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Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse

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ABSTRACT

The objective of this study was to investigate the degradation and mineralization of an azo-dye, the Congo red, in aqueous solutions using ozone. Phytotoxicity and the inhibitory effects on the microbial activity of the raw and the ozonated solutions were also carried out with the aim of water reuse and environment protection. Decolorization of the aqueous solutions, disappearance of the parent compound, chemical oxygen demand (COD) and total organic carbon (TOC) removal were the main parameters monitored in this study. To control the mineralization of the Congo red, pH of the ozonated solution and heteroatoms released from the mother molecule such NH_4^+, NO_3^- and SO_4^{2-} were determined. It was concluded that ozone by itself is strong enough to decolorize these aqueous solutions in the early stage of the oxidation process. Nonetheless, efficient mineralization had not been achieved. Significant drops in COD (54%) were registered. The extent of TOC removal was about 32%. Sulfur heteroatom was totally oxidized to SO_4^{2-} ions while the central –N=N– azo ring was partially converted to NH_4^+ and NO_3^-. Results of the kinetic studies showed that ozonation of the selected molecule was a pseudo-first-order reaction with respect to dye concentration. The obtained results also demonstrate that ozone process reduced the phytotoxicity of the raw solution and enhanced the biodegradability of the treated azo-dyes-wastewater. Hence, this show that ozone remains one of the effective technologies for the discoloration and the detoxification of organic dyes in wastewater.

1. Introduction

It is broadcasted that more than 60% of the dyes world production is consumed by textiles industries and more than half of this quantity is discharged into receiving water bodies more or less without treatment hampering thus the function of the ecological process. Moreover, different papers report that in most cases, biochemical oxygen demand/chemical oxygen demand ratio of the composite textile wastewater is around 0.25 implying the non-biodegradability of the organic matter therein [1–4]. Among the used dyes, azo-dyes are the most commonly utilized reagents owing to the presence of the azo-group which confers to these chemicals a certain resistance to light, acids, bases and oxygen, the desired proprieties for clothes' makers [5,6]. More than 53% of these commonly used azo-dyes are identified as non-biodegradable compounds [7]. As a consequence, wastewaters bearing such type of dyes are known to be highly resistant to the mostly widespread used conventional wastewater treatment method: the biological process [8–10]. Other technologies evaluated for dyes removal included: adsorption [11], coagulation, flocculation [12] and reverse osmosis processes [13,14]. Although these methods resulted in a significant color removal, they were either costly to apply in the actual field or enable to meet the discharge criteria of wastewater in term of chemical oxygen demand. Adsorbent regeneration, excess sludge production and the rapid fouling of the used membranes are some of other handicaps of these processes. It appears that applying a post-oxidation treatment able to degrade the so likely refractory molecules into smaller ones, which can be further oxidized by biological methods, remains the alternative way while dealing with colored wastewater. Within this regard, different oxidation processes such as NaOCl, H_2O_2 and O_3 as a single process or combined have been tested [15]. One aspect which is relevant to hypochlorite based decolorization process is that for environmental reason, the future use of chemicals containing chlorine should be restricted. The use of H_2O_2 is usually limited due to its relatively low oxidation power (1.78 V). As to ozone, which is considered one of the powerful oxidizing agents (2.07 V) [16], its application as a pretreatment for the improvement of wastewater biodegradability is thoroughly investigated [17–19]. It has been shown that ozone cleaves the conjugated bonds of azo-dyes chromophores,

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leading to color removal and enhancing the biodegradability of the treated wastewater [17,20]. In contrast, other studies [21] claim that short-term ozonation of a model aqueous azo-dye solution and dye-bath effluents from a textile dyeing and finishing industry formed toxic compounds. These results were proved by testing the biodegradability of the effluent and bioluminescence tests [21,22]. Likewise Martins et al. [23] have shown that in order to obtain high toxicity removal, longer ozonation periods with high ozone dozes have to be applied. Zhang et al. [24] reported that the major disadvantage of using ozone is the possible formation of toxic byproducts even from biodegradable substances. Hence, this makes it necessary to test the toxicity and the phytotoxicity of the compounds generated by ozonation to determining whether the treated wastewaters present a risk once discharged to the environment or planned to be reused. In the present work, a short-term ozonation of a widely used commercial azo-dye, the Congo red, was carried out. The dye was selected due to its complex chemical structure, high molecular weight, high solubility in water and its persistence one it is discharged into natural environment. The effect of some auxiliary dyeing additives on the ozonation process as well as the formation of potential toxic by-products and their inhibitory effects on the microbial activity and on a model plant were investigated.

