]**Odeyemi** Omolola Titilayo and **Gbadamosi** Mustapha Tunde

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Abstract

TiO_2 was synthesized by Sol-gel method and doped by Impregnation of Nitrogen from Ammonium Chloride to obtain 5% N-TiO_2. The undoped TiO_2 and N-doped TiO_2 photocatalysts were characterized by Fourier Transform Infrared (FTIR) Spectroscopy, X-Ray Diffraction (XRD) Crystallography and Scanning Electron Microscopy (SEM). Investigation of the activities of the photocatalysts for degradation of Indigo carmine dye in aqueous solution was carried out at different operating conditions of pH, temperature, catalyst concentration and dye concentration under aeration and UV- irradiation using a 20 Watt UV lamp in a specially constructed reactor made up of four compartments. The dye degradation reaction was monitored on a N4S UV-Spectrophotometer at 290 nm. The FTIR results attested the presence of N-H, Ti-O-Ti, Ti-O, H-O-H, O-H functional groups in the catalysts. The XRD Crystallography results show that 5% N- TiO_2 catalyst contains a mixture of anatase and rutile phase compared to undoped TiO_2 which contains pure anatase phase. The SEM results show decrease in particle size when TiO_2 was doped with Nitrogen. The degradation rate was found to comply with first order kinetics and optimum degradation was attained at the same pH and temperature of 3 and 40°C respectively for both photocatalysts. However, the dye and catalyst concentrations where optimum degradation was observed for 5 % N-TiO_2 and undoped TiO_2 were found to be 20 ppm, 0.025 g/l and 12.5 ppm, 0.05 g/l respectively. Percent degradation in the presence of both UV- Irradiation and catalyst was calculated to be 28.5 % and 34.14% for TiO_2 and 5% N- TiO_2 respectively. The percent degradation result shows a higher efficiency on 5% N- TiO_2 than undoped TiO_2.

Keywords: Degradation, Indigo carmine dye, 5 % N- TiO_2, Photocatalysts and TiO_2.

INTRODUCTION

Dyes are the most significant chemical constituents which impart colour to product of textile, pharmaceutical, paint, detergents, etc. industries. Indigo carmine, which is a synthetic dye, is highly coloured and toxic. It finds its uses mostly in dyeing of wool and silk (Klaus, 2003; Scharff, 1999). The structure is presented in Figure 1.

Dye molecules persist in the environment because many of them are not reactive towards light, acids, bases and oxygen (Rauf and Ashraf, 2009). Wastewater produced in textile industry is one of the sources of pollution because it contains complex mixture of polluting materials and minimized the concentration of oxygen in water receiving bodies (Tchobanoglous *et al.*, 2003). The limited success of conventional methods used in pollutant destruction leads to the use of advanced oxidation process (AOP) of photocatalysis using Titanium dioxide (TiO_2). This is because TiO_2 efficiently produce desired results without wasting energy and materials in industrial effluents treatment (Ghoreishi and Haghighi, 2003). Doping of TiO_2 enhances photocatalytic degradation of chemical species in wastewater. Non-metals such as boron, nitrogen, fluorine, and carbon are used to modify TiO_2 in order to enrich its photocatalytic activity. However, nitrogen has been observed as one of the most favourable dopant due to its stability and atomic size (Pelaez *et al.*, 2012).

In this research, TiO_2 was synthesized by Sol-gel method and 5% N- TiO_2 by Impregnation method. The samples were characterized by various techniques and comparison of their photocatalytic activities was examined to investigate the destructive power of TiO_2 and N-TiO_2 against uncatalyzed aqueous solution of indigo carmine dye.

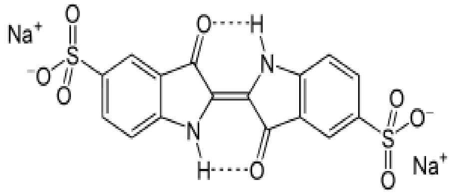

Figure 1: Structure of Indigo Carmine dye (Ahmed, 2013)

MATERIALS AND METHODS

Materials

Analytical grade reagents used are Ammonium Chloride, Ammonium Hydroxide, Hydrochloric Acid, Hydrogen Peroxide (Sigma Aldrich Chemical Company, USA), Potassium Hydrogen Phthalate, Ethanol, Titanium Trichloride (Tianjin Damao Chemicals Reagent, Tianjin, China) and Indigo Carmine Dye (molar mass 466.36 g/mol, density 1.01g/mL at 20 °C, very dark blue and water soluble obtained from Qualikems Analytical Reagent, Delhi, China).

