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Ponceau 6R dye decoloration and chromate reduction simultaneously in acid medium



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Abstract The degradation efficiency and kinetic degradation reaction of Ponceau 6R dye using potassium chromate have been investigated under various experimental conditions: different concentrations of H₂SO₄ and temperatures. The immediate change of the red coloration ($\lambda_{\max} = 518$ nm) to colorless was observed after addition of inorganic oxidizing agent (K₂CrO₄) into the protonated form of Ponceau 6R dye after 48 h. This observation could be attributed to the highest oxidized form of this dye obtained (the quinoid one), which undergoes a hydrolysis reaction to produce *p*-hydroquinone (H₂Q) by a mechanism similar to Schiff-base hydrolysis. The cationic form of this matrix is a crucial feature for the hydrolysis process. A kinetic model for oxidation of Ponceau 6R by the combination of chromate was developed based on experimental results. The observed kinetic reaction coefficient was determined and correlated as a function of UV spectral intensity of Ponceau 6R at 518 nm. The degradation rate follows pseudo-first order kinetics with respect to dye concentration.

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1. Introduction

Chromate [Cr(VI)] and azo dyes are common pollutants which may co-exist in some industrial effluents (Ng et al., 2010).

Azo dyes constitute the largest class of dyes used in industry (Nam et al., 2001; Pandey et al., 2007). More than two thousand azo dyes are known and over half of the commercial dye-stuffs are azo dyes. Azo dyes are broadly used in the textile industry, and also widely employed to color solvents, inks, paints, varnishes, paper, plastic, rubber, foods, drugs, and cosmetics (Shu and Huang, 1995). Azo dyes are resistant to aerobic biodegradation, since the conventional treatment (e.g., activated sludge) of wastewater contaminated with these dyes could not remove most azo dyes effectively (Nam et al., 2001; Suzuki et al., 2001).

Ponceau 6R, or Crystal ponceau 6R, Crystal scarlet, Brilliant crystal scarlet 6R, Acid red 44, or C.I. 16250, is a red

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azo dye. It is soluble in water and slightly soluble in ethanol. It is used as a food dye, with E number E126. It is also used in histology, for staining fibrin with the MSB Trichrome stain. It usually comes as disodium salt.

Chromium is extensively used in electroplating, leather processing and dyeing industries. The major oxidation states of chromium, Cr(III) and Cr(VI), are drastically different in physicochemical properties and toxicity (Kotaš and Stasicka, 2000). Cr(VI) is highly toxic, mutagenic and carcinogenic (O'Brien et al., 2003). The United States Environmental Protection Agency (USEPA) has listed Cr(VI) as one of the 17 chemicals posing the greatest threat to humans (Cheung and Gu, 2007). As an oxidizing agent, Cr(VI) produces reactive oxygen species (ROS) during its reduction. ROSs can easily combine with DNA–protein complexes and affect normal physiological function (Cheung and Gu, 2007).

Compared with Cr(VI), Cr(III) is much less toxic as cell membrane is nearly impermeable to Cr(III) (O'Brien et al., 2003). The environmental importance of these species is derived from the difference in toxicity of the different valence states of chromium. Hexavalent chromium is highly soluble, remarkably toxic and is a suspected carcinogen and mutagen. Cr(III), in contrast, is readily precipitated at a certain pH and exhibits no toxicity, even being considered an essential element to human metabolism at controlled levels (Paschoal et al., 2009). In general, Cr(III) has only approximate 1/1000 the toxicity of Cr(VI). Cr(III) is also known to be a trace essential element for glucose and lipid metabolism in mammals (Kotaš and Stasicka, 2000; Gómez and Callao, 2006; Mohan and Pittman, 2006).

Several authors have indicated that the possibility to reduce Cr(VI) using semiconducting materials such as TiO₂ (Litter, 1999; Chenthamarakshan and Rajeshwar, 2000); ZnO (Domenech and Munoz, 1987; Khalil et al., 1998); WO₃ (Wang et al., 1992); among others. On the other hand, the application of photocatalytic methods for the oxidation of dyes in wastewater using TiO₂ and UV-irradiation is a well-known process (Reutergardh and Iangphasuk, 1997; Kiriakidou et al., 1999; Wang, 2000).

