Decolourization of textile wastewater containing green cationic dye by AOPs

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Abstract. One of the main problems in the treatment of textile dyeing wastewater and dye manufacture wastewater is the removal of the dye colour. The colour of wastewater from today's new cationic dyes for polyacrylic fibres is much more difficult to treat by physical techniques such as adsorption and chemical coagulation to archive complete decolourization, because these dyes are very highly soluble in water.

The aim of the present work is to study the factors affecting the rate of decolourization of a textile wastewater witch contain water-soluble green cationic dyes derivatives of compact condensed system 2-aminopyridine. The investigated organic dyes have been treated by advanced oxidative process (AOPs). The following AOPs have been studied: Fe^{2+}/H_2O_2, O_3 and O_3/H_2O_2. The chemical treatability of cationic dyes from wastewater resulted from dyeing process by single ozonation and ozonation enhanced by ferrous iron salt ($FeSO_4 \cdot 7H_2O$) has been reported. The investigated processes followed the model of pseudo-first order reaction kinetic. Also, the VIS and HPLC methods were used, to demonstrate the degradation process of green cationic dyes derivatives from 2-aminothiazolo [4,5-b] pyridine.

Keywords: cationic dye, decolourization, AOPs, Fenton process, ozonation, O_3/H_2O_2, HPLC

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1. Introduction

In the last twenty years cationic dyes are produced and consumed annually in large quantities in textile industry, especially for dyeing of polyacrylic fibres. Cationic dyes include a broad spectrum of different chemical structures, primarily substituted aromatic compounds with heterocyclic groups. Generally, the cationic dyes have a great variety of colours and complex chemical structures and most of them are difficult to be direct biodegradable. Due to their complex chemical structure some of these dyes are suspected carcinogens. The environmental concern of these potentially carcinogenic pollutants in contaminated waters has drawn the attention of many research workers. First the colour in wastewaters is an obvious indicator of water pollution due to dye and pigment [1-3]. Also, the dyes in waters affect photosynthesis activity in environment due to reduced light penetration and may be toxic to some aquatic lives. Sometimes it is difficult to eliminate colour from wastewaters by conventional flocculation or biodegradation. Also, it is very difficult to remove dyes from wastewaters since cationic dyes are stable to light, heat and oxidizing agents and are hardly biodegradable.

It is known the fact that large amounts of coloured wastewaters that contain cationic dyes are generated especially from the textile finishing industry. The studies are estimated that almost 10% of cationic dyes used in textile production and dyeing process can be found in wastewater. Once dyeing is completed, the dyed polyacrylic fibres are washed off several times in order to remove unfixed dyes. This means that a significant amount of these synthetic dyes can be lost into wastewaters during processing operations [4-8]. In many cases this kind of wastewaters is resistant to biodegradation because of its complex structure and it usually contains toxic metabolic products such as aromatic amines compounds [8-11].

Several techniques ranging from physico-chemical (coagulation, adsorption, membrane separation, advanced oxidation processes) to biological methods for cationic dye removal are available. Biodegradation is an environmentally friendly and cost competitive alternative but the

conventional aerobic treatments have been proved ineffective while highly toxic aromatic amines can be formed by reductive fission under anaerobic conditions [2]. Coagulation/flocculation and other conventional techniques are known to be costly and only transfer of dyes from the liquid to the solid phase and thus other secondary problems arise [9].

Advanced oxidation processes have shown a great potential to decolourize and reduce recalcitrant organic compounds such as dyes, surfactants, other auxiliaries from dyeing process and finishing textile process. Moreover, they have been successfully used as pre-treatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes [11].

In this study, the decolourization of green cationic dyes derivatives from compact condensed system 2-aminothiazolo [4,5-b] pyridine has been investigated by applying Advanced Oxidation Process (AOPs).

2. Experimental

2.1. Materials and methods

Green cationic dyes (Fig. 1) are obtained for the first time by authors by original method.

