SÍNTESE ULTRASSÔNICA DIRETA DE NANOCOMPOSITOS WO₃/TiO₂ E APLICANDO-OS NA FOTODECOLORIZAÇÃO DO CORANTE AMARELO DE EOSINA

DIRECT ULTRASONIC SYNTHESIS OF WO₃/TiO₂ NANOCOMPOSITES AND APPLYING THEM IN THE PHOTODECOLORIZATION OF EOSIN YELLOW DYE

تحضير المتراكبات النانوية لـ (TiO₂ \ WO₃) مباشرةً بواسطة موجات فوق الصوتية وتطبيقها للزالة اللونية بالضوء لصبغة الايوسين الصفراء

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Received 12 January 2020; received in revised form 22 February 2020; accepted 08 March 2020

RESUMO

Esta pesquisa relatou um método direto, ecológico, econômico e simples de usar um instrumento ultrassônico como uma técnica verde para combinar WO₃ com TiO₂ nas proporções 0,5:1, 0,25:1 e 0,16:1 como compósitos 1, 2 e 3, respectivamente. Os dados de difração de raios-X em pó, identificaram os tamanhos médios dos retículos cristalinos dos WO₃ comerciais, TiO₂ comerciais e dos nanocompósitos de WO₃/TiO₂ preparados nas diferentes proporções, entre 17,897 nm e 48,672 nm. A análise de Microscopia de Força Atômica (MFA) observou que a morfologia da superfície de todas as amostras estudadas é esférica. Os tamanhos médios de cristal e os tamanhos dos compósitos preparados estão na faixa dos nanômetros, e esses valores aumentam com o aumento da quantidade de TiO₂ nos nano-compósitos preparados. A incorporação de W com Ti na matriz ocorreu com sucesso; porque o raio iônico do W⁶⁺ é menor que o do Ti⁴⁺. Foram investigados os valores de intervalo de banda para todas as amostras. Os intervalos de banda dos nanocompósitos preparados 1, 2, 3 e TiO₂ ocorrem como um tipo indireto, enquanto o intervalo de banda do WO₃ é encontrado como tipo direto. As amostras estudadas foram testadas utilizando-as como fotocatalisadores na descoloração de uma solução aquosa do corante amarelo eosina E_{descol.}%. A sequência de descoloração cresce da esquerda para a direita, conforme: E_{descol.}% (compósito 3) < E_{descol.}% (WO₃) < E_{descol.}% (TiO₂) < E_{descol.}% (compósito 2) < E_{descol.}% (compósito 1). A atividade do WO₃ é inibida com a adição de H₂O₂ à solução aquosa do corante amarelo de eosina devido à formação de ácido peroxotungstico (WO₃H₂O₂.H₂O ou WO₂(O₂)H₂O.nH₂O), mas a superfície modificada por incorporação de TiO₂, melhora a atividade, portanto, o nano-composto 1 na proporção de 0,5: 1 recebe uma eficiência máxima de fotodecoloração desse corante e passa de 25,11% para 73,88%.

Palavras-chave: Trióxido de tungstênio; Dióxido de titânio; Nanocompósito; Síntese verde; Eosina Corante amarelo.

ABSTRACT

This research reported a direct, environmentally friendly, economical, and simple method of using an ultrasonic instrument as a green technique to combine WO₃ with TiO₂ in ratios 0.5:1, 0.25:1, and 0.16:1 as composites 1, 2 and 3 respectively. Powder X-Ray Diffraction data identified the mean crystalline sizes of the commercial WO₃, commercial TiO₂, and of the prepared WO₃/TiO₂ nanocomposites in the different ratios in ranged from 17.897 nm to 48.672 nm. AFM analysis noted the surface morphology for all studied samples is spherical. The mean crystal sizes and practical sizes for prepared composites are found to be in the nanometer range, and these values rise with the raising in the TiO₂ quantity in prepared nano-composites. The incorporated of W with Ti in the matrix is successful happened; because the ionic radius of W⁶⁺ is fewer values than it for Ti⁴⁺. The band gaps values for all samples have been investigated. The band gaps of prepared nanocomposites 1, 2, 3, and TiO₂ are occurred as an indirect type, while the band gap of WO₃ is found as direct type. The studied samples were tested by using them as photocatalysts in the decolorization of an aqueous solution, the eosin yellow dye E_{decol.}%. The sequence of decoloration grows from the left to the right as: E_{decol.}% (composite 3) < E_{decol.}% (WO₃) < E_{decol.}% (TiO₂) < E_{decol.}% (composite 2) < E_{decol.}% (composite 1). The activity

