Decolourisation effects of Vat Green 01 textile dye and textile wastewater using H$_2$O$_2$/UV process

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Abstract

Wastewaters from textile industry contain various pollutants including a high content of organic matter, surfactants, additives and dyes. Dyes have obtained notoriety as hazardous substances, because most of them are toxic and considered to be resistant to biodegradation. Recently, advanced oxidation processes (AOP) have received considerable attention because it is possible to degrade organic compounds and colour from wastewaters. The decolourisation of Vat Green 01 textile dyestuff and real textile wastewater was investigated using UV radiation in the presence of H$_2$O$_2$ as function of pH, hydrogen peroxide concentration and dye concentration (in the study with the dyestuff). The results showed that the degradation increases as the initial H$_2$O$_2$ concentration increased up to a certain point at which hydrogen peroxide inhibited the wastewater photolytic degradation. The decolourisation rate follows pseudo-first order kinetic with the respect to the dye concentration.
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Keywords: Dyestuff; Textile wastewater; H$_2$O$_2$/UV

1. Introduction

Dyes pollutants from the textile industry are a major source of environmental contamination. Colour removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but also because of their colouring effect on natural waters [1,2].

Considerable amount of these pollutants draw off during the textile dyeing and finishing operations. Nowadays, coloured water is unattractive and generates more and more complains. Dyes have obtained notoriety as hazardous substances, because most of them are toxic and persistent in the environment [3].

Previous studies have demonstrated that traditional physical and chemical techniques such as coagulation, adsorption on activated carbon, ultra filtration, and reverse osmosis can be generally used efficiently to remove dyes from textile wastewater [4]. However, these processes are considered as non-destructive since they merely transfer the dye from liquid to solid wastes [1,5]. Consequently, the generation of the adsorbent material and post-treatment of solid wastes, which are expensive operations, are needed [3].

Effluents discharged from textile dyeing and finishing industries are categorized as the most difficult to be disposed by biological, chemical and physical technologies. Those effluents from textile industries are generally high in organic contents and strong colour, as well as contain surfactants and additives so that they are non-biodegradable as well as not meeting the effluent standards by traditional activated sludge treatment to result into the serious environmental contamination. Thus, the decolourisation technologies become major challenges as well as of increasing importance [6].

Currently, chemical methods, such as advanced oxidation processes (AOPs) seem more promising [1].

AOPs predominantly involve the generation of very powerful and non-selective oxidizing species, the hydroxyl radicals ($^\bullet$OH) for the destruction of refractory and hazardous pollutants observed in industrial wastewaters, surface waters and groundwater [7].

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Ultraviolet photolysis combined with hydrogen peroxide (UV/H_2O_2) is one of the most appropriate AOP technologies for removing toxic organics from water because it may occur in nature itself. This process involves the production of reactive and non-selective hydroxyl radicals ($^\bullet OH$) and can initiate the decolourisation reactions by reacting with the dye molecules [8]. The result of this reaction is the destruction of colour according to the following reactions:

$$H_2O_2 + h\nu \rightarrow 2^\bullet OH \tag{1}$$

$$^\bullet OH + dye \rightarrow oxidation\ product \tag{2}$$

The objective of this study was to investigate the effect of H_2O_2/UV in the treatment of the Vat Green 01 textile dyestuff and real textile wastewaters in batch reactors. The effects of the key operating variables, such as pH, hydrogen peroxide dosage, and dye concentration on the decolourisation kinetics were studied. The experiment was conducted by changing one variable at a time while keeping other parameters constant.

2. Experimental

2.1. Materials

Vat Green 01 textile dyestuff was supplied by a textile industry. The textile wastewater used in this work was obtained after physical–chemical treatment from an industrial textile treatment plant in Brazil. Its average chemical composition is given in Table 1.

Hydrogen peroxide (30 w/w) was used as received. The experimental dyestuff solutions were prepared using distilled water. The pH of the solution was adjusted using sodium hydroxide (NaOH) or by hydrochloric acid (HCl).

The Vat Green 01 textile dyestuff structure, according to the manufacturer, is showed in Fig. 1.

Table 1
Characterization of textile wastewater

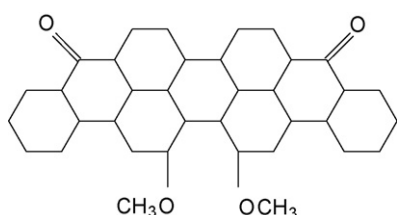|	
pH	9
COD (mg O_2 L^{-1})	750
BOD (mg O_2 L^{-1})	160
Total solids (g L^{-1})	8.33
Fixed solids (g L^{-1})	1.80
Volatile solids (g L^{-1})	6.53
NH_4^+ (mg L^{-1})	30
NO_3^- (mg L^{-1})	2

Fig. 1. Vat Green 01 dyestuff structure.

