Preparation of TiO_2 Nanoparticles Using $H_2O_2/TiOSO_4$ and Applications in Eosin Yellow Photocatalytic Degradation

Hind I. Hussein[1*], Firas H. Abdulrazzak[2]

Abstract

TiO_2 was synthesized in this work by chemical route, when the titanium oxysulfato ($TiOSO_4$) react with 4:6 H_2O_2/H_2O after is dissolved in deionized water. The yellow precipitate was drying at 100°C before heat treated at 400°C to obtain crystalline TiO_2. The sample were characterized using FT-IR and X-ray diffraction spectroscopy which identified that product was mixture between two form anatase and rutile. The photocatalytic activity of synthesized TiO_2 was tested in the degradation of Eousin yellow which compare with two form of TiO_2. Evaluated the results was shown that H_2O_2 was succeed to preparing TiO_2 from $TiOSO_4$ with higher activity then anatase and rutile forms.

Key Words: $TiOSO_4$, H_2O_2, Adsorption/Photodegradation, Anatase, Rutile.

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Introduction

May be TiO_2 was synthesized using many strategies but the researchers still until now trying to made it for more and more applications with higher activities. This behaviors towards synthesis TiO_2 can be related to physical and chemical properties that encourage to used it in huge applications (Eneyew *et al*, 2021) (Aljeboree *et al*, 2019). TiO_2 can preparing by top to down or down to top strategy such chemical and physical vapour deposition, spinning, electrochemical, and sol-gel method (Pardon *et al*, 2018, Layth *et al*, 2021).

TiO_2 shown three crystalline polymorphs: the stable forms were anatase, rutile and unstable form was brookite. The first two forms, anatase and rutile typically behave similar properties, and the main different represent by less weight, larger band gap and resistance to corrosion as compare with anatase. Generally, anatase stable until 700 degrees and brookite which is rarely exist however, is unstable and at high temperature converts to more stable within rutile form at high temperature. (Aljeboree, 2019, Muhammad *et al*, 2021).

The attentions in this properties pushed the researchers to modified many conditions that could decide the orientations of molecules crystalline nature and particle size with shape such temperature, solvent, precursor, precipitation reagent and many ether specific conditions (Peng *et al*, 2021).

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Effect of reagent concentrations or precipitation materials represent critical parameters for preparation method which used with titanium source such ($TiOCH_3$, $TiOC_2H_5$, $TiOC_3H_7$... etc.) or $TiCl_4$ and $TiOSO_4$ which common used for this purpose (Muhammad *et al*, 2021, Liqaa *et al*, 2019, Abdulrazzak 2019). Mostly $TiOSO_4$ could be represent the ideal precursor for synthesis TiO_2 because it is cheap and more safe for use as compare with the ether materials (Falah, *et al*, 2019, Paola *et al*, 2013). In this work we concern with synthesis TiO_2 from $TiOSO_4$ with H_2O_2 as precipitation method and as enhancement factor for increase the activities of TiO_2 by inter many free radical and anion species of OH from H_2O_2 and used Eosin yellow EY to decolorazation by synthesized TiO2.

Experiential

Materials and Method of Preparation

$TiOSO_4$, H_2O_2 (50% in purities) and Eosin Yellow (99% in purities) were purchased from Sigma-Aldrich. The TiO_2 Anatasee and Rutile were supplied from China Gansu, CNNC Hauyuan all of it were used without further purification.100mL of distilled water at 40 ^{0}C was used to dissolved 0.5 g of Titanyl sulfate ($TiOSO_4$) by magnetic stirrer until forming clear solution. 10 mL of H_2O_2/H_2O with volume ratios V_{H2O2}/V_{H2O} (4:6) were added for the solution and kept without stirring for 24 hours. The yellow precipitate was formed which washed until removed SO_4^{2-} were removed, drying the product for 3 hours at 100 ^{0}C before annealed for 2 hours at 400 ^{0}C with rate of heating 7.5 ^{0}C min^{-1}.