of WO₃ is inhibited with addition of H₂O₂ to the aqueous solution of eosin yellow dye because of the formation of peroxotungstic acid (WO₃H₂O₂.H₂O or WO₂(O₂)H₂O.nH₂O), but the modified surface by incorporation of TiO₂, improves the activity hence, nano-composite 1 in the ratio of 0.5:1 is given a maximum photodecolorization efficiency of this dye and changed from 25.11% to 73.88%.

Keywords: Tungsten Trioxide; Titanium dioxide; Nanocomposite; Green synthesis; Eosin Yellow dye.

المخلص:

نشر في هذا البحث بان استخدام جهاز الموجات فوق الصوتية كطريقة سهلة الاستخدام، صديقة للبيئة، اقتصادية وبسيطة، لذا يعتبر كتقنية خضراء، لدمج WO₃ مع TiO₂ ونسب 1:0.25 و 1:0.5 و 1:0.16 كمتراكبات 1، 2، و 3 على التوالي. شخّصت نتائج حيود الأشعة السينية للباودر بان معدل الحجوم البلورية للـ WO₃ التجاري، و TiO₂ التجاري، والنسب المختلفة المحضرة من المتراكبات النانوية (TiO₂WO₃) كان بمدى من 17.897 نانومتر الى 48.672 نانومتر. لوحظ من خلال نتائج تحليل الـ AFM مورفولوجية السطح لجميع العينات المدروسة بكونها دائرية الشكل. وجد ان جميع العينات المدروسة لها معدل حجوم بلورية وحجوم جسيمات ضمن المدى النانوي، اذ تزداد قيمها بزيادة كمية الـ TiO₂ في عينات المتراكبات النانوية المحضرة. تمت عملية تراكب W مع Ti في الشبكية بنجاح، لكون نصف القطر الايوني لـ W⁶⁺ يكون لها اقل قيمة نسبة الى نصف القطر الايوني لـ Ti⁴⁺. خمنت قيم فجوات الطاقة للعينات المدروسة. ظهر بان فجوات الطاقة غير مباشرة للمتراكبات النانوية 1، 2، و 3 المحضرة ولـ TiO₂ ايضا، بينما كانت فجوة الطاقة من نوع المباشر لـ WO₃. اختبرت العينات المدروسة باعتبارها عوامل مساعدة ضوئية لدراسة الازالة اللونية لصبغة الايوسين الصفراء من محلولها المائي، اذ كان تسلسل النسبة المئوية للازالة اللونية E_{decol.}% كالآتي:

$$E_{decol.}\% (\text{composite } 3) < E_{decol.}\% (\text{WO}_3) < E_{decol.}\% (\text{TiO}_2) < E_{decol.}\% (\text{composite } 2) < E_{decol.}\% (\text{composite } 1)$$

ثبطت كفاءة الـ WO₃ عند اضافة H₂O₂ الى المحلول المائي لصبغة الايوسين الصفراء بسبب تكون حامض فوق اوكسيد التنكستن بهيئة H₂O₂.WO₃.H₂O.nH₂O(O₂)H₂O، ولكن بتحويل سطحه بالتداخل مع TiO₂ ادى الى تحسين الفعالية، لذلك اعطى المتراكب النانوي 1 ذي النسبة (1:0.5) اعلى كفاءة للازالة اللونية لهذه الصبغة، وقد تغيرت القيمة من 25.11% الى 73.88%.

الكلمات المفتاحية: ثلاثي اوكسيد التنكستن، ثنائي اوكسيد التيتانيوم، المتراكب النانوي، التخليق الاخضر، صبغة الايوسين الصفراء.