Formula, notation

CD1

CD2

Properties

Green
λ_{max}=419 nm
Absorbance
1.198
ε = 29853

Green light
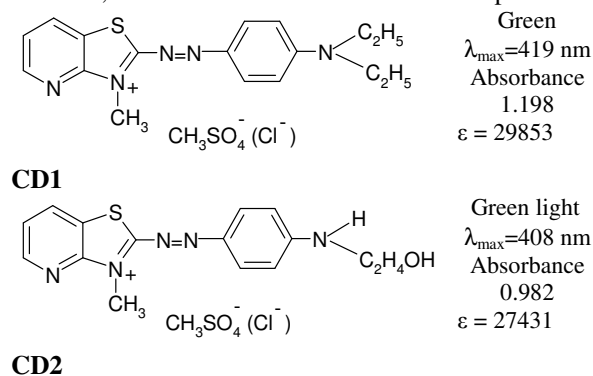λ_{max}=408 nm
Absorbance
0.982
ε = 27431

Fig.1. Green cationic dyes [12] derivatives of compact condensed system 2-aminothiazolo[4,5-b] pyridine [16]

The cationic dyes used for the dyeing of fibres are non-toxic [12, 13] in accordance with obtained results at the toxicological tests [14, 15]. So, these dyes can be used in the dyeing process respecting

the interdiction of ETAD (Ecological and Toxicological Agency of Dyes). The colours of dyed fibres are brightness with good fastness of washing (40^0C), alkaline perspiration, acid perspiration, ultraviolet radiation, cold water and hot water [12].

To demonstrate the fact that these cationic dyes, obtained by synthesis and used with success in dyeing process of polyacrylic fibres can be degraded in small organic molecules by AOPs it have analyzed two concentrations for green cationic dyes in water (100 ppm and 500 ppm).

Hydrogen peroxide and $FeSO_4 \cdot 7H_2O$ (Merck) were used without further purification. All the tests were carried out for 0.5L sample in batch mode at constant pH of 8.5.

2.2. Ozonation and O_3/H_2O_2 processes

Gas flow of ozone was 1 L/min (0.250 mg/L) and was generated from pure oxygen using ozone generation (Fig. 2). Other chemicals used throughout the study included hydrochloric acid and hydrogen peroxide [17]. Measurements of pH were obtained using pH-meter from DREL 2800/Complete Water Quality Control HACH-LANGE case. A Specord 250 UV-VIS spectrophotometer with double - monochromator, variable spectral resolution and cooled double detection and PC system was used to record absorbance and wavelength of maximum. (Table 1). Experiments were performed at room temperature at 1 L (O_3 and O_3/H_2O_2 process) batch reactors with magnetic stirring for one hour.
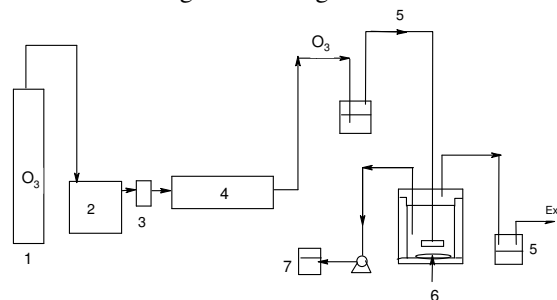

Fig. 2. Experimental set up of apparatus for ozonation process (1 - oxygen cylinder; 2- ozone generator; 3-flowmeter; 4-spectrophotomete; 5-KI scrubber; 6-stirring bar; 7-sampling port).

2.3. Fenton process

A graduated Pyrex glass vessel with magnetic stirring set up was used for Fenton process by using

optimised dosage of H_2O_2. The mixing of sample dye solutions with H_2O_2 and Ferrous sulphate was performed at 200 rpm for 10 min. The concentration of ferrous sulphate was varied from 50-200 mg/L to investigate its effect on decolourization of cationic dye solutions at 100 ppm and 500 ppm concentrations.

2.2. Analyses

The dyes decolourization in solution was monitored by high performance liquid chromatography using a Jasco 800 device, which are equipped with: quaternary pump; vacuum degasser for solvents; auto-sampler (for the automated injection in the chromatographic column of a previously selected quantity of sample and for automated washing of the syringe); column oven for the thermostating the chromatographic column; UV-VIS detector type Diode Array and alternative with fluorescence, with the possibility of simultaneous spectra acquisition; PC system.

