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Photocatalysis with titanium dioxide to remove colour of exhausted reactive dyebaths without pH modification

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ABSTRACT

This work is focused on photocatalytic decolourisation of residual textile dyebaths with ultra-fine titanium dioxide (TiO_2) without pH modification. Synthetic solutions were prepared with tertiary mixtures of three hydrolysed reactive dyes to simulate the industrial conditions. Two photocatalysts (referred as K1 and K2, respectively) were tested to remove colour of the synthetic dyebaths under UV light and solar light irradiation. The decolourisation treatment was also applied to residual cotton dyeing liquors containing the same trichromie of dyes. In all cases, K2 provided better results than K1. For synthetic and industrial effluents, the almost full decolourisation was reached with K2 both with UV and solar light irradiation. In all the experiments, decolourisation was achieved without any pH adjustment, which is an important advantage in order to simplify the process, to avoid chemicals consumption and to reduce the conductivity of the treated effluent. The use of solar light is also an additional advantage from a environmental point of view although it increases the treatment time.

Keywords: Photocatalysis; TiO_2; Decolourisation; Reactive dyebaths; pH adjustment; Solar light

1. Introduction

The textile industry consumes large amounts of water in their dyeing and finishing processes. High coloration and salinity levels are the main characteristics of textile wastewater. This problem is increased by the use of reactive dyes, widely used in the dyeing of cellulosic fibres as they offer high washing fastness and deep and brilliant colours. In opposite, these dyes have a low exhaustion degree (60–90%) caused by the simultaneous hydrolysis reaction. At alkaline pH, reactive dyes are fixed with a covalent bond to the ionised hydroxyl groups of cellulose, but this pH also promotes the dye hydrolysis. Consequently, the exhausted dyebaths contain large amounts of unfixed hydrolysed dyes which cannot to be reused in the same process.

In order to increase the exhaustion of reactive dyes, high amounts of electrolytes are added during the dyeing process (20–80 g l^{-1} of NaCl or Na_2SO_4). For this reason, many textile mills have difficulties to accomplish the current regulation related to the conductivity limits.

Although the physico-chemical wastewater treatments provide more than 95% colour removal, they produce a large amount of sludge and they do not achieve

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the required level of organic matter removal. Hence, the biological treatments are the most widely used, due to their efficiency in COD and BOD removal. However, some residual dyes have a poor biodegradability and biological treatments are not able to remove colour properly. Then, the application of specific treatments is required to accomplish the current regulations. There are different techniques to achieve colour removal, among them the most used are:

- Use of adsorbents [1,2].
- Filtration with membranes (nanofiltration and reverse osmosis) [3].
- Selection of microorganisms able to degrade dyes [4].
- Chemical oxidation processes [5,6].
- Electrochemical methods [7–10].
- Advanced oxidation methods [11–14].

Among the last ones, the heterogeneous photocatalysis with titanium dioxide provides good yield in organic matter degradation [15–17]. Its use in colour removal treatments has great advantages over other proposed techniques, namely, complete recovery of the titanium dioxide which can be reused, no addition of chemical products (the conductivity is not increased) and no generation of wastes.

The heterogeneous photocatalysis is a catalytic process based on photoactivation. The catalyst is promoted by radiant energy from visible and UV light. The photocatalyst acts as a conductor material in which surface redox reactions occur. In these reactions, free radicals are generated which attack the adjacent species by breaking their molecular bonds and oxidising or reducing them until they are converted in less complex and hazardous species. At the end of this process, the catalyst is not submitted to any physical change.

The heterogeneous photocatalysis with TiO_2 is based in the following factors:

- Incident energy on the system (UV or visible) which initiate the reaction.
- Activation of the semiconductor surface.
- Generation of the pair electron-gap.
- Hydroxyl radical production.

When a semiconductor is illuminated with light (hv) at higher energy than its *bandgap* energy (Eg = 3.2 eV for TiO_2), it produces electron-gap couples at high energy excited states (e^-/h^+). Part of these photoregenerated supports are combined inside the semiconductor, whereas the rest migrate to the particles surface where the electrons act as powerful reductors and the gaps as powerful oxidants able to initiate a wide range of redox reactions.

