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Research article

Influence of ozonation and biodegradation on toxicity of industrial textile wastewater

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A B S T R A C T

The textile industry demands huge volumes of high quality water which converts into wastewater contaminated by wide spectrum of chemicals. Estimation of textile wastewater influence on the aquatic systems is a very important issue. Therefore, closing of the water cycle within the factories is a promising method of decreasing its environmental impact as well as operational costs. Taking both reasons into account, the aim of this work was to establish the acute toxicity of the textile wastewater before and after separate chemical, biological as well as combined chemical-biological treatment. For the first time the effects of three different combinations of chemical and biological methods were investigated. The acute toxicity analysis were evaluated using the Microtox® toxicity test. Ozonation in two reactors of working volume 1 dm^3 (stirred cell) and 20 dm^3 (bubble column) were tested as chemical process, while biodegradation was conducted in two, different systems – Sequence Batch Reactors (SBR; working volume 1.5 dm^3) and Horizontal Continuous Flow Bioreactor (HCFB; working volume 12 dm^3). The untreated wastewater had the highest toxicity (EC50 value in range: 3–6%). Ozonation caused lower reduction of the toxicity than biodegradation. In the system with SBR the best results were obtained for the biodegradation followed by the ozonation and additional biodegradation – 96% of the toxicity removal. In the second system (with HCFB) two-stage treatment (biodegradation followed by the ozonation) led to the highest toxicity reduction (98%).

1. Introduction

The textile industry is known as a sector, which biggest impact on the environment is connected with primary water consumption and wastewater production (Rosi et al., 2007). Its water demand is estimated as 80–100 $m^3 \cdot Mg^{-1}$ of finished textile (Rosi et al., 2007). It is required to achieve environmentally sustainable development in the textile industry since closing of water cycle is highly recommended.

The wastewater discharged by this industry is loaded with high amounts of both organic and inorganic compounds. As a result it has a very complex composition. The effluents are characterized by alkaline reaction, significant salinity, intensive colour and toxicity. They contain: dyes, toxic heavy metals, pentachlorophenol, chlorine bleaching, halogen carriers, carcinogenic amines, free formaldehyde, biocides, salts, surfactants, disinfectants, solvents, and softeners (Jadhav et al., 2015). A lot of previously mentioned chemicals are xenobiotic substances. Among them dyes are found as especially important (Eren, 2012). First of all, the number of available colourants exceeds 100,000 (Yesiladali et al., 2006). It is one of a main reasons for extreme variability of the textile effluents. Secondly, they should be resistant to photo and biodegradation (Asghar et al., 2015), what makes their treatment very difficult. Usually, they pass through conventional wastewater treatment plants almost unchanged. As a result coloured wastewater is emitted to the aquatic environment, where creates problem to photosynthetic aquatic plants and algae (Sarayu and Sandhya, 2012). Thirdly, some of them or their degradation products are toxic, mutagenic or cytotoxic (Al et al., 2013; Bae and Freeman, 2007; Edwards et al., 2004; Lee et al., 2003; Mansour et al., 2007; Stammati et al., 2005; Umbuzeiro et al., 2005). What is more, the textile wastewater changes dramatically in the time (Eren, 2012). Its composition is strictly connected to the production profiles, which depend on the market demand. Even within one factory big

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differences can be observed – for instance related to the season and fashion trends (e.g. new colours).

Due to the above mentioned facts, the textile wastewater treatment is crucial but also an extremely complicated task. There are many methods which can be used – biological, chemical and physicochemical. The most often, it is impossible to obtain satisfactory effects using only one of them – the integration of different processes is necessary (Fu et al., 2011). Among the available techniques ozonation and biodegradation sound as the most environmentally friendly (Asghar et al., 2015; Imran et al., 2015).

The ozonation is known as process which generates no sludge. The residual ozone decomposes into water and oxygen (Asghar et al., 2015). However, the ozonation is suitable for complete decolourization rather than mineralization (Tosik, 2005). Additionally, ozone generation is expensive due to a high energy consumption. This is why this method must be coupled with the others. Depending on the pH value, the ozonation process follows two different routes. Under acidic conditions, ozone reacts directly with organic compounds as an electrophile. It attacks conjugated double bonds which are very often parts of the chromophores in dyes (Turhan et al., 2012). As a result, aldehydes, carboxylic acids and other by-products are formed (Asghar et al., 2015). At basic pH, ozonation mechanism changes from direct ozonation to complex chain mechanism. The ozone rapidly decomposes to produce the hydroxyl radical and other radical species (Turhan et al., 2012). The hydroxyl radicals lead to faster and further organics degradation than the ozone itself. For instance they are able to open aromatic rings of dyes (Asghar et al., 2015). Apparently, the rate of dyes oxidation grows with increasing solution pH (Turhan et al., 2012).