Photodegradation Experiments

In Wholly investigates of removal of EYs dye coolar has been performed via mixture 0.1 gm / 100 cm^3 of catalyst via 8 ppm of the EYs solution under UV light with intensities (1.4 m W) at 298.15 K. Utilizing a magnetic stirrer with 300 rpm at predetermined times 2 cm^3 of suspension reaction mixture was withdrawn every 30 minute, and using centrifuged at 8000 rps. Firstly, the mixture of EYs and catalyst were stirred in the dark to reach for equilibrium the absorption which was 30 min. before starting irradiation reaction. photo reaction was made by two mercury lamp (China) as a source of UV radiation. The absorbance wavelengths at 518nm of the solution was estimation utilizing ultraviolet-visible (UV-1100 spectrophotometer).

Characterization

The nature of function groups and the change in structure were determined by Shimadzu IRAinffinity-1 spectrophotometer with resolution 4 cm^{-1} and scanned between 500-4000cm^{-1}. The crystallography of $TiOSO_4$, synthesized TiO_2 and the two sample anatase and rutile for compare were analyzed by A (Riga Rotalflex-RU-200B) X-ray diffractometer. The 2theta angular region that taken was 15-80^o at scan rate 5^o /min. with resolution o.o2^o. The FT-IR for $TiOSO_4.2H_2O$ showed narrow and asymmetric stretches bonding at 1188.15-983.70 cm^{-1} which can be related to sulfite and sulfate (Jerson *et al*, 2018) anion connection to Ti^{+4} cation and that was reduce with samples after reaction with H_2O_2. A stretching vibration mode at 1360-1378 cm^{-1} that corresponds to a stretching vibration of S=O bonds (Esteban *et al*, 2014) The wide band between 3500 cm^{-1} and 2850 cm^{-1} refers to the vibrations of -OH groups and that mostly localize on the surface of $TiOSO_4$ material (Liziê *et al*, 2020).

The hydrophobic behavior of $TiOSO_4$ when adsorbed water which was appeared at 1639 cm^{-1} and that was disappear with synthesized TiO_2 beside change and variance in absorbance as compere with $TiOSO_4$. One of the clear change in structure was reduce the peaks that can be related to sulfite at 1100-900 cm^{-1} which refers to convert most of $TiOSO_4$ to TiO_2 and removed the peaks of H_2O absorption for synthesized TiO_2 and that may be related to calcination process. The vibration of Ti-O bond and polymer chains of Ti-O-Ti bond due to condensation can be observed between 850 cm^{-1} - 600 cm^{-1} (Daniela *et al*, 2017).