The photodegradation process [15,18] in the semiconductor surface can be expressed according to Eqs. (1)–(5):

$$\mathrm{TiO_2} + hv \rightarrow \mathrm{e^-} + \mathrm{h^+} \tag{1}$$

$$\mathrm{O_{2ads}} + \mathrm{e^-} \rightarrow \mathrm{O_2}^{\bullet -}{}_{\mathrm{ads}} \tag{2}$$

$$\mathrm{h^+} + \mathrm{H_2O_{ads}} \rightarrow \mathrm{HO^\bullet} + \mathrm{H^+} \tag{3}$$

$$\mathrm{h^+} + \mathrm{HO^-}{}_{\mathrm{ads}} \rightarrow \mathrm{HO} \tag{4}$$

$$\mathrm{R-H} + \mathrm{HO} \rightarrow \mathrm{RCOO^\bullet} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \text{inorganic ions} \tag{5}$$

In the illuminated semiconductor, the generated $OH^\bullet$ radicals are extremely powerful oxidant agents which attack the organic molecules adsorbed or closer to the catalyst surface. In the case of dyes, another degradation mechanism involving visible light can also occur as they are able to absorb part of the visible light. According to this mechanistic approach, the dye molecules irradiated with the visible light and adsorbed on the TiO_2 surface reach the corresponding excited states. These states mainly transfer electron to the TiO_2 particles conduction band (Eqs. (6) and (7)):

$$\mathrm{Dye} + hv \rightarrow \mathrm{Dye^\bullet} \tag{6}$$

$$\mathrm{Dye}^* + \mathrm{TiO_2} \rightarrow \mathrm{Dye^{\bullet +}} + \mathrm{e^-}\left(\mathrm{TiO_2}\right) \tag{7}$$

These reactions are highly dependent on the pH as it modifies the double electric interphase photocalyst (solid)-dyebath (liquid) which can influence the process of sorption-desorption and the separation of the electron-gap couples in the semiconductor particles surface [19].

The current studies on heterogeneous photocatalysis with titanium dioxide have been mainly carried out at acid pH [19,20]. At low pH, the dye sorption on the particles is increased with respect to the alkaline and neutral pH due to the electronegative charge of dye molecules that produces an electrostatic attraction. But a very strong adsorption reduces the active centres in the catalyst surface and consequently, diminishes its absorption of the light quantum. For this reason, some authors have reported the neutral pH as the most appropriated for the decolourisation [19,21]. In these cases, the structure was found to have also a clear influence [22,23].

However, the cotton dyeing effluents usually have a strong alkaline pH. In fact, reactive dyes, which are the most consumed for the cotton dyeing, require the addition of alkali to achieve a proper fixation. In this study, the TiO_2 was applied to remove the residual reactive dyes contained in synthetic and industrial exhausted dyebaths. As it is known, the pH could influence the colour removal efficiency. But from an environmental point of view, an increase of the effluent salinity is not convenient. For this reason, in this study the treatment was carried out at alkaline pH which is usual in the spent reactive dyeing effluents.

The main goal of this work was the application of two types of ultrafine TiO_2 (as commercial products) to remove colour of exhausted cotton dyeing wastewater containing hydrolysed reactive dyes at pH 10. The main factors which can influence the colour removal efficiency were studied: dye concentration, type and amount of catalyst.

2. Experimental

2.1. Reagents, materials and apparatus

2.1.1. Textile

The textile material was cotton filling face twill fabric prepared for dyeing (desized, scoured and bleached). The fabric density was 167.81 g m^{-2}, calculated by weighting a known surface of the textile in a conditioned room (temperature 20°C and relative humidity 60%).

2.1.2. Photocatalysts

Two commercial products kindly supplied by ZEUS QUÍMICA (Spain), were selected: KRONOS uvlp 7500 (referred as K1) and KRONOS vlp 7000 (referred as K2). The first is commercially indicated for photoactivity with UV light and the second one for high photoactivity with both UV and visible light. They are ultrafine powder containing up to 85% of titanium dioxide (TiO_2) and they are able to be used at alkaline pH. To carry out the experiments, they were dispersed by stirring into the hydrolysed dye solutions or the exhausted dyeing baths.

2.1.3. Dyes

Three commercial bifunctional reactive dyes, which constitute a dyeing trichromie, were studied: Procion Crimson H-EXL (PCH), Procion Blue H-EXL (PBH) and Procion Yellow H-EXL (PYH). They were kindly supplied by Dystar Hispania (Spain). Only the Colour Index of the Yellow has been published (C.I. Reactive Yellow 138:1). Their chemical structures and CAS numbers are presented in Fig. 1 [24,25]. For the dyeing process, dyes were used in water solution. To simulate a coloured wastewater, they were previously submitted to a hydrolysis procedure [7] and used in their hydrolysed form.