The biodegradation is the cheapest method of the textile wastewater treatment. It does not involve any chemicals. The most often biological processes lead to the detoxification of dyes (Ayed et al., 2010; Champagne and Ramsay, 2010; Chougule et al., 2014). Low concentrated wastewater containing disperse, vat, direct and basic dyes can be successfully treated in activated sludge systems. These types of dyes can be easily adsorbed onto activated sludge or flocculated (Frijters et al., 2006). The biodegradation of reactive dyes, especially azo dyes, demands specific sequence of the processes. Firstly, anaerobic conditions must be provided. In strongly reductive conditions – by potential redox below −350 mV – double bonds can be broken (Isik and Sponza, 2007). Thus aromatic amines are formed, which are not degraded in anaerobic process. Those amines may be further mineralised under aerobic conditions – for instance by the activated sludge process (Klepacz-Smółka et al., 2015; Popli and Patel, 2015). However, the biological processes have also specific limits. They can be used only for mineralization of biodegradable compounds. Moreover, microorganisms are sensitive to toxic compounds (Ganzenko et al., 2014). The pre-ozonation may be used for a very toxic effluents (Eremektar et al., 2007).

There are a lot of papers concerning the ozonation and the biodegradation of dyes (Ayed et al., 2010; Bonakdarpour et al., 2011; Champagne and Ramsay, 2010; Chougule et al., 2014; Fanchiang and Tseng, 2009; Oguz and Keskinler, 2008; Popli and Patel, 2015; Souza et al., 2010; Tabrizi et al., 2011; Tehrani-Bagha et al., 2010; Turhan et al., 2012; Zhang et al., 2015), however the textile wastewater contains many auxiliaries which may influence on the processes. This is the reason for researchers to concentrate on the industrial effluents last years (Anastasi et al., 2012; Fu et al., 2011; Iaconi, 2012; Jadhav et al., 2015; Lotito et al., 2012; Punzi et al., 2015; Qi et al., 2011; Somensi et al., 2010).

From the ecological point of view, the impact of the textile wastewater on the aquatic ecosystems is a very important aspect. Additionally, the wastewater reuse may be limited due to its toxicological effects. There is still not enough investigations dealing with the influence of the different processes on the real wastewater toxicity (Punzi et al., 2015). It is possible that treatment, especially the ozonation, might lead to the formation of the toxic products, which can be more dangerous for the environment than raw wastewater. Although there are different bioindicators used, the Microtox® assay is the most common method for the rapid estimation of the acute toxicity towards aquatic organisms (Ma et al., 2014).

The aim of this study was to determine the influence of the chemical, biological as well as combined chemical-biological treatment on the toxicity of the high-loaded effluents from the dyeing factory. Additionally, scaling-up of the processes was performed. As a chemical treatment the ozonation was selected. The biodegradation method was performed in Sequence Batch Reactors (SBR) as well as in horizontal continuous flow bioreactor (HCFB). Different combinations of chemical and biological processes were tested in two scales of the equipment used.

2. Materials and methods

The investigations were conducted in two systems. In the first system Sequence Batch Reactors (SBR) were used for the biodegradation and 1 dm^3 reactor working in semi-batch mode for the ozonation. In the second, the biodegradation was conducted in a horizontal continuous flow bioreactor (HCFB), while the ozonation in 20 dm^3 bubble column.

Three combinations of biological and chemical processes were tested: the ozonation followed by the biodegradation, the biodegradation followed by the ozonation and the biodegradation followed by the ozonation, and then second biodegradation.

2.1. The wastewater

The real wastewater was taken four times from the dyeing factory located in Lodz district, Poland. The experiments were carried out for samples collected in Winter (TW I - 22.03.15), Spring (TW II – 14.05.15) and Summer (TW III – 12.08.15 and TW IV – 09.06.15). The concentrated effluent stream was used – containing baths from washing with bleaching, dyeing and first rinse after dyeing. Previously mentioned baths are characterized by higher amounts of both organic and inorganic pollutants than washing without bleaching, rinses and neutralisation.

2.2. Ozonation experiments

The ozonation in a smaller scale was carried out in a semi-batch mode (heterogeneous gas–liquid system). Set-up was previously described by Bilińska et al. (2015). Two ozone doses were applied: 1.68 for TW I and 0.42 $gO_3 \cdot dm^{-3}$ for TW II and TW III. There was no pH correction.

While the ozonation in a bigger scale was performed in a glass column having a capacity of 20 dm^3. Diagram of the laboratory set-up is shown in Fig. 1. The ozone was fed into the reactor from the bottom of the reactor (1) with a ceramic diffuser brandol 60® (3). The column was connected with ozone generator manufactured by TOGC8X TROGEN LTD. (2), which is combined with integral compressor and oxygen concentrator. The ozone concentration in the gas phase at inlet and outlet of reactor was measured by ozone analyzer BMT 964 (4) manufactured by BMT MESSTECHNIK GMBH, Germany. Circulation of the liquid phase was forced by a peristaltic pump (5). Samples for analysis were collected using cell (6). The gas effluents from the reactor passed through a scrubber filled with silica gel with indicator (7) in order to remove moisture contained in the gas, and then directed to an ozone destructor (8). The process was conducted at a constant gas overpressure of 0.65 bar. The ozone dose equal to 0.42 $gO_3 \cdot dm^{-3}$ was applied to TW IV after biodegradation.