2.2. Photoreactor

All reactions were conducted in a 1500 mL capacity batch reactor. This model consists of 125 W medium-pressure mercury lamp, surround by a quartz thimble. The reactor has double walls to maintain constant temperature (28 °C) of the reaction. The pH of the solution or wastewater was adjusted to the desired value by addition of sodium hydroxide or by hydrochloric acid and then it was measured by Micronal pH-meter, model B474.

After the light of the reactor turn on precise amount of hydrogen peroxide (30%) were mixed with the 1500 mL solution (textile wastewater or dyestuff solution) by means of a magnetic stirrer. A specific H_2O_2 concentration was adjusted in the beginning of the treatment and no further H_2O_2 was added during the degradation.

2.3. Chemical analyses

All analyses were performed according to standard methods [9]. Chemical oxygen demand (COD) was realized according to colorimetric methods, biological oxygen demand (BOD) according to dilution method, ammonium (NH_4^+) according to Nessler method and nitrate (NO_3^-) according to Salicylic method.

The colour remove was compared using a Hach DR2500 spectrophotometer and measuring the absorbance.

The residual H_2O_2 was performed according to iodine method [10].

3. Results and discussion

The decolourisation of Vat Green 01 textile dyestuff and real textile wastewater were conducted using the H_2O_2/UV process under various operating conditions, such as pH, initial hydrogen peroxide concentration and dye concentration.

3.1. H_2O_2/UV reactions

Because of its inherent advantages (i.e. no sludge formation, significant reduction of COD in relatively short reaction times and easy handling), the H_2O_2/UV system has remained as the AOP most often applied for the treatment of hazardous/refractory pollutants observed in water or wastewater [5,11–14].

To examine the effect of pH and initial H_2O_2 concentration on the H_2O_2/UV treatment efficiency, advanced oxidation of the dyestuffs and textile wastewater was carried out for 2 h at different pH's and different H_2O_2 concentrations that was initially added to the reaction solution (0.25, 0.5, 0.75, 1 and 2 g/L).

At regular time intervals, samples were collected and analyzes by spectrophotometer to determine the decolourisation rate. Initial results demonstrated that neither H_2O_2 nor UV alone was able to appreciably decolourise of Vat Green 01 dyestuff and textile wastewater.
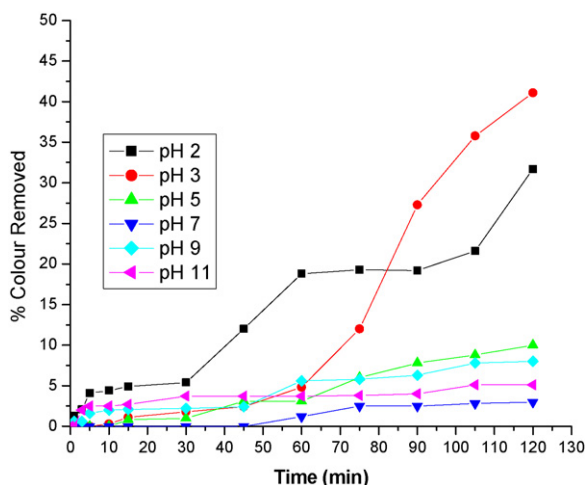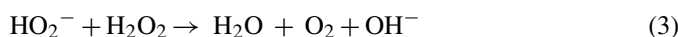
Fig. 2. Colour removal of Vat Green 01 dyestuff in different pH's, $[H_2O_2]_0 = 1$ g/L, $[dyestuff]_0 = 100$ ppm, 125 W and wavelength of the measurement 580 nm.
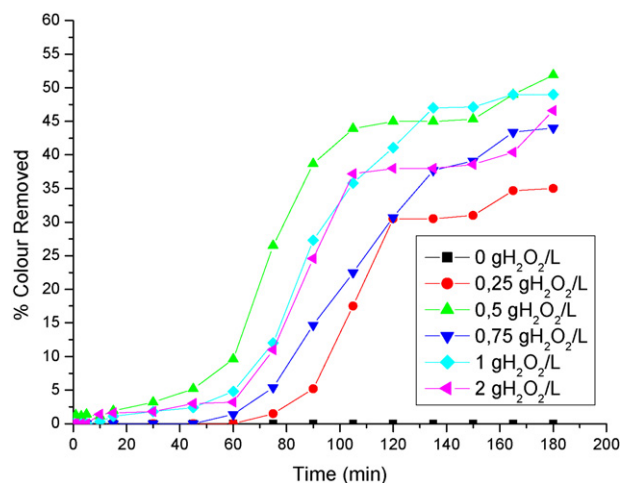

Fig. 3. Colour removal of Vat Green 01 dyestuff with different hydrogen peroxide dosage, pH 3, 125 W and wavelength of the measurement 580 nm.

