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Photocatalytic Degradation of Direct Blue 5b and Mordant Brown RH33 Azo Dye by Nano Al_2O_3 under UV Irradiation

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ABSTRACT

In this study, a chemical method including $AlCl_3$, ethanol and NH_3 solution are used for synthesis of nano Al_2O_3. The prepared nanoAl_2O_3 is characterized by applying the XRD and TEM techniques. The photocatalytic behavior of nano Al_2O_3 is applied to the photo catalytic degradation of Direct Blue 5b and Mordant Brown RH33dyes under UV irradiation technique. The effect of various parameters including catalyst dosage, pH and temperature on the degradation of two dyes are investigated. Finally, the efficiency of photo degradation by nano Al_2o_3 under UV irradiation for direct blue 5b and Mordant Brown RH33 found to be 93.7 and 93.2 respectively.

Key words: Nano Al_2O_3, XRD and TEM techniques**,** Direct Blue 5b and Mordant Brown RH33dyes

Introduction

Industrial wastewater is becoming important with the increasing diversity of industrial products. Dyes are released into the environment mainly from textile and dyestuff industries (Rezaei and Soltan, 2012). Azo dyes such as (Direct Blue 5b and Mordant Brown RH33) are the largest group of colorants, constituting 60-70% of all organic dyes produced in the world characterized by the presence of one or more azo bonds (-N=N-). The success of azo dyes is due to the their ease and cost effectiveness for synthesis as compared to natural dyes, and also their great structural diversity, high molar extinction coefficient, and stability towards light as well as to wetness. However, some azo dyes can show toxic effects, especially carcinogenic and mutagenic events. The toxic effects of the azo dyes may result from the direct action of the agent itself or of the aryl amine derivatives generated during reductive biotransformation of the azo bond (Pan *et al.,* 2012).

This could be the main reason for the received increasing attention of dyes removal from water sources. Photo degradation processes have been developed and found to be a convenient method to treat wastewater and removal of azo dyes in recent years. Various photocatalysts like metal oxides have been extensively used for the photo degradation processes. It should be noted that high surface area and high adsorption capacity of photo-catalyst is an important factor because the rate of the photo degradation process increased when dyes well adsorbed at the surface of the photo-catalyst (Valencia *et al*., 2012; Chuang *et al.,* 2008).

The aim of this study is to synthesize and the characterization of nanoparticles of aluminum oxide (Al_2O_3) via a sol gel method and the effects of their catalytic activity in the Photo-catalytic degradation of Direct Blue 5b and Mordant Brown RH33 by UV irradiation technique. According to the characteristic properties and photo-catalytic activity of Al_2O_3 depend on several factors such as morphology, size and crystalline structure of Al_2O_3.

Experimental

Chemicals

All reagents were purchased from Merck and used without further purification. The commercially available water-soluble acid chrome dye, Mordant Brown RH33 (MBRH33, Fig.1a) and azo dye Direct sky Blue 5B (DS5B, Fig.1b) is obtained from Sigma Aldrich company.

Physical characterization of Mordant Brown RH33 and azo dye Direct sky Blue 5B

To verify the structure of MBRH33 and DS5B the Fourier-transform infrared (FTIR) technique is measured as shown in Fig 2a and 2b.For MBRH33 CO, CN stretches are observed at 1628 cm^{-1}, 1511 cm^{-1}, respectively.

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Also for MBRH33 NH, NH2stretch are shown at 3448 cm-1, 3373 cm^{-1}, respectively. The N=N stretch characteristics for DS5B is observed at 1494 cm^{-1}. NH, OH is observed abroad bands at about 3454 cm^{-1} (Lee *et al.,* 2013).

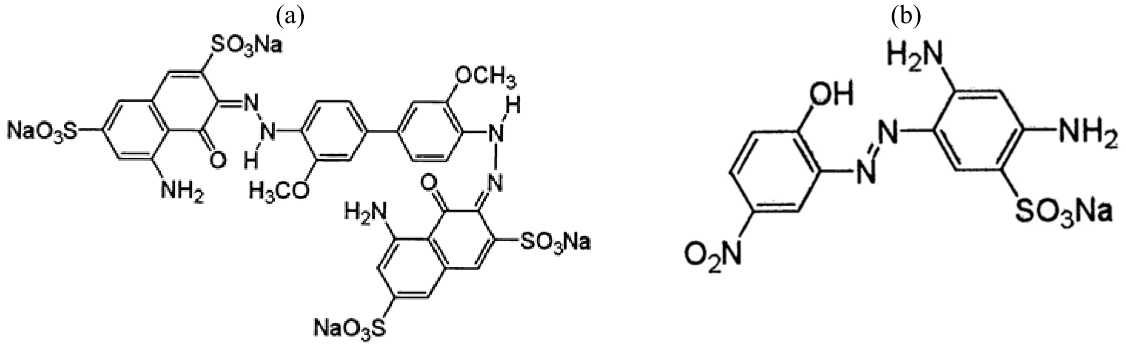

Fig. 1: Schematic diagram of Mordant Brown RH33 (1a) and Direct sky Blue 5B (1b).

