



Synergistic Effect of dark and photoreactions on the removal and photo-decolorization of azo carmosine dye (E122) as food dye using Rutile- TiO₂ suspension



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Abstract

Dark and photoreactions have been employed to handle the various hazardous organic water contaminants as Synergistic technologies. The removal (dark reaction) and the photo-decolorization (photoreaction) of azo carmosine dye (E122) as a food dye in an aqueous solution using Rutile- TiO₂ and UV-A light were investigated in this work. Various parameters such as oxidant agents and temperature were determined. In dark reaction, the adsorption capacity and percentage of carmoisine dye removal elevated with the depressing of the temperature. This dark reaction of carmoisine dye is exothermic, physical adsorption, less random, non-spontaneous, and quick response with low activation energy. The maximum value removal % is reached to 86 % when addition mixing of Fe(II) and H₂O₂ to dye solution. In photoreaction, the same oxidant agents were applied in the dye solution and found the reaction is a pseudo-first-order kinetic, exothermic reaction, fast (low activation energies), less random, and spontaneous. The maximum percentage of decolorization with the addition of mixing of Fe(II) and H₂O₂ equal to 64.28% at 30 min.

Keywords: Azo carmosine dye; Photocatalysts; E122; RutileTiO₂; food dye; removal.

1. Introduction

Organic and metallic organic contaminants of labs wastewater or industrial wastewater are a global problem for the environment, affect biodiversity and human health[1-4]. The elimination of organic compounds from wastewater before its discharge into the natural world is also important [4]. Dyes have long been commonly used widely in many industries, such as paper, dyeing, pulp, textiles, leather, plastics, cosmetics, paint, and food industries, as one of the most wastewater-causing contaminants [5]. Based on the European Food Safety Authority, azo food coloring is suspected of being hazardous in high concentration, as in the case of Carmoisine dye, which decomposed into aromatic amines by natural intestinal flora, which is the source of frequent headaches in adults, often distracting and hyperactive

in children [6]. As a result, azo dyes are extremely recalcitrant and are most persistent in the aquatic environment[7]. Carmoisine dye is used as a confectionery coloring agent for desserts, ice cream, gelatin beverages, medicine, and cosmetics[8]. It can be used Chemically, as a reagent by a spectrophotometric process to determine the concentration of diphenhydramine and this dye was often used in the textile industry and caused to create a high amount of wastewater[9]. Therefore, several manuscripts focused on the removal of these colored effluents were reported by researchers. Many treatment technologies have been developed for the decolorization[10] and degradation of dyes in wastewater effluents, using chemical adsorption[11], electrochemical process[12], bio-adsorption[13], biodegradation[14], sonochemical process [15]and

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advances oxidation processes (AOPs) such as UV/H₂O₂, UV/O₃, Fenton and photo-Fenton catalytic reactions[16]. AOPs are likely to be combined with the use of heterogeneous semiconductors in presence of light to create hydroxyl radicals that act as an oxidizing reagent for this process[17,18].TiO₂ has been used in AOPs as a vital photocatalyst to decolorize dyes from aqueous solutions[19,20]. This work aims to apply the rutile-TiO₂ suspension solution for decolorizing of Carmoisine dye from an aqueous solution in dark reaction and photoreaction. Varies parameters such as pH of the solution, oxidant agents, and temperature were examined to find the best conditions in dark reaction and photoreaction.

2. Experimental

2.1. Materials

All materials were used without any extra purification. Titanium dioxide (TiO₂) type rutile is used as a photocatalyst (Riedel -De-Haen AG, Seelze Hannover, Germany with purity 99.98%). The carmoisine dye (azorubine or E122 or Acid Red 14) with the molecular formula C₂₀H₁₂N₂Na₂O₇S₂, MWt = 524 g/mol, 87% purity, and λ_{max} 515 nm was supplied from Mumbai – India as a local dye.

2.2. Instruments

The dark reaction and photoreaction experiments were performed in a batch home-made reactor as shown in **Figure 1**. The light source of this reactor was horizontally located above the sampling glass container, as a high-pressure mercury lamp (UV- A), type Radium with 250 W at λ_{max} = 365 nm. The light intensity reaching the sample solution was calculated using a chemical actinometric solution and found to be 2.66x10⁻⁷ Einstein s⁻¹. The reactor is made of a wooden box, to prevent harmful irradiation[21] and which is covered inside with an Al sheet to focus the UV-A light in the sampling system.