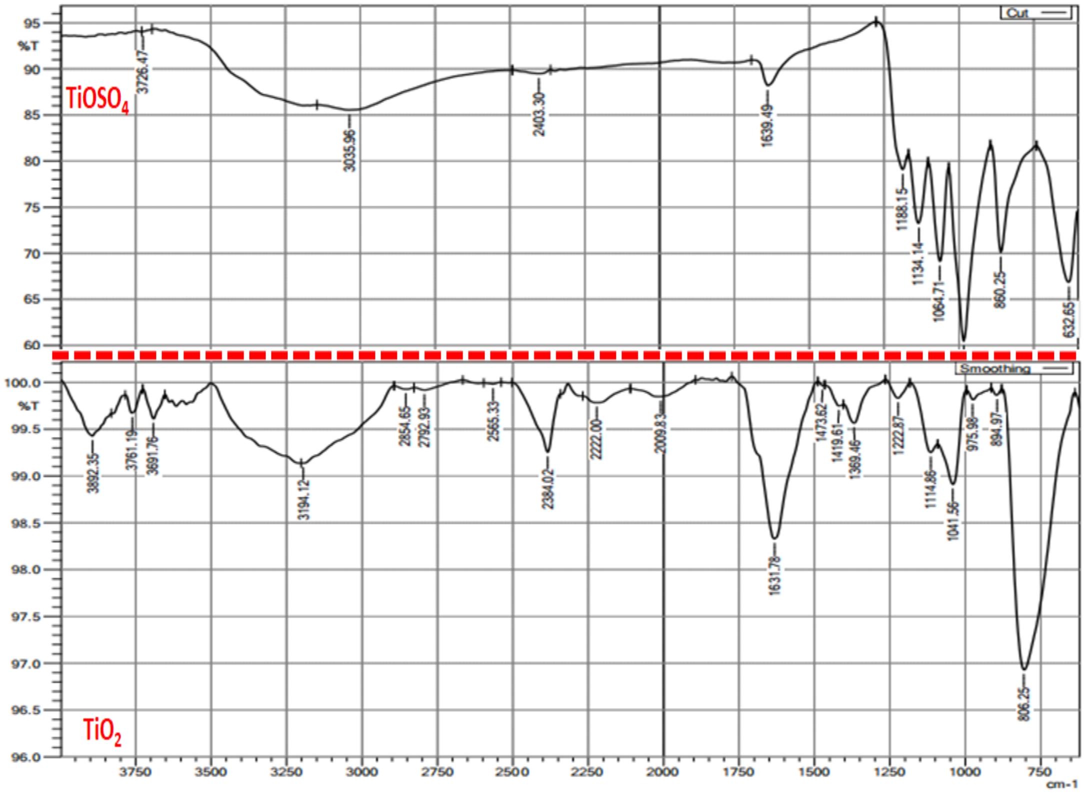

Figure 1. FT-IR spectroscopy for $TiOSO_4$ and synthesized TiO_2

The XRD analysis in Fig. 2 for synthesized TiO_2 and $TiOSO_4$ showed that H_2O_2 was succeed to make condensation process before precipitation when the clear change can be seen in crystallography structure.

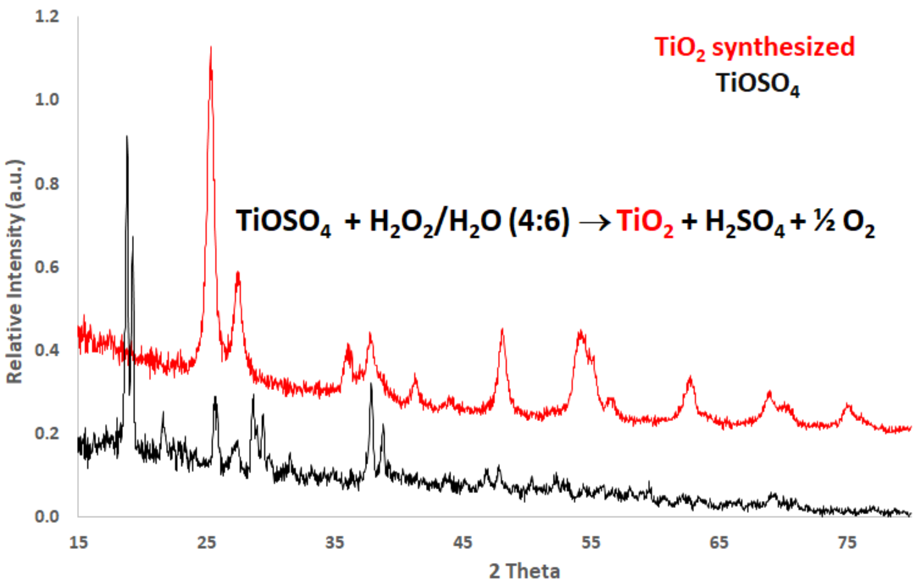

Figure 2. The XRD patterns for $TiOSO_4$ and synthesized TiO_2

Fig. 3 include XRD pattern for the synthesized TiO_2 after purification, drying and calcination with few peaks that can be related to two phases anatase and rutile . The anatase phase were represent by 25.24°, 38.29°, 48.1°, 55.11°, and 75.56° for the pure anatase and synthesized TiO_2 while Rutile was 27.55°, 36.21°, 41, 36° and 57.42°, however three shared peaks with variance in intensity, which is often favor anatase phase (Uddin *et al*, 2020). The most common peaks for synthesized TiO_2 were ≈ 25°, 38°, 48°, 55°, and 75° with planes of miller index 101, 004, 200, 211 and 215 respectively. The Debye-Scherrer equation (Francisco, *et al*, 2018) was used to estimated nanoparticles average diameter for synthesized and two types anatase, rutile TiO_2 according to equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where the wavelength λ of the CuKα radiation which used was 0.15418 nm, causing many differentiation peaks with 2θ at full width β of half maximum FWHM then average particle diameter for material D was calculated mostly at largest intensify. According to Debye-Scherrer equation the particle size was 88.2 nm, 8.6 nm and 11.22 nm for rutial, anatase and synthesized TiO_2 respectively, thus the average of synthesized TiO_2 was close to average of Anatase phase although there is ratios of rutile in synthesized sample.

