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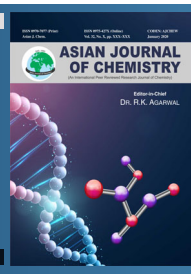

Synthesis of Spin Coated Tungsten Oxide for Photocatalytic Degradation of Rhodamine-B Dye

P.S. PATIL[1,*], A.N. KULKARNI[2], S.D. KHAIRNAR[1] and M.G. RAGHUWANSHI[1]

[1]Nanochemistry Laboratory, Department of Chemistry, N.T.V.S's G.T. Patil Arts, Commerce & Science College, Nandurbar-425412, India
[2]Department of Physics, N.T.V.S's G.T. Patil Arts, Commerce & Science College, Nandurbar-425412, India

*Corresponding author: E-mail: prafulpatil78@gmail.com

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Optical properties including band gap of many wide band gap semiconductor oxides like TiO_2, ZnO and SnO_2 has limitations over their bare use in photocatalytic applications. Thus, in view of above, tungsten oxide (WO_3), an intermediate band gap metal oxide has been selected to explore for photocatalytic degradation application. Present work deals with the preparation of WO_3 using a simple chemical solution based spin coating method. The prepared sample has been characterized for structural, morphological and photocatalytic properties. Degradation experiment of dye was carried out systematically at the optimized conditions of pH 4 and contact time (120 min) between dye and catalyst. For optimized conditions, WO_3 showed about 75% of degradation of rhodamine-B. This suggests that a huge scope to optimize preparative parameters for WO_3 to explore it as an alternative to conventional metal oxides.

Keywords: Photocatalytic degradation, Tungsten oxide, Rhodamine-B, Thin film, Spin coating.

INTRODUCTION

In our day to day life, numerous synthetic dyes, heavy metal ions, pesticides and waste ingredients from cosmetics, agriculture land, cloths, packing industry, leather accessories, sports items, paper, pharmaceuticals, plastics, printing, textiles industries *etc.* are polluting the water and air [1]. This led to honk a serious warning to environment [2-4]. Among these, dyes are the one of the major contaminants [5], nevertheless, only 12% of dyes are properly removed and/or separated [6]. And rest of the percentage of hazardous dyes, which is almost about 20-25% [7] contaminates the environment [8]. However, since the contamination is been majorly done through the water, this has a direct effect on the biodiversity [9].

In view of above, environmental hazard in addition to the water pollution has a depraved effect on human kind [10]. And hence, to execute a basic research in the area of the removal and/or degradation or separation of contaminants from waste-water has been the challenge for the researchers. In addition, the need for the researchers is to find the solution which is a simple and cost-effective method with tuneable aspects for the modification in the process if required [11,12]. As observed in literature, AOP is one of the most simple, cost effective, tuneable methods based on the materials in the nano regime, which has been employed successfully by the several researchers [13].

Of late, numerous semiconducting materials have been explored to remove various hazardous materials or contaminants using advanced photocatalytic oxidation process [14]. One of the important properties to be satisfied by the metal oxide is to have an ability to harvest electromagnetic spectrum principally from visible region with suitable opto-electric properties [15,16]. In view of this, WO_3 is a metal oxide, having enough photo-stability with steady physico-chemical properties has attracted the researchers [17,18]. In addition, it has very suitable intermediate optical band gap in the range of 2.4-2.8 eV, which allows it to harvest electromagnetic spectrum in the realm of 440-516 nm wavelength [19,20]. This makes it a suitable candidate as a photocatalyst for the removal of the hazardous contaminants.

However, in addition to suitable opto-electric properties, method of preparation of the photocatalyst also contributed to decide its photocatalytic ability [21,22]. This is because it helps to tailor the properties of the catalyst during its synthesis [21]. Many methods have been followed for the synthesis of WO_3 [23]. But, it has been always the look out to follow a simple and

low cost way for the synthesis of WO_3 with required properties to explore as a photocatalyst. Thus, in view of above, simple, chemical solution based technique *i.e.* spin coating has been employed in the present work. This is followed by the structural, optical and morphological characterizations. In addition to this, the prepared WO_3 in thin film has been explored for the photocatalytic degradation of rhodamine-B dye from aqueous solution with different concentrations [24,25]. The effect of pH of the solution, catalyst concentration and dye concentration over the photocatalytic behaviour of tungsten oxide (WO_3) has been studied systematically.

