USE OF ADVANCED OXIDATION PROCESSES FOR TEXTILE WASTEWATER TREATMENT – A REVIEW

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Abstract: *Recently, an increasing application of various AOPs for textile wastewater treatment has been observed for its advantages to conventional treatment methods. AOPs provide satisfactory result of textile effluent treatment. In this paper, on overview of use of ozone and ozone combined with other AOPs (O_3/H_2O_2, O_3/UV, O_3/US) for effluent decolouration and BOD/TOC elimination is given.*

Keywords: *O_3, O_3/H_2O_2, O_3/UV, O_3/US, dye mineralization, effluent decolouration*

1. Introduction

The shortage of water resources around the world increases the demands on the use of secondary sources, such as wastewater. In this perspective water recycling and re-use of treated effluent in high water consuming industrial sectors seem be to be a viable alternative to save valuable resources [1]. Advanced wastewater treatment by ozone and other oxidation technologies has a number of advantages compared to other technologies. Although some oxidation processes – use of ozone for disinfection of drinking water – have been known since the 19th century, the rapid development and application of advanced oxidation processes (AOPs) is a matter of development in the last decades. AOPs found application mainly in the oxidation of complex organic compounds which are difficult or impossible to degrade into simpler organic compounds by biological treatment. AOPs are based on generation and use of powerful but relatively non-selective highly reactive oxidizing species (primarily the hydroxyl radical OH• having high oxidation potential and low selectivity). These radicals are able to oxidize compounds that are not degradable by conventional oxidizing agents as oxygen O_2, ozone O_3 or chlorine Cl_2 [2]. The fact that the OH• radical attack is characterized by low selectivity is an important factor for a broad application of AOPs in a wide range of technologies.

To make the advantages of advanced wastewater treatment by small and medium enterprises, further cross cutting is needed. The proposed project AOP4Water aims to use AOPs in combination with biological treatment to define better and cost-efficient wastewater treatment. The project proposes use of ozone and use of ozone in combination with ultrasound (US), ozone with hydrogen peroxide, ozone with UV light. In the first stage of the project identification of main water uses and associated water quality and quantity requirements have been performed to evaluate the actual water uses in the different factories of the target industrial sector and to prepare water flow mass balance analysis for the chosen factories. This paper aims to provide an overview of recent use of ozone and selected AOP in textile industry.

2. Textile industry

Textile industry is very water intensive. Water is used through the whole textile production from cleaning of raw material to many washing through textile production or as a principal medium in various processes. Processes in the textile industry can be divided into mechanical and finishing operations. During mechanical operations fabrics are manufactured of fibre by spinning, weaving and knitting. Sizing is one of the technological steps of weaving of cotton and its blends. In terms of water consumption mechanical operations are not very water demanding. The second process is finishing (wet processing) providing the textiles with the main functional characteristics (appearance, feel, absorbency, softness, water repellence, crease resistance). During finishing a significant amount of water is consumed and also a significant amount of waste and pollution are produced. According to the material composition these processes are used desizing, scouring, bleaching, mercerization, carbonizing, fulling, washing, dyeing, finishing.

2.1 Wastewater management in textile industry

The main environmental issues arising from textile manufacturing regard primarily emissions to water and air and energy consumption. However, the major environmental concern in textile industry is the amount of water being discharged as well as its chemical content and load. Water is the principal medium for removing impurities, applying dyes and finishing agents, and for steam generation. The primary water consumption reaches 80–100 m^3/ton of finished textile and wastewater discharge 115–175 kg of COD/ton of finished textile; a large range of organic chemicals, low biodegradability, colour, and salinity in discharged water are also of environmental concern [3]. Major pollutants specifically found in textile wastewater are suspended solids, highly recalcitrant chemical oxygen demand, dyes giving intense colour and other soluble substances [4].

Pollution load and content is related to the processes used. A large percentage of the total emission load from textile industry activities is attributable to substances that are already on the raw material before it enters the finishing mill (e.g. impurities and associated materials for natural fibres, preparation agents, spinning lubricants, sizing agents, etc.). All these substances are usually removed from the fibre during the pretreatment process before colouring and finishing [5]. Secondly, significant amounts of water are consumed during wet processing. Bulk of water is utilised in washing at the end of each process. Dying is another important source of pollution in textile industry wastewaters containing dyes and other chemical compounds mainly from dyeing and finishing processes. Polluting substances can originate from the dyes themselves (e.g. aquatic toxicity, metals, colour), auxiliaries contained in the dye formulation (e.g. dispersing agents, anti-foaming agents, etc.), basic chemicals and auxiliaries used in dyeing processes (e.g. alkali, salts, reducing and oxidising agents, etc.) and residual contaminants present on the fibre (e.g. residues of pesticides on wool, spin finishes on synthetic fibres) [5]. However, strong colouration of the textile industry wastewater is of the major environmental concern and if not treated properly it can cause serious problems in the environment.