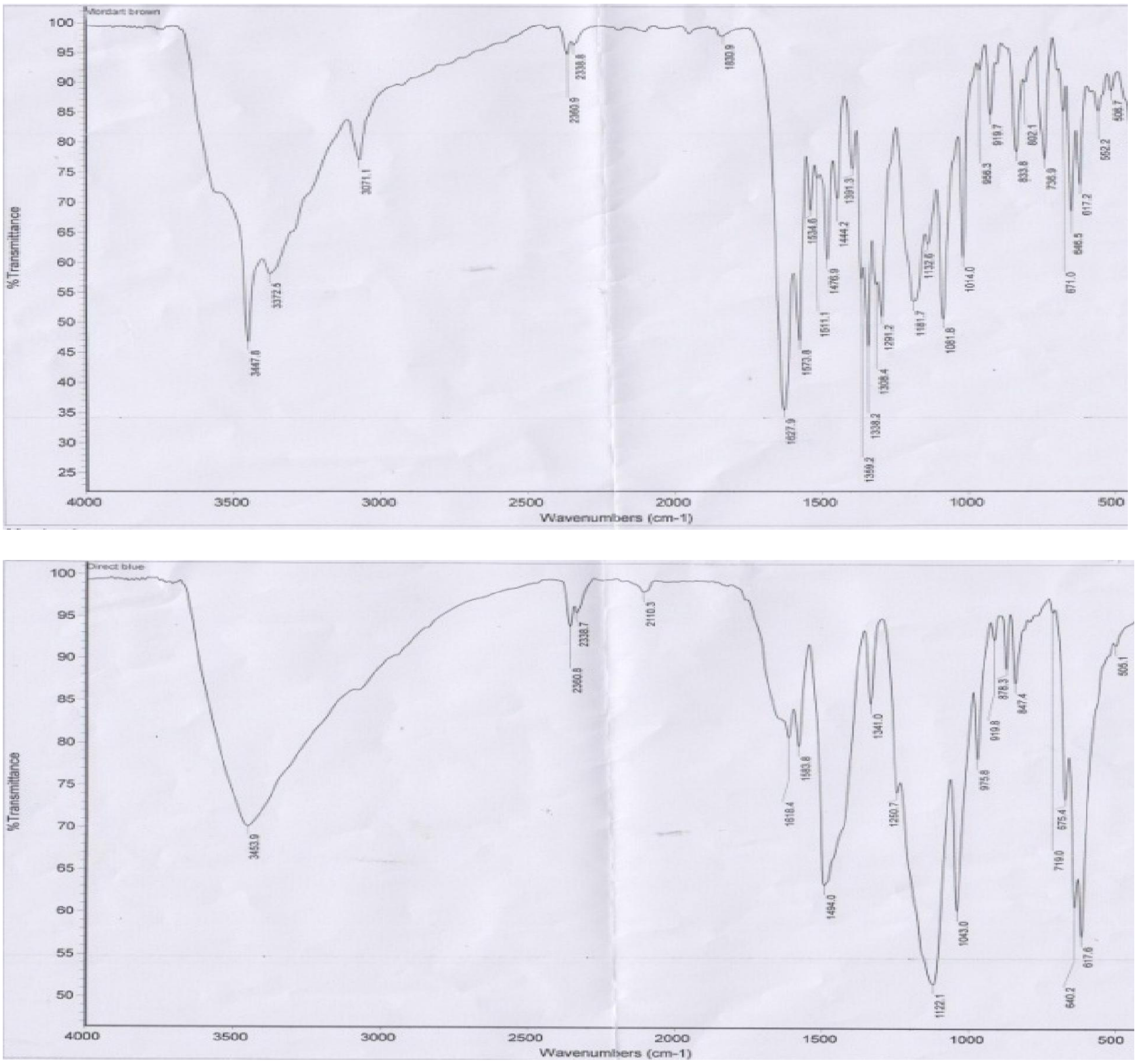

Fig. 2: FTIR of Mordant Brown RH33 (2a) and Direct sky Blue 5B (2b).

Synthesis procedure of nano Al_2O_3

Al_2O_3 nanoparticles were prepared via sol-gel method using the precursor aluminum trichloride ($AlCl_3$) as the starting materials. 28% of ammonia solution was added dropwise to stirred ethanolic solution of aluminum trichloride ($AlCl_3$) (0.1 M). The gel was left to digest for 30 hours at room temperature. After filtration in water pump, drying at 100°C for 24 h in an oven, and annealing at 1000°C for two hours, the mechanism of nanoAl_2O_3 is illustrated in the following equations.

(i) $NH_3.H_2O \longrightarrow NH4+OH-$
(ii) $M\text{-}Cl+NH_4OH \longrightarrow M\text{-}OH+NH_4Cl$
(iii) $M\text{-}OH + R\text{-}OH \longrightarrow H_2O + M\text{-}O\text{-}R$
(iv) $M\text{-}OR + M\text{-}OH \longrightarrow R\text{-}OH + M\text{-}O\text{-}M$

Physical characterization of nano Al_2O_3

XRD data were collected from the synthesized powders for phase identification and determination of crystallite size by Bruker-AXS D8Advance (for 2θ range from 0 to 80° with a step size of 0.01° (2θ)) -using Cu-Kα radiation. TEM image was taken by The JEOL JEM 2100 microscope to examine the shape and size of nano-composite.

