

Photodecolourization of ponceau 4R by heterogeneous photocatalysis

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Abstract

The photodecolourization of ponceau 4R dye has been carried out using a combination of TiO_2 and UV irradiation ($\lambda = 254 \text{ nm}$) at a pH of 6. Dye decolourization was also assessed by adding low concentrations of inorganic oxidants, such as $\text{Na}_2\text{S}_2\text{O}_8$ (5×10^{-4} to $1.8 \times 10^{-2} \text{ M}$) and NaIO_4 (1×10^{-4} to $5 \times 10^{-4} \text{ M}$) to TiO_2 in the presence of UV radiation. It was observed that dye decolourization was enhanced using UV/ TiO_2 / $\text{Na}_2\text{S}_2\text{O}_8$ and UV/ TiO_2 / NaIO_4 catalytic systems over UV/ TiO_2 alone. First-order kinetics adequately described the disappearance of the dye. Reaction rate orders with respect to the oxidant species were 0.46, 0.58, and 1.55 for, respectively, TiO_2 , $\text{Na}_2\text{S}_2\text{O}_8$, and NaIO_4 . The most effective catalytic system for dye decolourization was found to be UV/ TiO_2 / NaIO_4 . The influence of dye concentration varying from 4×10^{-5} to $1 \times 10^{-4} \text{ M}$ on the degradation rate was studied. It can be seen that the degradation rate increases with the increase in dye concentration.

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1. Introduction

Textile dyeing generates large quantities of liquid effluents, and although there are increasing incentives to practice greater economy in the use of water through recycling schemes [1], most dye wastewaters are discharged into the environment. The most common dyes present in textile industry wastewater are the azo dyes [2]. Due to the stability of the modern dyes, biological treatment methods for textile effluents are ineffective [3–5]. In recent years, due to the non-toxic, insoluble, inexpensive, and highly reactive nature of TiO_2 under UV irradiation, the TiO_2 photocatalytic degradation technique has been used to oxidize wastewater containing dyes and has attracted much attention as an alternative to conventional methods [6].

This work investigates the decolourization of ponceau 4R in aqueous medium by different photocatalytic systems (UV/ TiO_2 , UV/ TiO_2 / $\text{Na}_2\text{S}_2\text{O}_8$, and UV/ TiO_2 / NaIO_4) in a slurry batch reactor. The effect of initial dye concentration on the degradation rate was also examined.

2. Experimental procedures

2.1. Reagents

Ponceau 4R (Fig. 1) was obtained from Fluka, whereas TiO_2 (Degussa P25) with average particle size of 30 nm and surface area of $50 \text{ m}^2 \text{ g}^{-1}$ was obtained from Aldrich. The other chemicals ($\text{Na}_2\text{S}_2\text{O}_8$, NaIO_4 , acid and alkali for pH adjustment) were purchased from Fisher.

2.2. Irradiation experiments

The photochemical reactor employed in this study consists of a 1000 ml cylindrical reservoir (Fig. 2). Irradiation was performed with a low pressure mercury vapour source with a UV output at 254 nm (43 W, Voltarc Tubes Inc., USA) located 10 cm from the surface of reservoir solution. The UV intensity at the centre point of the reservoir solution was measured using a UV radiometer (Model UVX, UV Products Ltd., Cambridge) equipped with a sensor with peak sensitivity at 254 nm was 4 mW cm^{-2} . Aqueous solution of dye ($1 \times 10^{-4} \text{ M}$) was prepared before each measurement. The initial working volume of the reactor was 1000 ml of the dye solution and TiO_2 (0.7, 1.5, or 3 g l^{-1}). The solution was stirred magnetically and the temperature was kept constant at $20 \pm 1 \text{ }^\circ\text{C}$. A stream of air was sparged

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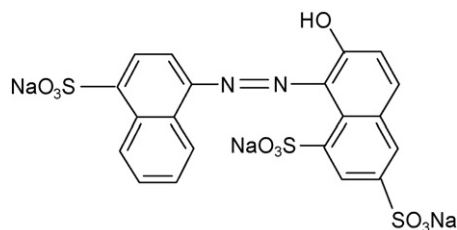


Fig. 1. Structure of ponceau 4R.