1. INTRODUCTION

The tungsten trioxide (WO₃) also known as tungsten (VI) oxide is one of the transition metal oxides, which is classified as an n-type semiconductor with a wide range of band gap between 2.5 eV to 2.8 eV at room temperature (Yan *et al.*, 2015; Huang *et al.*, 2014; Walle *et al.*, 2012). In addition, it is chemically stable, non-toxic, insoluble in water, and acidic medium, but it can be dissolved in strong alkali solutions or HF, as represented in Equations 1 and 2 (Cotton *et al.*, 1980; Rollinson *et al.*, 1975; Lassner *et al.*, 1999)

The tungsten trioxide is also called as tungstic acid, and is a highly condensed and amorphous substance with a reduced water content, that depends on the ratios of WO₃: H₂O such (1:2), (1:1) and (2:1) for WO₃.2H₂O (white color), WO₃.H₂O (yellow color) and 2WO₃.H₂O (orange-yellow color) respectively. The second ratio (1:1) is the most common, and it is an amorphous yellow powder. Therefore, it can be

used as a pigment for bright yellow glasses, in ceramics and paints (Lassner *et al.*, 1999; Rao, 2013). The crystal structure of WO₃ depends on the temperature; the triclinic (δ-WO₃) appears in the range of temperatures from -50 to 17 °C. The monoclinic form consists of two types: monoclinic II (ε-WO₃) and monoclinic I (γ-WO₃), the first is synthesized at temperatures ranging from -143 °C to -50 °C, while the second type appears in the range of temperatures from 17 °C to 330 °C, the last type (i.e., γ-WO₃) is recognized as the most common, as the commercial form of WO₃ structure, and it is highly thermally stable up to 150 °C. The orthorhombic form (β-WO₃) is prepared in temperatures ranging from 320 °C to 740 °C, and the tetragonal form (α-WO₃) appears in temperatures above 740 °C (Rollinson and *et al.*, 1975; Lassner and *et al.*, 1999; Rao, 2013; Cazzanelli and *et al.*, 1999). As represented in Equations 3 to 6.

monoclinic $I \xrightarrow{(330-740)^\circ\text{C}}$ orthorhombic (Eq. 5)

orthorhombic $\xrightarrow{\text{Above } (740)^\circ\text{C}}$ tetragonal (Eq. 6)

The WO_3 pure or modified - bulk or nanoparticle - have been extensively utilized in fields such as gas-sensors (Staerz *et al.*, 2018; Leidinger *et al.*, 2015), self-cleaning surfaces (Garlisi *et al.*, 2015; Bianchi *et al.*, 2013), photocatalyst for water splitting (Kalanur, 2019; Stoll *et al.*, 2017), dye-sensitized solar cells (Zheng *et al.*, 2010; Yong *et al.*, 2013), antibacterial agents (Syed *et al.*, 2010; Stankic *et al.*, 2016), photoelectron-catalysis (Goulart *et al.*, 2019), used as a new anode material for lithium-ion batteries (Li and Fu, 2010).

In order to improve the photocatalytic activity of the WO_3 , the WO_3 has been incorporated with the TiO_2 by using the Microwave-assisted hydrothermal process (Ren *et al.*, 2011), Sol-gel method (Cabrera *et al.*, 2012; Dominguez *et al.*, 2017), co-precipitation (Luévanó Hipolito *et al.*, 2014). In this work, the purpose is to improve the properties of WO_3 by incorporating it with TiO_2 as a composite in different ratios (0.5:1), (0.25:1), and (0.16:1) by using a direct ultrasonic synthesis. The morphology and optical properties for the commercial WO_3 , the commercial TiO_2 , and their composites of $(\text{WO}_3/\text{TiO}_2)$ as photocatalysts are ongoing.

2. MATERIALS AND METHODS

In this research, all chemicals were employed as received without any additional purification. The tungsten trioxide (WO_3), as $\text{WO}_3 \cdot \text{H}_2\text{O}$ (yellow color), and the titanium dioxide (TiO_2) as rutile were purchased from Riedel-De-Haen AG, Seelze, Hannover, Germany. Suitable compounds to determine the light intensity in photoreaction experimental was used without any purification. Eosin yellow dye (Acid red 87 dye) was supplied by CDH from India, with the molecular composition $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$, and molecular weight 691.86. The Eosin yellow dye has some unique physical and chemical characteristics, which are listed in Table 1.

In this research, the essential instruments, which were employed to prepare and investigate the characterizations consisted of a sensitive balance model (BL 210 S, Sartorius, Germany), X-Ray Diffraction spectrophotometer model Lab

X- XRD 6000 (Shimadzu, Japan), hot plate stirrer model Heido (Mr. Hei-Standard, Germany), UV-Visible spectrophotometer model AA-1800 (Shimadzu Japan), centrifuge (Hettich- Universal II, Germany), AFM model AA 3000 (Advanced Angstrom Inc., USA), and ultrasound model DAIHAN (Scientific, Korea).