Photocatalytic degradation procedure

The experiments are carried by using the Mercury lamp (220 v) with 100 ml Dye solution prepared in appropriate concentration using dieionzed water. Dye solutions are stirred in the dark for different time after the addition of (nano Al_2O_3) as photocatalyst to reach the adsorption equilibrium on the surface of the photocatalyst. The suspension solution is irradiated. The photo catalyst is isolated from heterogeneous solution by centrifuging before any absorbance measurement at 3000 rpm for 10 min to remove the catalyst particles completely. The progress of photocatalytic decolonization is monitored by measuring the absorbance of the solution samples at the maximum wavelength of each dye (λmax=442 nm for MBRH33) and (λmax 600 nm for Direct sky blue 5B). Initial decolonization rate constants (k_1) are determined from the slope of ln (A_0/A_t) versus t (min) plot According to Eqn (1):-

$$\ln(A_o) = ak_1t + \ln(A_t) \qquad (1)$$

Where A_o and A_t are the absorbance at zero time and at (t) time respectively

Results and Discussion

The prepared sample was characterized with XRD and TEM techniques. The X-ray diffraction pattern of nano Al_2O_3, whereas the characteristic peaks of Al_2O_3 are 25.50, 35.11, 37.72, 43.29, 46.13, 52.52, 57.44, 66.47 and 68.16. Meanwhile these peaks are in conformity with a single-phase with a monoclinic structure (Kamil *et al.,* 2016).

The average crystal size of the nanoparticles is calculated by the Debye–Scherer formula (2), and found to be 31 nm for Al_2O_3.

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

Where, k is the shape factor, D is the crystallite size, θ is the diffraction angle, β is the full width half maximum of diffraction angles in radians.

The surface morphology and grain size of the prepared Al_2O_3 nano-powders were characterized by TEM techniques. The average profile size is about 2.5 nm.

Photocatalytic activity

Photocatalytic degradation of Direct Blue 5B and Mordant Brown RH33 dye was investigated using the prepared Al_2O_3 nano-catalyst by UV irradiation technique. The characteristic absorption peak of Direct Blue 5B solution was found λ_{max}= 600 nm and for Mordant Brown RH33 λ_{max} = 442 nm as shown in figures (4) and (5). The spectra of Direct Blue 5B consist of two bands at 600and 320 nm .Where the spectra of Mordant Brown RH33 show bands at 222, 374,442 and 446 nm.

Degradation of Direct Blue 5B and Mordant Brown RH33 was visualized by a decrease in peak intensity within 30 min of incubation time and its concentration was calculated from the standard calibration curve of absorbance against concentration. The following equation was used for the evaluation of degradation rate by using Eqn. (3).

$$R = \frac{(C_o - C_t)}{C_o} * 100 \qquad (3)$$

Where R is degradation rate, C_0 and C_t are the concentration of Direct Blue 5B and Mordant Brown RH33 at UV irradiation time zero and t respectively.

