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TiO₂ Nanoparticles Sensitized by Safranin O Dye using UV-A Light System

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Abstract. This study examined the photocatalytic decolorization of safranin O dye by using TiO₂ nanopowder as a photocatalyst, under illumination with using artificial UV-A- light. The behavior of this reaction was pseudo first order and the maximum of removal was 88.176% in 100 min. at 30 °C. The increased of reaction temperature enhances the photoreaction, with positive ΔH that equal to 20.552 kJ mol⁻¹ and given low activation energy reach to 22.609 kJ mol⁻¹. The Fenton reaction was applied in aqueous solution of this dye with the using TiO₂ nanopowder and given maximum photo decolorization efficiency.

Keywords. Safranin O, TiO₂ nanopowder, basic red 2 dye, photo-decolorization, oxidant agent, Fenton reaction.

1. Introduction. Titania (TiO₂) is one of an important n-type semiconductor which used as photo catalyst. This material is found as a white crystalline powder with three main types of crystal structures in natural: Anatase, Rutile and Brookite^{1,2}. Anatase and brookite can transform to rutile by calcinations at about 900 °C and both have metastable structures. However, rutile is more stable, less band gap (3.02 eV) and have a maximum density (4240 kg m⁻³)³⁻⁷ compared with anatase and brookite.

In general, anatase and rutile have a same structure (tetragonal structure), but brookite has orthorhombic crystal system³. The TiO₂ bulk and nanopowder have good properties like high photocatalytic activity with high chemical and biological stability, low cost, non-toxicity and suitable optical-electronic properties⁸⁻¹⁰. These reasonable properties for titania were attracted considerable attention toward published many researchers in different fields such as, using it in produced a hydrogen energy from oxidation of methanol after metalized it^{11,12}, using it as photocatalyst¹³⁻¹⁶, enhanced the efficiency of solar cells¹⁷⁻¹⁹, treatment of tumor cells²⁰⁻²², using it in UV protectors in skin²³⁻²⁵ and using it as inhibitor for some enzyme to treat some diseases in human body²⁶. Many researches confirmed that the TiO₂ nanoparticles are have a more active than TiO₂ bulk, so, that due to it has a low particle or (crystal) sizes which leads to high numbers of active sites with depressing the no. of defects in the inner grains. Moreover, it has a low melting point, a high of porosity, low phase transition temperature, and reduced the lattice constants²⁷⁻²⁹.

The aim of this project was to exploit the created of hydroxyl radical in aqueous solution of safranin O dye, to investigate the decolorization of it in present TiO₂ nanopowder at optimum conditions.

2. Experimental

2.1. Chemicals. In this project, the chemicals were employed without any pre-treatment. Titanium dioxide nanopowder was purchased from US Research nanomaterial Inc, USA with 99.9% purity. Safranin O dye (C₂₀H₁₉ N₄Cl) was supplied from BDH - England. This dye is also called basic red 2 dye or basic dye. Basis on



IUPAC, it can be called 2,8-dimethyl-3,7-diamino-phenazine. It is fully soluble in water with M.Wt equal to $350.85 \text{ g mol}^{-1}$, beyond to the xanthene dyes class, used as redox indicator in analytical chemistry, and employed for the detection of cartilage or employed as a counterstain in some staining protocols^{30,31}.

2.2. Method. By basing on the homemade photoreactor in Figure 1, the series of the photoreaction experiments were conducted by mixing 100 mL from aqueous solution of safranin O dye with a suitable amount of TiO_2 nanopowder as suspension solution.