Methods

Synthesis of the photocatalysts

A 100 cm^3 of 10% $TiCl_3$ (containing 15% HCl), 100 cm^3 distilled water, 200 cm^3 of 30% H_2O_2 and 200 cm^3 NH_4OH solution was magnetically stirred for 24 hrs, aged for 72 hrs, washed, dried and calcined at 400 °C for 1 hr to obtain

TiO_2 photocatalyst (Molea and Popescu, 2011). A 0.25 g of ammonium chloride was dissolved in solution of ethanol and water (3:1 v/v) and added to 4.75 g of TiO_2. The reaction mixture was refluxed for 180 mins, heated and calcined at 400 °C for 1 hr to obtain 5% N-TiO_2 photocatalyst (Kumar *et al.*, 2015).

Characterization

The synthesized photocatalysts were characterized by Fourier Transmission Infrared Spectroscopy (FTIR) using Nicolet iS5 FTIR machine. The FTIR instrument was cleaned and calibrated. The main power of the instrument and computer was switched on and software icon was opened after 15 mins. The sample holder was also cleaned perfectly. Moisture free potassium bromide (KBR) of spectroscopic grade was crushed in a clean mortar and pestle, filled alone into the sample holder and scan as the background. The particle size of the catalyst was reduced to particle size less than 5 mm in diameter by mixing 2 mg of catalyst with 200 mg of KBR in a mortar and pestle. The mixed sample was placed close to the chamber compartment and scan to obtain the sample spectrum. The sample and standard infrared spectrum was merged and split to the peak to get the % purity of the sample.

X-Ray Diffraction (XRD) Crystallography analysis was carried out using Bruker AXS D8 Advance (USA). The catalyst was filled into the sample holder until it is slightly overfull, and plexiglass was placed on the top surface of sample to compress the catalyst in the specimen holder. The specimen holder and plexiglass cover were carefully placed on the tabletop and the plexiglass cover was lifted. The specimen holder containing the sample was placed into the specimen carrier and then placed in the X-ray diffractometer before data collection procedure was run on the system. Scanning Electron Microscopy (SEM) analysis was performed using FEI Quanta 200-HiVac Mode. The catalyst was filled on an appropriately sized round aluminum disc, measured with plastic measuring tool to determine sample's height. The aluminum disc was copulated into a brass stub before sliding the stub into the sample mount. The chamber door was closed, and a Pump was clicked in the computer interface.

Photocatalytic Activities

Photodegradation of indigo carmine dye by TiO_2 and 5% N-TiO_2 was achieved under varying values of pH, temperature, dye and catalyst concentration using 20 W UV- lamp and aeration in reactor. About 5 cm^3 supernatant solution was withdrawn at regular interval of 15 mins up to 120 mins reaction time and the absorbances were recorded (Daneshvar *et al.*, 2003). Optimum parameters used in dye degradation were chosen using first order rate constant and percent degradation by each photocatalyst was calculated using the equation (Odeyemi *et al.*, 2018):

$$D(\%) = (A_o - A)/A_o \times 100 \qquad (1)$$

where D represents degradation, A_o is initial absorbance before addition of catalyst and A is absorbance of dye at time t.

The dye degradation reaction was equally conducted in the absence of the photocatalyst using UV-irradiation only.

Effect of pH on Degradation of Indigo Carmine Dye

About 5 ppm dye solution was prepared from the stock solution by dilution using buffer solutions in the range 1 to 8 in a 200 cm^3 volumetric flask and degradation followed using 0.05 g/l catalyst at 30°C for 120 mins on stream. The absorbances of the initial and final supernatant solutions were taken and recorded (Ahmed, 2013).

Effect of Dye Concentration on its Degradation

Indigo carmine dye solution ranging from 2.5 ppm to 25 ppm was degraded at pH 3 by 0.05 g/l catalyst concentration and temperature of 30°C (Susheela, 2012).

