

Comparison of UV/H₂O₂ and UV/S₂O₈²⁻ processes for the decoloration of azo dyes Congo Red in various kinds of water.

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The wastewater from textile industries containing non-biodegradable and toxic dye compounds is an important source of environmental contamination. This study aims at investigating the decoloration of Congo Red (C.I name.Direct Red 28, C.I. DR28) dye in aqueous solution by the UV/H₂O₂ and UV/S₂O₈²⁻ processes. Congo Red dye was dissolved in various kinds of water such as distilled water, drinking water and river water. Aqueous Congo Red dye solutions were irradiated with low-pressure mercury vapour lamp emitting at 254 nm in a batch photoreactor. The efficiency of the decoloration was monitored by measuring the absorbance change as a function of irradiation time using UV-visible spectroscopic analysis.

Results showed that an almost complete decoloration of dyes (90%) in distilled water in UV/H₂O₂ process was possible to achieve after 90 min of irradiation. In drinking water and in river water the maximum colour removal efficiency of Congo Red, was only 61.0% and 50.5% respectively, after 90min of irradiation. The using of UV/S₂O₈²⁻ process, enhanced considerably the colour removal, the efficiencies being 92.8%, 88.0% , 80.1% in distilled water, in drinking water and in river water respectively, only after 60 min of irradiation.

Keywords: Congo Red, azo dyes, decoloration, photodecomposition, hydrogen peroxide, persulfate

Introduction

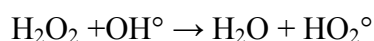
The textile and dyestuff industries are the primary sources of the release of dyes into the environment. Approximately 10000 different dyestuffs are used in textile industry [1], and among them azo dyes is used over 50% of all dyes. Azo dyes, which contain one or more azo bonds, are among the most widely used synthetic dyes and usually are major pollutants in dye wastewaters [2]. Due to the presence of large degree of aromatics in these dyes and their stability, conventional treatment methods such as coagulation/flocculation, activated carbon adsorption or membrane techniques are ineffective for decoloration and degradation, because these methods can only transfer the contaminants from one phase to another, leaving the final environmental problem unsolved [3].

During the last decades, many investigators have demonstrated that non-biodegradable and refractory organic compounds including azo dye can be mineralized successfully and completely by the advanced oxidation processes (AOP). Among this technique, sonolysis, sonocatalytic approach [3,4], photocatalytic process [5,6], radiolysis process [7] are the most used. The use of ultraviolet radiation (UV) in the presence of hydrogen peroxide (H₂O₂) is also a very promising technique [8]. Mercury lamps emitting at 254 nm are the most commonly used in order to dissociate H₂O₂ into hydroxyl radicals which are very powerful oxidizing species. The hydroxyl radical is formed by the homolytic splitting of the H₂O₂ oxygen–oxygen bonds by UV light of wavelength low 300nm [9].



Many research have reported the complete decoloration and mineralization of dyes by UV/H₂O₂ process [10-14].

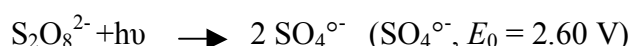
Galindo and Kalt demonstrated also that the UV/H₂O₂ process is able to destroy totally the chromophore structure of azo dyes. The reaction rate of azo dyes depends on the basic structure of the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of dyes. Numerous researchers show that the decoloration efficiency of dyes depends on the operational parameters [1,15,16]. The decoloration efficiency increases as the initial concentration of H₂O₂ and light intensity are increased but it decreases when the initial concentration of dyes is increased. However, at high concentrations of H₂O₂ the increase in dye decoloration started decreasing. This is because of the reason that at high concentrations, the solution undergoes self quenching of OH° radicals by added amounts of H₂O₂ to produce HO₂° radicals.



The existences of a scavenger of OH° radicals have also an effect in the decoloration efficiency [17].

The persulfate also could be a good candidate for the photochemical oxidation technique. Persulfate (S₂O₈²⁻) is a strong oxidant ($E_0 = 2.05 \text{ V}$) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator in the petrochemical industry [18]. The persulfate is normally available as a salt associated with ammonium, sodium, or potassium. It has also been reported to be effective for degrading organics in hazardous wastewaters in acidic or basic media through direct chemical oxidation (DCO), where persulfate is used as a sacrificial reagent [19,20]. The thermal or photochemical activated decomposition of S₂O₈²⁻ ion to SO₄^{°-} radical has been proposed as a method to accelerate the process because the reactions of persulfate are generally slow at normal temperature [20].