2.1.4. Auxiliary products

An aqueous solution of NaCl (30%) was prepared as dyeing electrolyte. In order to simulate the final dyeing pH, a buffer solution pH 10 containing 10.7 ml l^{-1} of sodium hydroxide (NaOH) 0.1 M and 50 ml l^{-1} of sodium carbonate (Na_2CO_3) 0.05 M was prepared to adjust the final volume of dyes solutions. The solutions were prepared with deionised water. All these compounds were supplied by Sigma Aldrich Co. (Spain).

2.1.5. Apparatus

To carry out the experiments, the following equipment was used: a magnetic and thermical stirrer SBS, a mixer SILVERSON L4RT, a UV lamp 300 W OSRAM ULTRA-VITALUX (maximum emission wavelength: 360 nm), a lab centrifuge P-Selecta, filters Cromafil 45 nm MACHEREY-NAGEL PET 45/25 and a spectrophotometer DATACOLOR 650 TM. The analyses of Total Organic Carbon content were performed with a TOC analyser (Shimadzu 5050A, Germany).

2.2. Sample preparation

2.2.1. Hydrolysed dye solutions

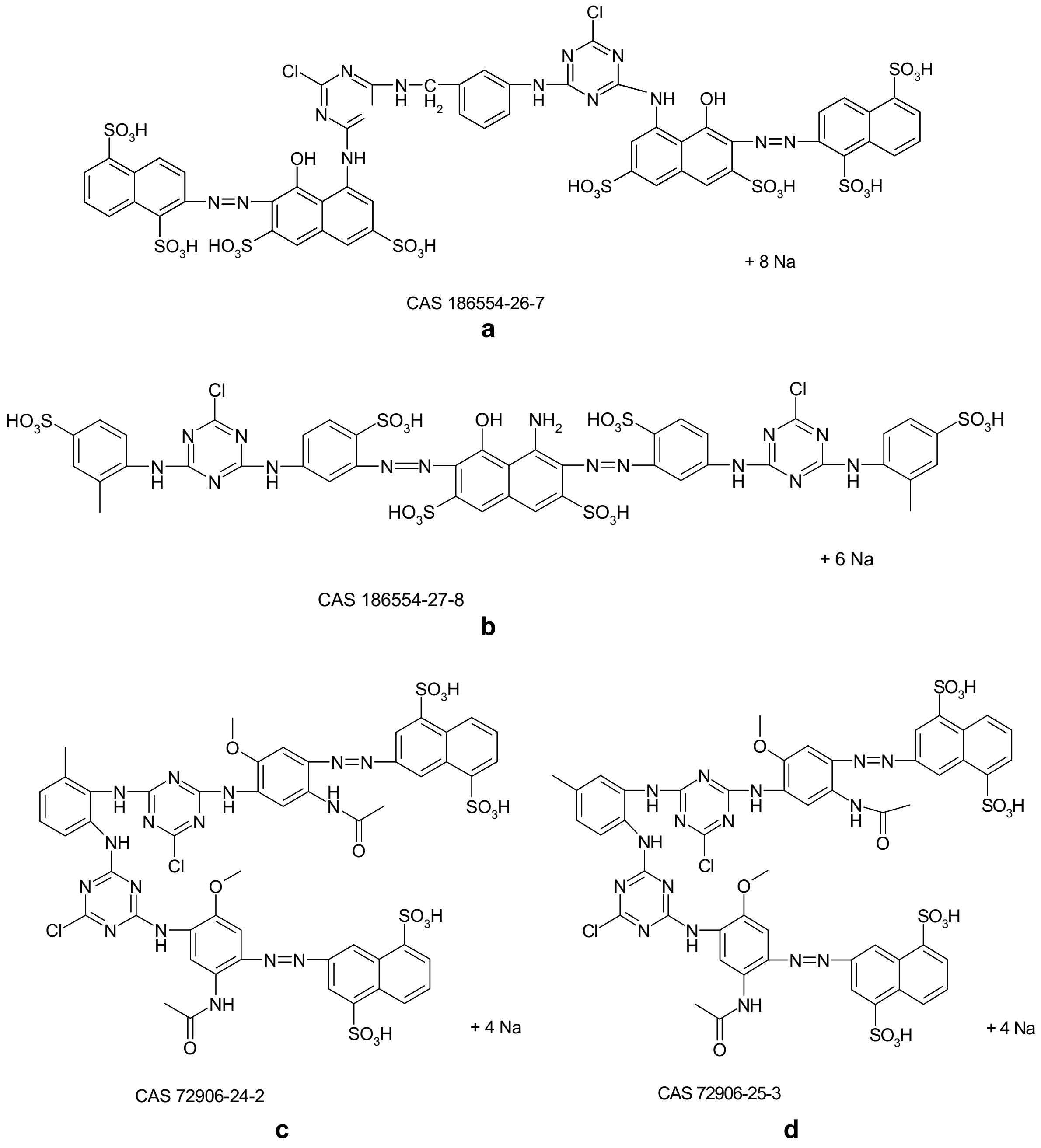
Simulated exhausted dyebaths were prepared by hydrolysis of dye solutions. With this purpose, solutions of individual reactive dyes were boiled with sodium hydroxide (Sigma Aldrich Co., Spain), as follows: deionised water (about 10% of the total volume) and the amount of NaOH 0.65 M necessary to reach pH 12 were added to the weighted dyes. Solutions were boiled for 1 h to ensure a total dye hydrolysis. They were let to cool, then diluted almost to the final volume and finally, adjusted to pH 10 with hydrochloric acid (Sigma Aldrich Co., Spain).