2.1. Synthesis of the $(\text{WO}_3/\text{TiO}_2)$ composites

Based on the ultrasonic technique with using (ultrasonic, 60 kHz, type DAIHAN Scientific, Korea), a series of steps, as in Figure 1, were performed to synthesize the WO_3/TiO_2 composites in the ratios of 0.5:1, 0.25:1 and 0.16:1. The ultrasonic method is an active method, used to generate sufficient energy for a bond formed. The WO_3 suspension solution and the TiO_2 suspension solution that dissolved in distilled water (type IV reagent water) were mixed in the ultrasound reactor for 5 hours.

2.2 Application of prepared $(\text{WO}_3/\text{TiO}_2)$ composites on decolorization of eosin yellow dye solution.

After analyzed the morphology using AFM and the optical properties using the Tuce equation of prepared $(\text{WO}_3/\text{TiO}_2)$ composites, it's found that the composites were successfully prepared as nano-photocatalysts. The active path to test the influence of the TiO_2 chosen to be combined with WO_3 is implemented, which raised the photocatalytic activity with the application of them as a composite on the decolorization of an aqueous solution of eosin yellow dye.

Exactly 0.1000 g of TiO_2 , or WO_3 , or $(\text{WO}_3/\text{TiO}_2)$ composites (0.5:1, or 0.25:1 or 0.16:1) were added to 100 mL of 5 ppm of eosin yellow dye solutions with the natural dye solution pH (6.09) and then mixed the dye solution with photocatalyst together to produce a homogeneous suspension solution with using a Teflon bar and a magnetic stirrer. The formed mixture was allowed to stay in the dark for 30 min to get ready for the photocatalytic step (Ahmed *et al.*, 2018a; Marhoon *et al.*, 2019; Kzar *et al.*, 2019). In a wooden box, a 250 watts UV-A lamp (Radium-Germany) was applied over the mention suspensions solutions at regular intervals time with a light intensity equal to $2.66 \cdot 10^{-7}$ Einstein $\cdot \text{s}^{-1}$. Approximately 2.5 ml of the mixture was collected in a plastic test tube. And then, the photocatalyst was separated by centrifuge from the dye solution twice at 4000 rpm for 15 minutes. The dye solution was analyzed using the UV-Vis spectrophotometer (AA-1800, Shimadzu) to determine the residual

concentration of eosin yellow dye at a maximum wavelength (516 nm (Ahmed, 2018). The kinetic study of this photodecolorization was implemented by calculating the apparent rate constant ($k_{app.}$) (Hussein *et al.*, 2018; Ahmed *et al.*, 2018b) and photodecolorization efficiency ($E_{decol.}\%$) (Jasim, and Ahmed, 2019; Rangel *et al.*, 2018) used from C_o and C_t , referring to the initial concentration of eosin yellow dye without illumination (dark reaction for 30 min) and the concentration of the same dye in according with Equations 7 and 8 at t time of illumination.

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app.}t \quad (\text{Eq.7})$$

$$E_{decol.}\% = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \quad (\text{Eq.8})$$

3. RESULTS AND DISCUSSION:

In order to prove that the nanocomposites 1, 2, and 3 were successfully prepared, the characteristics of prepared nanocomposites were studied and compared with the commercial WO_3 and the commercial TiO_2 .

3.1. Structural characterization

The X-ray diffraction (XRD) analysis was carried out on Lab X- XRD 6000, Shimadzu X-ray diffraction spectrophotometer with a Cu K α radiation source at λ equal to 1.540 Å. On the basis of the resulted peaks in Figure 2, that found the peaks of the commercial WO_3 and the commercial TiO_2 are sharp, but the peaks of the all prepared composites are broad and have low intensities that indicated the gain on nanocomposites from WO_3/TiO_2 . The mean crystal sizes (L) in nm for all the samples was calculated from the Debye-Scherrer, Equation 9 (Ahmed *et al.*, 2014; Ahmed *et al.*, 2012; Mahammed *et al.*, 2017).

$$L = \frac{k \lambda}{\beta \cos \theta} \quad (\text{Eq. 9})$$

In Equation 9, λ is the wavelength of Cu as the source of the instrument in (nm), β is the full width at half maximum intensity in (radian), k is shaped constant, and θ is the Bragg diffraction angle.