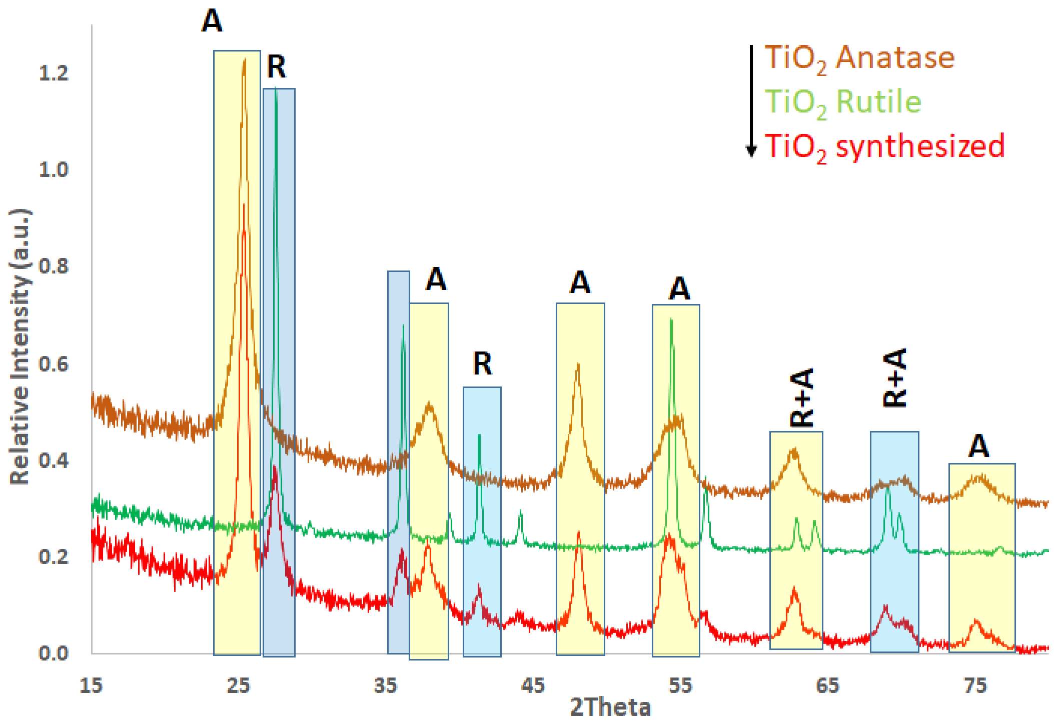

Figure 3. The XRD patterns for synthesized TiO_2 and compare with TiO_2 Anatase and Rutile forms

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The XRD analysis within detection limits confirm that the volume ratios of H_2O_2:H_2O (4:6) succeed to preparing TiO_2 nanoparticles in tetragonal crystal structure with high purity.

Results: Activity of synthesized TiO_2

The activities of synthesized TiO_2 was tested with Photocatalysis reaction when activated uses UV-light in exist H_2O/O_2, as heterogeneous photocatalysis and make compare with the two types of TiO_2 rutile and Anatase. The results for photocataltic decolourization of EY were plotted in Fig. 4, which shows two part of reaction: the first at dark without UV-light and that represent the adsorption reaction which take 30 min for the equilibrium time while the ether with UV-light. The percentage removal by adsorption (%) of EY (Hanan 2021) by the catalysts was calculated as follows:

$$\text{Adsorption } \% = \frac{Ci - Ce}{Ci} \times 100 \qquad (2)$$

The removal of dyes in the dark reaction did not reach to 1% for anatase and rutialle phase of TiO_2 while with synthesized TiO_2 was 8%. The photo-reaction was done without adding firstly, photocatalyst by using UV-light illumination for five hours which shows no degradation of EYs. After using the photocatalyst the activities for three materials were shows variance and clear change for all.