Photolysis of S₂O₈²⁻ produces sulphate radical anions SO₄^{°-} with 100% photochemical efficiency, yielding SO₄^{°-} as summarized in the following reactions [21]:



The quantum yield of SO₄^{°-} formation varies according to literature. Its values extend from 0.5 to 1.4. Criquet et al estimated this value to 0.52 [22]. SO₄^{°-} are highly reactive and selective oxidizing species, and are able to initiate the oxidation and mineralization of organic substrates [23]. Similar to hydroxyl radicals, sulphate radicals may react with organics by electron transfer, hydrogen abstraction, or addition mechanisms [24].

Kamel et al investigated the influence of parameters in the two systems UV/H₂O₂ and UV/S₂O₈²⁻ for the decoloration of congo red such as the effects of the initial concentration of H₂O₂ and S₂O₈²⁻, the initial concentration of dye, the light intensity [25].

In this work, the decoloration of congo red by H₂O₂ photochemically assisted and S₂O₈²⁻ photochemically assisted in various kinds of water has been studied. The congo red is one of the most common reactive azo dye used in textile industry [26].

The main objective of this work is to compare the effectiveness of UV/H₂O₂ and UV/S₂O₈²⁻ process for the decoloration of azo dyes in the different kinds of water. The study is based on monitoring reduction in the solution absorbance at the wavelength that corresponds to the maximum absorbance of the sample.

Materials and experimental methods

Congo red, which is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid ($C_{32}H_{22}N_6Na_2O_6S_2$) named commercially C.I. Acid Red 28, was obtained from LABOSI (its purity was 99%) and was used without further purification. The characteristics of the dye are as follows.

Colour index 22120, $M_w = 696.68 \text{ g mol}^{-1}$, $\lambda_{\max} = 500 \text{ nm}$ and the structure:

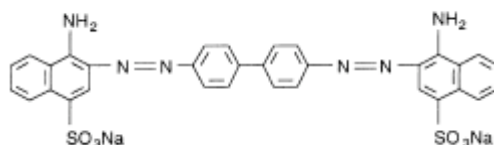


Fig.1 Chemical structure of congo red

Hydrogen peroxide (30% w/w) was obtained from CARLO ERBA and the sodium persulfate from Sigma-Aldrick $98\% M = 238.1 \text{ g mol}^{-1}$. The optical absorption spectrum of dye was recorded on a 190 DEL SAFAS UV-VIS spectrophotometer. All of the experiments were performed with a low-pressure mercury lamp, encased in a quartz tube, which emitted monochromatic radiation at 254nm the equivalent in energy ($E = 472.4 \text{ kJ E}^{-1}$). The intensity given by photon flux was $9.2 \cdot 10^{-6} \text{ Einstein s}^{-1}$. This intensity was determined by means of the chemical actinometer hydrogen peroxide. The low-pressure mercury UV lamp was inserted directly into a well-stirred batch reactor made of borosilicate with a total volume of 5l. The outside of the reactor was covered with an aluminium sheet.

Hydrogen peroxide was determined by the $TiCl_4$ colorimetric method [27] and persulfate concentration was determined by absorption spectrophotometry at 610nm of discoloration of alcian blue [28].

The photolysis experiments were performed using a 5 l solution containing the congo red. The initial concentration of congo red was 0.02mM. Samples were withdrawn from a sample point at certain time intervals and analyzed for decoloration of congo red. Decoloration of dye solutions was checked and controlled by measuring the absorbance of dye solutions at different intervals using a UV-vis 190 Del Safas Spectrophotometer. The maximum values of absorbance of the dye were at 340nm and 500nm. The variation of pH of the sample before and after the irradiation was measured with a pH-meter Takusel. For the buffer solution, the pH of the dye solutions was fixed with phosphate buffer with ionic strength of $5 \cdot 10^{-3} \text{ M l}^{-1}$ and pH of 7.2.