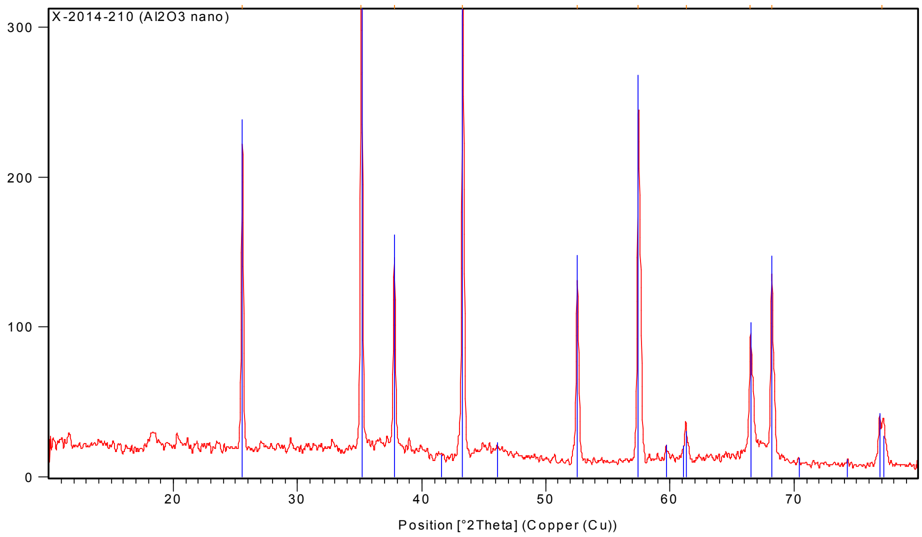

Fig. 3: XRD pattern of Al_2O_3 nano-powder

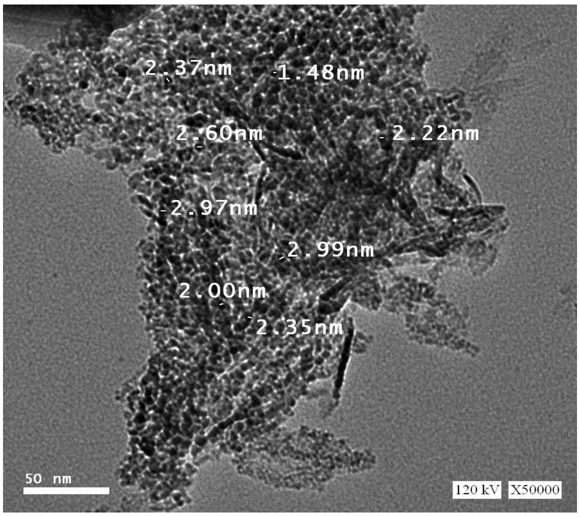

Fig. 4: TEM image of Al_2O_3 nanoparticles

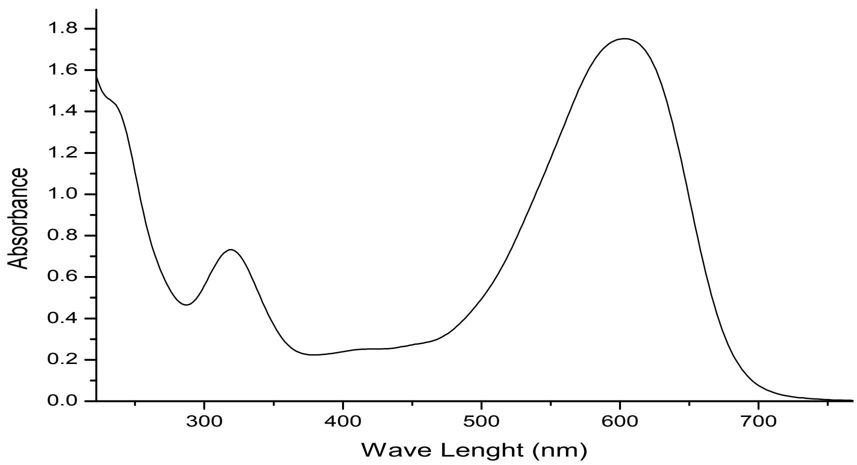

Fig. 5: The UV-vis spectrum of Direct Blue 5B in water.

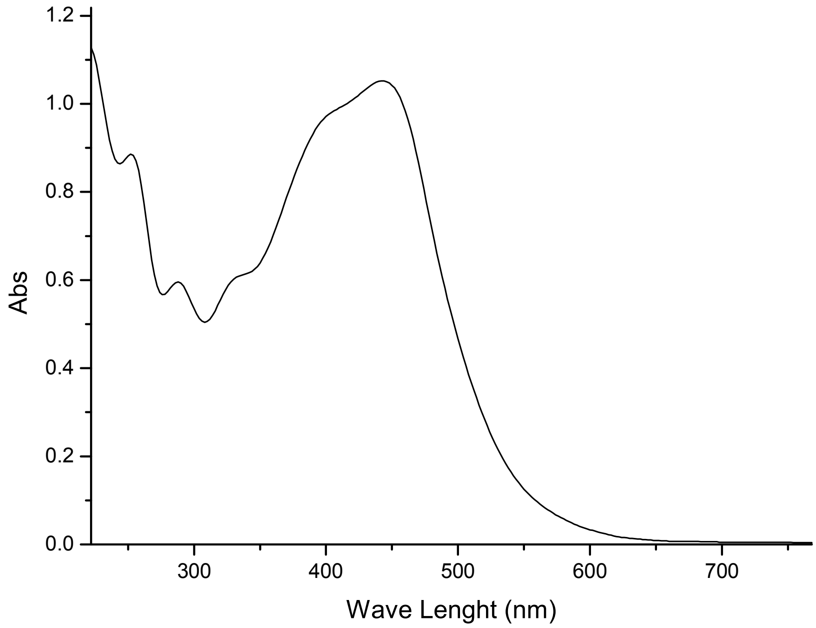

Fig. 6: The UV-vis spectrum of Mordant Brown RH33 in water.

Effect of catalyst amount-

Initially, the effect of catalyst concentration on the Direct Blue 5b degradation was investigated and the results are shown in the Figures for Mordant Brown RH33 and Direct Blue 5b. It is revealed that the degradation of the two dyes increased with increasing the catalyst amount in the range of 0.1 g to 0.15 g. Afterwards due to reducing of the light penetration into the suspension, a decrease in the two dyes degradation was occurred.

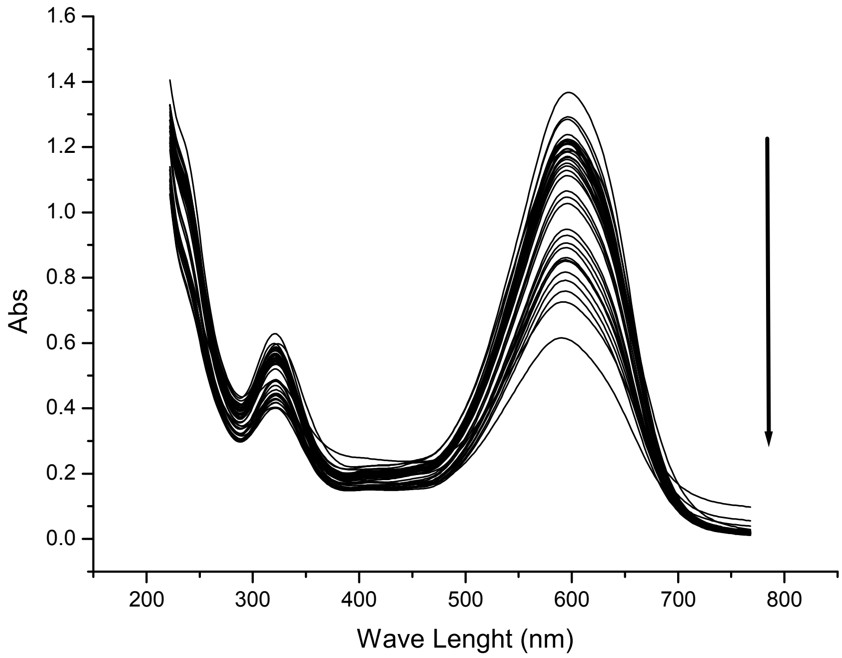

Fig. 7: Irradiation of100 ml of Direct Sky Blue 5B 10^{-4} M with 0.1g Al_2O_3 from zero time to 30 minute.