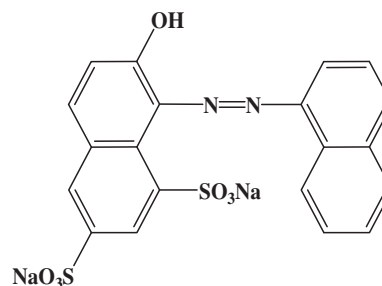
Since chromium ions and azo dyes are likely to be present together in industrial wastewaters, the investigation of the co-removal of Cr(VI) and azo dyes is urgently needed (Ng et al., 2010). While there are extensive studies on chromate reduction and azo dye decolorization/degradation, few studies have focused on the co-treatment of these two pollutants (Aksu et al., 2007; Kim et al., 2008; Aksu et al., 2009; Paschoal et al., 2009; Ng et al., 2010).

In the present study, deceleration (red color $\lambda = 518$ nm) immediately of the Ponceau 6R dye after addition of the inorganic oxidizing agent (K₂CrO₄) has been proposed.

2. Experimental

2.1. Materials

Ponceau 6R, Molecular Formula = C₂₀H₁₂N₂O₇S₂Na₂, Molecular Weight = 502.446, $\lambda_{\max} = 518 \pm 2$ nm, Class = Azo Dye, C.I. number 16250, C.I. name Acid red 44, having structure (Scheme 1) was purchased from Aldrich. All other chemicals used throughout this study were of analytical reagent grade of the highest commercial pure reagents. All glassware were washed with nitric acid (1:1) before being used.



Scheme 1 Structure of Ponceau 6R dye.

2.2. Instrumentation

The absorption spectra were recorded on a Perkin-Elmer Lambda 35, (scan speed 8 nm s⁻¹). The absorption spectra were taken over the wavelength range 200–1100 nm. A Heto temperature (type HAAKe C 10) was used for the accelerated kinetic studies.

2.3. Procedure

Ten milliliters of a solution containing H₂SO₄ (500 mmol was placed in the calibrated flask. The background spectrogram of this solution was recorded. A known concentration of the analyte (Ponceau 6R and K₂CrO₄) was added to the same cell by means of a micropipette (Voa Co., UK). The absorption spectra were recorded against the reagent blank. All absorption spectra in this study are those obtained after the base line correction for the blank reagent. A reagent blank was prepared in similar manner without analyte. All measurements were carried out at room temperature (24 ± 1 °C), except for temperature dependence studies.

2.4. Kinetic measurements

Generally, when reaction mechanisms are unknown, the rate law describing a particular chemical reaction can be deduced from experimentally measured time-concentration data for one or all of the reactants (Levenspiel, 1972; Grasso and Weber, 1989).

All kinetic measurements were carried out with respective Ponceau 6R concentrations at least 10 μmol fold in excess of the chromate concentration (100 μmol) at temperatures of 298, 308 K, and different concentrations of sulfuric acid.

3. Results and discussion

3.1. Degradation and reduction reaction

Fig. 1 shows that the addition of oxidant (K₂CrO₄) into Ponceau 6R (100 μmol). The immediate change of the red coloration ($\lambda_{\max} = 518$ nm) to colorless was observed after addition of inorganic oxidizing agent (K₂CrO₄) into the protonated form of Ponceau 6R dye after 48 h. This observation could be attributed to the highest oxidized form of this dye obtained (the quinoid one), which undergoes a hydrolysis reaction to produce *p*-hydroquinone (H₂Q) by a mechanism similar to Schiff-base hydrolysis (Ahmed, 2008). The cationic form of this matrix is a crucial feature for the hydrolysis process.

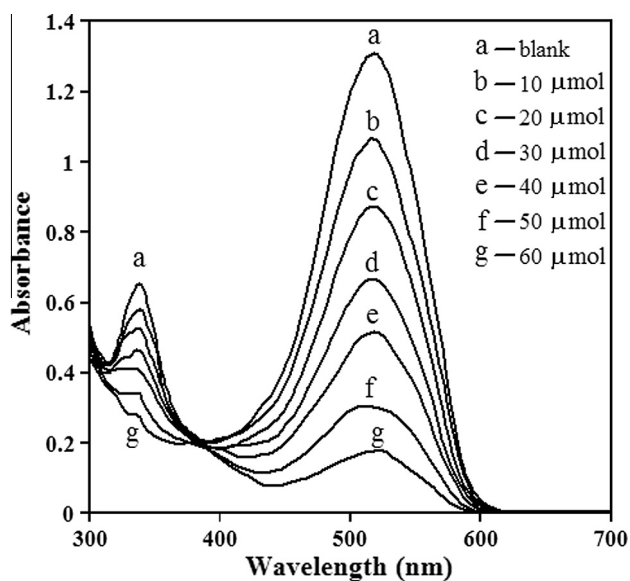


Figure 1 UV-Vis spectral of Ponceau 6R dye with different concentration of chromate oxidant.

