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Ozonation pre and post-treatment of denim textile mill effluents: Effect of cleaner production measures

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ABSTRACT

Denim production, which is one of the leading sub-sectors of textile industry that generates considerable amount of wastewater with high pollution load both from dyeing and finishing processes. This sub-sector is therefore to consider cleaner production opportunities for these processes to reduce its wastewater generation and pollution load. In a denim-producing plant, the wastewater treatability studies have revealed that the most technically applicable cleaner production alternatives are caustic recovery from alkaline finishing wastewaters, and reuse of indigo dyeing wastewaters via the application of membrane filtration. In the present study, impact of the changes in the final effluent quality due to the foreseen cleaner production measures were considered in reference to the evaluation of impact on ozonation treatment of the effluent from a denim-producing plant. Ozonation was applied as pretreatment to the effluent from the plant before the foreseen measures (chemical oxygen demand, COD = 2750 mg/L; color = 3950 Pt–Co), and to the simulated effluent after the foreseen measures (COD = 3100 mg/L; color = 4500 Pt–Co); and also as post-treatment to the biologically treated effluent (COD = 800 mg/L; color = 3700 Pt–Co) before the foreseen measures. When applied to the effluent before the foreseen measures as pretreatment, ozonation provided 86% color and 46% COD removal with 3240 mg/h ozone dose in 70 min. However, less satisfactory results were obtained with the wastewater after the measures; with 86% color and 31% COD removals at 3960 mg/h ozone dose in 80 min. In parallel to the decrease observed in COD removal, ozone consumption was also much higher than that for the wastewater before the cleaner production measures. The findings have indicated that the environmental benefits to be brought by cleaner production measures have to be balanced against the risks to be encountered in the treatment of the final effluent.

1. Introduction

The textile industry is a water intensive sector and production of textiles affords a great variety of processing steps requiring use of large amounts of water and chemicals. This fact has put efforts on the minimization of use of, and where applicable reuse of, raw materials and water within the production steps. Being a water intensive sector (typically 200–400 L per kg of fabric); in textile industry, liquid discharges are of primary concern rather than gaseous emissions and solid wastes. Given the great variety of fibers, chemicals and other auxiliaries in use, textile manufacturing processes generate wastewaters containing metals, phenols, toxic compounds and/or phosphates. These constituents which are mostly resistant to conventional biological treatment, can pass untreated through the conventional wastewater treatment systems (Hu et al., 2016).

For the removal of the recalcitrant organics, conventional treatment methods are inappropriate and chemical oxidation methods are known to be much more effective (Ciardelli et al., 2001). Chemical oxidation with ozone is one of the most suitable chemical oxidation processes for effective color removal from textile effluents, with simultaneous interaction and breakdown of refractory organic matter resistant to biodegradation (Dogruel et al., 2002). Chromophore groups, generally organic compounds with conjugated double bonds can be broken by ozone (directly or indirectly) into smaller forms, decreasing the color of the effluent (Oguz and Keskinler, 2008). However, a complete mineralization by

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ozonation is usually not efficient and economically feasible, whereas, its application in one step for color removal and partial oxidation to improve biodegradability seems to be more promising (Gupta et al., 2015). The conversion of refractory organic matter into more biodegradable intermediates by ozonation, allowing for efficient COD removal by succeeding biological degradation is generally reported to reduce the operational costs (Van Aken et al., 2011). Post-ozonation, on the other hand, may provide better COD removal and have a polishing effect on the effluent quality (Dogruel et al., 2002).

The capability of ozone in oxidizing various pollutants in the water by direct attack on the different bonds; is further enhanced in the presence of H_2O_2 due to the generation of highly reactive OH• radicals. The dissociation of H_2O_2 results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals (Gogate and Pandit, 2004). When hydroxyl radical concentration is elevated, the oxidation rate is further increased.

Ozone can be applied either before or after the biological treatment process. Best results concerning color removal are achieved if the wastewater has been previously pretreated in order to remove other constituents so that the ozone oxidizing power is "consumed" only or at least at a maximum proportion in color removal. But still, in some cases, pre-ozonation may be expected to ease biological treatment by converting the more slowly biodegradable COD into simpler compounds or by reducing the amount of inert organic matter.