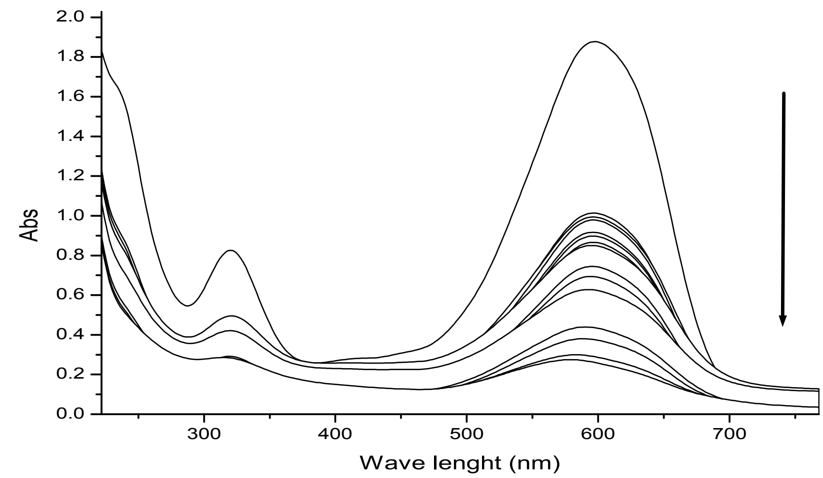

Fig. 8: Irradiation of100ml of Direct Sky Blue 5B 10^{-4} M with 0.13g of $Al_2O_3$from zero to 30 minute.

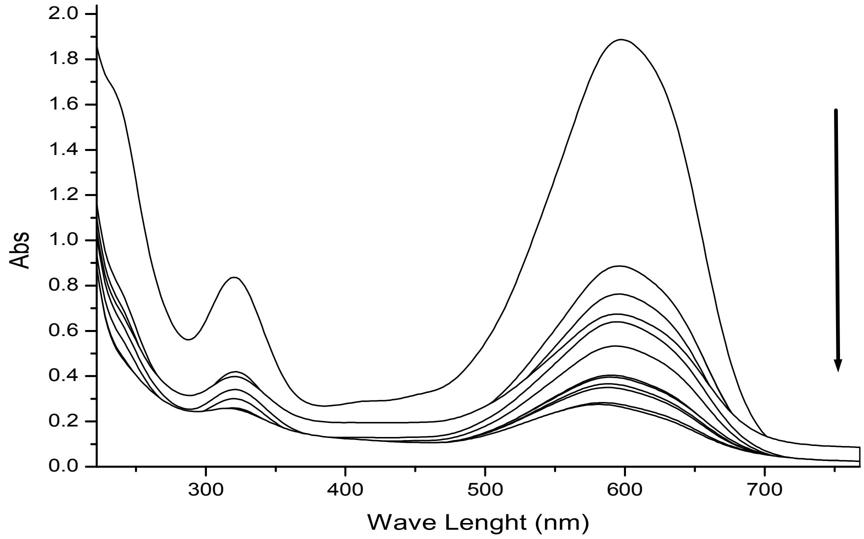

Fig. 9: Irradiation of 100 ml of Direct Sky Blue 5B10^{-4} M with 0.15g of Al_2O_3 from zero time to 30 minute.

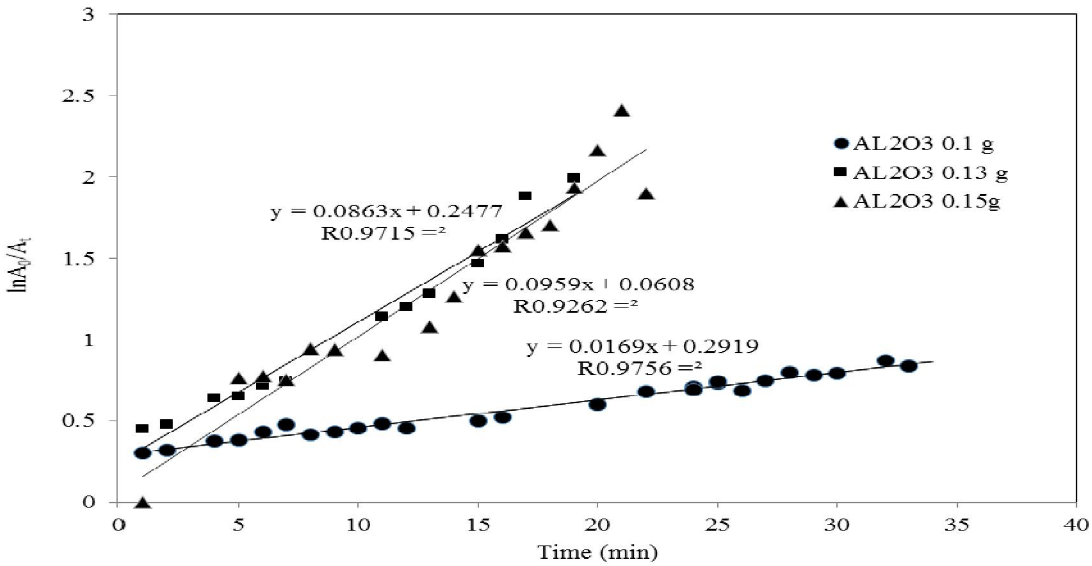

Fig. 10: Plot of ln (A_0/A_t) versus time.