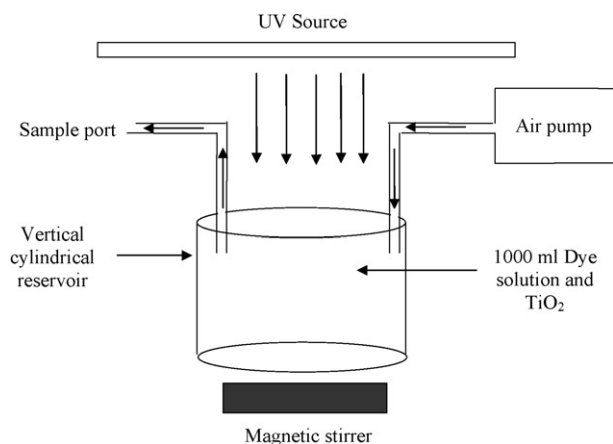


Fig. 2. Schematic diagram of the batch photoreactor.

into the reactor at a flow rate of 2800 ml min^{-1} during the reaction. The pH of the solution was 6 (the natural pH of the dye solution at the concentration employed here). The dye–catalyst mixture was irradiated immediately after addition of the catalyst to the dye solution to minimize the effect of dye adsorption on the catalyst surface, and to be sure that the decrease in absorbance is mostly due to dye degradation rather than adsorption on catalyst surface.

2.3. Analytical procedure

Analytical determination of the dye was carried out by measuring the absorbance decrease at a wavelength of 508 nm (the maximum absorbance of the dye) using UV–visible Spectrophotometer (1601 PC, Shimadzu). Aliquots of solution drawn from the reactor at different intervals of time were filtered through $0.2 \mu\text{m}$ polyethersulfone membrane to remove the catalyst (TiO_2).

3. Results and discussion

The decolourization of ponceau 4R was carried out by different catalytic systems using UV/ TiO_2 , UV/ $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$, and UV/ $\text{TiO}_2/\text{IO}_4^-$. The most effective system for decolourization of the dye will be assessed.

3.1. Effect of TiO_2 concentration

Irradiation of TiO_2 (0.7 g l^{-1}) with UV light of wavelength 254 nm resulted in decolourization of ponceau 4R dye. This can

be explained as follows: TiO_2 has a band gap of 3.2 eV, therefore TiO_2 is photoexcited by near-UV illumination ($\lambda \leq 380 \text{ nm}$). Excitation of TiO_2 with light of wavelength shorter than the band gap results in formation of electron–hole pairs as follows:



These electrons and holes may either recombine, releasing heat, or they may migrate to the surface of the semiconductor, where they can undergo redox reactions with molecules and ions on and near the surface [7].

The positively charged holes reaching the surface react within a few picoseconds with water or hydroxide ions to produce hydroxyl radicals, which are the primary oxidizing species due to their highly electrophilic character.

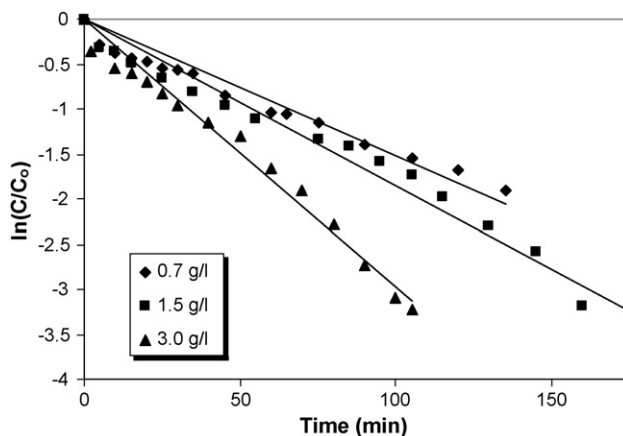


The hydroxyl radical reacts readily with surface adsorbed dye molecules, either by electron or hydrogen atom abstraction, forming organic radical cations, or by addition reactions to unsaturated bonds [8].

Since holes at the particle interface usually react faster than electrons, the particles under illumination contain an excess of electrons. Removal of these excess of electrons is necessary to complete the oxidation reaction, by preventing the recombination of electrons with holes. The most easily available and economic electron acceptor is molecular oxygen. Thus, in the presence of air or oxygen, the predominant reaction of electrons is that with O_2 as electron acceptor [9],



The effect of increasing TiO_2 from 0.7 to 3 g l^{-1} on the decolourization of the studied dye was investigated (Fig. 3). Plotting the experimental data in this form is diagnostic of the first-order kinetics. The lines shown in the figure were obtained using least squares linear regression techniques. Increasing the loading of TiO_2 from 0.7 to 3 g l^{-1} resulted in an increase in the rate of dye decolourization.