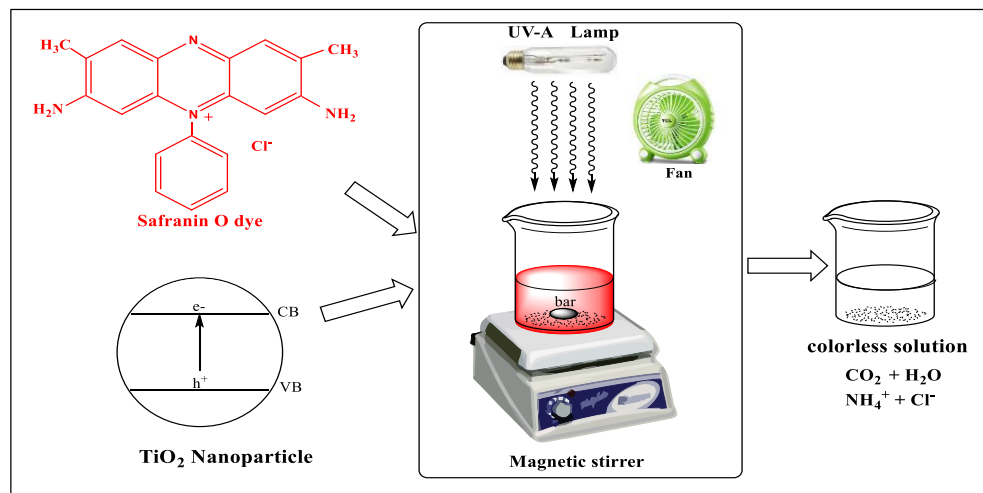


Fig. 1 Homemade photoreactor setup to decolorize Safranin O dye.

In fact, the equilibrium time for this reaction was closely performed at 30 min as adsorption process. After this step, the solution was exposed to UV-A light-(as HPML-type Radium (125 watts)), which has calculated light intensity equal to $9.1 \times 10^{-8} \text{ einstein s}^{-1}$ using chemical actinometer^{32,33}. After regular exposed times of irradiation, about 3 mL collected from the mixture, and then double filtered to ensure from all TiO_2 nanopowder molecules must remove. The absorbance of the filtered dye solution was carried out using UV-Visible spectrometer at 530 nm. The apparent rate constant (k_{app}) and percentage of photodecolorization efficiency PDE % were described by mentioned in the references^{10,34,35}.

3. Results and Discussion

3.1. Effect of TiO_2 dose on the photodecolorization rate of Safranin O dye

Figure 2 (a) and (b) clearly displays the rate constant for decolorization of this dye in presence TiO_2 raises with the increasing the dosage of TiO_2 that due to increase the active site to adsorb the dye before the irradiation process³⁶. The maximum value of apparent rate constant is obtained at 175 mg/ 100 mL with efficiency (PDE %) equal to 88.176 at 100 min. That pointed out the increased in active site on photocatalyst surface, which enhanced to adsorb of dye molecules with hydroxyl radicals, this case will accelerate the decolorization of the dye according to the first possible of Langmuir-Hinshelwood (L-H) kinetics model. This model is having four suggested cases^{27,36,37}:

The reaction is happened between ($\text{Dye}_{(\text{ads.})}$ and $\cdot\text{OH}_{(\text{ads.})}$), the reaction is happened between ($\text{Dye}_{(\text{ads.})}$ and $\cdot\text{OH}_{(\text{soln.})}$), he reaction is happened between ($\text{Dye}_{(\text{soln.})}$

and $\text{OH}_{(\text{soln.})}$) and the reaction is happened between ($\text{Dye}_{(\text{sol.})}$) and $\text{OH}_{(\text{ads.})}$).

From the other hand, after using 175 mg/100 mL of TiO_2 nanopowder, the rate of reaction depresses, that based on the raised of the solution turbidity and declined the transmittance of light, which caused inhibited the hydroxyl radical formation, this effect is called screen effect^{9,38, 39}.