The individual hydrolysed dye solutions were mixed in the appropriate rates to obtain two synthetic trichromies effluents containing 0.05 and 0.25 g l^{-1} of total hydrolysed dyes (0.0167 and 0.0833 g l^{-1} of each dye, respectively). In both cases, 30 ml of NaCl solution (30% w/v) was added, as the typical industrial dyeing effluents contain a similar amount of this salt which acts as dyeing electrolyte. The final volume was adjusted to 250 ml with the buffer solution pH 10.

2.2.2. Dyeing and washing exhausted liquors

Three fabric samples were dyed (1 g of sample in 100 ml of dyeing liquor) with an initial amount of 0.036 g of the dyes trichromie (concentration of each dye in the liquor 0.12 g l^{-1}, non hydrolysed), 4 g of NaCl and 100 ml of the buffer solution pH 10.

The dyeings were carried out as follows: the fabric was placed into the dyebath (liquor) while stirring at room temperature during 10 min. The temperature was increased to 80°C in 30 min. These conditions were maintained during 60 min. The total dyeing process lasted 100 min. In order to operate at a constant volume, deionised water was added when necessary.



CAS 186554-26-7
a

CAS 186554-27-8
b

CAS 72906-24-2
c

CAS 72906-25-3
d

Fig. 1. Chemical structure and CAS number of the dyes: Crimson Procion H-EXL (a), Navy Blue Procion H-EXL (mixture of a and b), Yellow Procion H-EXL (mixture of c and d).

After the dyeing, a two step fabric washing (liquor ratio 1/100) was performed as follows: scouring at room temperature (10 min, 100 ml) and final washing (30 min, 100 ml) in boiling water.

Finally, the exhausted dyebath (about 50 ml, the rest was absorbed onto the textile) and the two residual washing liquors (about 180–190 ml) were collected, mixed and adjusted to a total volume of 250 ml. This solution contained the residual hydrolysed unfixed dyes whose concentration was analyzed by UV-visible spectroscopy. The content of each dye in the wastewater was found in the range of 0.016–0.018 g l^{-1} (total dye concentration of 0.05 g l^{-1}).

2.3. *Sample treatments*

The experimental conditions of the different colour removal tests are presented in Table 1. Photocatalysts

Table 1
Description of samples and treatment conditions

Sample	Test	Dye concentration (g l^{-1})	Catalyst K1 (g l^{-1})	Catalyst K2 (g l^{-1})	Irradiation
Synthetic liquor	A1	0.05	1	–	UV lamp
	A2$_{SL}$	0.05	–	1	Solar light
	A2$_{UV}$	0.05	–	1	UV lamp
Synthetic liquor	B1	0.05	2	–	UV lamp
	B2$_{SL}$	0.05	–	2	Solar light
	B2$_{UV}$	0.05	–	2	UV light
Synthetic liquor	C1	0.25	2	–	UV lamp
	C2$_{SL}$	0.25	–	2	Solar light
	C2$_{UV}$	0.25	–	2	UV lamp
Residual textile dyeing liquor	D1	0.05	2	–	UV lamp
	D2$_{SL}$	0.05	–	2	Solar light
	D2$_{UV}$	0.05	–	2	UV lamp

K1 and K2 were dispersed in the synthetic dye solutions or in the exhausted dyebaths at 1 or 2 g l^{-1}, according to the test conditions. The solutions were stirred in the dark during 30 min at high speed (9800 rpm) to ensure the equilibrium adsorption/desorption and to avoid the starting of reactions [23].