Fig. 3. First-order model for UV-induced decolourization of ponceau 4R in the presence of TiO_2 (g l^{-1}).

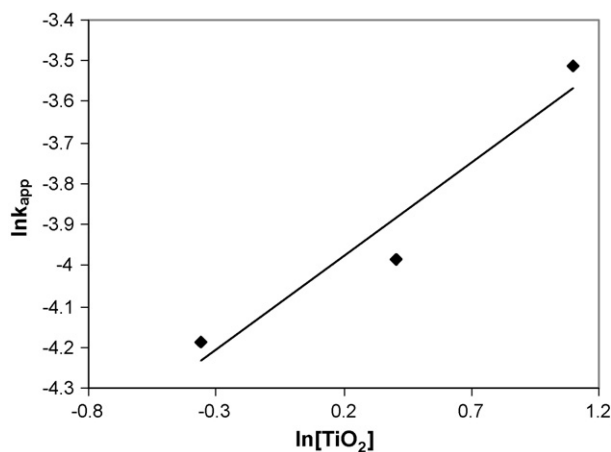


Fig. 4. The influence of TiO_2 concentration on the apparent first-order rate constant.

The results of analysis of the effects of TiO_2 concentration according to a power law model [10]:

$$k_{\text{app}} = k'[\text{TiO}_2]^n \quad (5)$$

where k_{app} is the apparent rate constant, k' the true rate constant, and n is an exponent shown in Fig. 4. The reaction order with respect to TiO_2 concentration is 0.46.

Increasing the concentration of TiO_2 from 0.7 to 3 g l^{-1} leads to an increase in the number of photons absorbed by TiO_2 from the UV source. Therefore, excitation of more electrons from the valance to the conduction band will be observed and the concentration of holes will be increased. Thus, increasing the number of hydroxyl radicals generated and the decolourization rate also will be enhanced [11–13].

3.2. Effect of addition of $\text{S}_2\text{O}_8^{2-}$ to TiO_2

In the irradiated aqueous TiO_2 suspensions, oxygen on TiO_2 surface provides a natural sink for the photogenerated electrons. OH radicals are then formed via the oxidation of TiO_2 surface-sorbed H_2O or hydroxyl ions by the surviving holes. The introduction of a more effective electron acceptor than oxygen might be beneficial [14–16].

Fig. 5 shows the effect of addition of persulfate to TiO_2 (0.7 g l^{-1}) on decolourization of ponceau 4R dye. It was found that addition of a low concentration of the persulfate ($5 \times 10^{-4} \text{ M}$) to TiO_2 (0.7 g l^{-1}) enhances the rate of decolourization over UV/ TiO_2 only.

The reaction rate order with respect to persulfate, obtained from Fig. 6, was found to be 0.58.

The persulfate anions can trap the photogenerated conduction band electrons of TiO_2 more than O_2 , and generate strong oxidizing $\text{SO}_4^{\bullet-}$ according to the following reaction [14]:



Sulfate radical anion is also generated at wavelength of 254 nm and can participate in reactions with the solvent, accord-

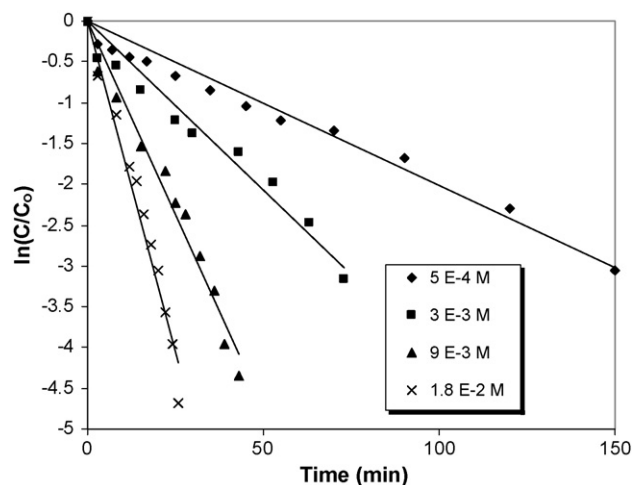
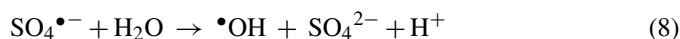


Fig. 5. First-order model for UV-induced decolourization of ponceau 4R in the presence of TiO_2 (0.7 g l^{-1}) and different concentrations of sodium persulfate (M).

ing to the following reactions [17–19]:



Sulfate radical does also react with H_2O_2 according to:



Thus, HO_2^{\bullet} generated can also participate in the photodegradation reaction.