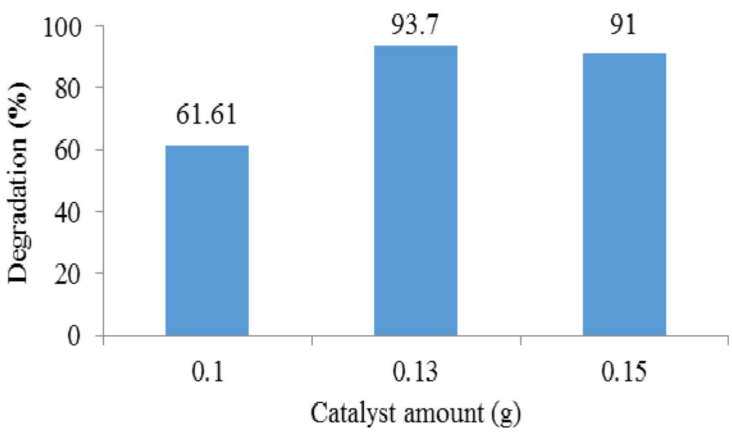

Fig. 11: Photo-catalytic degradation of Direct Blue 5B versus time

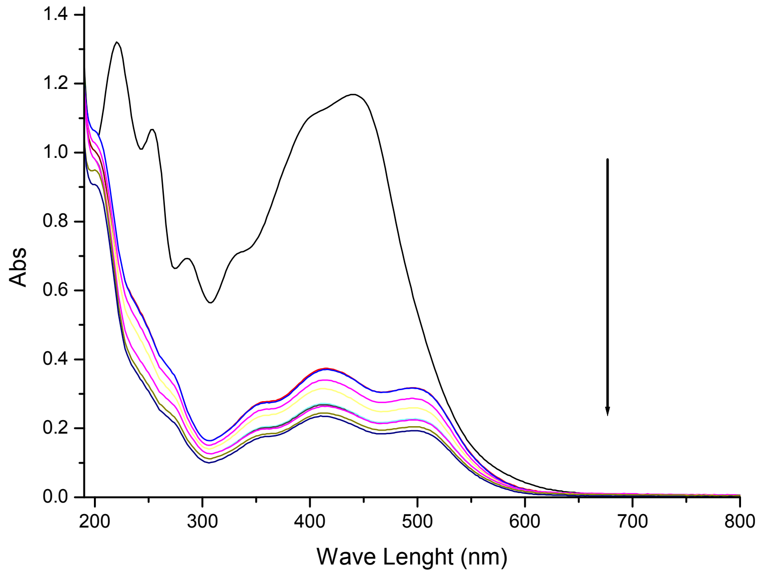

Fig. 12: Irradiation of100 ml of Mordant Brown RH33 10^{-4}M with0.1g Al_2O_3 From zero time to 30 minute.

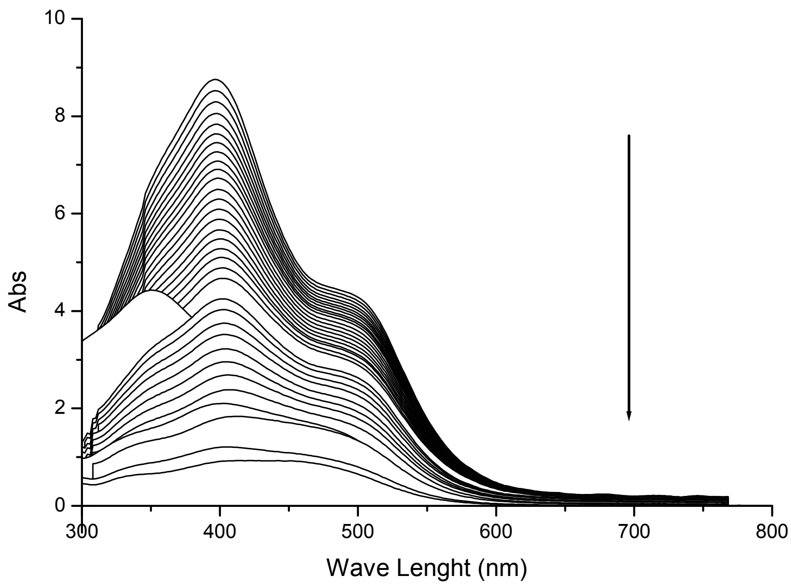

Fig. 13: Irradiation of100ml of Mordant Brown RH33$10^{-4}$ with0.13 g Al_2O_3 From zero time to 30 minute