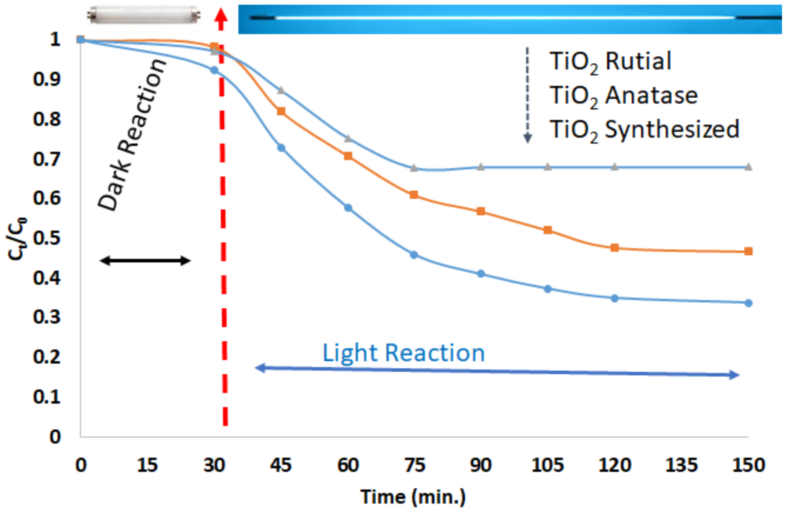


Figure 4. The process of adsorption/photocatalytic removal of 8 ppm EY by 100 mg rutile, anatase, and synthesized TiO_2 at 298.15 K

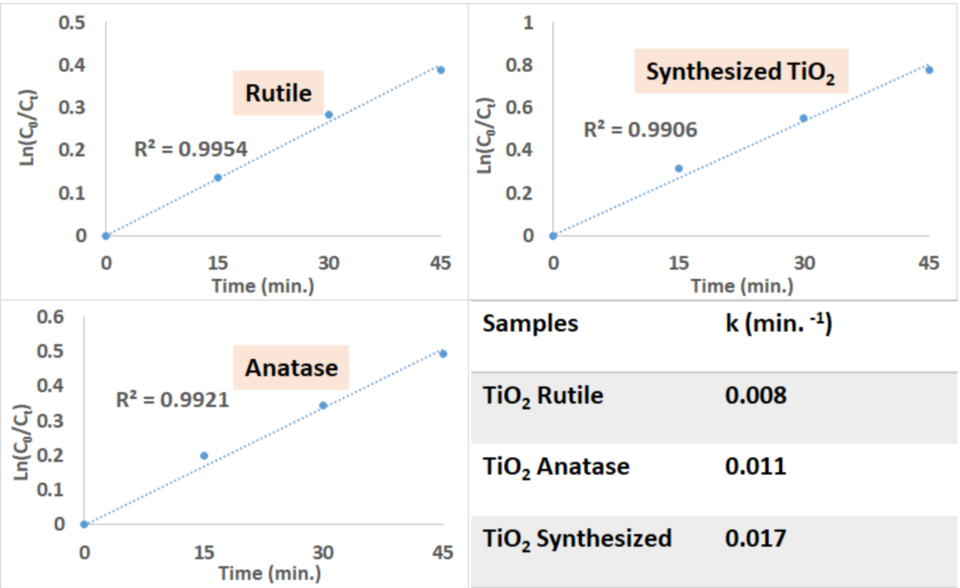
Degradation rate was calculated from the amount of the dye in the solution after viral times as follows:

$$\text{Degradation ratio } \% = \frac{C_0 - C_e}{C_e} \times 100 \qquad (3)$$

Where C_0 and C_e are the initial and equilibrium concentrations of EYs dye (mol/L). The adsorption/photocatalysis kinetic study was accrued using rutile, anatase and synthesized TiO_2 as catalysts. Irradiated reaction by UV- light with efficiency removal reached to 28%, 51% and 68% respectively in 150 minutes as shown in Fig. 4. The experiments, was accrued with kept the mass of the catalysts, dyes concentration, pH and temperature constant. The kinetic studies were applied by using Langmuir-Hinshelwood kinetic model of pseudo-first order (Zhang *et al,* 2017, Ali *et al,* 2017) when plotted Ln (C_0/C_t) versus t, and shows linear behaviors for degradation of EYs dye under UV-light.

