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Combination of sonophotolysis and aerobic activated sludge processes for treatment of synthetic pharmaceutical wastewater

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HIGHLIGHTS

- Aerobic activated sludge process was only able for partial TOC removal from a SPWW.
- UV/US/H_2O_2 process at optimum condition was able to remove more than 90% TOC in SPWW.
- Effects of various operational parameters on the UV/US/H_2O_2 process were studied.
- Combined UV/US/H_2O_2 and aerobic AS resulted in higher mineralization while lower oxidant consumption.
- Combined processes reduced retention time in both sonophotoreactor and bioreactor.

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ABSTRACT

The performance and effectiveness of sonophotolytic process, aerobic activated sludge (AS) process, and their combination in reduction of total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD) from a synthetic pharmaceutical wastewater (SPWW) are evaluated. Batch mode experiments are performed to obtain optimal experimental operating conditions of the sonophotolytic process. An ultrasonic power of 140 W, initial pH solution of 2, and air flow rate of 3 L min^{-1} are found to be optimal operating conditions. The initial optimum molar ratio of H_2O_2/TOC was found to be 13.77 for the sonophotolytic process operated in batch mode. In continuous mode, a 90% TOC reduction was obtained in the sonophotolytic process after 180 min retention time, whereas only 67% in an aerobic AS process for retention time of 48 h. However, combined sonophotolytic and aerobic AS processes improved the biodegradability of the SPWW with 98% TOC and 99% COD removal while reducing the retention time in sonophotoreactor and aerobic AS bioreactor to 120 min and 24 h, respectively. Besides, the consumption of H_2O_2 was reduced significantly in the combined processes.

1. Introduction

Pharmaceutical industries are characterized by a large number of products, processes, plant sizes as well as the magnitude and the quality of produced wastewater. For manufacturing each type of product, several processes and raw materials may be required [1]. During the last few decades, the production and consumption of pharmaceutical compounds have been increased significantly, mainly due to the developments in medical science and also the considerable growth in the world population. Nowadays, a huge amount of medicines is manufactured each year for human and animal consumptions [2]. Therefore, an enormous amount of wastewater is generated in pharmaceutical industries [3]. Pharmaceutical wastewaters are generally categorized as one of the main complex and toxic industrial wastewaters with high BOD, COD, total suspended solid (TSS), toxicity and odor as well as low BOD/COD ratio. Moreover, wastewater from pharmaceutical industry might contain various amounts of organic solvents, catalysts, raw materials, and reaction intermediates which make their treatment procedure complicated [1,4,5].

Most treatment methods of pharmaceutical wastewater are physico-chemical and conventional biological processes. Coagulation-flocculation and activated carbon adsorption are frequent examples of physico-chemical mechanisms. Suarez et al. [6] applied coagulation-flocculation as pre-treatment for hospital wastewater. The treatment was able to reduce TSS by about 92% and COD up to 70%. However, the removal of most pharmaceutical components such as antibiotics were marginal. Activated carbon in both powdered (PAC) and granular (GAC) forms was also used for the removal of micropollutants. More than 90% removal of estrogens was reported by both GAC and PAC processes [7]. Also, up

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to 90% removal of endocrine disrupting material by PAC was observed [8]. Biological methods are known as the most common and cost-effective choices of the treatment. In the case of industrial pharmaceutical wastewater, aerobic AS process with long hydraulic retention time (HRT) is a very frequent treatment option [9]. Membrane bioreactors (MBR) are also aerobic technologies which have been used alone or in combination with AS process to treat pharmaceutical wastewaters. About 99% COD and 95% BOD of a real pharmaceutical manufacturing wastewater was removed by MBR [10,11].

Even though conventional biological methods are economical choice of treatment, several types of industrial wastewater such as those from petrochemical, pharmaceutical, leather, dye, pulp and paper and pesticide manufacturing plants contain considerable amount of organic compounds which are nonbiodegradable and refractory to microorganisms applied in biological treatment systems. These pollutants cannot be removed by conventional wastewater treatment plants and the standard regulations cannot be reached. Also, the release of these substances into the environment and their presence in drinking water may have harmful effects on both humans and ecosystems [12–14]. Considering the aforementioned issues, additional treatment steps seem to be indispensable. Among technologies used to remove nonbiodegradable substances, advanced oxidation processes (AOPs) are influential treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants [15]. AOPs are of great interest and used by several researchers to treat different types of pollutants during past few decades [16–22]. AOPs such as UV/H_2O_2, Fenton, etc. could be described as an oxidation method based on the intermediacy of highly reactive species such as hydroxyl radicals ($^{\cdot}OH$) in a procedure leading to the degradation of target contaminants [23]. The application of ultrasound irradiation (US) or sonolysis in water and wastewater treatment has received a lot of attention in recent years and several studies have been reported [24]. Several advantages of sonolytic process such as avoiding consumption of chemical oxidants or catalysts, safety, and lower demand for the clarification of aqueous solution, make their application simple and desirable [25].