The mean crystalline sizes of the WO_3 , TiO_2 , and the prepared WO_3/TiO_2 composites 1, 2, and 3 were found equal to 17.897 nm, 48.672

nm, 40.084 nm, 43.456 nm, and 42.703 nm respectively. The addition of TiO_2 in different ratios for WO_3 leads to raising the mean crystal size and improvement of the optical properties. The peaks positions at 2θ equal to 27.46° , 36.10° , 41.26° , 54.34° , 56.32° , and 69.02° were beyond the diffractions of the TiO_2 at (110), (101), (111), (211), (220) and (301). The highest peak at crystal planer (110) with 2θ was equal to 27.46° corresponds to the rutile phase, which is in agreement with the standard diffraction data (JCDs card No. 00-021-1276) (Filippo *et al.*, 2015). On the other hand, XRD peaks at 2θ equal to 16.60° , 25.72° , 34.24° , 34.99° , 49.68° , 52.74° , 56.29° , 57.24° , and 62.78° which assigned to (020), (111), (200), (131), (202), (222), (311), (113) and (133) plane as orthorhombic $\text{WO}_3 \cdot \text{H}_2\text{O}$ phase (JCDs card No. 00-043-679) (Elnouby *et al.*, 2013). The incorporation between WO_3 and TiO_2 was proved by the redshift occurred toward the essential position peaks with 2θ from 27.46° , 54.34° and 36.10° to $(27.56^\circ - 27.60^\circ)$, $(54.42^\circ - 54.46^\circ)$ and $(36.19^\circ - 36.23^\circ)$, this change ensured that the metal bond was generated between W and Ti in the crystal lattice (Ahmed *et al.*, 2014; Mohammed and Ahmed, 2018; Fakhri and Ahmed, 2019).

3.2. Surface Morphology of photo-catalysts

The atomic force microscopy images are presented in Figure 3. It was noted that the particle sizes of the WO_3 and the TiO_2 are 65.310 nm and 56.220 nm, respectively. Besides, the particle sizes of the prepared WO_3/TiO_2 composites are increased when compared to those of the WO_3 and TiO_2 . This change is due to the agglomeration of WO_3 and TiO_2 particles in the matrix, and the particle sizes of the composites 1, 2, and 3 are equal to 71.270 nm, 93.160 nm, and 94.290 nm for the ratios 0.5:1, 0.25:1 and 0.16:1 respectively. The elevation in the particle sizes for the prepared composites increases when it is increased the ratio of TiO_2 that is attributed to the high ionic radius of the Ti^{4+} (0.61 Å) (Ahmed *et al.*, 2014; Ghosh and Biswas, 2003), making it suitable to be incorporated with W^{6+} with low ionic radius (0.51 Å) (Ghosh and Biswas, 2003).

In Figures 3 and 4, the TiO_2 has more roughness average than the roughness average of the prepared composites 1, 2, and 3. This is due to the inverse relation between average roughness value and particle size. Hence, TiO_2 has a smaller practical size (56.220 nm), so it has the highest roughness value (27.9 nm).

3.3. Optical properties of photocatalysts

The optical band gaps of all the samples in this research were obtained from the absorption coefficient (α) data in Equation 10, which was calculated by analyzing the variation on the absorbance of suspension solution (A) Tauc relation in Equation 11 depends on the Plank's constant (h), the frequency (ν) of the incident photon, the optical constant (k), m is a constant value which is equal to $\frac{1}{2}$ and 2 for a direct transition and indirect transition respectively (Fakhri and Ahmed, 2019; Tauc *et al.*, 1996).

$$\alpha = 2.3026 A/t \quad (\text{Eq. 10})$$

$$\alpha h\nu = k(h\nu - E_g)^m \quad (\text{Eq. 11})$$

The optical band gap deduced from the Tauc plot was displayed in Figure 11. Hence, the linear variation of $(\alpha h\nu)^2$ vs. $h\nu$ indicated that the transition in TiO_2 is indirect allowed and all composites 1, 2 and 3 are indirect allowed also, but, the linear variation of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ indicated that the transition in WO_3 is direct allowed with band gap equal to 2.719 eV. Moreover, the optical band gaps for the prepared composites 1, 2, and 3 were found to be an indirect band gap, and the band gap values decrease compared to the band gap of TiO_2 alone (3.063 eV), they are equal to 2.765 eV, 2.837 eV, and 2.988 eV respectively.