Irradiation treatments were performed in two ways: with a UV lamp or under solar light (only for photocatalyst K2). In the first case, samples were placed under the UV lamp (21 cm) with constant stirring (700 rpm) in order to accomplish a proper homogenisation, aeration and light action. Samples were irradiated during several hours and aliquots of 10 ml were collected during the treatments at 0, 15, 30, 75, 105, 135, 180, 210, 240, 270 and 300 min, from the beginning of the experiment.

Longer UV expositions were applied in the experiments performed with residual dyeing liquors (D1, D2$_{SL}$ and D2$_{UV}$), as they contained organic matter extracted from the cotton fabric. In these cases, the experiments were extended to 23 h of irradiation. Samples were aerated and stirred during the treatment to maintain the temperature.

2.4. Colour removal experiments

Colour removal in % was calculated from the ratio of the absorbance reduction at time t versus the initial absorbance, at the maximum wavelength of each dye (520 nm for PCH, 630 nm for PBH and 420 nm for PYH) according to the following expression:

$$\text{Colour removal (\%)} = \frac{\text{Absorbance}\,(t = 0) - \text{Absorbance}\,(t)}{\text{Absorbance}\,(t = 0)} \times 100$$

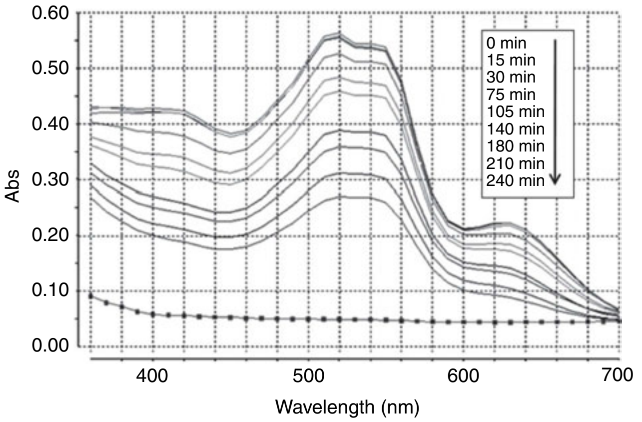


Fig. 2. Spectrum evolution registred along a colour removal experiment for a trichromie with a total dye concentration of 0.05 g l^{-1}.

Experiments were carried out in triplicate. Values which caused a coefficient of variation higher than 5% were discarded. Prior to the spectroscopic analysis, samples were centrifugated for 20–30 min at 2300 rpm to remove the photocatalyst and then filtered though a 45 µm filter. A blank was run for each experiment. The UV-visible spectra of the collected samples show the evolution of the decolourisation. Fig. 2 corresponds to a typical experiment, the rest of trials showed a similar tendency.

In order to provide an easy method for industrial applications, the evolution of each dye is calculated from its absorbance at the maximum wavelength in the visible region. The absorbance at each maximum wavelength was only attributed to one dye. The possible effect of the other two dyes was not corrected as their contribution was not significant to evaluate the yield of the experiment.

3. Results and discussion

3.1. Effect of the type of photocatalyst on simulated dyebaths

The experiments carried out with K2 were catalysed by ultraviolet light and by solar light, whereas K1 experiments were only activated with ultraviolet irradiation due to the low activity of K1 under solar light (according to the supplier information). Results obtained under these conditions are plotted in Fig. 3.

The highest colour removal was observed in the experiment where K2 was irradiated with UV light (A2$_{UV}$). In this experiment, all dyes reached more than 95% decolourisation after 240 min of UV irradiation. Also, it can be seen that the treatment with K2 under solar light (A2$_{SL}$) is faster that K1 with UV irradiation (A1). In the experiment A2$_{SL}$ values of 60–75% of colour removal are reached after 240 min of solar light