Effects of Catalyst loading on Indigo Carmine Dye Degradation

Indigo carmine dye was degraded using different catalyst concentration loading from 0.025 g/l to 0.175 g/l at constant optimum dye concentration, pH 3 and temperature of 30°C (Ahmed, 2013).

Effect of Temperature on Photocatalysts Activity

Temperature within the range 30 to 60°C was monitored for the dye degradation (Mehrotra *et al.*, 2005; Mozia *et al.*, 2009; Soares *et al.*, 2007).

RESULTS AND DISCUSSION

Characterization of TiO_2 and 5 %N- TiO_2

Fourier Transform Infrared (FTIR) spectroscopy.

Fourier Transform Infrared analysis was carried out on the photocatalysts before usage and the spectra obtained are presented as Figures 2(a) and (b). It was observed that both spectra showed a broad peak at 400 – 1000 cm^{-1} and deformation vibrations at 1600 – 1630 cm^{-1}, which are caused by Ti-O stretching and H-O-H bending vibrations respectively. The spectrum of N- TiO_2 gave strong signals in the region 1000 - 1700 cm^{-1} while TiO_2 control peak was at 1630.27 cm^{-1} which are representations of adsorbed water (Chen and Mao, 2007).

The observed broad band at 3200 - 3600 cm^{-1} was due to O-H stretching vibration (Mugundan *et al.*, 2015). In essence, the FTIR results show presence of water molecules and hydroxyl groups in the photocatalysts which are part of the necessary requirement for degradation of dye molecules in solution (Mugundan *et al.*, 2015). The spectra of N-TiO_2 also showed bands at 3417 cm^{-1} and 1630 cm^{-1} indicating N-H stretching and bending vibrations respectively. This shows that there was bonding of the Nitrogen with the TiO_2 material (Nolan *et al.*, 2012).

X-Ray Diffraction Crystallography.

The XRD patterns of TiO_2 and 5% N-TiO_2, showing strong diffraction peaks, are presented in Figure 3. The crystallite sizes of both catalysts were calculated by Debye Scherrer formula to be 13.38 nm and 11.45 nm