The HPLC method use the following reagents: the Nucleosil® 100-5 C_{18} PPN (5 µm particles size) columns were considered to be the most appropriate for the cationic dyes because they allow retention times long enough for an efficient separation and prevent the clogging of the column [19]. For both dyes the mobile phase was Trimethylammonium acetate 0.1 M:acetonitrile:water = 90:8:2 (v/v) with a flow of 1 mL/min. Linear gradient elution was used, from 0% to 20% in acetonitrile in 20 minutes.

3. Results and Discussions

It is known very well the fact that the restraint efficiency of cationic dyes on fibre is situated between 80 and 90%. So, 10 – 20% from these dyes are founded in residual waters resulted from dyeing fibres. These dyes must be removed by degradation as AOPs. In these procedures the molecules of dyes are decomposed in simple and biodegradable molecules.

O_3 and O_3/H_2O_2 processes are strongly pH dependent. Experiments were conducted at pH of 8.5. Ozone can oxidize organic matter in water either directly or through the hydroxyl radicals produced during the decomposition of ozone. The direct oxidation with molecular ozone is of primary importance under acidic conditions, however it is

relatively slow compared to the hydroxyl free radical oxidation in neutral and basic solution. The experimental set up shown in the Fig. 2 has been used the oxidative mineralization in ozone and hydrogen peroxide process. In ozonation process, using 1 L/min gas flow, one hour, at pH 8.5, only 82.1% for CD1, respectively 81.9% for CD2, colour was removed. This could be explained by the fact that an increase in ozone exposure time enhanced the mass transfer and reaction rate of dye solution. The decrease in colour removal efficiency (Fig.3) with increase in dye solution may be attributed to the competition of ozone between parent dye molecules and reaction by-products.
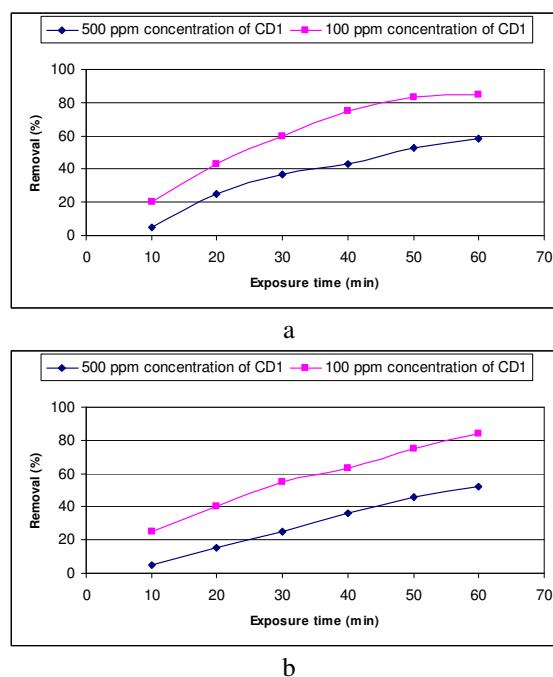

a

b

Fig. 3. Effect of ozone exposure time on colour removal at pH = 8.5; a – results for **CD1** and b – results for **CD2**.

The addition of H_2O_2 (optimal dosage 250 mg/L) to the O_3 enhanced the ozone decomposition because of higher rates hydroxyl radical's production which influenced overall process efficiency. Colour removal (97.91% for the first dye CD1, and 96.93% for the second cationic dye noted with CD2) was achieved applying O_3/H_2O_2 process. An increase in colour removal is observed with the