Various kinds of water such as distilled water, drinking water and river water were used to prepare the dyes solution with the concentration of 0.02mM. The initial concentration of hydrogen peroxide and persulfate in the dyes solution are 1mM.

The degree of decoloration, i.e. the removal degree of colour at the λ_{\max} of the sample (500 nm) was calculated with the relation

$$DD(\%) = \frac{A_0 - A_t}{A_0}$$

where A_0 is the initial absorbance of the wastewater sample and A_t the absorbance at time t of the photodegradation.

Fig. 2 shows the absorption spectra of the sample, $0.02 \cdot 10^{-3} \text{ M}$ of dyes. The absorption spectrum of the sample is characterised by two main bands, one in the visible range

($\lambda_{\text{max}} = 500 \text{ nm}$) responsible for the red colour and other in the UV region ($\lambda_{\text{max}} = 340 \text{ nm}$). The 500 nm bands arise from chromophore structure ($-\text{N}=\text{N}-$) of azo dyes whereas the 340nm bands are characteristics of the naphthalene ring of the dyes which absorption wavelength is higher than of benzene ring [29]. The ionic strength has an effect on the absorbance of the sample [30]

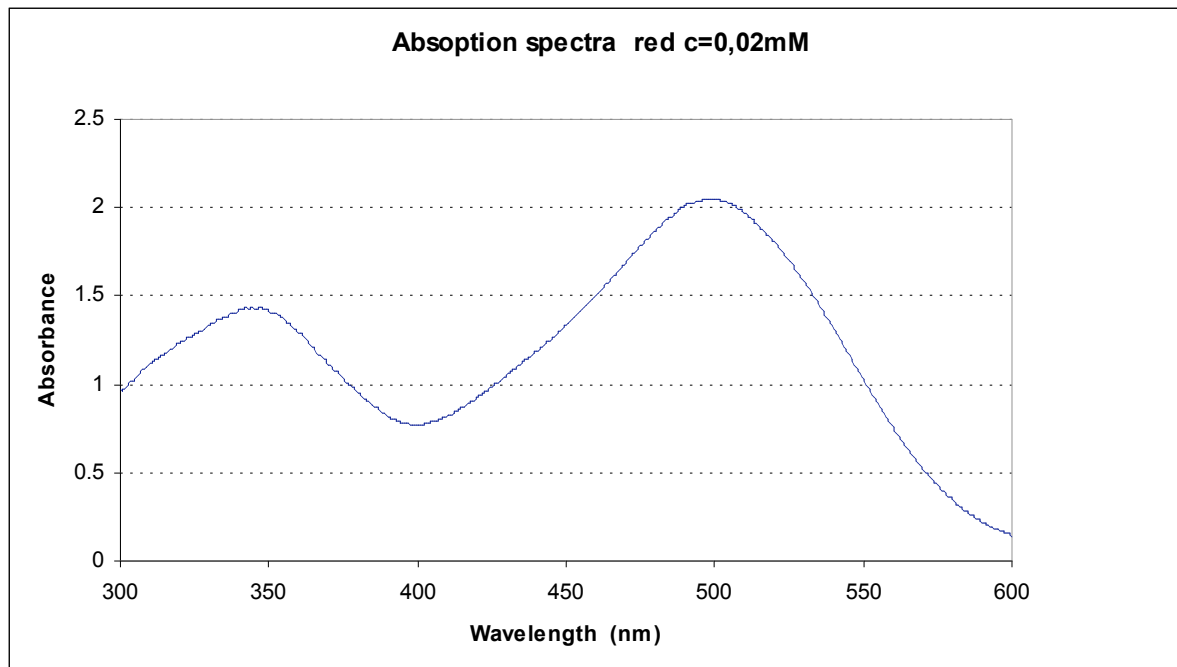


Fig. 2 Absorption spectra of the congo red in distilled water

Results and Discussion

In Fig. 3 and Fig. 4, the results obtained by treating the sample with H_2O_2 alone, or $\text{S}_2\text{O}_8^{2-}$ alone and in combination with $\text{H}_2\text{O}_2/\text{UV}$ and $\text{S}_2\text{O}_8^{2-}/\text{UV}$ are reported. From Fig. 3, it is possible to observe that the action of H_2O_2 alone did not show any decolouration capacity, although H_2O_2 can be a relatively powerful oxidant. On the other hand, UV used alone yielded a slower rate of decoloration [31]. The dyes molecules absorb photon, the UV energy will be transferred to the dyes molecules and the electronic structures of the dyes are excited. Thus, molecules excited states are unstable and short lived and will dispense their excitation energy in some physical way or undergo chemical reactions and form new species.