EXPERIMENTAL

Tungsten hexachloride (WCl_6, Alfa Aesar), acetyl acetone (Loba Chemie), methanol (Qualigens) and polyethylene glycol (Qualigens) were used in pure form without further purification. Further, double distilled water has been used to prepare stock solutions and cleaning processes. Soda lime glass was used as a substrate for the deposition of thin film.

Substrate cleaning: Substrate is one of the important parameters which decide the proper nucleation and growth of the film in chemical solution deposition method. Thus, it is necessary to clean and prepare the substrate to obtain the uniform and adherent film. Prior to the deposition of the film, glass substrate were cleaned ultrasonically in the presence of double distilled water. It was then followed by drying substrate for 10 min at room temperature. Finally, the substrate was cleaned by acetone before to use for the film deposition [26].

Preparation of WO_3 thin film: Fig. 1 shows the stepwise process for the preparation of WO_3 thin film.

Photocatalytic degradation study: The analysis of photocatalytic performance of WO_3 was carried out through photocatalytic removal of rhodamine-B (50 mL of 5, 10, 15 and 20 mg/L solution) under UV-visible light into the photocatalytic reactor (Lelesil Innovative System, Mumbai, 160 W mercury vapor lamp) in the time range of 15 to 120 min, respectively.

Characterizations: The crystal phase in the prepared WO_3 thin film was examined by X-ray diffraction (XRD) study using (XRD- Bruker D8 Advance X-ray diffractometer, Germany). Scanning electron microscope (SEM) with EDXS (Hitachi S-4800, Japan) was used to study the surface morphology of the prepared thin film. A UV-visible double beam spectrophotometer (Systronics-2203) was used to analyze the photocatalytic behaviour of prepared WO_3 thin film through the degradation of rhodamine-B dye under UV light for different concentrations.

RESULTS AND DISCUSSION

Surface morphological analysis of WO_3 thin film: Fig. 2 shows the scanning electron micrographs for different resolutions showing the morphology evolution of the WO_3 crystals in the deposited thin film. It can be observed that the crystals have been arranged to form clusters. However, on the time scale the clusters are agglomerated to have sphere-like morphology. To verify such formation through agglomeration, scanning of the deposited film has been carried out for different resolutions. However, at higher resolution, the SEM images showed the