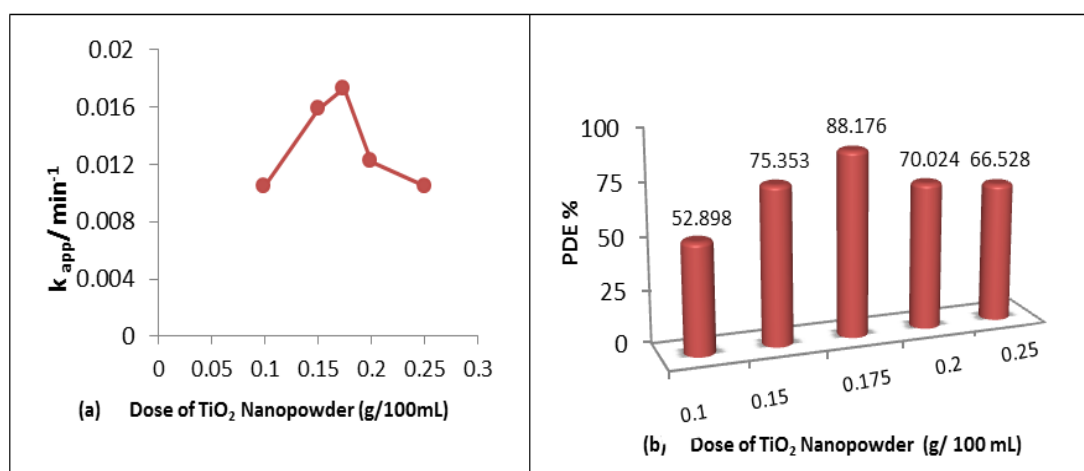


Fig. 2 Effect of TiO_2 nanopowder dose on the (a) apparent rate constant of photo-reaction and (b) PDE %, at conditions: cat. dose = (0.1-0.25) g/100mL, Safranin O dye conc.= 25 ppm, and $T = 303.15\text{K}$.

3.2. Effect of Temperature on the photodecolorization rate of Safranin O dye

Briefly, the application of different temperatures on a suspension solution of this dye leads to find the activation energy ΔE_a from plotting Arrhenius equation^{33, 40-43}, the thermodynamics function like ΔH^\ddagger with ΔS^\ddagger from plotting Eyring equation^{34,43- 46} and Gibbs free energy ΔG^\ddagger by using Gibbs equation^{33,45}. From Figure 3 (a) and (b) results, the thermodynamics function and activation energy were determined, as listed in table 1. The increased in temperature causes to raise in the rate of reaction and speed of producing of hydroxyl radical and other species such as (O_2^- and HOO^\cdot)³³ which leads to form a hydroxyl radical at last. These results proved that the photo - decolorization of safranin O dye with the presence of TiO_2 nanopowder is endothermic and fast. Moreover, the negative value of entropy indicates to decolorize for the chromophoric groups of this dye by degradation it to other small species, but the positive value of ΔG^\ddagger refers to the reaction is non-spontaneous. These results are in agreement with the reported in references^{33,47,48}.

Table 1 The kinetic and thermodynamic functions for the photo-decolorization process of safranin O dye in suspension of TiO_2 under UV-A.

E_a kJ mol^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger_{303.15}$ kJ mol^{-1}
22.609	20.552	-3.060	21.479