3.3. Effect of addition of IO_4^- to TiO_2

The effect of addition of periodate to TiO_2 (0.7 g l^{-1}) for decolourization of the studied dye is shown in Fig. 7. It can be seen that addition of very low concentration of periodate ($1 \times 10^{-4} \text{ M}$) to TiO_2 (0.7 g l^{-1}) resulted in higher decolourization rate than UV/ TiO_2 and UV/ $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$. Also increasing the concentration of periodate to $5 \times 10^{-4} \text{ M}$ resulted in complete decolourization of the dye after about 8 min of UV irradiation, indicating the effectiveness of periodate over persulfate.

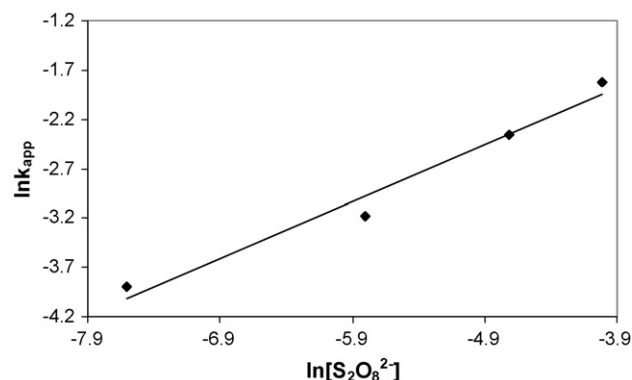


Fig. 6. The influence of sodium persulfate concentration on the apparent first-order rate constant.

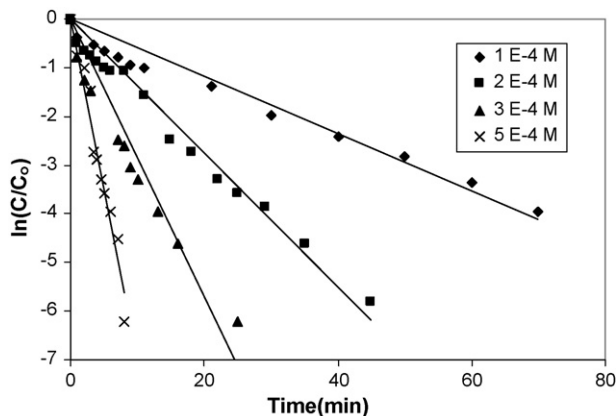
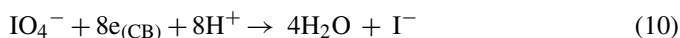


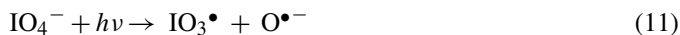
Fig. 7. First-order model for UV-induced decolorization of ponceau 4R in the presence of TiO_2 (0.7 g l^{-1}) and different concentrations of sodium periodate (M).

The reaction rate order with respect to periodate was found to be 1.55 (Fig. 8) higher than that for persulfate.

The enhancement of dye decolorization may be due to the scavenging of the photogenerated conduction band electrons of the excited TiO_2 which is more efficient than trapping with O_2 or $\text{S}_2\text{O}_8^{2-}$ as follows [14]:



Also, the photolytic decomposition of periodate under UV irradiation (254 nm) involves the formation of a number of highly reactive radical- and non-radical intermediates (IO_3^\bullet , $\bullet\text{OH}$, and IO_4^\bullet) as follows [20]:



This study has shown that the two oxidants, persulfate and periodate, enhance the rate of UV-induced decolorization of the azo dye ponceau 4R in the presence of TiO_2 . The rate of decolorization was greatest in the presence of periodate