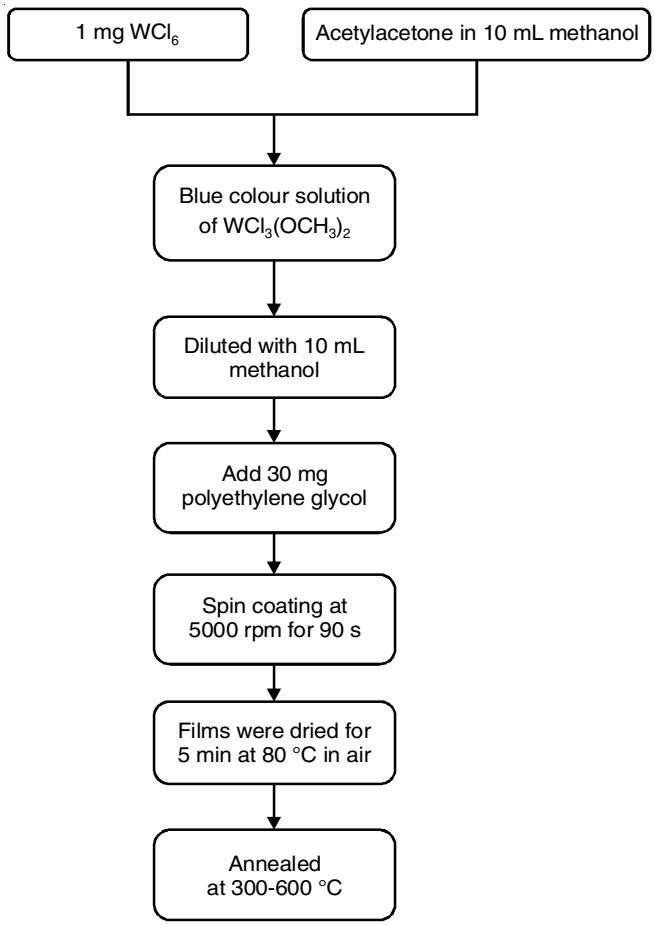

Fig. 1. Schematic flowchart showing stepwise procedure followed for the preparation of WO_3 thin film

cauliflower like bunch morphology obtained from the combination of the well-arranged spheres. Emergence of such cauliflower like morphology obtained through chemical solution deposition can be attributed to the heterogeneous nucleation, where the substrate used for the deposition would have played an important role [27]. The deposition may be a cluster by cluster mechanism [28].

Literature suggests that such sphere like morphology in the nano-regime (at 300 nm resolution) would accelerate the photocatalytic degradation [29]. This might be due to the suitable surface to volume ratio achieved in the present case [30].

Structural analysis of WO_3 thin film: Fig. 3 shows the XRD spectra of WO_3 thin film. The well-resolved diffraction peaks along (020) and (022) in the X-ray diffractogram confirmed the monoclinic phase of WO_3 (JCPDS card No. 83-0951).

However, the diffractogram of WO_3 thin film revealed a definite peak having dominant orientation along (020) plane around $2\theta \sim 23.58^{\circ}$. Observed preferred growth of the crystal along (020) plane might be attributed to the nucleation and growth of WO_3 crystals through cluster by cluster mechanism during the deposition of WO_3 film as discussed above. This is in close agreement with the results discussed earlier [31].

Elemental analysis of WO_3 thin film: The elemental analysis of WO_3 thin film was analyzed by EDXS and presented in Fig. 4. The peaks for tungsten and oxygen in the EDXS