3.1.1. Vat Green 01 dyestuff

It has several works about the decolourisation of textile dyestuffs in the literature [1,6,15–20] but most of them are with the same textile dyestuff (Direct Blue 199, Acid Orange 7, Acid Blue 74 and Reactive Black 5). In this work was tested another kind of dyestuff (Vat Green 01) because the textile wastewater studied in this work contain Vat Green 01. According to Brazilian Textile Industry where the wastewater used in this work was colleted, the Vat Green 01 is very difficult to degrade by conventional treatment methods.

At first were performed reactions with 1 g H_2O_2/L, 100 ppm of dyestuff and different pH range between 2 and 11. The solutions of dyestuff were adjusted to the desired pH by addition of HCl or NaOH. The different concentrations of acid or base have been chosen in order to add the minimum quantity of these species to avoid the volume of the reaction mixture. The decolourisation rate of Vat Green 01 dyestuff in different pH's are shown in Fig. 2. At 120 min of reaction, it was verified that in pH 3 there was a better colour remove about 41%. It was observed that the Vat Green 01 dyestuff degradation has pH dependency, the better results are in pH's 2 and 3; the worst are in pH's 5, 7, 9 and 11.

According to some authors [21,22], the photochemical degradation rate of H_2O_2 is variable under certain pH conditions and this can affect the H_2O_2/UV reaction to degrade different contaminants. Under alkaline conditions hydrogen peroxide deprotonates with formation of the H_2O_2/HO_2^- equilibrium. The HO_2^- species reacts with a non-dissociated molecule of H_2O_2 according to reaction (3), which leads to dioxygen and water, instead of producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of $^\bullet OH$ is lower than expected:

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \qquad (3)$$

Furthermore, the deactivation of $^\bullet OH$ is more important when the pH of the solution is high. The reaction of $^\bullet OH$ with HO_2^- is approximately 100 times faster than its reaction with H_2O_2.

In acid pH's concomitant with acidification of the solution by HCl, increasing amounts of conjugated base were added to the solution. The anion Cl^- is able to react with hydroxyl radical leading to inorganic radical ions. These inorganic radical anions show a much lower reactivity than $^\bullet OH$, so that they do not take part in the dye decolourisation. There is also a drastic competition between the dye and the anions with respect to $^\bullet OH$. The self-decomposition rate of hydrogen peroxide is strongly dependent on pH, the kinetic constants dependents if the pH is 2, 3, 4, 5, 7 or others [17]. Then, the reaction rate is depending of the pH.

Found the better pH was verified the better hydrogen peroxide concentration to the process. The results from the irradiation of the Vat Green 01 dyestuff (100 ppm), in pH 3 and using different concentrations of H_2O_2 are summarized in Fig. 3. The removal efficiency increases with increasing H_2O_2 concentration up to a certain point at which hydrogen peroxide started to inhibit the wastewater photolytic degradation because the two opposing effects. With increasing H_2O_2 concentration: (A) more hydroxyl radicals are available to attack the aromatic rings and the rate of reaction increases (Eq. (1)) and (B) above the limiting point, hydroxyl radicals efficiently react with H_2O_2 and produces $HO_2^\bullet$ (Eq. (4)). Because $HO_2^\bullet$ radicals are less reactive than $^\bullet OH$, increasing $HO_2^\bullet$ results in negligible contribution [23]:

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \qquad (4)$$
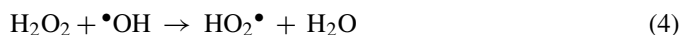
It was verified that the efficiency of the process increased in parallel until 0.5 g/L of hydrogen peroxide dosage where the remove rate was 52% of colour, after this point the efficiency decrease because of the plenty of H_2O_2 in the reaction medium. When the hydrogen peroxide concentration becomes high, the excess hydrogen peroxide consumes hydroxyl radicals and it performed like a hydroxyl radical scavengers.

This excellent concentration value depends of the wastewater composition to be treated. Because of this is very important optimized the H_2O_2 dosage to improve the reaction performance.
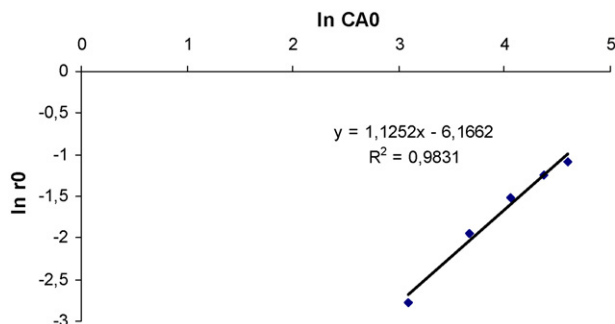
Fig. 4. ln–ln plot of initial rate (mg/L min) vs. initial concentration of Vat Green 01 dyestuff (mg/L). pH 3, $H_2O_2 = 1$ g/L and 125 W.