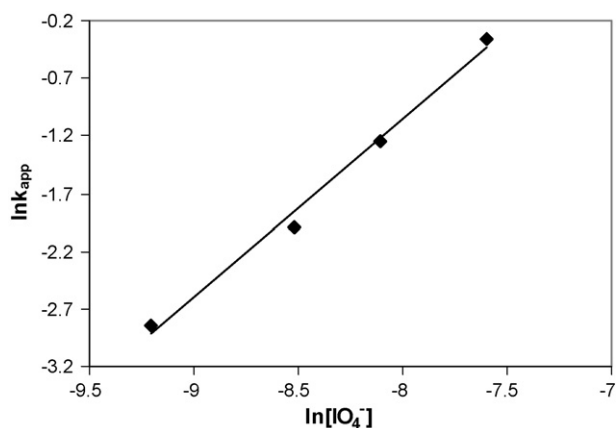


Fig. 8. The influence of sodium periodate concentration on the apparent first-order rate constant.

or persulfate and slowest for UV/ TiO_2 . The rate enhancing effects of these oxidants does not appear to have been studied previously with reference to ponceau 4R dye but studied for other organic dyes. Qamar et al. [21] found that the addition of peroxide or periodate enhanced the rate of breakdown of Chrysoidine R and Acid Red 29 dyes when irradiated with UV in the presence of TiO_2 . The reaction rate was found to follow the order: UV/ TiO_2 / $\text{S}_2\text{O}_8^{2-}$ > UV/ TiO_2 / H_2O_2 > UV/ TiO_2 . Similarly, Qamar et al. [22] reported enhanced rates of photocatalytic degradation of chromotrope 2B and amido black 10 B in the presence of H_2O_2 , KBrO_3 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The degradation rate was in the order UV/ TiO_2 / BrO_3^- > UV/ TiO_2 / $\text{S}_2\text{O}_8^{2-}$ > UV/ TiO_2 / H_2O_2 > UV/ TiO_2 . Qamar et al. [23] found a beneficial effect in adding H_2O_2 or KBrO_3 to UV irradiated suspensions of TiO_2 to degrade Chrysoidine Y azo dye compared to UV/ TiO_2 alone. Saquib and Muneer [24] studied the photocatalytic degradation of Acid Orange 8 dye in aqueous suspensions in the presence of inorganic oxidants (H_2O_2 or KBrO_3). The degradation rate of the dye was enhanced and H_2O_2 was found to be the more effective oxidant. Also Saquib and Muneer [25] found that the addition of H_2O_2 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ enhanced the degradation rate of gentian violet in the presence of UV and TiO_2 . They found that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ had a greater effect than H_2O_2 . Similarly, Augugliaro et al. [26] reported increased rates of photocatalytic degradation of Methyl Orange and Orange II dyes in the presence of H_2O_2 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The photocatalytic degradation of Remazol Brilliant Blue R dye under sunlight and artificial light source has been studied by Saquib and Muneer [27] in the presence of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, and KBrO_3 . It was found that all additives increase the degradation rate of the dye under sunlight, whereas under UV light $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 show a higher activity than that of H_2O_2 or TiO_2 . Sadik et al. [28] investigated the effect of H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$ addition on the decolorization of indophenol dye in the presence of ZnO photocatalyst. Addition of low concentration of H_2O_2 or $\text{Na}_2\text{S}_2\text{O}_8$ to ZnO irradiated with UV ($\lambda = 254 \text{ nm}$) resulted in an enhancement in the rate of dye decolorization compared to ZnO only. It was observed that UV/ZnO/ $\text{S}_2\text{O}_8^{2-}$ is the most effective catalytic system than that of UV/ZnO/ H_2O_2 or UV/ZnO. Also, the photodecolorization of neutral red dye by UV/ZnO, UV/ZnO/ $\text{S}_2\text{O}_8^{2-}$ and UV/ZnO/ IO_4^- systems was reported by Sadik et al. [6]. They found that the decolorization rate follows the order: UV/ZnO/ IO_4^- > UV/ZnO/ $\text{S}_2\text{O}_8^{2-}$ > UV/ZnO. Similarly, Wang and Hong [17] found that the addition of 10^{-2} M of KIO_4 , $\text{K}_2\text{S}_2\text{O}_8$, or H_2O_2 into the UV/ TiO_2 system with a TiO_2 concentration of 25 mg l^{-1} resulted in a much faster degradation rate of 2-chlorobiphenyl compared to that in the UV/ TiO_2 system. The most effective oxidant for the degradation is found to be KIO_4 .