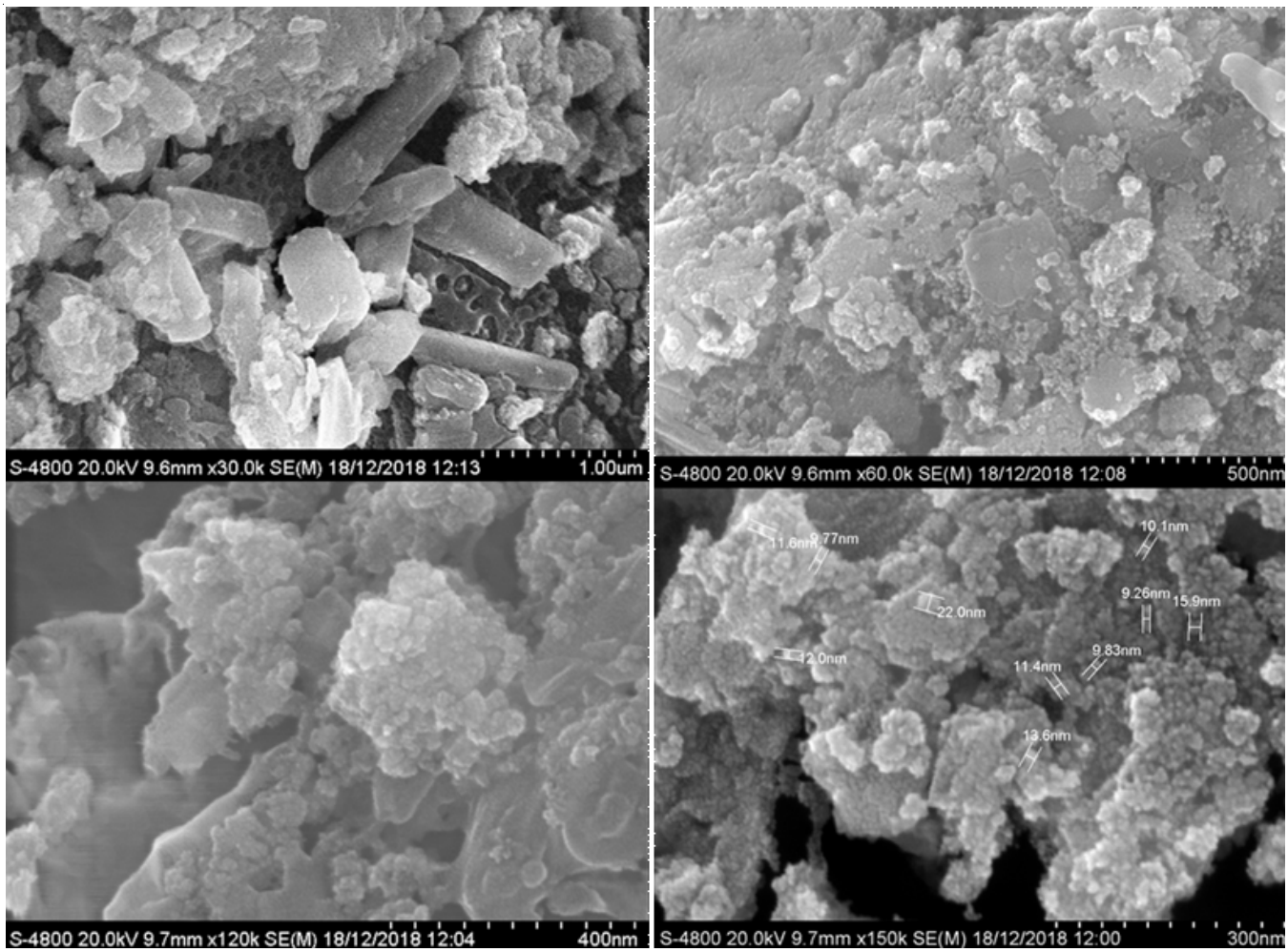

Fig. 2. Scanning electron micrographs for different resolutions of WO_3

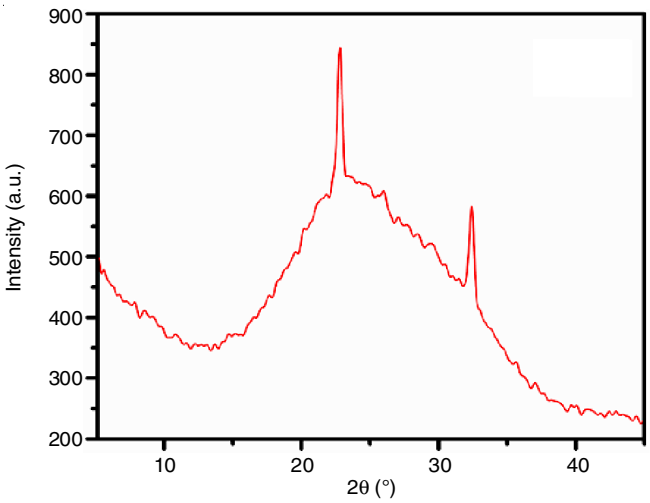

Fig. 3. X-ray diffractogram of WO_3thin film

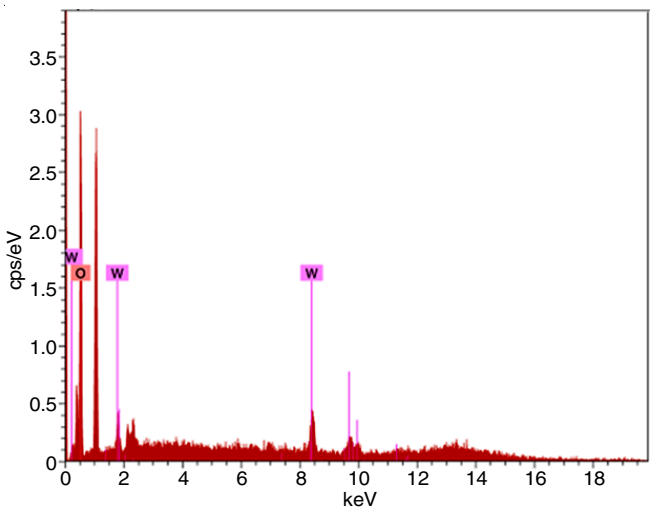

Fig. 4. EDXS spectrum showing % atomic ratio of elements in WO_3 thin film

spectrum qualitatively confirmed the stoichiometric formation of WO_3 as a product. The elemental mapping clearly indicates 24:76 atomic % proportion of W:O, respectively in WO_3 thin film. This gives a confirmed qualitative formation of WO_3 thin film.

Effect of concentration of rhodamine-B dye during photodegradation: The temporal percentage degradation of rhodamine-B dye using WO_3 is presented in Fig. 5. It revealed a steady variation *i.e.* relative enhancement in the degradation activity for WO_3 with a decrease in the rhodamine-B dye concentration from 20 to 5 mg/L, respectively [32]. The maximum percentages degradation for 20 mg/L concentration of rhod-