A study was undertaken as the first application and evaluation of Best Available Techniques (BAT) within the context of the EU's Industrial Emission Directive to a textile mill in Turkey. The objective of the project was to develop a "best practice example" for the textile sector. In the project (CAYDAG-105Y088); for a denim manufacturing textile mill in Kayseri, Turkey, BAT requirements were determined, several better-water management or cleaner production measures were identified targeting at the minimization, and where applicable, reuse of both water and raw materials. In this context; a series of alternative cleaner production opportunities were foreseen for the management of different wastewater streams from the mill. The opportunities considered in the present study are caustic recovery from alkaline finishing wastewaters and water reclamation from indigo dyeing wastewaters by membrane filtration. After these cleaner production measures are taken in the mill, it is expected that there will be reduction in the volume of wastewater from dyeing and finishing operations. Moreover, there will be an increase in the strength of the wastewater from indigo dyeing, as the reject stream from membrane filtration will be going to the already existing wastewater treatment plant applying activated sludge process. On the other side, caustic recovery from finishing wastewaters will yield a finishing wastewater with a lower caustic content which is again the reject stream from the membrane filtration of caustic finishing wastewater. It is expected that these reject streams and the wastewaters from other units will come together to form the overall wastewater flowing into the activated sludge plant. As the reject streams are high in strength, it is expected that the overall wastewater after the foreseen cleaner production measures will be higher in strength and lower in biodegradability.

In the present study which is a part of the above mentioned investigation; ozonation was considered as an option for improving biodegradability of textile wastewater constituents (Asghar et al., 2015) which are mostly resistant to conventional biological treatment due to the chromophore groups of the textile dyes (Vishnu et al., 2008; Souza et al., 2010). As Asghar et al. (2015) indicated, ozone reacts selectively and slowly with organics, it is sometimes combined with catalysts that can convert it to hydroxyl radicals known to be the most important and most reactive oxidants which are capable of reacting with all types of solutes that can be subjected to oxidization. De Moraes et al. (2000) studied the degradation and toxicity reduction of textile effluent combining the photocatalytic process with ozonation and indicated reductions of 95% for color, 60% for total organic carbon and 50% for toxicity of the effluent. Nonetheless, Gianluca and Nicola (2001) reported that color removal from textile wastewater treated biologically was dependent on the initial COD value of the textile wastewater. According to Jianging and Tingwei (2001), ozonation at a dose of 30 mg/cm^3 increased the rate of biodegradability of textile wastewater by a factor of 1.6 and the increase in the degradation rate was influenced by the type of dye and its concentration.

As indicated above, all the studies about the ozonation of textile wastewaters, dealt with various types of textile wastewaters (synthetic or real) without considering possible effects of cleaner production measures such as water reuse or chemical recovery practices on the end-of-pipe treatment process. The studies dealing with the effects of cleaner production measures are all limited to the assessment of decrease in point source pollution (Bezama et al., 2012), environmental impacts (Yilmaz et al., 2015), or econometric influences (Castillo-Vergara et al., 2015). The goal of this study was to explore the possible effects of applying certain cleaner production measures (water reclamation for indigo dyeing wastewater and caustic recovery for mercerizing wastewater) on the end-of-pipe treatment of the resulting effluent and to see the effects on the performance of ozonation when applied as pretreatment.

The research for pretreatment of the overall plant effluents was carried out in two parts; of which the first is with the already existing overall plant wastewater and the second is with the wastewater expected (simulated wastewater) after the application of cleaner production measures which are the reuse of caustic in the alkaline finishing process wastewater and the reuse of indigo dyeing wastewater following membrane filtration. For the post treatment, ozonation experiments were conducted with the wastewater from the effluent of the biological wastewater treatment plant existing in the textile mill. In all the ozonation and ozonation + H_2O_2 application tests; color, COD, 5-day biochemical oxygen demand (BOD_5), ozone utilization ratio and BOD_5/COD parameters were measured to determine the treatment efficiency. As the first stage in experimental studies, pH effect was investigated to determine the optimum pH to be maintained in further ozonation tests.

2. Experimental

2.1. Wastewaters

Ozonation experiments were conducted on three different wastewater samples obtained from denim manufacturing textile mill in Kayseri, Turkey. The first is the so called "before the cleaner production measures" wastewater, which was taken from the influent of the wastewater treatment plant of the mill. This wastewater is mainly from dyeing and finishing processes (Table 1). The second is the wastewater so called "after cleaner production measures" that was prepared using the wastewater samples

Table 1
Wastewater streams forming the overall plant wastewater before and after the foreseen cleaner production measures.

Process	Before measures (% by volume)	After measures (% by volume)
Dyeing	35	24
Finishing	45	31
Other	20	45