2.3. Procedure

The first step (dark reaction) was done by mixing 100 mL of 10 ppm of carmoisine dye with 0.2 g of TiO₂ by magnetic stirrer and Teflon bar for 15 min to allow for reaching the suspension solution to equilibration state. The adsorption capacities (q_e) and the percentage of removal (E_{re}%) were calculated as following equations 1 and 2[22-24], after centrifuged and read the absorption at 510 nm.

$$q_e = \frac{(C_o - C_e)}{m} \cdot V \quad \dots (1)$$

$$E_{re} \% = \frac{(C_o - C_e)}{C_o} \cdot 100 \quad \dots(2)$$

Where, C_o and C_e are the initial and equilibrium dye concentrations in solution m is the mass (g) of adsorbent and V is the volume in L of adsorbate (carmoisine dye).

In the second step, the suspension solution was exposed to UV-A light for 30 min. In regular times, about 3.5 mL of suspension solution was isolated in the test tube. Then, double centrifuged (Hettich) for collected solutions was achieved at 4000 rpm and 15 min to ensure all the fine TiO₂ particles were separated. The filtered dye solution absorption was measured with a UV-Visible spectrophotometer (type AA-1800, Shimadzu) at 512 nm. The kinetic study for decolorization of carmoisine dye was investigated with founding the apparent rate constant (k_{app.}) and efficiency of dye photodecolorization (E_{decolor.} %) based on Langmuir-Hinshelwood (L-H) model by depending on the below equations 3 and 4[25-27].

$$\ln \left(\frac{C_o}{C_t} \right) = k_{app} \cdot t \quad \dots(3)$$

$$E_{decol.} \% = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \quad \dots(4)$$

Where: C_o and C_t are an initial concentration of carmoisine dye in (dark reaction) at time of irradiation = 0 and a concentration of the same dye at time t of irradiation.

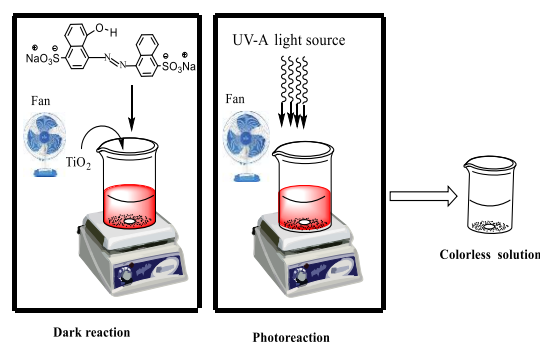


Fig. 1. Schematic diagram of dark and photo decolorization of carmoisine dye using a homemade photoreactor

3. Results and Discussion

3.1. Effect of Addition Oxidant Agents on Dark Reaction

Figure 2 explains the effect of adding the oxidant agents such as (1x 10⁻⁵ M) H₂O₂, (1x 10⁻⁵ M) Fe(II), mixing of Fe (II) + H₂O₂, and K₂S₂O₈ on the adsorption process of Carmoisine dye on TiO₂ surface at 30 min and 298.15 K. The maximum

removal of this dye obtains besides mixture from Fe(II) and H₂O₂ as Fenton reaction that attitudes to increase the activity for degradation of this dye and leads to an increase in the removal efficiency from 82.42 % to 86.91% at 30 min. while, the efficiency of removal for this dye depresses, when adding the other studied oxidant agents that attitude to increase the comparative of these oxidant agents on adsorption with dye.