3.4. Effect of using the different photocatalysts on the Photo- decolorization of eosin yellow dye

A series of photo-experiments have been conducted in order to detect the best photocatalytic activity behavior of studied samples primarily, there are a series of photo-experiments were performed. The activities of commercial TiO_2 , WO_3 , and prepared composite 1 are roughly identical in the constant rate values shown in figure 7, but the composite 1 is more effective than that for other samples. This is due to many reasons: first, the WO_3 surface defect raises with forming a composite, which results in the depressed in the recombination process by increasing a surface ability to move the charge from the high conductive band of TiO_2 to the low conductive band of WO_3 . While, the positive charge in WO_3 valance band leaps during combined to the valance band of TiO_2 (Asim *et al.*, 2013; Sajjad *et al.*, 2003). In Figure 6, this

case is displayed schematically. The second cause illustrated that the addition of TiO_2 during combined would elevate the acidity of the WO_3 surface, leading to the formation of high amounts of hydroxyl radicals in present light (Asim *et al.*, 2013; Sajjad *et al.*, 2003). The basic start for the photoreaction is Hydroxyl radical. The third cause is based on the reduced band gap since the two semiconductors were combined. Consequently, the lower conductive band in a vacuum owns the new band gap for a new case, and its operation is elevated toward the use of visible light. Therefore, W^{+5} may be generated during the electron transfer to the reducible species surface. That will assist and improve the optical properties of the photocatalyst (Sajjad *et al.*, 2003). The efficiency of WO_3 increases from 18.951 % to 25.1119 % at 90 min, with combined it with TiO_2 and generated a composite 1.

3.5. Effect of H_2O_2 addition on photocatalysts in eosin yellow dye Photo- decolorization

Now the effect of hydrogen peroxide addition will be studied after the best composite was chosen, which was prepared in using an ultrasonic technique. Figure 8 demonstrates the efficiency of photocatalytic for eosin yellow dye decolorization, which declines with the use of TiO_2 and WO_3 , but the efficiency of this reaction increases with the use of composite 1. This action due to the WO_3 can be reacted with hydrogen peroxide and produced Peroxotungstic acid such as $(\text{WO}_3 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ or $\text{WO}_2 (\text{O}_2) \cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O})$ (Pecquenard *et al.*, 1998), which will inhibit its photoactivity of it because Peroxotungstic acid is used as inorganic photoresists (Pecquenard *et al.*, 1998; Kudo *et al.*, 1991).

Alternatively, peroxotungstic acid assumes that the produced peroxo polytungstate anions are linked together by a hydrogen bond (Pecquenard *et al.*, 1998). This anionic species can reduce the acidity of the WO_3 surface and decline the adsorption of hydroxyl ion, which necessary to form hydroxyl radical under UV-light. On the other hand, the H_2O_2 addition to the TiO_2 suspension solution did not improve the decolorization rate constant and efficiency of the decolorization of eosin yellow dye. That attitude to self-decomposition of H_2O_2 or acting as a scavenger for hydroxyl radicals has finally formed water and liberated oxygen free molecules (Hussein *et al.*, 2018; Ahmed *et al.*, 2018b; Kumar *et al.*, 2011; Mashkour *et al.*, 2011). Inversely, the addition of H_2O_2 to suspension solution of composite 1 leads to improve the

photodecolorization from 25.11% to 73.887. This due to raising the WO_3 acidity following the combination with TiO_2 and induced a high hydroxyl radical species (Asim *et al.*, 2013; Sajjad *et al.*, 2003). This species will increase the probability of the chromophoric group electrophilic attack in studied dye (Arslan *et al.*, 2000).

3.6. Mechanism of photodecolorization of eosin yellow dye

Initially, when UV-A light focuses on surface of dye suspension solution containing photocatalysts such as WO_3 , or TiO_2 or WO_3/TiO_2 nanocomposite, this leads to the formation of hydroxyl radical and other species such as superoxide anion and peroxide radical, which will starts the attachment with the chromophore groups in the dye and induces the decolorization of dye with continuous irradiation from its solution for 90 min. But with irradiation, the dye generated CO_2 and H_2O at the solution pH of reaches to 7 for several hours. The suggested mechanism for decolorization of eosin yellow dye was indicated in Figure 9 (Ahmed, 2018).