Table 2
Colour and COD removal of textile wastewater applying different H_2O_2/UV conditions

Sample	pH	H_2O_2 (g/L)	Color removal (%)	COD removal (%)
ETF 1	3	1	74	69
ETF 2	7	1	49	37
ETF 3	11	1	59	13
ETF 4	3	0.5	28	14
ETF 5	3	2	67	47
ETF 6	3	1.5	73	50

Founded the best pH and hydrogen peroxide concentration, it was studied the kinetics of degradation following the initial velocity method. According to Fig. 4, the kinetics of degradation to the Vat Green 01 dyestuff is pseudo-first order.

Some works has studied the kinetics of degradation of another kind of dyestuff [15–17,24,25] and the most of them founded pseudo-first order or first order kinetics. The model applied was different and the kinetics constants "*k*" founded has also different values to the same dyestuff.

In this work, the "*k*" is calculated by linear regression shown in Fig. 4, and his value was 2.99×10^{-3} min^{-1}. This value is very small and this can explain why the degradation of Vat Green 01 dyestuff is slow compared with other dyestuffs.

3.1.2. Textile wastewater

Several papers shown decolourisation reactions with only one dyestuff [2,17,26,27], but a few demonstrated reactions of real wastewater.

At first, reactions on three different pH's were performed to treat the textile wastewater: 3, 7 and 11, to be compared to the colour removal of the dyestuff solution. This is shown in Fig. 5.

As in the reaction of the Vat Green 01 dyestuff, the best colour removal was found in pH 3, but the textile wastewater reached about 70%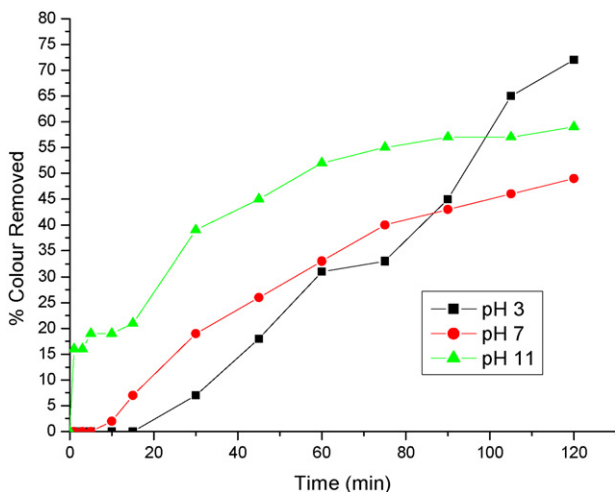 colour removal in 2 h (Fig. 5). This can be explained by the kinetic pathways favourable of the real textile wastewater and the different auxiliary chemicals that promote or not the oxidation.

Table 2 shows different H_2O_2/UV conditions to treat the textile wastewater. According to this table, different from Vat Green 01 dyestuff where the best H_2O_2 dosage was 0.5 g/L, to textile wastewater the best H_2O_2 concentration reached up to 1.0 g/L. After this point, a higher concentration began to inhibit the wastewater photolytic degradation because it acted as a free-radical scavenger itself, thereby decreasing the hydroxyl radicals concentration.

It was observed that after H_2O_2/UV treatment, using the best optimization parameters, there is still about 225 mg O_2/L of COD. This implies that the textile wastewater used in this work still needs further treatment. The H_2O_2/UV process should be used associated with biological treatment. The best form of this association, after or before, depends of the characteristics of the wastewater to be treated.

4. Conclusion

The H_2O_2/UV process was not so efficient to degradation of Vat Green 01 dyestuff where the maximum remove rate was 41%. While to textile wastewater, which contain the Vat Green 01 dyestuff, the process reached 70% of colour remove. This can be explained by the kinetic pathways favourable of the real textile wastewater and the different auxiliary chemicals that promote or not the oxidation.

The COD remove rate of the textile wastewater reached 69% in the same condition where the colour remove was 70%. This remove rate was not so high and this implies that the textile wastewater used in this work still needs further treatment. The best option is associate this process with biological treatment.

The best H_2O_2 dosage to the process was 0.5 g/L to the Vat Green 01 dyestuff and 1.0 g/L to the textile wastewater. Up to these values the H_2O_2/UV process efficiency decreased because of the plenty of H_2O_2 in the reaction medium. When the hydrogen peroxide concentration becomes high, the excess hydrogen peroxide consumes hydroxyl radicals and it performed like a hydroxyl radical scavengers. The optimum dosage depends of the composition of the wastewater to be treated.

Fig. 5. Colour removal of Textile Wastewater in different pH's, $H_2O_2 = 1$ g/L, 125 W and wavelength of the measurement 365 nm.

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