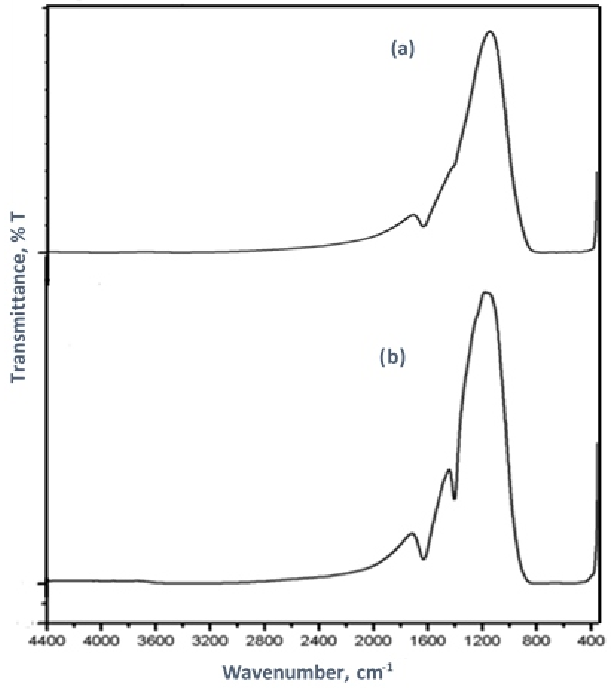

Figure 2: FTIR Spectra of (a) undoped TiO_2 (b) 5% N-TiO_2

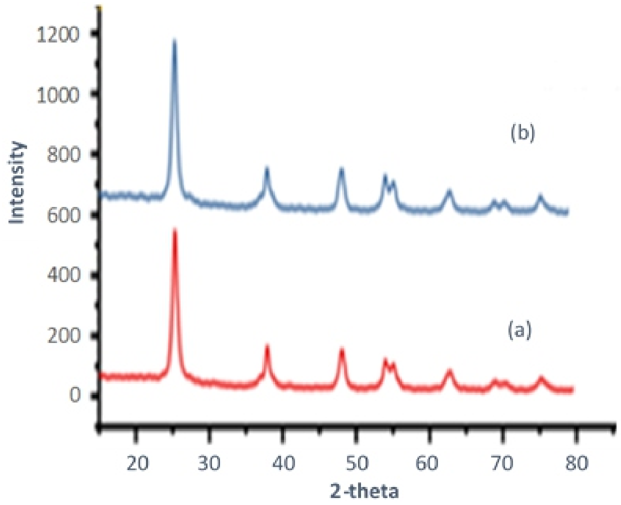

Figure 3: XRD patterns of (a) undoped TiO_2 and (b) 5% N-TiO_2

for undoped TiO_2 and 5% N- TiO_2 respectively (Borchert *et al.*, 2005). From the results, N- doped TiO_2 was observed to contain a mixture of anatase and rutile phase while TiO_2 was dominated by anatase phase only. This is due to the support of N-doping in formation of oxygen vacancies needed for anatase to rutile transformation by rearrangement of required atoms (Martyanov *et al.*, 2004).

Scanning Electron Microscopy

The micrograph obtained using Scanning Electron Microscopy shows the results in nanometric dimensions and are presented in Figures 4(a) and (b). Particle size of 5% N- TiO_2 was observed to be smaller compared to undoped TiO_2 (Kumar *et al.*, 2015) and effective degradation was expected by doped catalyst in comparison with undoped (Chanderia *et al.*, 2017).

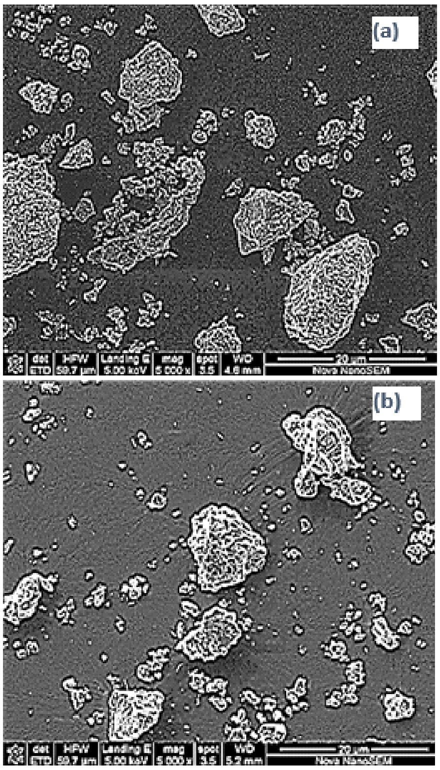

Figure 4: SEM Micrographs of (a) undoped TiO_2 and (b) 5 % N-TiO_2

Photocatalytic Degradation of Indigo Carmine Dye

Effect of pH

Photocatalytic degradation of Indigo carmine dye mainly depends on pH of the reaction solution due to amphoteric behavior of TiO_2 (Ahmed, 2013; Wang *et al.*, 2008). Degradation of Indigo carmine dye was very strong in acidic pH due to the production of anionic dye when dissolved in acidic medium. The effect of pH on dye degradation results is presented in Figure 5(a). Effectual degradation by both catalysts was observed at acidic pH of 3 which was found to be the optimum (Ahmed, 2013; Wang *et al.*, 2008).

Effect of Dye Concentration

It was observed that the rate constant for the reaction decreased with increase in dye concentration and later increased with increase in dye concentration up to the optimum concentration. The results of effect of dye concentration on its degradation is presented in Figure 5(b). The decrease at first may be due to present of plenty catalyst sites in dye solution which shows faster degradation and higher percent degradation. As the dye concentration increases, the rate constant later increases which may be due to the presence of more active sites on the catalyst than molecules in solution (Munusamy *et al.*, 2013). On the other hand, the decrease in rate constant was attributed to the presence of more dye molecules than catalyst sites which reduced the amount of light penetrating the solution (Daneshvar *et al.*, 2003). Optimum dye concentration