4. CONCLUSIONS

The results indicated that the composites prepared using the direct ultrasonic method in distilled water were actually prepared using different ratios of 0.5:1, 0.25:1, and 0.16:1 from WO_3 with the TiO_2 as composites 1, 2 and 3 respectively. It is dependent on the energy provided by the ultrasonic instrument. The phase composition and morphologies of all commercial and prepared samples were estimated by XRD and AFM. The agglomeration between the WO_3 and the TiO_2 was obtained. Hence, the AFM analysis deduced to the particle sizes of prepared composites 1, 2, and 3 were much larger than those of their components alone with smaller surface roughness.

The roughness of the TiO_2 with a small particle size value was considered to have a maximum value. In the primary experiments, the raised of the efficiency of photocatalytic decolorization (E%) of the eosin yellow dye from aqueous solution using the studied photocatalysts was sequenced to:

E% composite 3 < E% WO_3 < E% TiO_2 < E% composite 2 < E% composite 1, and when H_2O_2 is added the sequences will be WO_3 < TiO_2 < composite 1.

5. ACKNOWLEDGMENTS:

The researchers gratefully acknowledge to the university of Kerbala, college of science, for implementing the assistance during performed this project in graduate labs. Also, the distinction acknowledgment goes to Dr. Abed Al-Kareem Al-Samaraee (the University of Baghdad, College of Science, department of chemistry) and Dr. Ayad Fadi Al-Kaim (the University of Babylon, College of Science for women, department of chemistry) to perform some essential analyses such as AFM analysis and UV-Visible spectrophotometer with Labsphere diffuse reflectance accessory.

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Table 1. The Distinctive Physical And Chemical Characteristics of The Eosin Yellow Dye (Ahmed, 2018).

Values	Parameters
Structure
2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate xanthene	IUPAC name
brilliant red-brown powder dye slightly yellowish in aqueous solution	Class
Acidic	Natural
(515-518) nm	$\lambda_{\max}$

Figure 1. The schematic for full steps of prepared WO₃/TiO₂ composites

Figure 2. XRD pattern of commercial WO_3 and commercial TiO_2 and its prepared nanocomposites.

Figure 3. Three-dimensional AFM image of (a) commercial WO_3 , (b) commercial TiO_2 , (c) $(\text{WO}_3/\text{TiO}_2)$ composite 1 (0.5:1), (d) $(\text{WO}_3/\text{TiO}_2)$ composite 2 (0.25:1), and (e) $(\text{WO}_3/\text{TiO}_2)$ composite 3 (0.16:1).

Figure 4. The roughness averages with the studied samples (depended on particle sizes).

Figure 5. Tauc plot a) for WO₃ as a direct band gap. b) for TiO₂ and prepared (WO₃/ TiO₂) composites 1,2, and 3 as indirect band gaps.

Figure 6. Charge transfer between WO_3 and TiO_2 .

Figure 7. Photocatalytic decolorization of eosin yellow dye with employing WO_3 , TiO_2 and prepared $(\text{WO}_3/\text{TiO}_2)$ composites 1,2 and 3 nanoparticle.at 25 °C, 200 mg of catalyst's dose, initial pH 6.09 and 5ppm of eosin yellow dye (a) Relation between appearance rate constant and studied samples and (b) $E_{decol.}\%$ for 90 min verse studied samples.

Figure 8. Effect of using H₂O₂ on Photocatalytic decolorization of eosin yellow dye with employing optimum dose 500 mg WO₃, 500 mg TiO₂, and 200 mg prepared (WO₃/TiO₂) composite 1nanoparticle as best doses. At 10⁻² mmol of H₂O₂, 25 °C, 5ppm of eosin yellow dye, and initial pH 6.09 (a) Relation between appearance rate constant and studied samples and (b) $E_{decol} \%$ for 90 min verse studied samples.

Figure 9. The schematic diagram for the most probable decolorization mechanism of eosin yellow dye in the presence of UV/ WO_3 , or TiO_2 or WO_3/TiO_2 nanocomposite.