The photocatalytic degradation in the previous studies was carried out for different types of organic dyes having different chemical structures and under different experimental conditions. In accordance with our results presented here for ponceau 4R, all the work studied in literatures shows that the UV/ TiO_2 / IO_4^- had a greater effect than UV/ TiO_2 / $\text{S}_2\text{O}_8^{2-}$ or UV/ TiO_2 in photodegradation of dyes. These results are in agreement with our results for photodecolorization of ponceau 4R.

Table 1
Effect of initial ponceau 4R concentration on the kinetic parameters

Initial dye concentration, C_0 (mol l ⁻¹)	Apparent rate constant, k_{app} (min ⁻¹)	Initial reaction rate, r_{in} (mol l ⁻¹ min ⁻¹) $r_{in} = k_{app} \times C_0$	$t_{1/2}$ (min)	$t_{1/2}^*$ (min)	k (mol l ⁻¹ min ⁻¹)	K (mol ⁻¹ l)
4×10^{-5}	11.87×10^{-2}	4.75×10^{-6}	5.84	4.72	6.71×10^{-6}	59346.6
5×10^{-5}	9.99×10^{-2}	5.0×10^{-6}	6.94	5.47		
8×10^{-5}	6.78×10^{-2}	5.42×10^{-6}	10.22	7.7		
1×10^{-4}	5.86×10^{-2}	5.86×10^{-6}	11.83	9.19		

$t_{1/2}$: experimental half-life time; $t_{1/2}^*$: theoretical half-life time; k : reactivity constant; K : Langmuir adsorption constant.

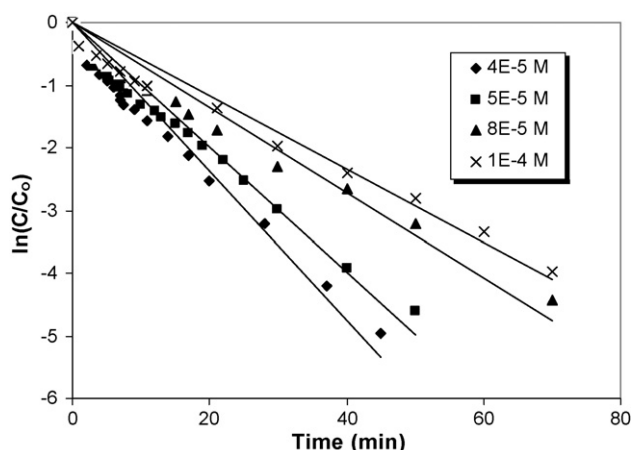


Fig. 9. Effect of initial ponceau 4R concentration (M) in the presence of TiO₂ (0.7 g l⁻¹) and IO₄⁻ (1 × 10⁻⁴ M).

3.4. Effect of initial dye concentration

As the effect of pollutant concentration is of importance in any process of water treatment, it is necessary to investigate the effect of initial concentration on the photocatalytic degradation of ponceau 4R, as shown in Fig. 9. The straight-line relationship of $\ln(C/C_0)$ versus irradiation time is obtained. This photodegradation follows a first-order expression up to an initial concentration of 1×10^{-4} M. The apparent first-order rate constant (k_{app}) decreased with the increasing of concentration of ponceau 4R when other parameters are kept constant, as shown in Table 1.

In heterogeneous media, the dependence of the rate of degradation on the concentration of the solutes often follows the Langmuir–Hinshelwood expression, with the initial rate ($R_{initial}$) being [29,30]:

$$\frac{1}{R_{initial}} = \frac{1}{k} + \frac{1}{Kk} \frac{1}{C_0} \quad (14)$$

where C_0 is the initial concentration of the substrate, K taken to represent the Langmuir adsorption constant, and k is a reactivity constant, providing a measure of the reactivity of the surface of the catalyst with the substrate. A linear expression can be conveniently obtained by plotting reciprocal initial rate against reciprocal initial concentration (Fig. 10). The linear transform of this expression yields $k = 6.71 \times 10^{-6}$ mol l⁻¹ min⁻¹ and $K = 59346.6$ mol⁻¹ l.