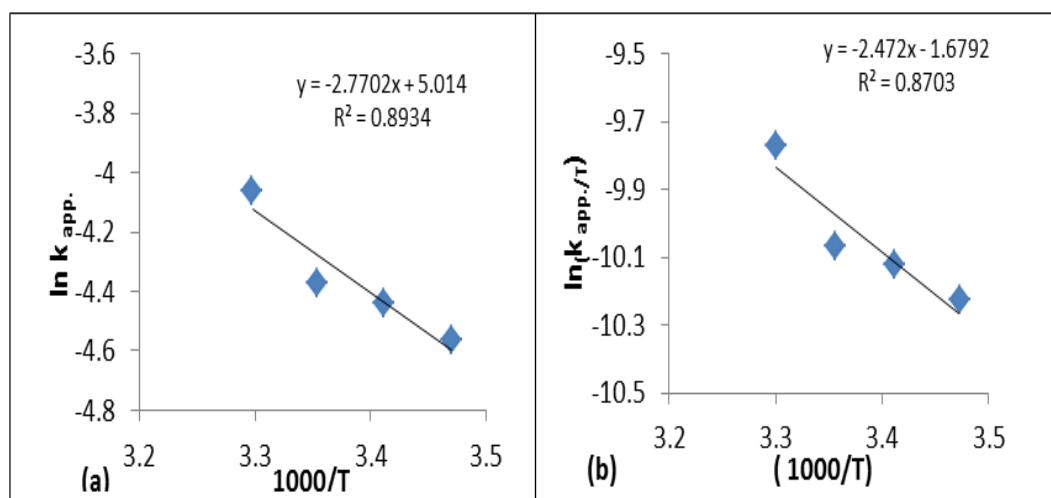


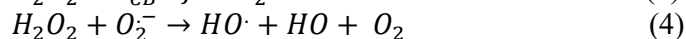
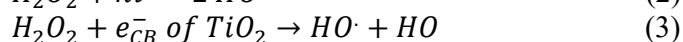
Fig. 3 Effect of temperature on photo-decolorization of safranin O dye from suspension solution of TiO_2 at the range in temperature (288-303) K (a) Arrhenius equation plot and (b) Eyring equation plot.

3.3. Effect of oxidant agents on the photo-decolorization rate of safranin O dye.

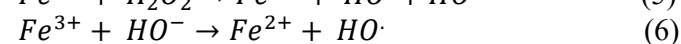
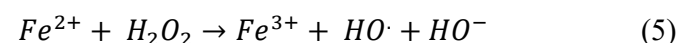
The addition of oxidant agents such as H_2O_2 and $Fe(II)$ on the suspension solution of safranin O dye with TiO_2 nanopowder was done. The rate of reaction increases with addition 0.1 % H_2O_2 but decreases with the addition of 1×10^{-4} M from $Fe(II)$ with the efficiency equal to 92.73 and 85.923 respectively, these results are shown in Figure 4 (a) and (b). The decreased in the rate of reaction and efficiency with the using $Fe(II)$ alone (in this concentration) was interpenetrated to scavenge of hydroxyl radical by using the $Fe(II)^{47}$ according to equation 1.



Whereas, the addition of 0.1% H_2O_2 alone or as the mixture from (0.1% H_2O_2 with 1×10^{-4} M from $Fe(II)$) as (Fenton reaction), that accelerates the photo-decolorization reaction, hence, that attitude to produce a hydroxyl radicals according to the following equations^{50,51}.



The Fenton reaction is enhanced this photo-decolorization of safranin O by increasing the efficiency from 88.176 to 98.838 by producing a high amount of hydroxyl radicals, as noted in the following equations⁵²⁻⁵⁵.