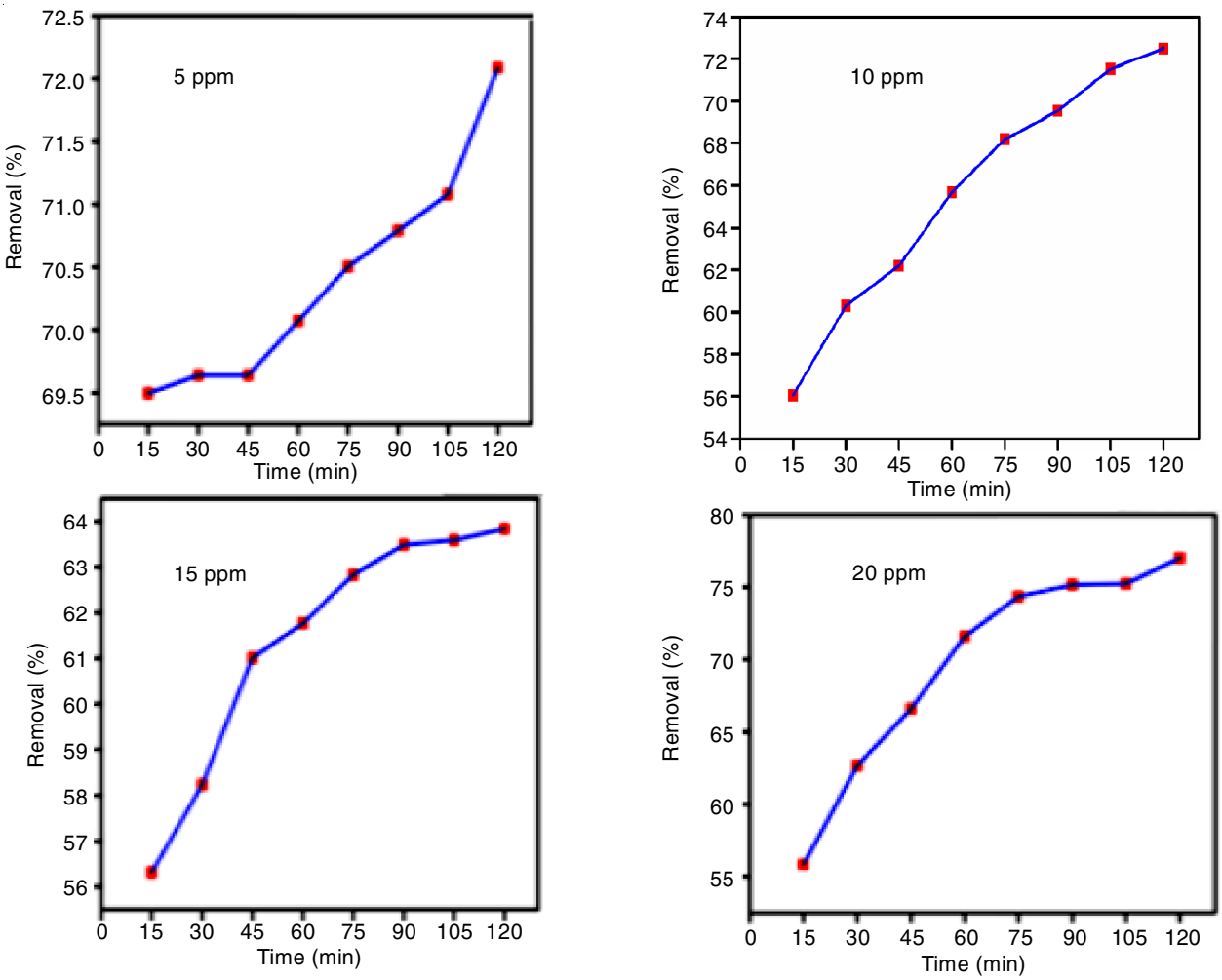

Fig. 5. Time dependent percentage removal of rhodamine-B dye (for different concentrations) during the photocatalytic degradation using WO_3 thin film

amine-B dye solution was about 75%. For higher concentration of dye, optical band gap of catalyst might helped to degrade the dye and thus the degradation enhanced [33]. The obtained results are in agreement with the reported results [31].

Analysis of time dependent optical absorbance of rhodamine-B dye (for different concentrations) during photocatalytic degradation: Fig. 6 shows the time dependent optical absorbance of rhodamine-B dye for different concentrations measured during its photocatalytic degradation using WO_3 thin film. The continuous decrease in the optical absorbance with increasing time suggests the decrease in the number density of the dye molecules [31]. This gives the qualitative confirmation of the successful degradation of rhodamine-B dye using WO_3 thin film under illumination.

Kinetic analysis of photocatalytic degradation of rhodamine-B dye using WO_3 thin film: Photocatalytic degradation kinetics of rhodamine-B has been described using the standard equation discussed in the literature [34].

$$\ln\frac{C_o}{C_t} = kt \qquad (1)$$

where, C_o is the initial concentration at time t = 0 and C_t is the final concentration at time t for rhodamine B dye, respectively.

Fig. 7 represents the variation in ($\ln C_o/C_t$) as a function of irradiation time. Nature of the graphs plotted ($\ln C_o/C_t$) *versus* time for different concentrations revealed that the photocatalytic degradation efficiency of rhodamine-B has followed the pseudo first-order reaction kinetics [35-37].

However, the results of photocatalytic degradation obtained in the present study have been compared with the various metal oxides reported in the literature and presented in Table-1.

TABLE-1
PHOTOCATALYTIC DEGRADATION OF RHODAMINE-B USING VARIOUS METAL OXIDES AS PHOTOCATALYST

Metal oxide	Dye/ contaminant removed	Removal (%)	Ref
ZnO/SnO_2	Rhodamine B	~ 20	[38]
Cu_2O		60	[39]
Bi_2O_3		58.4	[40]
α-Fe_2O_3		~84	[41]
ZnO		38	[42]
MgO		15	[42]
Co_3O_4		32	[43]
$ZnWO_4$		71	[44]
TiO_2		62	[45]
WO_3		75	Present Study