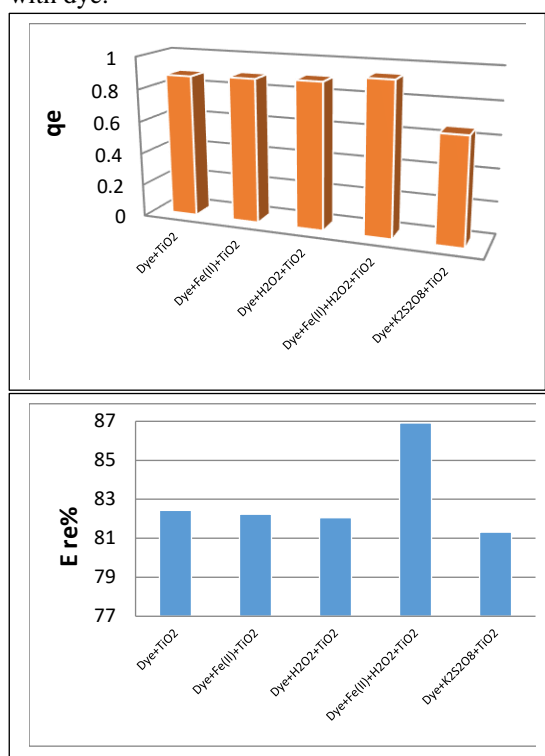


Fig. 2. Relation of (a) q_e and (b) E_{re} % for dark reaction in (Carmoisine dye / oxidant agents/ TiO₂) systems.

3.2. Effect of oxidant agents on photoreaction

The influence of addition for oxidant agent in the current light and TiO₂ on the photo decolorization of carmoisine dye is presented in **figure 3** (a and b). The rate of this photoreaction and the efficiency of carmoisine dye decolorization explain, the rise of rate and the E_{decolo} % of photodecolorization for this dye when addition mixture of (1x 10⁻⁵ M) H₂O₂ and (1x 10⁻⁵ M) Fe(II) as Fenton reaction and addition (1x 10⁻⁷ M) K₂S₂O₈ at 298.15 K and 30 min. The magnitude of E_{decolo} % of this dye for Fenton reaction from the increase from 24.46% to 42.85% and the addition of K₂S₂O₈ will increase of E_{decolo} % from 24.46% to 30.0 % . That due to the presence of K₂S₂O₈ and Fenton reaction in solution under the light will enhance the production of hydroxyl radicals that regarded as the power of photodecolorization parameter[28-30].

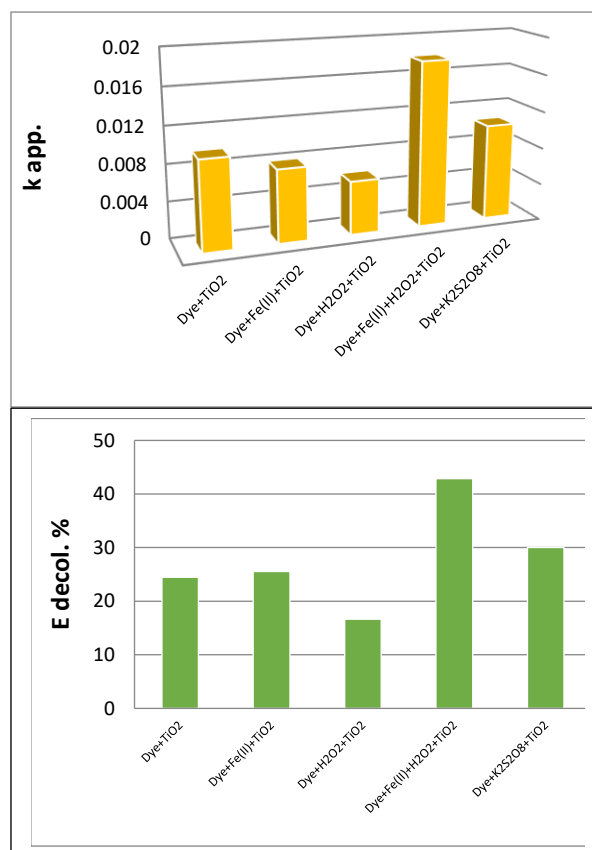
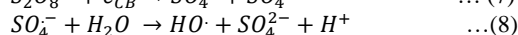
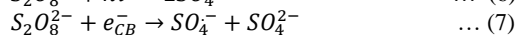
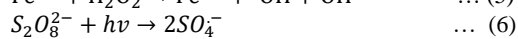
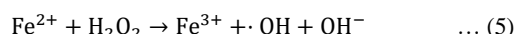
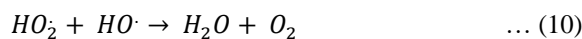
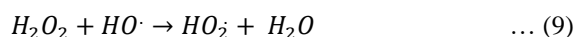


Fig. 3. Relation of (a) k_{app} and (b) $E_{decolorization}$ % for photo reaction in (Carmoisine dye / oxidant agents/ TiO₂) systems.