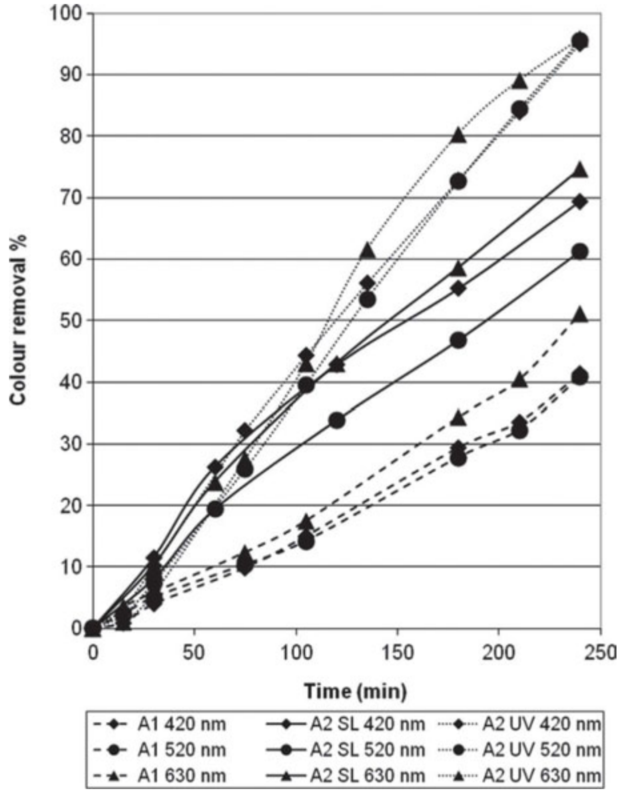


Fig. 3. Colour removal measured at the maximum wavelength of each dye for tests carried out to synthetic liquors (total dye concentration = 0.05 g l^{-1}) with a photocatalyst concentration of 1 g l^{-1}.

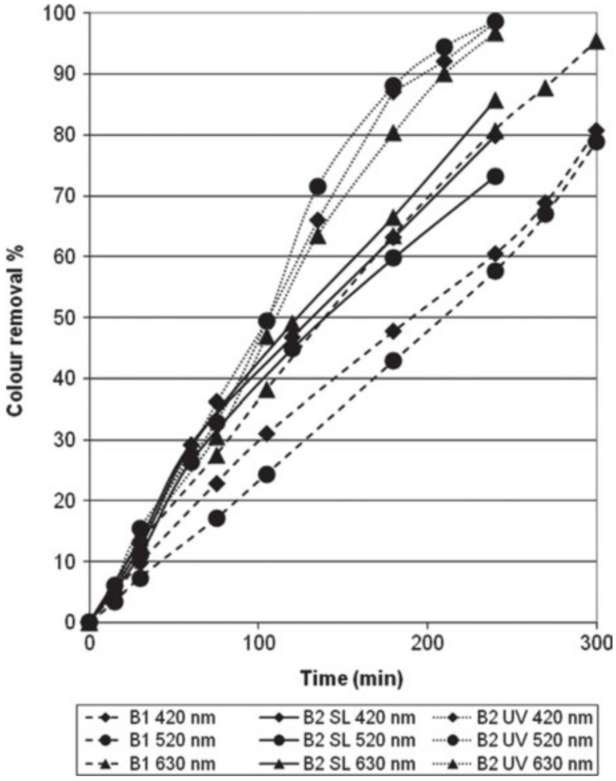


Fig. 4. Colour removal of synthetic liquors (total dye concentration = 0.05 g l^{-1}) with a photocatalyst concentration of 2 g l^{-1}.

exposition, whereas values of 40–50% are obtained in experiment A1. In summary, the use of K2 implies an important energy saving and consequently, the process is more sustainable.

3.2. *Effect of the photocatalyst concentration*

The photocatalyst concentration was doubled in experiments B1, $B2_{SL}$ and $B2_{UV}$ with respect to experiments A1, $A2_{SL}$ and $A2_{UV}$ in order to evaluate its effect on colour removal. The results of these experiments are shown in Fig. 4.

Experiments A and B were carried out at the same dye concentration (0.05 g l^{-1}). In general, better colour removal results were obtained when the ratio photocatalyst/dye was doubled from 20/1 to 40/1. But, the effect of the photocatalyst concentration was higher for K1, and for K2 with solar light than for K2 irradiated with UV light. The colour removal was significantly higher in the experiment B1 than in the experiment A1. After 240 min, 58–80% decolourisation was reached in the experiment B1 versus 40–50% in the experiment A1.

In the same way, the results obtained in the experiment $B2_{SL}$ reached 75–85% of colour removal, significantly higher than the results obtained in the experiment $A2_{SL}$ (60–75% of colour removal).

The photocatalyst concentration has a lower effect when K2 is irradiated with UV light. In fact, the results of the experiment $A2_{UV}$ were very good and the reduction of the treatment time in the experiment $B2_{UV}$ is not significant. By another hand, it is observed that the colour removal in experiment $B2_{UV}$ follows a pseudo-first order kinetic according to the Langmuir-Hinshelwood's heterogeneous catalytic model.

The higher is the photocatalyst concentration, the higher is its total surface and the number of active sites. But at very high dose, the incident light is attenuated as the disperse light is increased. Moreover, the density of superficial gaps and electrons is reduced by the interaction between particles whereas the deactivation of activated molecules is increased [19].