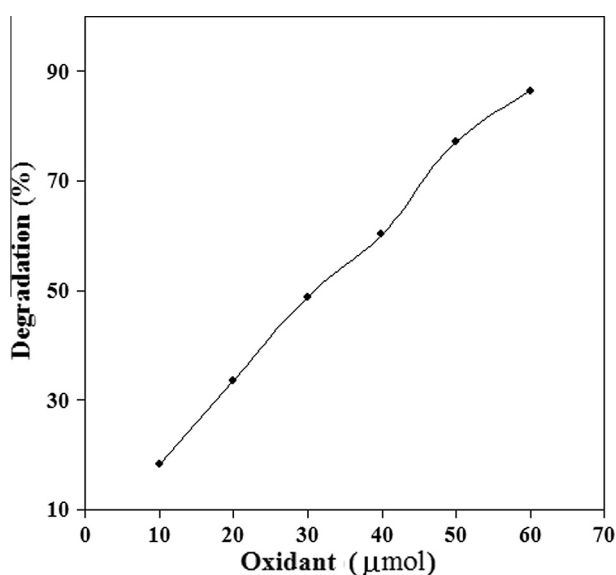


Figure 2 Relation between the degradation efficiency of reducer (Ponceau 6R) and oxidant (K_2CrO_4) concentration.

The decreases in absorbance at $\lambda_{max} = 518$ nm (red coloration) with increasing the concentration of the oxidant (K_2CrO_4) at constant concentration of the dye was analyzed using a linear-regression program (Ahmed, 2008) according the following equation:

$$A_{(\text{reducer})} = a + bC_{(\text{oxidant/mol})} \quad (1)$$

Where A , C are the absorbance of Ponceau 6R (reducer) and concentration of the potassium chromate (oxidant), and a , b are the intercept and slope, respectively, of the straight line of the calibration plot. The lower limit of detection of the oxidant, Cr(VI), is as low as 5.20 ppm (mg/L), suggesting the pos-

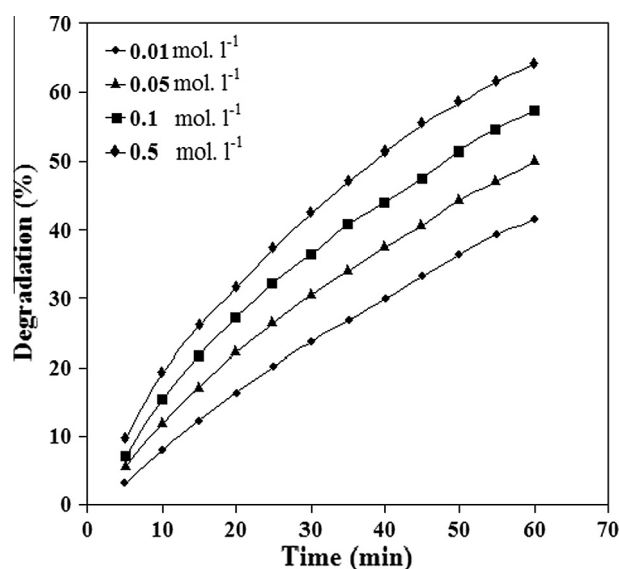


Figure 3 Degradation efficiencies of Ponceau 6R with potassium chromate in different concentrations of H_2SO_4 at 25 °C.

sible application of this procedure for determination of Cr(VI) in real sample, without any pretreatment such as analyte separation and/or preconcentration. The slope of the calibration plot in this calculation is due to the hydrolysis constant ($K_h = 1.946 \times 10^4 \text{ mol}^{-1} \text{ L}$) of this dye.