On the contrary, the addition of (1x 10⁻⁵ M) H₂O₂ and (1x 10⁻⁵ M) Fe(II) alone will decline these factors, that attitude to act them as a scavenger of hydroxyl radicals[21,31], according to the following equations below [21,32-34].



3.3. Effect of Temperature on dark Reaction without and with Fenton reaction

The temperature of the adsorption process is another important functional Physico-chemical parameter, and it is the adsorption capacity of the adsorbent differs considerably [35]. The results indicated that a decrease in adsorption capability resulted when the temperature was increased from (283.15 to 298.15)K using Fenton reaction. This trait suggested that the adsorption of Carmoisine dye was

exothermic. The sorption distribution coefficient (k_d) was calculated using equation 12 [19,36]. Meanwhile, the thermodynamics parameters such as a change in enthalpy ΔH° , change in Gibbs energy (ΔG°) and change in entropy ΔS° can be calculated by using equation 12, Gibbs equation (eq. 13), Van't Hoff equations (eq. 14) in the same ranged of temperatures [36-38].

$$k_d = \frac{C_{ads}}{C_e} \quad \dots(12)$$

$$\Delta G^\circ = -RT \ln k_d \quad \dots(13)$$

$$\ln k_d = \frac{-\Delta H^\circ}{RT} + \left(\frac{\Delta S^\circ}{R}\right) \quad \dots(14)$$

Here, C_{ads} is the amount (carmoisine dye) in the catalyst surface (TiO_2) at equilibrium (mg/L), C_e is the total dissolved residual dye in the solution at equilibrium (mg/L).

The results that calculated depending on **figure 4** demonstrate to the ΔH° values without and with the using Fenton reaction equal to (-3.806 kJ mol⁻¹) and (-4.842 kJ mol⁻¹) respectively, these values are less than 100 kJ mol⁻¹ [36], hence, this adsorption reaction for Carmoisine dye regards as physical adsorption and the negative value indicating to the natural reaction is exothermic. The addition of Fe(II) and H₂O₂ (as Fenton reaction) to the aqueous solution of carmoisine dye leads to depression in ΔH° values in the mentioned range of temperatures, which improves the adsorption process.

The negative ΔS° magnitudes without and with the using Fento reaction are -0.025 kJ mol⁻¹ and -0.0312 kJ mol⁻¹ respectively, the entropy for using Fenton reaction is less value and favor in adsorption reaction. The low values of entropies can be indicated to the associative adsorption mechanism has happened without a change in the internal structures of the catalyst (TiO_2) and strong binding of dye ions onto the active sites[39, 40]. Based on **figure 5**, The positive values of ΔG° without and with the using Fenton reaction are ranged to (3.518-3.830) kJ mol⁻¹ and (3.954- 4.691) kJ mol⁻¹ with the raising the temperature ensures the processes are exothermic, non-spontaneous[36,37].

At different temperatures, the activation energy (E_a) equation for the dark reaction[22,23] was calculated using equation 15.

$$E_a = \Delta H^\circ + RT \quad \dots(15)$$

At (283.15-298.15) K, the activation energies without and with the using Fenton reaction ranged from (-1.45 to -1.32) kJ mol⁻¹ and (-2.363 to -1.287)

kJ mol⁻¹ found to be less 4.2 kJ mol⁻¹, that attitude to obtain the sorption process[36]. Based on the range of activation energy for using Fenton reaction, the sorption reaction of carmoisine dye in the presence Fe(II) and H₂O₂ on TiO_2 surface is fast compared with than sorption reaction of carmoisine dye on TiO_2 surface without Fenton reaction.