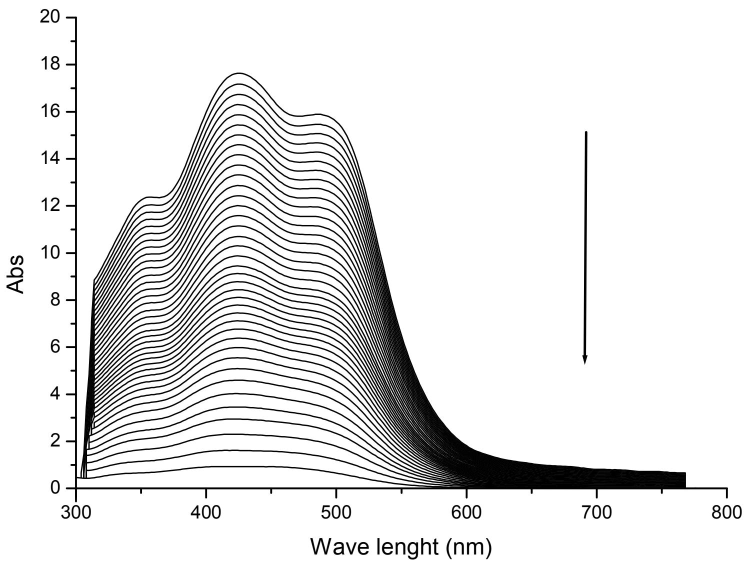

Fig. 14: Irradiation of 100 ml of Mordant Brown RH33$10^{-4}$ with0.15g Al_2O_3 From zero time to 30 minute.

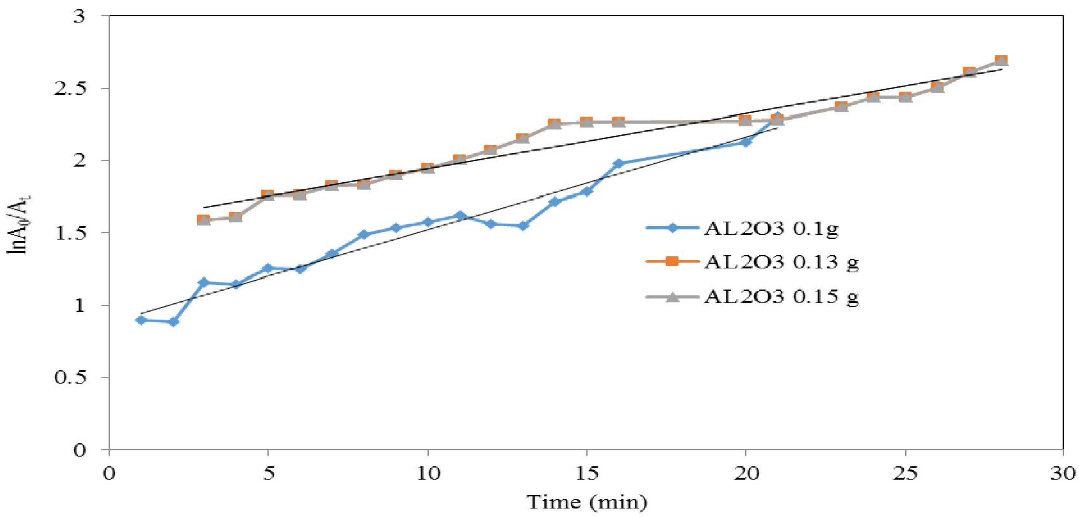

Fig. 15**:** Plot of ln (A_0/A_t) versus time

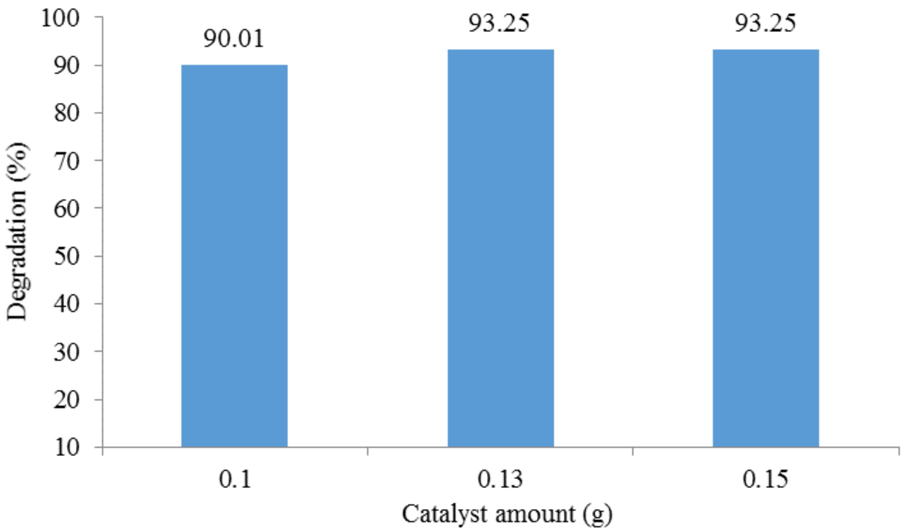

Fig. 16: Photo-catalytic degradation of Mordant Brown RH33 versus time

Effect of pH levels on the photo-degradation of Direct Blue 5B and Mordant Brown RH33

It is believed that the pH value can influenced the photo-catalytic activity of metal oxides such as Al_2O_3. This is due to the amphoteric behavior of metal oxides. In fact the pH value influences the surface charge properties of metal oxides. Thus reactions which take place on the surface of metal oxides occurred via different mechanism at different pH values. In basic conditions the surface of most metal oxides is negatively charged whereas in acidic conditions becomes positive ((Lizama *et al.,* 2002; Akyol *et al.,* 2004; Akpan and Hameed, 2009; Pakmehr *et al.,* 2015). For a wide pH value range, Direct Blue 5b and Mordant Brown RH33 molecules save their negative charges. Therefore, the ability of the two dyes is adsorbed on the surface of metal oxides increased when the solution pH value is acidic. The effect of acidic and basic media on the photo-degradation of two dyes was therefore investigated. Change of pH value was done by the using of NaOH and HCl for basic and acidic conditions respectively. In acidic medium (pH=3), photodegradation increases whereas in basic media (pH=10), a decrease is observed as shown in Figures (17 and 18).