$$\ln \frac{C_0}{C_t} = k_r\, K\, t = k_{app}\, t \qquad (4)$$

When C_0 represents 8 ppm of the initial concentration of the dye and C_t represent the concentration of EYs after different time. The K and k_r refers to equilibrium constant and kinetic constant of degradation reaction respectively and that was substituted by apparent constant rate for degradation k_{app} in the photocatalytic reaction. Comparing the rate constants which estimated in tables that listed with Fig. 5, all of catalysts are in the same order reaction, and it is possible to note that synthesized TiO_2 behave a greater efficiency in the removal of EYs dye in dark and irradiation with UV-light.



Samples	k (min. $^{-1}$)
TiO_2 Rutile	0.008
TiO_2 Anatase	0.011
TiO_2 Synthesized	0.017

Figure 5. The kinetic of photocatalytic removal and the value of rate constant (k) for 8 ppm EYs by 100 mg rutile, anatase, and synthesized TiO_2 at 298.15 K

Discussion

The critical parameters that limit an efficient of semiconductor such TiO_2 as photocatalyst is band gap or the charge couple e^-/h^+ in the conduction CB and valance VB band respectively (Dorian and Charles 2011) (Jerson *et al*, 2018) the equation below refers to the general requirements of mechanism for producing active site on the TiO_2 surface towards typical photocatalytic reaction:

$$TiO_2 + hv\ (\text{UV-light}) \longrightarrow TiO2^{e-\ CB}_{h+VB} \quad (5)$$

$$TiO2^{e-\ CB}_{h+VB} \longrightarrow TiO_2 + \text{heat} \quad (6)$$

$$TiO_2 + H_2O\ (\text{absorbed}) \longrightarrow TiO_2 + OH^- + H^+ \quad (7)$$

$$TiO2^{e-\ CB}_{h+VB} + O_2\ (\text{absorbed}) \longrightarrow O_2^- \quad (8)$$

$$TiO2^{e-\ CB}_{h+VB} + OH^-(\text{absorbed}) \longrightarrow OH^* \quad (9)$$

$$O_2^-\ \text{OR/AND}\ OH^* + \text{Organic Materials} \longrightarrow H_2O + CO_2 + \text{OETHERS} \quad (10)$$

From equations 5-10 it could be seen two species responsible to EYs decolourization which is influence directly with the crystalline structure. However anatase was more active then rutile (Peng *et al*, 2021) and in the same time create mixture in continent or structure of synthesized TiO_2 can achieve more activates due to forming synergistic effect . The enhancement in activities can due to also to the size of synthesized materials when include mixture of two phases anatase/rutile with very small particle size (Paola *et al*, 2013) as compare with pure anatase and Rutile with value of particle size between 8-88 nm . all of that crate less particle size in nano scale with high surface area causing reduce band gap to make more active species such hydroxide and oxide with free radicals and anionic behavior on the surface of TiO_2 as shown in equations previously.

Conclusion

In order to find the simplest and cheapest method for synthesis TiO_2 and using it in many applications such photocatalytic reaction, we used specific ratios of H_2O_2/H_2O with $TiOSO_4$ in ambient conditions to reach for the best results in efficiency. The FT-IR analysis shown that complete conversion for $TiOSO_4$ to TiO_2 and XRD analysis improve the double form for the product which is anatase\rutile. The efficiency of synthesized TiO_2 can be related to the mixture morphology for the product which include both anatase and rutile. H_2O_2 was successfully used as a precipitation reagent for synthesized TiO_2 which could make specific control in the physio-chemical properties for the product when make balance in the value of anatase and rutile. The photodegradation results showed that adsorption of EYs on the surface of synthesized TiO_2 was enhance the decolourization efficiency performance.

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