2. Materials and methods

2.1. Oxidation process

Congo red was purchased from Merk as a commercially available dye with 98% purity. The dye's chemical structure and its main characteristics are shown in Fig. 1. All aqueous ozonated solutions of Congo red were prepared with ultra pure water and had a concentration of 0.30 g/l to simulate a medium loaded textile wastewater. Ozonation was conducted in a 100 ml cylindrical glass reactor using a glass bubble diffuser as shown in Fig. 2. All connections from the ozone generator to the reaction vessel were Teflon made tubing. Due to small reactor volume, a fresh dye sample of 50 ml was used for each run. A Triligaz ozone generator was used to produce ozone from the oxygen feed gas with a flow rate of 2.7 g of O_3/h corresponding to its minimum producing capacity enabling us following the kinetics studies. The ozone leaving the reactor was trapped by tow-sequential bubblers containing a potassium iodine (KI) aqueous solution (2%). The influence of some salts that may coexist with the dye on the ozone decolorization efficiency was investigated.

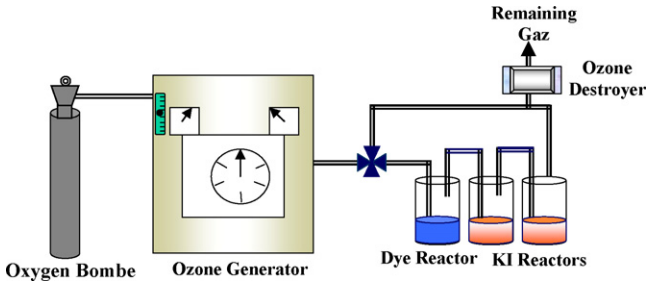

Fig. 2. Sketch of the experimental apparatus used for the ozonation.

Experiments were also conducted using the advanced oxidation process (O_3/H_2O_2). Therefore, hydrogen peroxide (31%, w/w) was added to the Congo red aqueous solution to achieve a final concentration of 7.5 mM just before the ozone containing gas entered the reactor.

2.2. Monitored parameters

Oxidation advancement was followed by monitoring the fading of color, chemical oxygen demand (COD), total organic carbon (TOC) and pH. These parameters were analyzed according to the standard methods described in the Japanese International Standard (JIS) handbook [25]. Absorbance was determined using a Hitachi U-2000 UV/vis spectrophotometer. Total organic carbon was measured using a Shimadzu-TOC-5000A analyzer (catalytic oxidation on Pt at 680 °C) via calibration using standards of potassium phthalate.

2.3. Inorganic ions evolution during the ozonation

To control the mineralization of the Congo red, heteroatoms, released from the mother molecule, such NH_4^+, NO_3^- and SO_4^{2-} were quantified using an ionic chromatography (HIC-6A Shimadzu type) equipped with a conductivity detector and a Shim-pack column. The separation was achieved using an isocratic elution at a flow rate of 1.0 ml/min. A mobile phase of 1 mM of tris(hydroxymethyl)aminomethane and 1 mM of phthalic acid was used for nitrite, nitrate and sulfate ions and a 25 mM of metasulfonic acid in the case of ammonia.

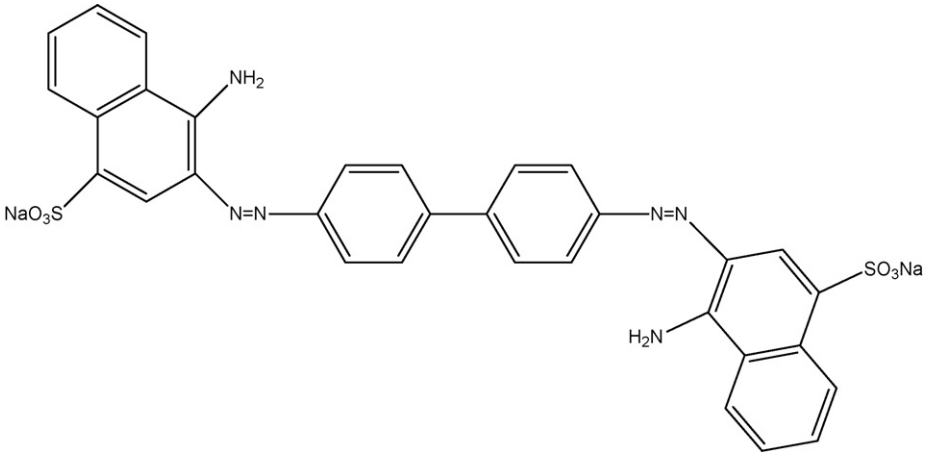

Fig. 1. Chemical structure of the studied molecule (molecular formula, $C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight = 696.68 g, solubility in water at 25 °C = 25 g/l; λ_{max} at pH 7 = 550 nm; color index = 22120).