2.2. Use of ozone for textile industry wastewater treatment

Textile industry produces large quantities of highly coloured effluent, which is generally toxic and resistant to destruct by conventional treatment methods. Low biodegradability of many fibre acid, direct and reactive dyes allows them to pass untreated through the sewerage works due to their high water solubility and relatively low molecular weight [6]. Important advantage of use AOP and their combinations is the destructive character of AOP to conventional such as activated carbon adsorption, coagulation, flocculation or precipitation. Besides not satisfactory treatment result, sludge is created when conventional methods are used causing another source of problems [7].

Ozonation is relatively effective in reducing colouration of various dye origins and toxic effects of textile effluents; the main environmental concern related textile wastewater effluent discharge. Dissolved in water ozone reacts with many organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidant like hydroxyl radical [2]. Use of ozone for wastewater treatment in textile industry to remove colouration and lower toxicity has been documented in several studies; however sufficient effect on BOD/TOC removal was not confirmed. Baban et al. [8] applied ozone (C_{O3}=18.5 mg/l; input rate) to treat remaining composite wastewater (spent dye baths and first and second rinses) from woollen textile finishing industries. The results indicated that 40 min ozonation of biologically treated wastewater yielded almost colourless effluent with a decolourization efficiency of around 98–99% and with a corresponding ozone absorption rate of 58.0 mg/l. Biological treatment followed by 10 min ozone oxidation reduced the overall toxicity significantly (92%); however ozonation has a slight effect on COD removal [8]. Similar results have been achieved in study of Selchuk [9]. The study confirmed almost complete colour absorbances (over 98%) in 20 min ozone contact time, while COD removal (37%) was very low and almost stable in 30 min ozonation period. The toxicity of wastewater reduced after colour degradation by 85% at the transferred ozone concentration of 82.3 mg L^{-1} [9].

Commercial dyes used in textile industry can be classified according to their chemical composition (azo, antrachinone, sulphur, triphenilmethane, indigoid, phtalocyanine, etc.) or according to their application class (acid, direct, disperse, metal complex, chrome, reactive, etc.) [5]. Azo-dyes are the most commercially used dyes and comprise of a nitrogen double bonds (–N=N–), and when attached to molecules they become monoazo, diazo or polyazo dyes. Azo dyes, with the exception of few simply structured dyes, resist biodegradation under aerobic conditions. On the other hand, azo bond is vulnerable to reductive cleavage and its degradation products include colourless aromatic amines which are known to be toxic and potentially carcinogenic [10]. The study of Wang et al. [11] documented significant effect on colour removal and increased biodegradability and COD, TOC reductions about 40% and 25% for 6 h ozonation; however, short-term ozonation led to a formation of highly toxic by-products. Similar results for decolouration, COD and TOC removal were achieved by Chu et al. [12] on practical textile wastewater treatment. Use of ozone for decolouration textile industry effluent was also documented for reactive dyes that are widely used for dyeing of cotton [13-15]. The latter two studies [14-15] also investigated the possibility of recycling of ozone treated effluent. Ozonation provided satisfactory decolouration after a relatively short period ozonation (for example 10 minutes) [15]. Ozonation also proved to be efficient for colour removal caused by dispersed dyes (complete decolorization in

1 min at the ozone dose of 50 mg dm^{-3}, provided the colloidal and suspended particles were previously removed from the wastewater); however, removal of COD was not sufficient to reach discharge standards [16].

The main factors affecting ozonation performance are pH, the nature and concentration of oxidisable organics, applied ozone dose, competition between the target compound and biodegradable by-products, the presence of oxidant scavengers, and the efficiency of ozone mass transfer [17-18]. Although increased ozone doses has a positive effect on decolourisation of acid dye solutions effluents and the efficiency of the treatment increases with higher pH (pH range 5–9), an adverse effect of buffered solutions was reported [19]. Increase of the mass transfer rate of ozone and enhancement of efficiency of the ozonation process was achieved by using a microbubble generator that enabled high intensity microbubble solution, utilization of almost all input ozone and faster decolourization and organic reduction [12].