The combination $\text{H}_2\text{O}_2/\text{UV}$ was more effective in the decoloration of dyes in distilled water than UV alone. Dyes are attacked by UV photon and by hydroxyl radical, which is a powerful oxidant generated from the photolysis of H_2O_2 by UV light, making possible the degradation of the dyes. The destruction of azo bond $\text{N}=\text{N}$ in the chromophore of azo dyes led to decoloration of dye solutions.

According to the works of Bali et al [31] the Congo red showed more resistance to $\text{UV}/\text{H}_2\text{O}_2$ process than the others dyes and the maximum decoloration efficiency obtained was around 70% at a H_2O_2 concentration of 50mM after 120 min of irradiation.

The results (Fig. 4) also showed that $\text{S}_2\text{O}_8^{2-}$ alone was not able to appreciably decolorize the congo red. This result is in good agreement with the works of Kamel et al under the same concentration of $\text{S}_2\text{O}_8^{2-}$ (10^{-3} M) [25]. An important decrease in the concentration of the dye occurs when the solution was irradiated with UV in presence of $\text{S}_2\text{O}_8^{2-}$. This decrease of the concentration of the dyes was due of the radical sulphate ions generated by the photolysis of persulfate ions.

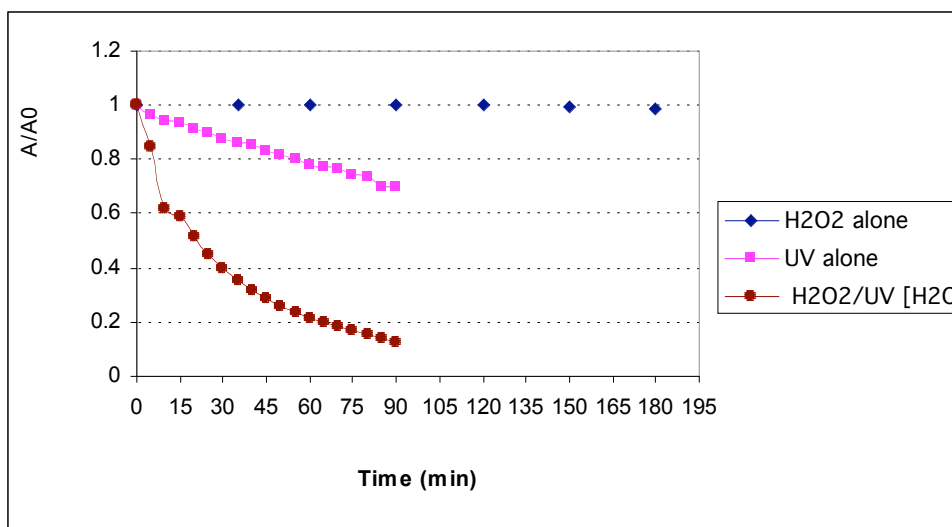


Fig. 3 Decoloration of congo red in the distilled water by H₂O₂ alone, UV alone, UV/H₂O₂

Fig 5 and 6 are the results of the residual coloration (A/A_0) of the dye solution in various kinds of water. It can be observed that the degree of decoloration of the dye solution depends on the kind of water. Under the same conditions, the degree of decoloration of the dye in the distilled water reaches 90% with H₂O₂ after irradiation time of 90min, and 92.8 % with S₂O₈²⁻ after 60min. The degree of decoloration of dye solutions in drinking water and river water reaches 61% and 50.5 % respectively with H₂O₂ and 88.0% and 80.1% respectively with S₂O₈²⁻. The experiments results indicated that the decoloration of dye solutions mainly depends on the type of water in which dye is dissolved. The difference in the decoloration efficiency is apparently due to the presence of scavenging of radicals. The drinking water in this experiment contains Cl⁻ and HCO₃⁻.