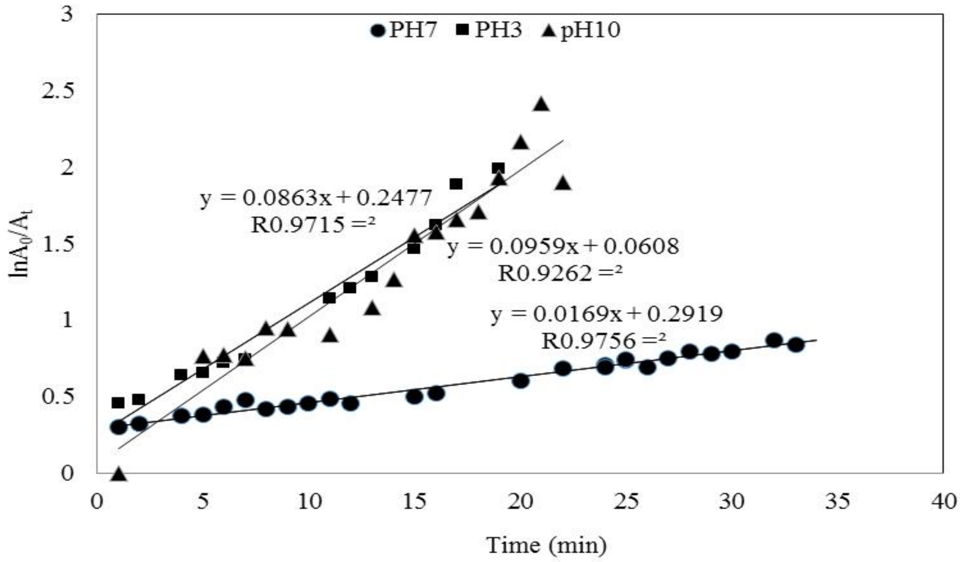

Fig. 17: Plot of ln (A_o/A_t) versus time for the degradation of Direct sky Blue 5b effect of initial pH solution.

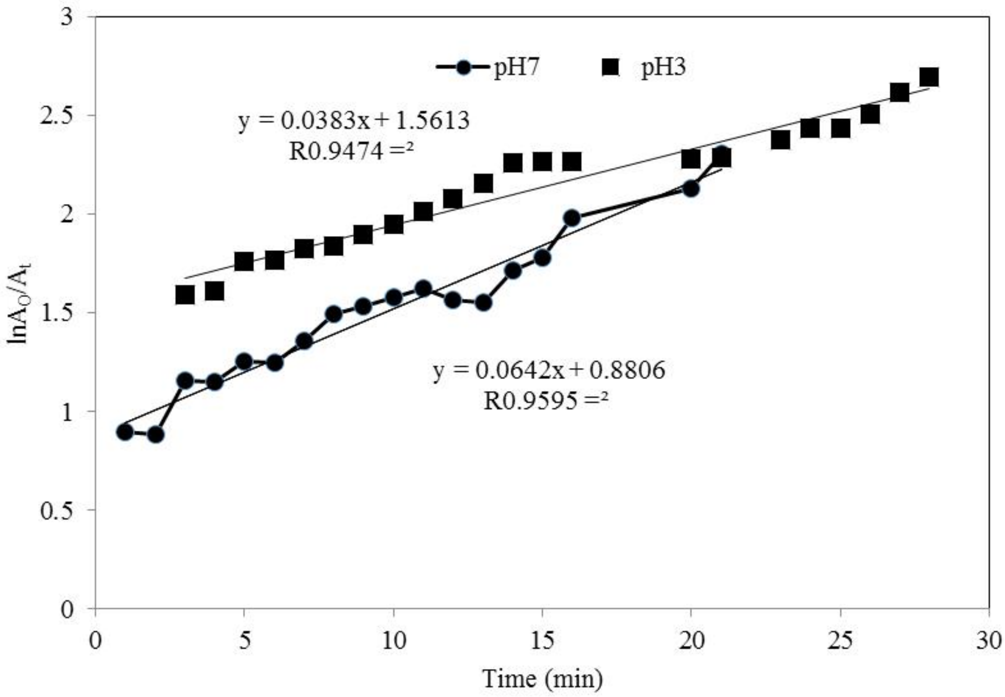

Fig. 18: Plot of ln (A_o/A_t) versus time for the degradation of Mordant Brown RH33 effect of initial pH solution.

Conclusions

The present work concentrated on the chemical preparation of Al_2O_3 nano particles using ethanol and aluminum trichloride ($AlCl_3$) precursors. The synthesized nanoparticles have been characterized using Powder XRD and TEM techniques. The photocatalytic behavior of the as prepared sample was evaluated by degradation of *Direct Blue 5B and Mordant Brown RH33* .Implying different concentrations of catalyst showed that the catalyst played a key role in the photo-catalytic degradation of *Direct Blue 5B and Mordant Brown RH33.*

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