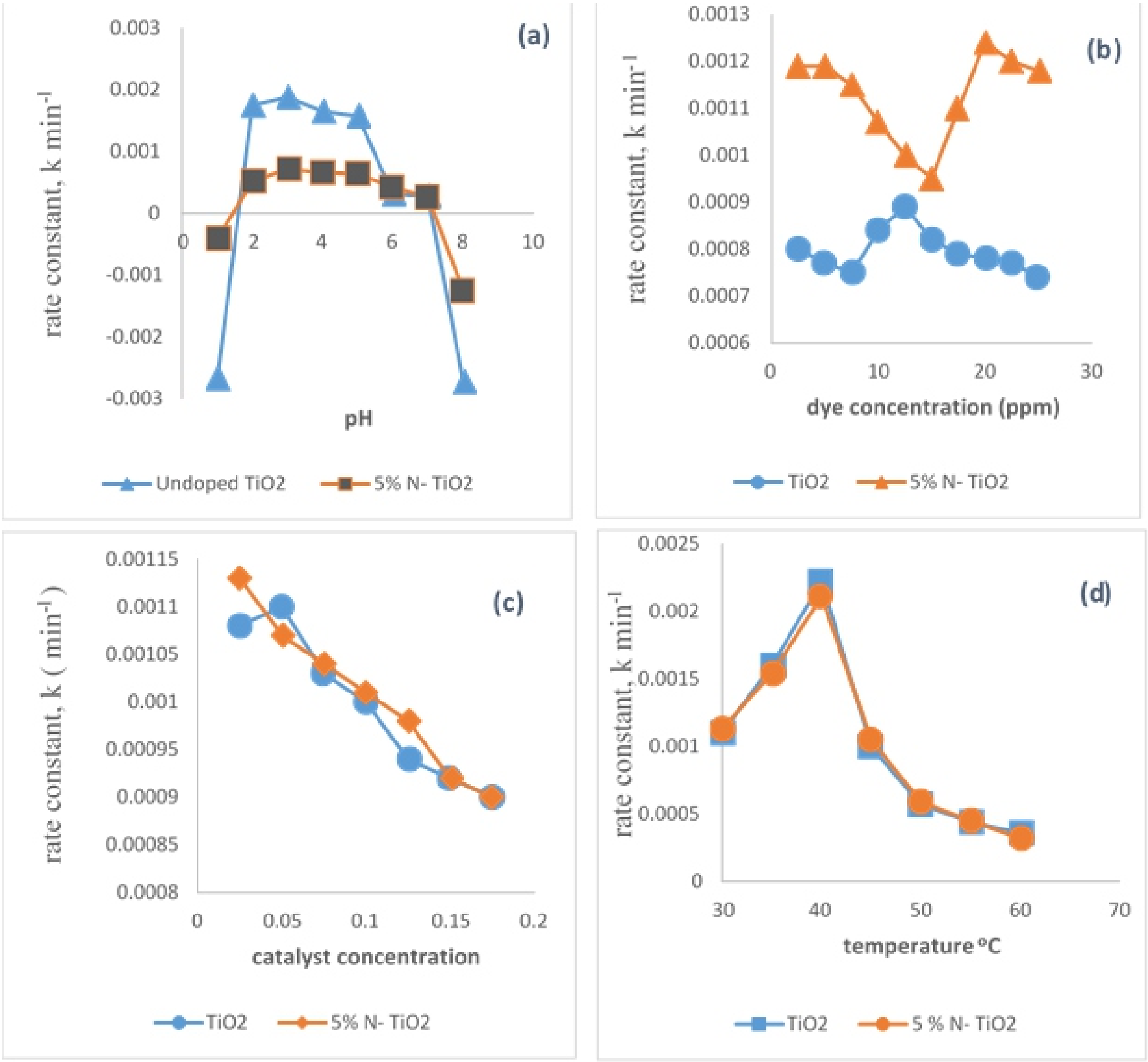

Figure 5: Effect of (a) pH (b) dye concentration (c) catalyst concentration and (d) temperature on indigo carmine dye degradation

attained by TiO_2 and 5 % N- TiO_2 was 12.5 ppm and 20 ppm respectively. This variation was observed to be attributed to the difference in the catalysts surface area.