2.3. Use of ozone and hydrogen peroxide for textile industry wastewater treatment

Hydrogen peroxide is relatively inexpensive, readily available chemical oxidant that accelerates decomposition of ozone and enhances formation of hydroxyl radical. The addition of both hydrogen peroxide and ozone to wastewater accelerates decomposition of ozone and enhances production of hydroxyl radical [20]. H_2O_2 acts as a catalyst and accelerates the decomposition of ozone to hydroxyl radical [21]. Higher pH positively influences dissociation of H_2O_2 into HO^{2-} ions that initiate decomposition of ozone more effectively than OH• [22]. Rapid and complete decolourization of textile industry effluent can be achieved; however this combination like use of ozone alone is not able to bring complete mineralisation either [23]. Kurbus et al. [24] tested performance of H_2O_2/O_3 to remove colour, COD and TOC for several vinylsulphone reactive dyes solutions in a pilot scale plant. The study showed that decolourisation took a long time (90 min) than other combinations tested; COD removal obtained after decolourisation was satisfactory (about 300 mgL^{-1} from the initial dye concentrations around 1 500 mgL^{-1}). Low performance of the combination was explained by pH; alkaline conditions enable reaction of hydrogen peroxide with NaOH resulting in formation of sodium peroxide (Na_2O_2) and decreasing concentration of hydrogen peroxide for formation of hydroxyl radicals [24].

2.4. Ozone and ultrasound (US)

Sonochemical reactions are induced upon high-intensity acoustic irradiation of liquids at frequencies that produce cavitation (typically in the range 20–1000 kHz). Cavitation refers to formation, growth, and implosive collapse of gas- or vapour-filled cavities (bubbles) in a liquid matrix. Collapse of the cavities produces localized high-temperature (about 5 000°C) and high-pressure (about 50 MPa) hotspots [10]. During collapse, water vapour and gas trapped inside the bubble are fragmented and dissociate into a variety of radicals, including hydroxyl. When ozone is introduced into a sonolysis system, the ultrasonic irradiation enhances the mass transfer, dispersion, and solubility of O_3, and it enhances the production of additional OH• [25]. Recently, attention has been given to the use of ultrasound in combination with ozone for textile industry wastewater treatment. The studies proved that combination of ozone with ultrasound is effective for removal of colour, COD and TOC [16, 10]. Use of ultrasound alone for removal of TOC and colour caused by azo dyes appeared to be rather inefficient

[10]. Similar results were achieved in the another study [28] proving that combination was more effective form mineralization of reactive dye C.I. Reactive Blue than use of ozone or ultrasound alone.

Combination of ultrasound with ozone or ultrasound with ozone and UV provides better results in terms of dye degradation and effluent decolourization. The study of Tezcanli-Guyer and Ince [26] compared performance of various AOP (ozone, ultrasound and UV) on degradation of azo dyes. The study showed that ozone in combination with ultrasound (520 kHz) has similar performance like combination of ozone with UV for decolouration of textile wastewater, while combination of ozone, ultrasound and UV was more than 25 % than each. The synergic effect of the latter combination was attributed to enhanced ozone diffusion by mechanical effects of ultrasound, and photolysis of ultrasound-generated H_2O_2 to produce hydroxyl radicals [26].

2.5. Ozone with UV light

UV-based advanced oxidation processes are based on formation of hydroxyl radicals OH• through the direct ozonation and photolysis reactions and hydroxyl radical oxidation [28]. Ozone combined with UV light demonstrated to be effective mean for textile wastewater treatment. Azbar et al. [29] studied efficiency of several AOP combinations for colour and COD for a polyester and acetate fibre dyeing effluent. The study showed that combination of ozone and UV light reached COD removal of 94% and colour removal of 93%. However, among the AOPs tested (O_3, O_3/UV, H_2O_2/UV and O_3/H_2O_2/UV), the combination of ozone, UV and peroxide appeared to be the most efficient in terms of COD and colour removal with a 99% and 96% [29]. Decolouration effect of UV/O_3 combination was successfully tested on six azo dyes effluent; more than 95% of colour was removed in less than 11.5 minutes for all six azo dyes (initial dye concentration 20.0 mg dm^{-3}, oxygen flow rate 6.0 $dm^3 min^{-1}$) [30]. The study showed dependence of the chemical structure of the dye on the efficiency of the process. The more azo bonds (–N=N–) the more difficult the process of decolourization is [30]. Ozone combined with UV also proved to be more efficient for BOD elimination. Efficiency of BOD elimination on biologically treated textile industry effluent was almost six times higher for ozone combined with UV after 30 minutes contact time [31].

3. Conclusions

This review confirmed that AOP have a significant potential for textile industry wastewater treatment. Large quantities of colours and other contaminants present in textile wastewaters pose significant demands on its treatment. As single treatment method cannot effectively remove all contaminants from wastewaters, preliminary laboratory tests have to be carried out before selecting final treatment method considering that the efficiency of AOP is compound specific and thus have an effect on efficiency of the treatment. The actual laboratory testing textile industry wastewaters in relation to cost-effectiveness of the treatment will be performed in the next stage of the AOP4WATER project.

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