3.2. Degradation of dye efficiency

The percentage of Ponceau 6R dye degradation was calculated using the following equation:

$$\text{Degradation}(\%) = \frac{A_o - A_t}{A_o} \times 100 \quad (2)$$

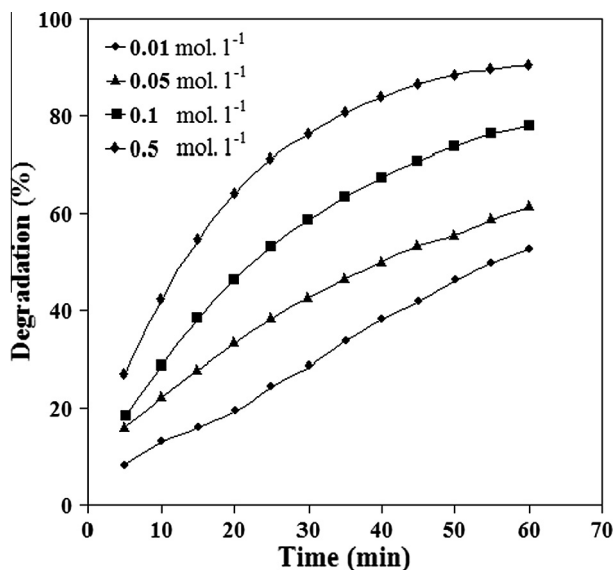


Figure 4 Degradation efficiencies of ponceau 6R with potassium chromate in different concentrations of H_2SO_4 at 35 °C.

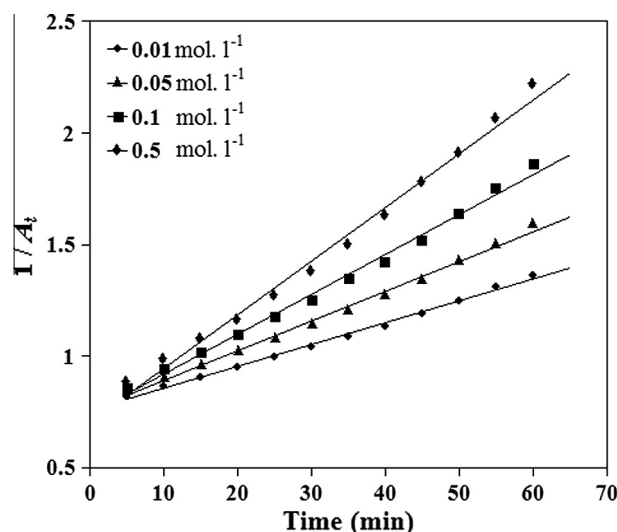


Figure 6 Pseudo-second order curve of degradation of Ponceau 6R with potassium chromate in different concentrations of H_2SO_4 at 25 °C.

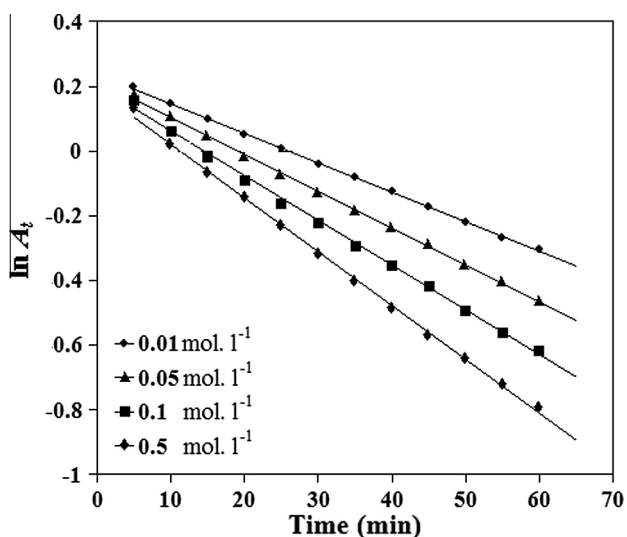


Figure 5 Pseudo-first order curve of degradation of Ponceau 6R with potassium chromate in different concentration of H_2SO_4 at 25 °C.