Barakat [26] also studied the photodegradation of Procion Yellow H-EXL dye over TiO_2 suspension. The author found that the optimum pH was 5. At this pH a dosage of 1 g l^{-1} of TiO_2 reached a colour removal of almost 90% in solutions of 50 mgl^{-1} of dye in 180 min of UV irradiation whereas at pH 9, the colour removal was lower than 30% with the same irradiation time. In our work, all the experiments were carried out at pH 10, the usual pH of the reactive residual dye baths. For the same dye concentration (50 mg l^{-1}) a colour removal around 90% was obtained after 210 min when the dosage of the photocatalyst K2 is 1 g l^{-1} (experiment A2 UV). The treatment time was reduced to 180 min when the photocatalyst concentration was 2 g l^{-1} (experiment B2 UV). The other two studied dyes (Procion Crimson H-EXL and Procion Blue H-EXL) showed similar behavior.

The photocatalyst K2 was able to degrade reactive dyes at alkaline pH. In contrast, the photocatalyst K1 showed poorer results, as in the case of Barakat studies at alkaline pH. Several authors [12,13,26] presented high colour removal yields when the treatment was carried out at acid pH. However, in the case of reactive dye effluents, it is more convenient to perform the treatment at alkaline pH in order to avoid the addition of acid which produces an increase of the effluent conductivity.

3.3. Effect of the dye concentration

In experiments C1, $C2_{SL}$ and $C2_{UV}$ the dye concentration was 0.25 g l^{-1} (ratio photocatalyst/dye 8/1). The results of colour removal are presented in Fig. 5.

As in the previous series of experiments, the highest colour removal was obtained in the experiment with K2 and UV irradiation ($C2_{UV}$). However, the colour removal only reached values of 65–75% after 300 min of UV irradiation. In fact, an irradiation period of 1100 min was necessary to reach 98% of colour removal.

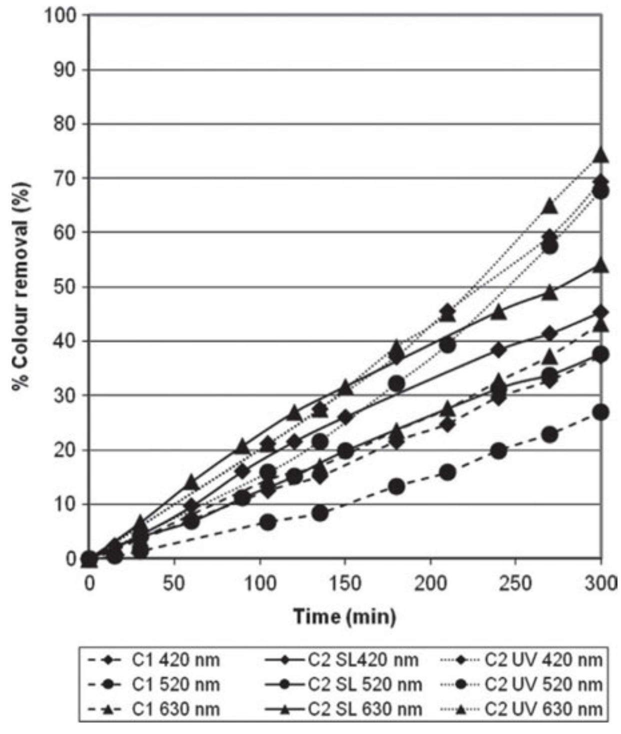


Fig. 5. Colour removal of synthetic liquors (total dye concentration = 0.25 g l^{-1}) with a photocatalyst concentration of 2 g l^{-1}.

The effect of dye concentration is studied from the results obtained in experiments B and C (Figs. 4 and 5), as they were performed at the same concentration of titanium dioxide (2 g l^{-1}). It can be seen that the dose of photocatalyst in experiments C (ratio photocatalyst/dye 8/1) was clearly insufficient. In the case of the photocatalyst K1, values between 25–50% were obtained after 300 min of UV irradiation in the experiment C1, whereas a higher level of colour removal was observed in the experiment B1 for all the wavelengths: 79–95% at the same irradiation period. The same behaviour is observed for photocatalyst K2 with solar light, very low colour removal values are obtained in the experiment $C2_{SL}$ (37–55%) with respect to the results obtained in the experiment $B2_{SL}$ (75–85%).