Sonochemical reactions are principally due to a phenomenon named acoustic cavitation. The phenomenon is the process of formation, expansion, and sudden implosion of gas microbubbles. The acoustic cavitation leads to the generation of high local pressure (as high as 1000 atm) and high temperature (as high as 5000 K). It is known that under these extreme conditions, the pyrolysis of water molecules results in the formation of hydroxyl radicals as follows (Eq. (1)) [26,27]:

$$H_2O \xrightarrow{US} .H + {}^{\cdot}OH \quad (1)$$

Generally, US waves at frequencies in the range of 20-1000 kHz can produce cavitation in aqueous solutions [28]. The cavitation acts as a means of concentrating the diffusing energy of ultrasound into microbubbles. During sonolysis, three types of sonochemical reactions can take place. First, the pyrolytic reactions which happen due to the high pressure and temperature inside the cavitation bubbles; second, the free radical attack which is performed by the produced reactive radicals in the interfacial area between the bubbles and the liquid phase, and third, the generation of hydroxyl radicals in the liquid bulk solution [29,30]. Organics components with low solubility and/or high volatility are expected to go through fast sonochemical degradation since they have a tendency to accumulate inside or around the gas–liquid interface. Therefore, sonolysis may be a proper method for the removal of pharmaceutical micropollutants.

Even though AOPs are very effective in treating almost all organic compounds, some flaws prevent their commercial applications. The high requirement of oxidant/catalyst dosage, high electrical power consumption, and precise pH adjustment are some of these drawbacks which make operational cost of AOPs high [31]. Therefore, to overcome the aforementioned problems and to find efficient and economical treatment, the combination of advanced oxidation and biological processes as a potential alternative has attracted attention of many researchers. Carballa et al. [32] combined ozonation and anaerobic digestion for the removal of 11 pharmaceutical components and reported that the ozonation pretreatment improved the efficiency of the biological post treatment. In another study, Sitori et al. [33] achieved 95% dissolved organic carbon removal (DOC) from an industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatments. Fenton was also combined with sequential batch reactor to treat a real pharmaceutical wastewater containing two antibiotics where 89% COD removal was achieved [34]. In these studies, generally, AOPs are applied as a pre-treatment to degrade refractory compounds and to improve the biodegradability level of the wastewater. The produced biodegradable intermediates could be mineralized in a subsequent low cost biological step. Finding the optimum retention time of the wastewater in an AOP reactor is a challenging issue. On one side, in order to reduce the cost of AOPs, lower dosage of chemicals and lower retention times should be applied to achieve small percentage of mineralization. On the other hand, a very low mineralization causes the formation of intermediates which are still toxic and similar to the parent compounds. Therefore, the selection of the point to transfer the effluent of an AOP reactor to the bioreactor should be performed carefully. Two factors are important in combined processes, the biodegradability of the wastewater after photochemical oxidation and the presence of residual oxidants such as H_2O_2, which are inhibitory to microorganism in biological treatment systems.

In this study, the remediation of a synthetic pharmaceutical wastewater was carried out by means of a sonophotolytic process ($UV/US/H_2O_2$) alone and sonophotolysis as a pre-treatment for the aerobic AS process. The effects of operating parameters, such as US power, H_2O_2 concentration, pH, and HRT in both sonophotolysis and aerobic AS processes were investigated. Furthermore, the effluent of the sonophotoreactor was analyzed to evaluate the changes in the biodegradability of the wastewater as well as residual concentration of H_2O_2. Based on the results obtained, the optimal HRT for both the sonophotoreactor and the bioreactor are found and the combined treatment was performed under optimal operating conditions. To the best of the authors' knowledge, this is one of the first reports studying the combination of the sonophotolytic process and biological treatment without using H_2O_2 neutralizer. Results of this study can help having an efficient treatment of industrial pharmaceutical wastewater.

2. Materials and methods

2.1. Materials

The SPWW was prepared based on a list of components reported in a study by Badawy et al. [35]. The components were detected in the wastewater generated by a pharmaceutical and chemical company in Cairo, Egypt. The wastewater contained chloramphenicol, diclofenac, salicylic acid, and paracetamol which were the main products of the production plant. Also, some by-products including p-aminophenol, nitrobenzene, benzoic acid, and phenol were detected in the raw wastewater [35]. Three sets of concentrations in distilled water were chosen to conduct the experimental runs. Characteristics of these three sets are shown in Table 1. The 30% (w/w) H_2O_2 (Sigma–Aldrich) was used as received. Also, NaOH and H_2SO_4 solutions (VWR, Canada) were