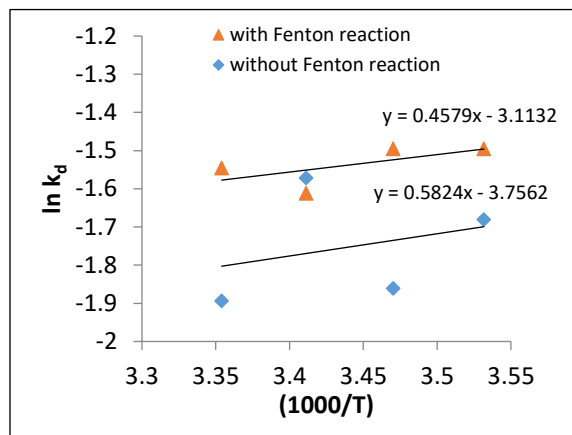


Fig. 4. The relation between $\ln k_d$ and $(1000/T)$ for adsorption of Carmoisine dye the Fenton reaction on TiO_2 surface.

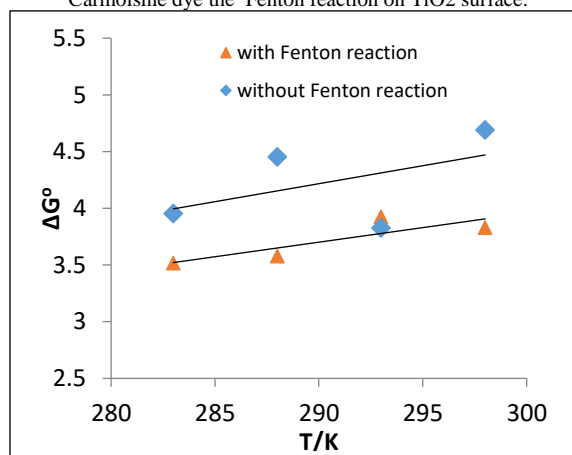


Fig. 5. Relation of Gibb's free energy change (ΔG°) versus temperature for an exothermic process of adsorption of Carmoisine dye on TiO_2 surface using Fenton reaction in temperature ranged (283.15-298.15) K.

3.4. Effect of Temperature on Photo Reaction without and with Fenton reaction

Under UV-A light, the influence of increased temperature in range (283.15- 298.15) K elevates the efficiency of photodecolorization of this dye in the presence of TiO_2 . The activation energy (E_a) and thermodynamic function (ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger) were determined using the Arrhenius equation (eq.16)[41,42], Eyring-Polanyi equation(eq. 17), and the Gibbs equation(eq. 18), respectively[43-48].

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \quad \dots(16)$$

$$\ln \left(\frac{k_{app}}{T} \right) = \frac{-\Delta H^\ddagger}{RT} + \left(\ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \right) \quad \dots(17)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad \dots(18)$$

Figures 6 and 7 Turn out, Arrhenius equation plot and Eyring equation plot for photodecolorization of Carmoisine dye from TiO₂ suspension solution without and with the using Fenton reaction (mixing from (1x10⁻⁵ M) Fe(III) + (1x 10⁻⁵ M) H₂O₂).

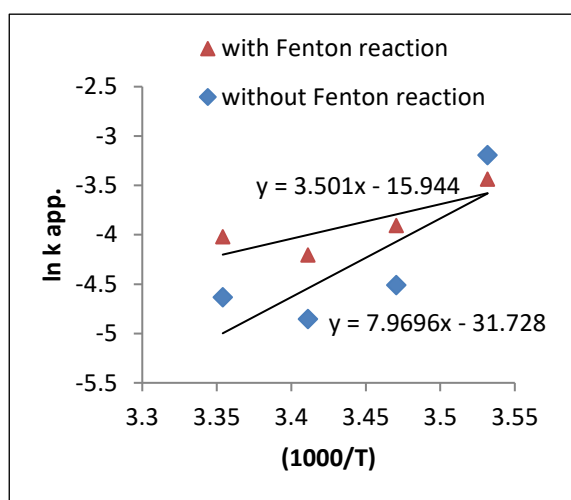


Fig. 6. Arrhenius equation plot for photodecolorization of Carmoisine dye on TiO₂ surface without and with the using Fenton reaction in temperature ranged (283.15-298.15) K.