At higher dye concentration respect to photocatalyst amount, the photodegradation efficiency is decreased. This can be attributed to the higher dye adsorption on the catalyst surface which diminishes the amount of hydroxyl groups, and consequently, the degradation is reduced. In addition, the amount of photons absorbed by the catalyst is lower, which also reduces the photodegradation [22].

3.4. Effect of the photocatalyst on residual dyeing liquors

At this point, colour removal experiments were carried out on residual textile dyebaths. From the results obtained in synthetic dyebaths a ratio catalyst/dye of 40/1 was selected. This optimised ratio agrees with other authors [18] and it is important to remark that a high photocatalyst concentration is not an environmental or economical problem as it is recovered for a new process.

Fig. 6 corresponds to colour removal obtained in experiments D1 (photocatalyst K1), $D2_{SL}$ (photocatalysts K2 with solar light) and $D2_{UV}$ (photocatalysts K2 with ultraviolet light). As expected, the treatment time of residual dyebaths is higher than synthetic dyebaths due to the presence of organic matter extracted from the cotton fabric. From TOC measurements, it was established that the residual dyebaths contain 480 mgC l^{-1} whereas the synthetic dyebaths have 24 mgC l^{-1} (both at a dye concentration of 0.05 gl^{-1}). This technique is not selective and other compounds can produce interferences on the dye adsorption process. However, high levels of colour removal are reached, even in the presence of these other compounds.

As expected, the yield of K2 was increased by performing the treatment with UV light as can be seen in Fig. 6. The best yield is obtained for experiments $D2_{UV}$ which provide the lower treatment time. In all cases, values are higher than 85% after 850 min: 88.53% at 420 nm; 93.14% at 520 nm and 96.85% for 630 nm).

By another hand, high levels of colour removal were also obtained when K2 was irradiated with solar

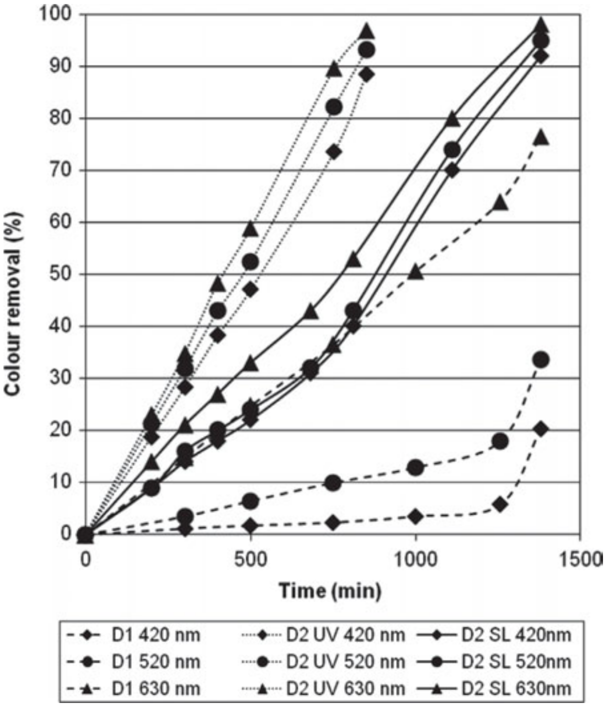


Fig. 6. Colour removal measured at the maximum wavelength of each dye for tests carried out to residual dyeing liquors (total dye concentration = 0.05 g l^{-1}; photocatalyst concentration = 2 g l^{-1}).

light: colour removal is higher than 90% after 1350 min of solar exposition. Although the treatment was slower under these conditions, it implies an important energy saving and consequently, a more sustainable process.

4. Conclusions

The photocatalysis with TiO_2 using solar light or UV light is a promising technique to remove reactive dyes from wastewater. All the experiments were performed at pH 10, without adjusting the pH which demonstrated the possibility to carry out the decolourisation process at high pH values.

The photocatalyst K2 with solar light showed better results than the photocatalyst K1 with UV light. Thus, the use of K2 implies an important energy saving. The yield of K2 is improved with UV light as it was confirmed in the treatment of residual textile dyebaths.

The ratio catalyst/dye 40/1 provided the best results. This high amount of catalyst with respect to the dye concentration does not imply a less sustainable or more expensive treatment since the catalyst is recovered at the end of the process.

Colour removal in residual dyebaths was slower than in synthetic dyebaths due to the presence of organic matter extracted from the cotton fabric. In spite of that, the photocatalyst K2 reached more than 90% of colour removal after 1380 min (23 h) of irradiation with solar light. The treatment time was reduced to 850 min (14 h) with UV light.

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