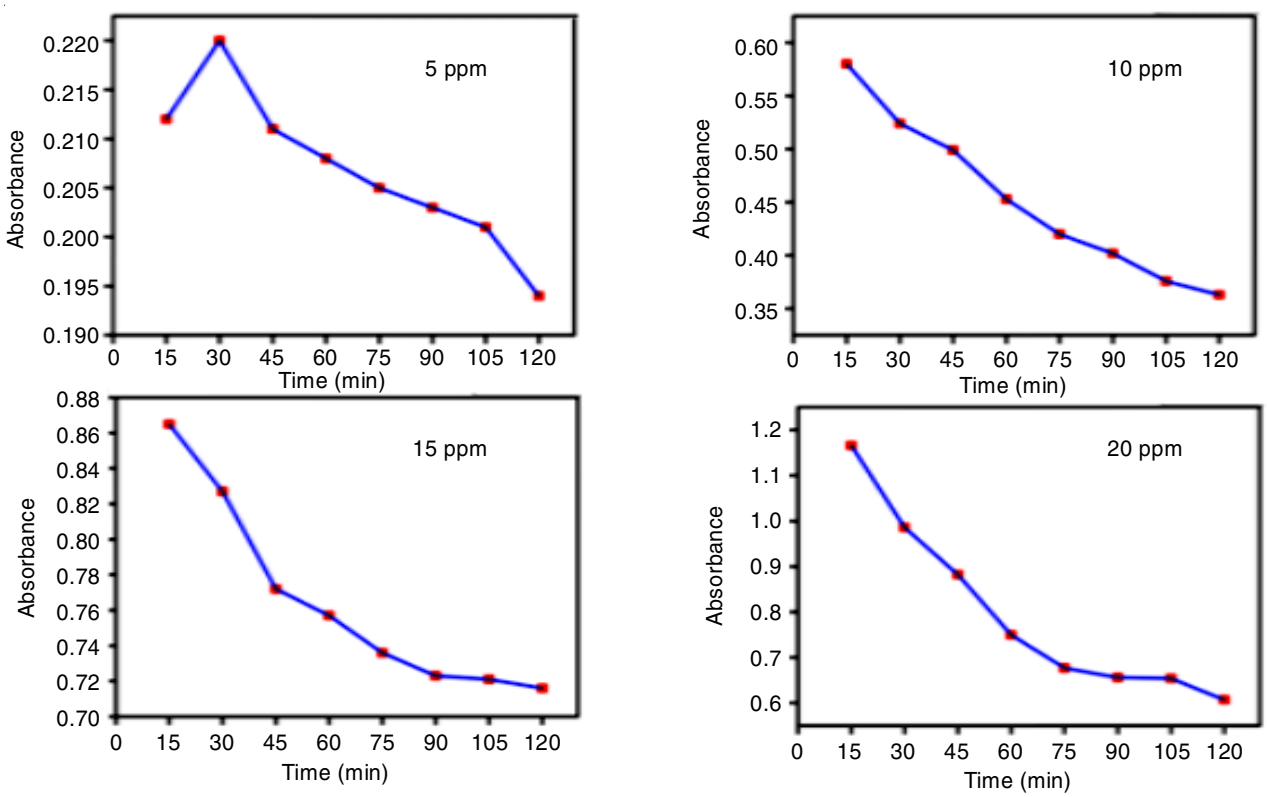

Fig. 6. Time dependent optical absorbance of rhodamine-B dye (for different concentrations) during the photocatalytic degradation using WO_3 thin film