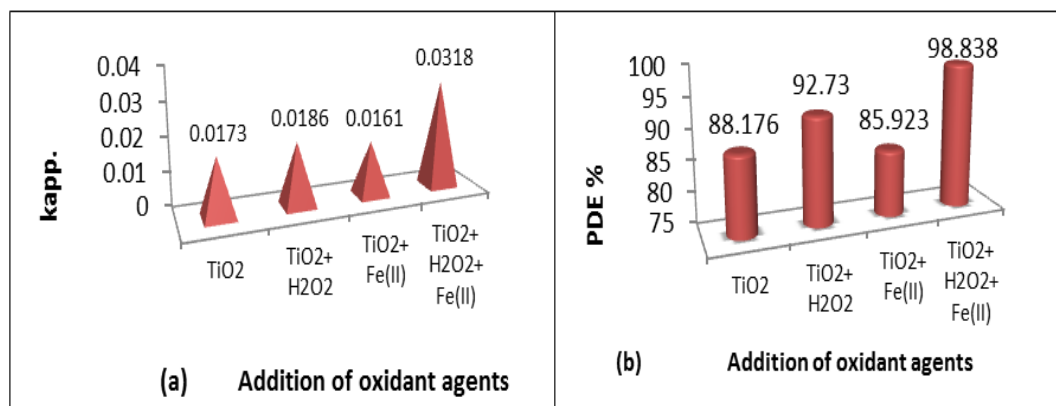
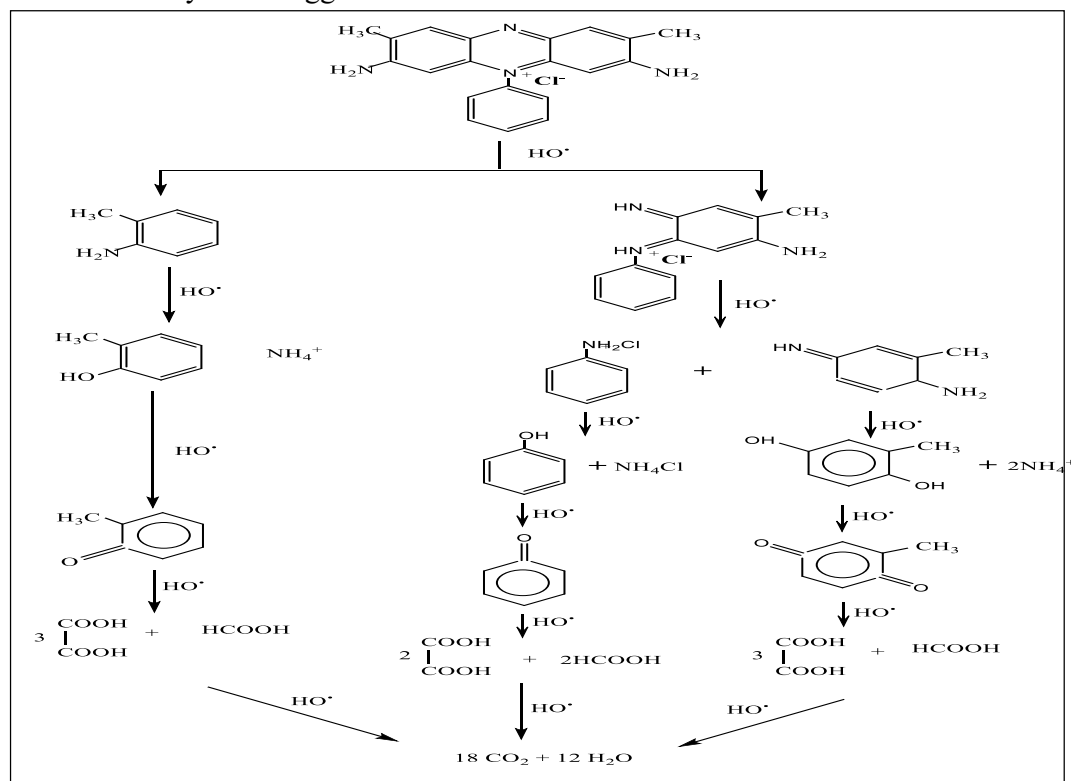


Fig. 4 Effect of addition oxidant agents on the photo- decolourization of 25 ppm from safranin O dye with 175 mg/100 mL of TiO₂ nanopowder, at 0.1% H₂O₂ and 1×10^{-4} M from Fe(II). a) Relation between rate constant (k_{app}) verse used oxidation agent with sample b) Relation between efficiency (PDE%) verse used oxidation agent with the sample.

3.4. Mechanism

In order to form hydroxyl radical on TiO₂ nanopowder surface must focus a light on the suspension solution of TiO₂ nanopowder. The hydroxyl radical is regarded a power force to start the photo-decolorization of dye and generated of hydroxyl radicals by series of redox process^{46, 54,55}. The photooxidation process of hydroxyl ion by hole of semiconductor is formed HO[•]. Moreover, the photoreduction process for O₂ environment is leaded to produce 2HO[•]^{36,54}. The mechanism of decolorization of safranin O dye was suggested in scheme 1.



Scheme 1 Suggested mechanism for decolorization of safranin O dye in TiO₂ nanopowder- UV-A light system.

3.5. Conclusions

In this study, the main conclusions were investigated. The photocatalytic decolorization process of safranin O dye in suspension solution of TiO₂ nanopowder under UV-A light system was done. This photoreaction is found to be fast, endothermic and obeyed the pseudo first order with low activation energy.

The efficiency for decolorization of safranin O dye with the using the best amount of TiO₂ nanopowder under addition some oxidant agents have followed by the sequences:

PDE% using Fe(II) < PDE% without oxidant agents < PDE% using H₂O₂ < PDE% using (mixture from H₂O₂ and Fe(II)).

The using of Fenton reaction was enhanced the efficiency that changed from 88.176% to 98.838% at 100 min.

The suitable mechanism was suggested to obtain the decolorization and degradation of this dye with form CO₂ and H₂O (mineralization process) at final pH equal to 7.

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