Fig. 11 shows the change of half-life time (min) with the initial ponceau 4R concentration. $t_{1/2}$ and $t_{1/2}^*$ represent the

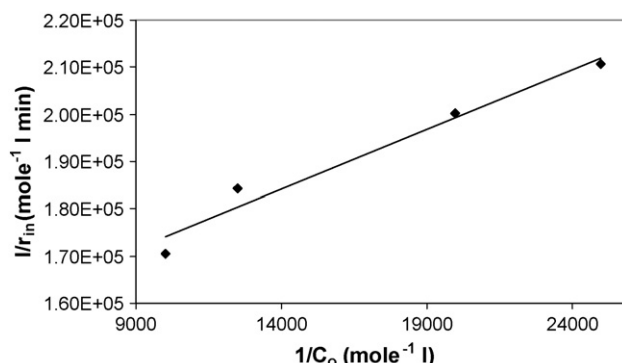


Fig. 10. Change of initial rate (r_{in}) with initial ponceau 4R concentrations using UV/TiO₂ (0.7 g l⁻¹) and IO₄⁻ (1 × 10⁻⁴ M).

experimental and theoretical half-life times, respectively.

$$t_{1/2} = \frac{0.693}{k_{app}} \quad (15)$$

$$t_{1/2}^* = \frac{0.5C_0}{k} + \frac{\ln 2}{kK} \quad (16)$$

It can be seen that at low initial dye concentration (4×10^{-5} M), the difference between $t_{1/2}$ and $t_{1/2}^*$ is small as shown from Table 1 ($t_{1/2} = 5.84$ min and $t_{1/2}^* = 4.72$ min). This may be explained as follows: at low dye concentration (4×10^{-5} M), the intermediate products concentration formed during the degradation of the parental dye is very low. They may compete with the dye molecules for the limited adsorp-

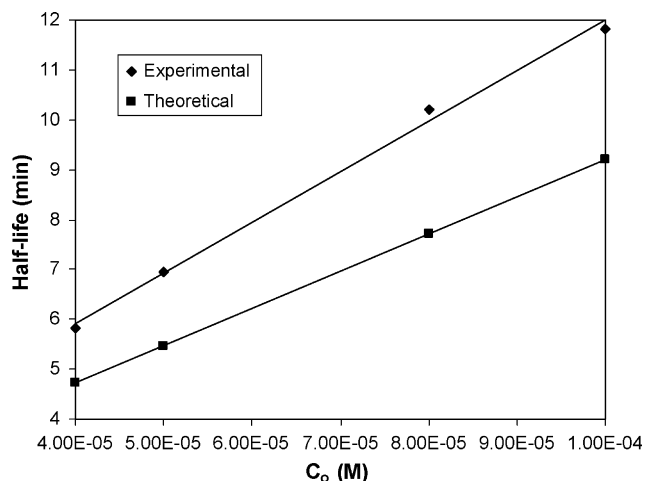


Fig. 11. Change of half-life (min) with initial ponceau 4R concentration using UV/TiO₂ (0.7 g l⁻¹) and IO₄⁻ (1 × 10⁻⁴ M).

tion and catalytic sites on the TiO₂ particles. This effect may be neglected as the intermediates concentration is very low, so $t_{1/2}$ increases a bit relative to $t_{1/2}^*$. However, the difference between $t_{1/2}$ and $t_{1/2}^*$ increases with increasing the initial dye concentrations (5×10^{-5} to 1×10^{-4} M) due to increasing the intermediates concentration and thus inhibit the dye degradation. Thus, $t_{1/2}$ will be increased compared to $t_{1/2}^*$ [31–34]. Another possible cause for such results is the UV-screening effect of the dye itself. At a high dye concentration, a low amount of UV may be absorbed by the TiO₂ particles and thus reduces the efficiency of the catalytic reaction [35]. Similar observations have also been reported for the degradation of other dyes and organic compounds [36–38].

4. Conclusions

Photodecolourization of ponceau 4R was carried out using Degussa P25 TiO₂ and ultraviolet (UV). The effect of addition of electron acceptor, such as Na₂S₂O₈ or NaIO₄, on the degradation kinetics of the dye compound was investigated as well. It was found that UV/TiO₂/Na₂S₂O₈ and UV/TiO₂/NaIO₄ systems were more effective than UV/TiO₂ system. The most effective system for the dye decolourization was UV/TiO₂/NaIO₄. It can be seen also that the photodecolourization follows a first-order kinetics and Langmuir–Hinshelwood behaviour.

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