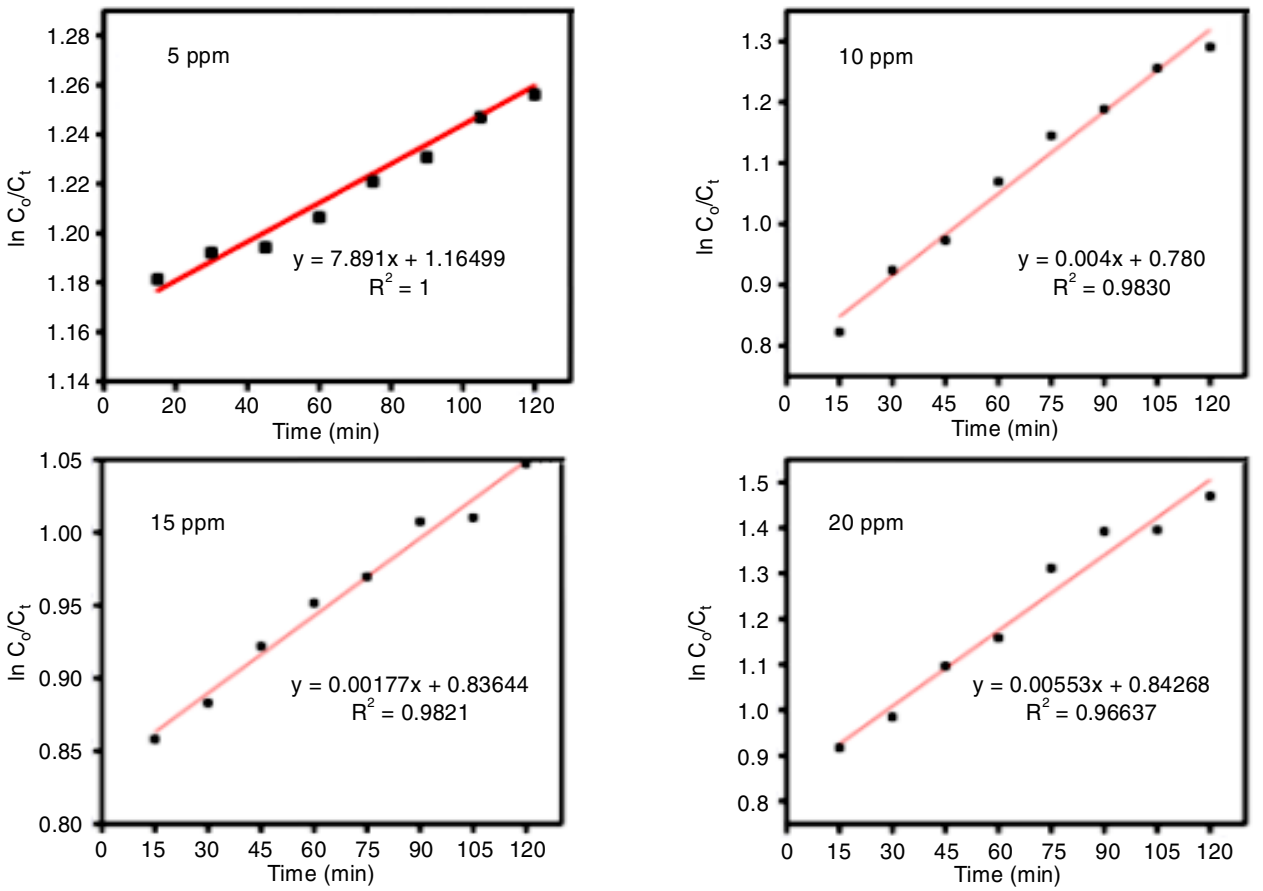

Fig. 7. Kinetics for different concentrations of rhodamine-B dye during the photocatalytic degradation using WO_3 thin film

This comparison suggests WO_3, a suitable alternative candidate as a photocatalyst to the conventional metal oxides.

Conclusion

The nanostructured tungsten oxide (WO_3) thin film was successfully deposited on glass substrate by spin coating, a simple chemical solution deposition technique. Structural, morphological and optical properties illustrated that spinning time play a significant role in the growth process. From X-ray diffraction analysis, the nanocrystalline WO_3 with monoclinic crystal structure was confirmed. The SEM images of sample showed a well-defined nanospheres of increasing size as a function of prolonged spinning time and can be attributed to the cluster by cluster deposition mechanism. In addition, the photocatalytic performance of WO_3 was studied for the removal of rhodamine-B dye as a function of contact time. From the study, it may be concluded that contact time and pH of dye has a profound influence on all the degradation parameters, thus, effecting the degradation percentage of dye. It is implicited that the overall degradation efficiency of WO_3 can be improved through monolayer deposition, composite structures and doping, which will decrease the possible recombination losses of charge carriers. In nut shell, a contact time of 120 min and dye concentration of about 20 mg/L found to be best performance for the use of WO_3 as a photocatalyst for the removal of rhodamine-B dye.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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