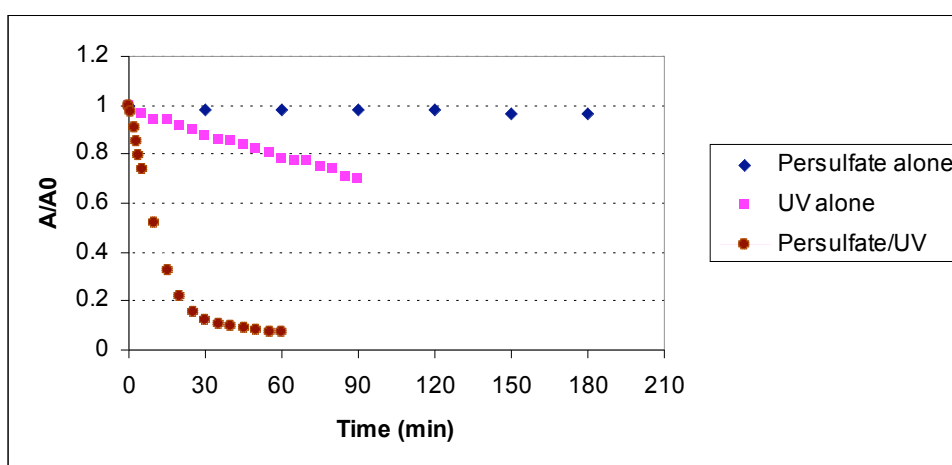
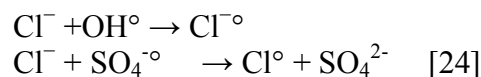
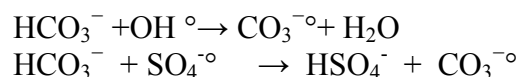


Fig.4 Decoloration of congo red in the distilled water by S₂O₈²⁻ alone, UV alone, UV/ S₂O₈²⁻

In the presence of these ions, dye decoloration decreased slightly. This can be explained on the basis that the presence of these ions scavenge the OH[°] radicals or SO₄[°] radical according to the following reactions thus causing a decrease in percentage decoloration [32]



The decrease of the effectiveness of decoloration in the river water may be due to the presence of others organic compounds which react with the radicals in competition with the dyes.

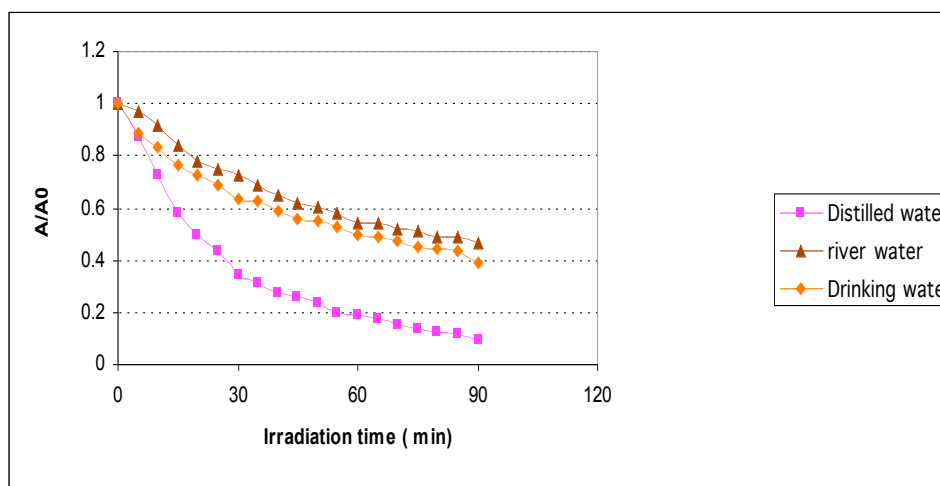


Fig. 5 Decoloration of congo red in the various kind of water by UV/H₂O₂

The results show also that the UV/S₂O₈²⁻ process is more effective than the UV/H₂O₂. The efficiency of the developed process is based primarily in the high oxidizing strength of the sulphate radicals formed. The sulphate radicals are stronger oxidants than the hydroxyl, especially at neutral pH [33], and this might explain in part the higher decoloration of the sample.