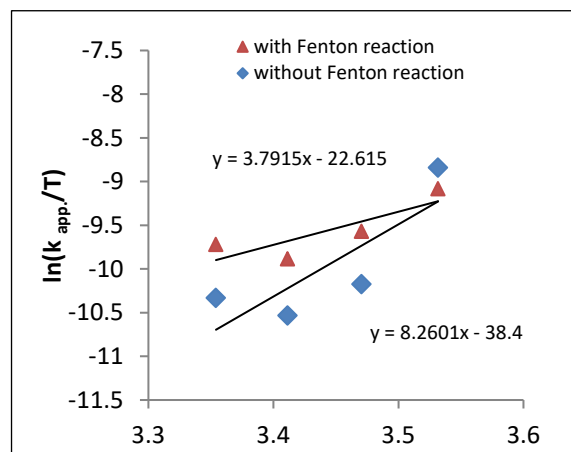
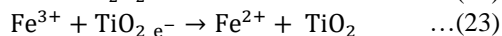
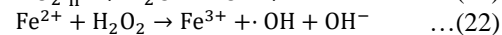
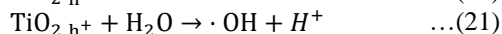
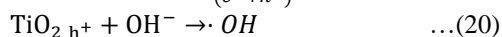
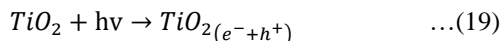


Fig. 7. Eyring equation plot for photodecolorization of Carmoisine dye on TiO₂ surface without and with the using Fenton reaction in temperature ranged (283.15-298.15) K.

Based on **figures 6 and 7 and Table 1**, the activation energy for photo reaction during without and with the addition of Fenton is found to be lower that refers to the reaction is fast in both cases. The enthalpies values refer to both reactions are exothermic, but the photo Fenton is favor

thermodynamically because the enthalpy with using photo Fenton reaction is more than values without Photo Fenton reaction, which enhances the generalization of hydroxyl radical, according to the following equation[49-52].



In both cases, The photoreaction for decolorization of this dye is exothermic (-ΔH[‡]), less random(-ΔS[‡]) and spontaneous (-ΔG[‡]). These results are in agreement with the reported in reference [53].

Table 1. The thermodynamic Parameters and activation energy for photodecolorization of Carmoisine dye on TiO₂ Surface without and with the using Photo Fenton reaction.

Studied Process	E _a kJ mol ⁻¹	ΔH [‡] kJ mol ⁻¹	ΔS [‡] J mol ⁻¹ K ⁻¹	ΔG [‡] _{283.15} kJ mol ⁻¹
Photoreaction of Carmoisine dye in TiO ₂ suspension solution	-66.259	-71.500	-7.480	-69.400
Photo Fenton reaction of Carmoisine dye in TiO ₂ suspension solution	-29.107	-31.522	-5.580	-29.900

3.5. Mechanism of photocatalytic decolorization of carmoisine dye.

This mechanism relies on three essential requirements suitable photocatalyst, source of light such as UV or Visible or solar, and colored solution like dye solution. when a source of light is filled on the suspension solution of TiO₂ with carmoisine dye, the h⁺ -e⁻ pairs will create on photocatalyst[54,55]. Series of redox sequence process will start and generate hydroxyl radicals HO· with reduction potential 2.8 V when hydroxyl ion reacts with photo hole in valance band of photocatalyst[56-60]. The other species can be generated by reacting environmental oxygen with the photoelectron on the conductive band such as superoxide radical O₂⁻ and then produces a peroxide radical HOO· the last species can be reacted with hydrogen ion in an aqueous solution and produces hydrogen peroxide. Hydrogen peroxide in the presence of light will split to double hydroxyl radicals ions[61-65]. The most acceptance mechanism for decolorization of carmoisine was suggested in figure 8[10].