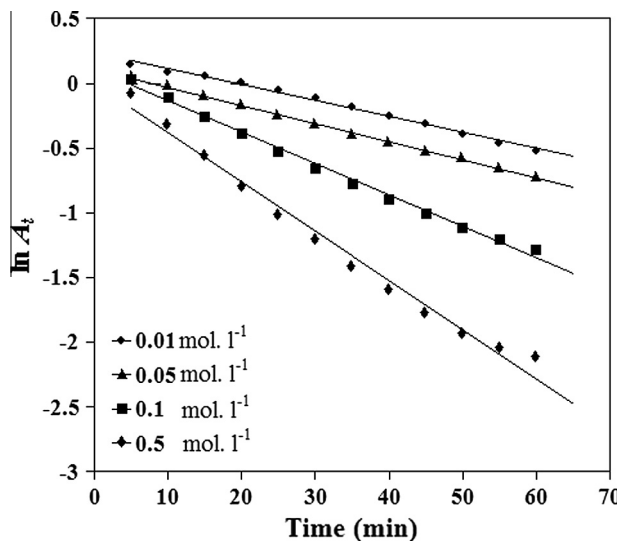


Figure 7 Pseudo-first order curve of degradation of Ponceau 6R with potassium chromate in different concentration of H_2SO_4 at 35 °C.

where A_o is the initial absorbance of dye before the reaction, and A_t is the absorbance of dye after beginning the reaction.

Increase in the dosage of potassium chromate from 10 to 60 μmol has a pronounced effect on the degradation efficiency of Ponceau 6R (Fig. 2). The decolorization efficiency reached nearly 90% at higher concentration of potassium chromate.

Figs. 3 and 4 show the variation in the percentage oxidation of Ponceau 6R as a function of contact time with different concentration of sulfuric acid at temperatures 298 and 308 K. It is observed that in all cases the percentage oxidation is comparatively increasing with contact time. On other hand, with increasing of acid concentrations the oxidation efficiencies were increased.

3.3. Degradation kinetic studies

Degradation kinetics is the important physicochemical studies for the evaluation of the basic traits of a good oxidation and reduction rates. The kinetics of decoloration processes was summarized and presented in Figs. 5–8.

The rate constants were calculated by using pseudo-first order and pseudo-second order kinetic models. The first order expression is given as

$$\ln A_t = \ln A_o - k_1 t \tag{3}$$

where A_o is the initial absorbance of Ponceau 6R dye before beginning the oxidation process (without oxidant), A_t the absorbance of dye after oxidation at any given time t , and k_1

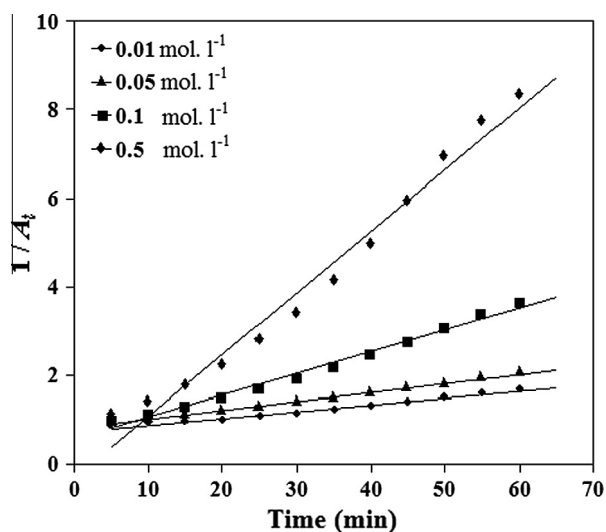


Figure 8 Pseudo-second order curve of degradation of Ponceau 6R with potassium chromate in different concentration of H_2SO_4 at 35°C .

is the rate constant. The values of k_1 were calculated from slope of the linear plot of $\ln A_t$ versus t (Figs. 5 and 7).

The pseudo-second-order kinetic rate equation is given as

$$\frac{1}{A_t} = \frac{1}{A_o} + k_2 t \quad (4)$$

where k_2 is the rate constant of pseudo-second order reaction. The values of k_2 were calculated from the slope of the linear plots of $1/A_t$ versus t (Figs. 6 and 8).