increase in ozonation exposure time in both concentrations of cationic dyes at optimal H_2O_2 dosage. Initially hydrogen peroxide is dissociated into hydroperoxide ions, which further attack the ozone molecules resulting in the formation of hydroxyl radicals. The decrease in colour removal (Fig. 4) with increase in dye concentration is due to the fact number of dye molecules increased for a fixed no of HO^* radicals.
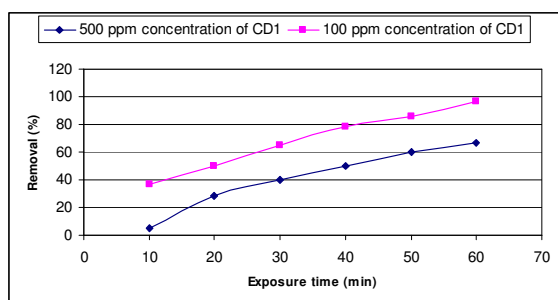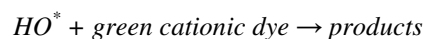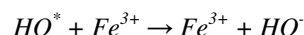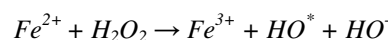

a
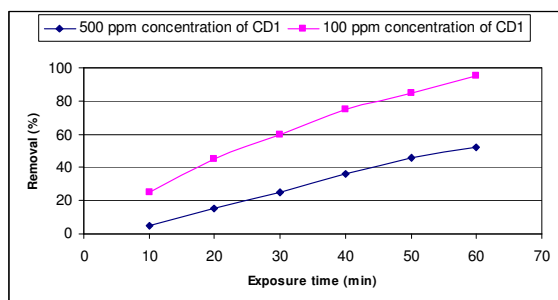
b

Fig. 4. Effect of ozone exposure time on colour removal in O_3/H_2O_2 process (pH = 8.5); a – **CD1**; b – **CD2**.

The both cationic dyes were decolorized fast by O_3/H_2O_2 process in 60 min. However, decolourization means just disappearing of chromophoric part of the dye molecule and splitting in smaller organic parts.

Fenton's reagent, a mixture of H_2O_2 and Fe^{2+}, which can generate great amount of HO^* radicals with powerful oxidizing ability has been proposed for the degradation of green cationic dyes derivatives from compact condensed system 2-aminothiazolo[4,5-b] pyridine. In general, the hydroxyl radical has a high oxidation po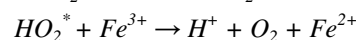tential (2.8 eV), a very short live, but reactive and it attacks dyes by either abstracting a hydrogen atom or adding itself to double bonds.
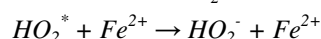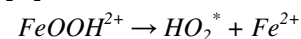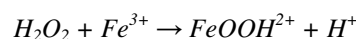
The Fenton process can be defined as the oxidation of organic compounds in an aqueous solution by using Fenton reagent (ferrous ion and hydrogen peroxide). The accepted mechanism of Fenton reaction to form hydroxyl radicals is [20]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^* + HO^-$$

$$HO^* + Fe^{3+} \rightarrow Fe^{3+} + HO^-$$

$$HO^* + green\ cationic\ dye \rightarrow products$$

The HO^* radicals formed in these reactions will then attack the cationic dyes present in wastewater.

Also, Fe^{2+} can be regenerated through the reaction of Fe^{3+} with hydrogen peroxide (Fenton-like-reaction):

$$H_2O_2 + Fe^{3+} \rightarrow FeOOH^{2+} + H^+$$
$$FeOOH^{2+} \rightarrow HO_2^* + Fe^{2+}$$
$$HO_2^* + Fe^{2+} \rightarrow HO_2^- + Fe^{2+}$$
$$HO_2^* + Fe^{3+} \rightarrow H^+ + O_2 + Fe^{2+}$$

When large amounts of Fe^{2+} are present either in Fenton reaction or Fenton-like-reaction system, the degradation of cationic dyes are very fast because large amount of HO^* radical are produced.