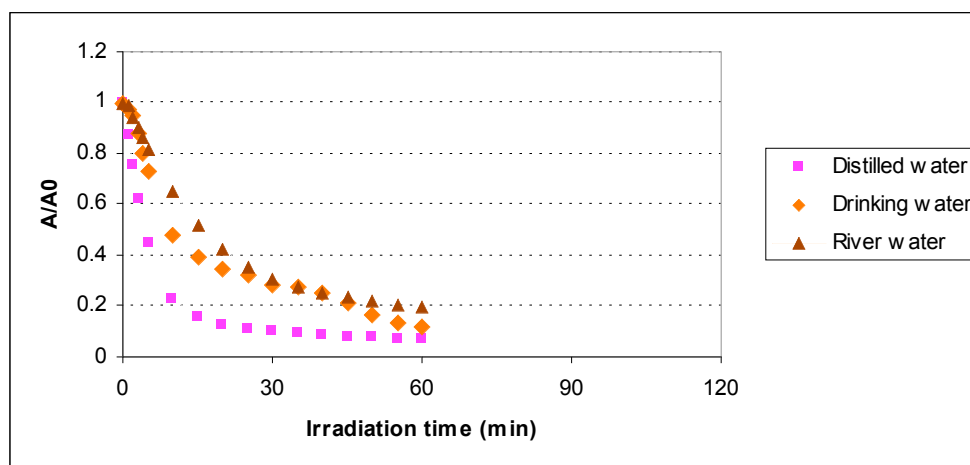


Fig.6 Decoloration of congo red in the various kinds of water by UV/ S₂O₈²⁻

It is observed also that the decoloration of congo red in the system UV/ S₂O₈²⁻ occurs more quickly than in UV/H₂O₂. It may be explained by the results of the work of George P. Anipsitakis et al. [24, 34]. They showed an important property of the oxidants such as

hydrogen peroxide and persulfate, based in the energy of their O–O bond. This bond in potassium persulfate has been estimated to be 33.5kcal/mol whereas in hydrogen peroxide it is 51kcal/mol. Another research have reported the distance of the O–O bonds of these oxidants; 1.453 Å in solid H₂O₂, and 1.497 Å in (NH₄)₂S₂O₈. This suggests that persulfate is cleaved more easily than hydrogen peroxide, indeed the persulfate might be more easily activated than hydrogen peroxide, and thus the resulting sulphate radicals might be formed more readily than hydroxyl radicals [33]. In the other hand, the enhancement of decoloration efficiency may be due to the presence of the two radicals OH° and SO₄° in the medium [25]. According to the results of Kamel et al, the initial rate of decoloration in the UV/persulfate is higher than which of UV/peroxide [25]. They demonstrated that the decoloration of congo red by the UV/H₂O₂ process follows a pseudo-first-order kinetics law and the apparent rate constants varying with the concentration of the H₂O₂. These values are 0.09 mg L⁻¹ min⁻¹ and 1.1 mg L⁻¹ min⁻¹ for the hydrogen peroxide concentration 10⁻³ and 2.10⁻³ respectively. These values are lower than the rate decoloration with the UV/S₂O₈²⁻ process in the same concentration of hydrogen peroxide. These might be the reason that decoloration occurs more rapidly in UV/ S₂O₈²⁻ system than in UV/H₂O₂.

Conclusion

Advanced Oxidation Processes represent a powerful treatment for refractory and/or toxic pollutants in textile wastewaters. The results presented here show that for the congo red, the use of UV with persulfate method was considered more efficient than the photochemical assisted with hydrogen peroxide for the decoloration. The photochemical with persulfate treatment showed 80.1% colour reduction in the dye solution, even the dyes were dissolved in the river water. These results suggest that the S₂O₈²⁻/UV process may be envisaged as a method for treatment of coloured waste waters for decoloration in the textile industries. This investigation can be continued by studying the efficiency of this system process under different controlled conditions, by identifying the intermediates by-products and their biodegradability; the parameters in industry application and the cost effectiveness.

Acknowledgments

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