Effect of Catalyst Concentration

The result for the effect of catalyst concentration at optimum conditions by both catalysts is presented in Figure 5(c). The rate constant decreased linearly as catalyst concentration increased. This decrease was due to cloudiness of dye solution by excess catalyst resulting in scattering of UV- Irradiation (Reza *et al.*, 2017). The optimum catalyst concentrations were 0.025 g/l and 0.05 g/l for 5% N-TiO_2 and TiO_2 respectively. The difference in catalyst concentration shows that the particles of the doped catalysts were finer than the undoped which in turn attribute higher surface area to the doped than undoped. Therefore, under the same conditions of pH and temperature, more of the undoped catalyst than the doped catalyst was required for degradation of the dye molecule.

Effect of Temperature

The result for effect of temperature on dye degradation over a temperature range of 30 °C to 60 °C at various optimum conditions is presented in Figure 5(d). Maximum dye degradation was attained at temperature of 40 °C for both catalysts. The rate constant increased as the temperature increased up to an optimum of 40 °C after which it decreased with further increase in temperature. The increase at first, as the temperature increased, could be explained to be due to the increase in the kinetic energy of the colliding molecules of the dye and the catalysts (Mehrotra *et al.*, 2005). Soares *et al.*, (2007) also observed operating temperature range to be between 40°C to 50°C in their study of the effect of temperature on reaction and at lower temperature, the reaction was limited by desorption of the product formed which caused surface degradation and reactant adsorption to be slower. In this study however, beyond the optimum temperature of 40°C where the degradation decreased, it was observed that adsorption of the dye

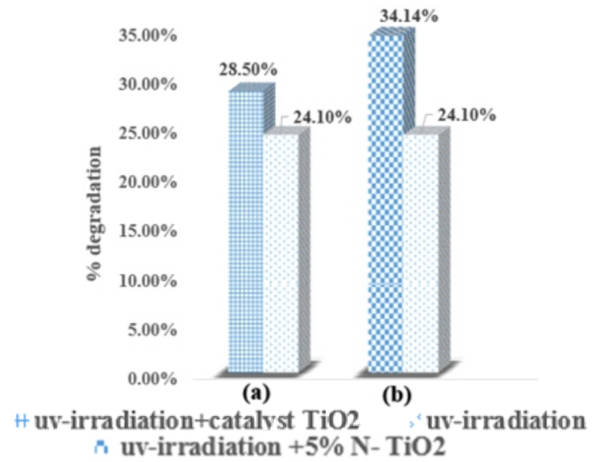

Figure 6: Comparison of Relative Activities of the Catalysts (a) UV-Irradiation + Undoped TiO_2) with UV-Irradiation alone (b) UV-Irradiation + 5% N-TiO_2 with UV-Irradiation alone

which is the limiting reaction was disfavoured while desorption of the products was enhanced (Mozia *et al.*, 2009).

Relative Activities of Photocatalysts

The relative activities of the TiO_2 and 5 % N-TiO_2 photocatalysts under their optimum experimental conditions are presented in Figure 6. Maximum degradation observed in the presence of the catalysts was 28.50% and 34.14% for TiO_2 and 5% N-TiO_2 respectively. It is of great concern to observe that these percentages were very low as compared to what has been obtained in related literatures that have been cited. However, it is also worthy of note that in photocatalysis, charge carriers tend to quickly recombine more often than not in some active catalysts as explained by Mamba *et al.*, 2014 which tend to stop or slow down the process occasionally. On the other hand, since the scope of the work relates more to comparing the activities of an undoped with the doped, then it was observed that the activity of the TiO_2 photocatalyst was enhanced by the Nitrogen doping. Comparing these results with that obtained in the presence of the UV-light only, where the degradation was 24.1% (Figure 6), it was also observed that even though the indigo carmine dye could be degraded in the absence of the catalysts, the presence of same could increase the rate of the degradation process.

CONCLUSIONS

Titanium dioxide (TiO_2) was successfully synthesized and doped with Nitrogen from Ammonium Chloride, characterized by FTIR, XRD and SEM, and used in the degradation of Indigo carmine dye in aqueous solution. Effective degradation was achieved by both catalysts and optimum pH 3 and temperature 40°C were identified for both catalysts whereas different optimal dye and catalyst concentrations were obtained. Degradation in the presence of a photocatalyst was also found to be more efficient than in the absence of the photocatalyst.

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