Initially an increase in colour removal was observed with the increase in ferrous sulphate amount for all concentrations of green cationic dyes. The removal of colour decreased beyond 100 mg/L of $FeSO_4$ concentration. Maximum value of colour removal was at 100 mg/L (Fig. 5). The specialty literature shows the fact that the rate of decolourization increases with an increase in the concentration of ferrous ions [20]. The decrease of colour removal after a specific concentration of ferrous sulphate could be explained as ferrous ions catalyze H_2O_2 to form hydroxyl radicals quickly at the initial stage of reaction. The amount of unutilized iron salts increases which would result an increase in the TDS and colour contents of the residual water.
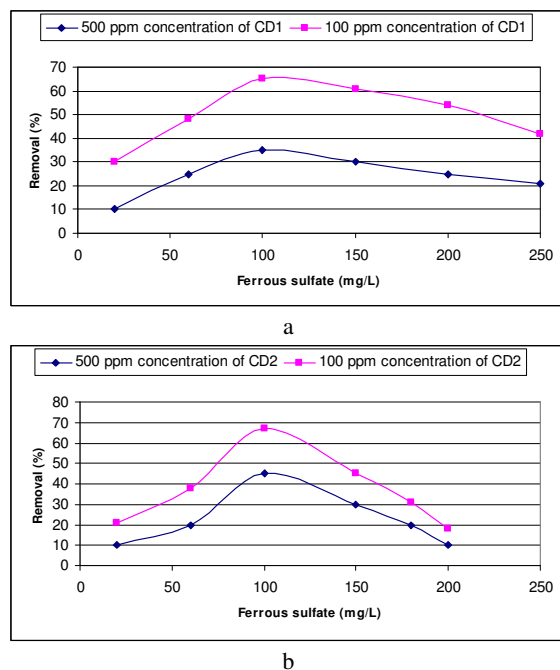
a

b

Fig. 5. Effect of ferrous sulphate concentration on colour removal a – **CD1**; b – **CD2**.

The major kinetic pathway of cationic dyes degradation could be expressed as follows [3]:

$$\frac{dC_A}{dt} = -k \cdot C_A \cdot C_{HO^\bullet}$$

where, C_A represented concentration of dye, $C_{HO^\bullet}$ denoted hydroxyl radical concentration and k is the first order rate constant. Assuming hydroxyl radical concentration reached equilibrium, than $C_{HO^\bullet}$ could be treated as a constant.

The decolourization rate was found to follow pseudo-first order kinetics with respect to the dye concentration as rate constant was affected by changing the initial concentration of dye.

The expression of equations is [3]:

$$\frac{dC_A}{dt} = -k \cdot C_A \qquad (1)$$

$$\ln(\frac{C_0}{C_A}) = -k \cdot t \qquad (2)$$

The values of rate constants have been calculated using a specially software and are presented in Table 1. The highest values can be observed for **CD1** and **CD2** decolourization by O_3/H_2O_2 process.

Table 1. Rate constants of green cationic dyes oxidative degradation

AOPs	Rate constant, k [min⁻¹]	
	CD1	CD2
Fe^{2+}/H_2O_2	0.054	0.050
O_3	0.031	0.034
O_3/H_2O_2	0.068	0.066

The HPLC chromatograms (see Experimental part) of green cationic dyes **CD1** (as example) at both concentrations is presented in Fig. 6.
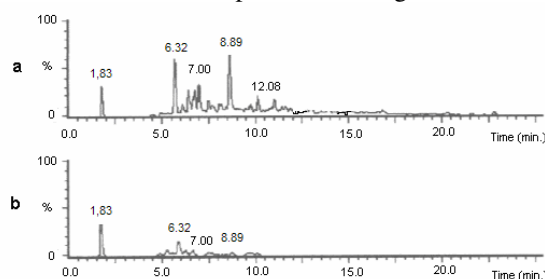

Fig. 6. The HPLC chromatograms for dye CD1 initial (a) and after decolourization with O_3/H_2O_2 (b)

The dye concentration decreases comparative with the initial concentration after 30 minutes of the treatment and several products are formed and identified. Very low concentrations (traces) of products formed during the treatment prove extensive degradation and mineralization, which is very important from the environmental point of view.

4. Conclusions

In this study were analyzed some oxidative methods Fe(II)/H₂O₂, O₃ and O₃/H₂O₂ for degrade of cationic dyes which are used with success in dyeing process. Almost 10 – 20% from these dyes are founded in residual waters resulted from dyeing polyacrylic fibres. The experimental results demonstrate that the most effective AOPs for the dyes decolourization were O₃/H₂O₂ and Fe²⁺/H₂O₂. The investigated processes followed the model of pseudo-first order reaction kinetic. Also, the HPLC method was used, for demonstrated the degradation process of green cationic dyes.

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