The results of the kinetics parameters for oxidation of ponceau 6R dye at various concentrations of sulfuric acid and temperatures, calculated from the linear plots of pseudo-first order and pseudo-second order kinetics models are presented in Table 1. Pseudo-first order model provides better correlation than pseudo-second order model. The low correlation coefficient values obtained for the pseudo-second order model indicates that oxidation of dye did not follow the pseudo-second order reaction. The insufficiency of the pseudo-second order model to fit the kinetics data could possibly be due to the limitations of dye concentration controlling the reaction process. The experimental data were observed to fit well to the pseudo-first order equation. The correlation coefficients (r^2) for the linear plots of $\ln A_t$ against t for the pseudo-first order equation were larger than pseudo-second order at all concentrations of acid and temperatures.

3.4. Thermodynamic activation parameters of oxidation reaction

Thermodynamic activation parameters were calculated from the results of the rate constants of pseudo-first order as a function of the reciprocal of the temperature in Kelvin. The activation energy of the reaction of Ponceau 6R with chromate was calculated by measuring the reaction rate at two different temperatures. Rate data as a function of temperature, fit to point-slope form of Arrhenius equation, will yield an estimate of the activation energy.

$$\frac{\ln k_{308}}{\ln k_{298}} = \frac{-E_a}{R} \left(\frac{1}{T_{308}} - \frac{1}{T_{298}} \right) \quad (5)$$

Where, k_{298} , k_{308} are the rate constants of the oxidation reaction at two different temperatures $T_{298} = 298\text{ K}$ and

Table 1 Kinetic degradation parameters of Ponceau 6R dye.

Temp. (K)	Acid conc. (M)	Pseudo-first order			Pseudo-second order		
		k_1	r^2	$t_{1/2}$ (min)	k_2	r^2	$t_{1/2}$ (min)
298	0.01	0.009	0.9995	75.8	0.010	0.9964	81.4
	0.05	0.010	0.9991	61.0	0.013	0.9951	59.4
	0.10	0.014	0.9980	50.2	0.018	0.9936	44.4
	0.50	0.017	0.9985	41.6	0.024	0.9913	32.9
308	0.01	0.012	0.9922	56.2	0.015	0.9723	53.2
	0.05	0.014	0.9980	49.1	0.020	0.9946	39.4
	0.10	0.024	0.9946	28.6	0.049	0.9889	16.2
	0.50	0.038	0.9861	18.2	0.139	0.9765	5.7

Table 2 Thermodynamic degradation parameters of Ponceau 6R dye.

Temp. (K)	Acid conc. (M)	E_a (kJ/mol)	ΔH^\ddagger (kJ/mol)	$-\Delta S^\ddagger$ (J/mol)	ΔG^\ddagger (kJ/mol)
298	0.01	22.0	19.5	219	84.7
	0.05	25.7	23.2	205	84.4
	0.10	41.1	38.7	151	83.6
	0.50	61.4	58.9	81	83.1
308	0.01	22.0	19.4	219	86.8
	0.05	25.7	23.1	206	86.4
	0.10	41.1	38.6	151	85.1
	0.50	61.4	58.8	81	83.9

$T_{308} = 308$ K, respectively, $R = 8.314$ J/K mol, and E_a is the activation energy.

The other thermodynamic activation parameters were calculated as follows; the enthalpy of activation (ΔH^*) was calculated from the activation energy using the equation:

$$\Delta H^* = E_a - RT \quad (6)$$

The entropy of activation (ΔS^*) in each reaction was then evaluated as follows:

$$k = \frac{KT}{h} \cdot e^{\frac{\Delta S^*}{R}} \cdot e^{\frac{-\Delta H^*}{RT}} \quad (7)$$

Where k is the rate constant, K Boltzmann constant, and h Planck's constant. The value of ΔG^* has been calculated at 298 and 308 K from the relation;

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

The values of the activation parameter are recorded in Table 2. The negative value of entropies of activation (ΔS^*) indicate that the reaction occurs between ions of similar charge (Shukla and Kesaryani, 1984).

4. Conclusion

The decoloration and kinetic degradation reaction of Ponceau 6R dye using potassium chromate have been studied. The immediate change of the red coloration ($\lambda_{\max} = 518$ nm) to colorless was observed after addition of inorganic oxidizing agent (K_2CrO_4) into the protonated form of Ponceau 6R dye after 48 h. This observation could be attributed to the highest oxidized form of this dye obtained (the quinoid one), which undergoes a hydrolysis reaction to produce *p*-hydroquinone (H_2Q) by a mechanism similar to Schiff-base hydrolysis. The cationic form of this matrix is a crucial feature for the hydrolysis process.

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