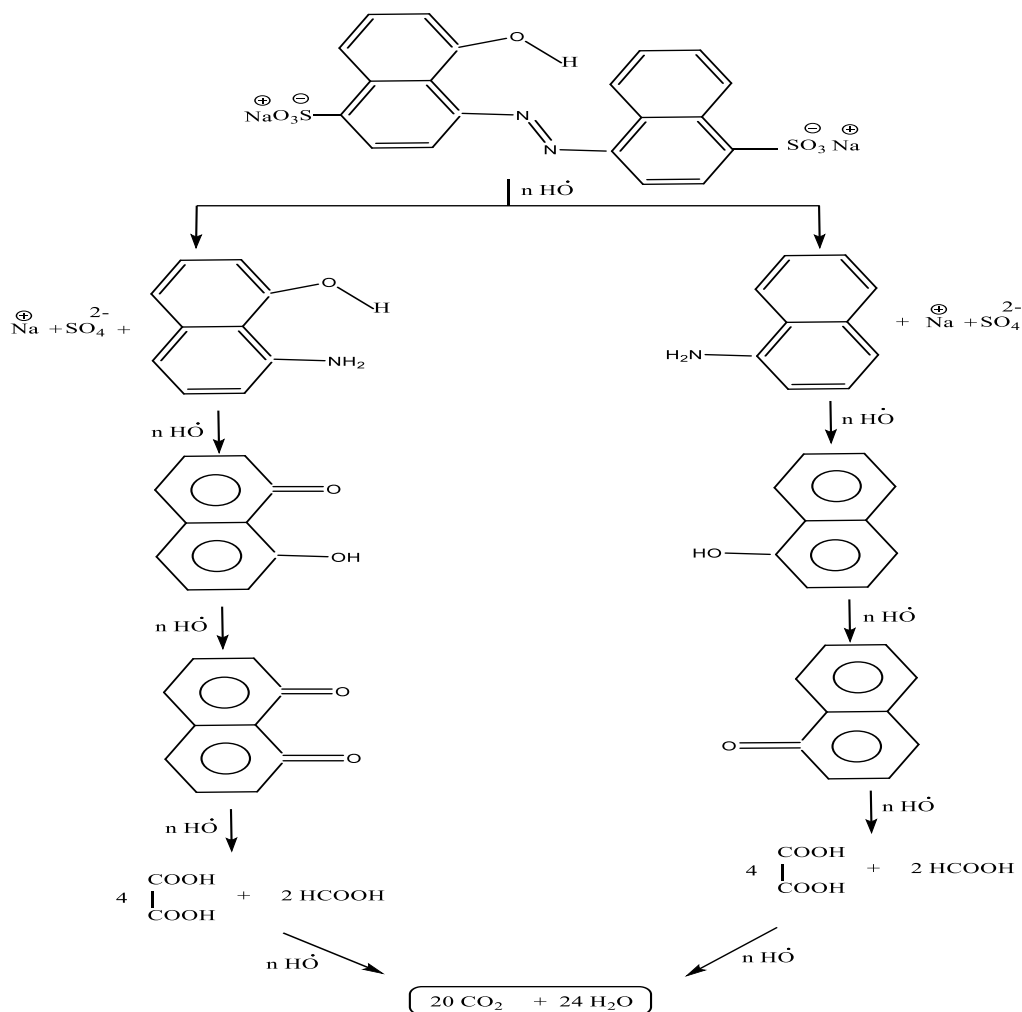


Fig. 8. Schematic of suggested mechanism of carmoisine dye photo decolorization in presence photocatalyst.

4. Conclusions

In this work, based on the results in dark and photoreaction, it can be observed that the adsorption of that Carmoisine dye on the rutile- TiO_2 surface is performed. The percentage and adsorption capacity of removal Carmoisine dye rise with depressing of the temperature at equilibrium time equal to 15 min. The Oxidant agents such as Fe(II) , H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, and mixing of $\text{Fe(II)} + \text{H}_2\text{O}_2$ was examined in dark and photoreaction and found the addition of mixing of $\text{Fe(II)} + \text{H}_2\text{O}_2$ as a Fenton reaction is elevated the removal and decolorization of this dye. Moreover, the addition of $\text{K}_2\text{S}_2\text{O}_8$ to carmoisine solution with TiO_2 under the light causes an increase in decolorization efficiency. The photoreaction of this dye is obeyed to pseudo-first-order kinetics. At a range of temperature from 283.15 to 298.15, the thermodynamics parameters were determined, and found the dark and photoreactions without and with the using the oxidant agent are exothermic, less random, and spontaneous.

5. Conflicts of interest

“There are no conflicts to declare”.

6. Formatting of funding sources

Self

7. Acknowledgments

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