Journal of Industrial and Engineering Chemistry 25 (2015) 329–337

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Studies on enhancing the biodegradation of tannins by ozonation and Fenton's oxidation process

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ARTICLE INFO

Article history:
Received 29 May 2014
Received in revised form 2 November 2014
Accepted 16 November 2014
Available online 24 November 2014

Keywords:
Advanced oxidation process
Biodegradation
Fenton's reagent
Ozonation
Tannins

ABSTRACT

Tannins are used in vegetable tanning and re-tanning processes. The biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio of 0.196 indicated that tannins are recalcitrant and persistent. Ozonation as pre-treatment resulted in 20% and 49% of COD and total phenol removal due to mineralization and the BOD_5/COD ratio increased to 0.298. Fenton's reagent pre-treatment resulted in 51% and 85% reduction of COD and phenol removal due to mineralization, with subsequent improvement in BOD_5/COD ratio from 0.196 to 0.443. Wastewater pre-treated with Fenton's reagent resulted in BOD_5 and COD of 26 and 210 mg/L in the aerobic treated final effluent.

Introduction

Tanneries generally adopt either mineral tanning using chromium salts or vegetable tanning using tannins. Tannins are plant based polyphenolic compounds, subdivided into hydrolysable tannins and condensed tannins (proanthocyanidins). Hydrolysable tannins are present in plants as gallotannins and condensed tannins. The most common type of tannin found in forage and browse legumes are polymers of flavonol units [1]. Tannins combine with proteins in the hides/skins to form leather. Vegetable tanning materials used by the tanners contain not only tan but also non-tans consisting of sugary matter, gallic acid, soluble mineral salts, and other organic acids. Although non-tans do not tan leathers, their nature and quantity have important effects on the physical and chemicals characteristics of the tanned leather. Tannins are used mainly in vegetable tanning and also in the re-tanning process. Usually, a blend of about 70% of condensed tannins, and the remaining made up of hydrolyzable tannins, are used by the tanners for vegetable tanning process. Among condensed tannins, wattle extract is preferred because of its usefulness in the production of sole and heavy leathers, mainly due to its weighting and filling properties. Wattle extract penetrates hides faster and does not build sediments in the liquor. Chrome tanned leathers are mostly re-tanned to modify the properties of the finished leather to suit modern demand [2].

During vegetable tanning process, to ensure full penetration and reaction of tannins with skin collagen, an excess of vegetable tannin extracts is used in tanneries. Consequently, many tannin and non-tannin components inevitably remain in the wastewater [3]. Most of the difficult to biodegrade complex organic chemicals like dyes, syntans, vegetable tannin, fatliquors present in the wastewater are applied in the post-tanning (retanning, dyeing and fatliquoring) operations. In the effluent treatment plants, all the sectional streams are mixed as composite wastewater and treated. Post-tanning chemicals in the wastewater cause environmental problems due to their recalcitrant nature and toxicity to the microbes. Tannins, in particular, tend to absorb more light, heat and retain less oxygen than unprocessed water in the biological systems, thereby reducing the efficiency of the treatment process [3,4]. Considering the low biodegradability and persistent nature tannins exist even after conventional chemical and/or biological wastewater treatment process.

An iron pillared inter-layered clay as catalyst of the photo-Fenton process to oxidize phenolic compounds was examined. The selected clay was bentonite and the phenolic compounds were phenol, 4-chlorophenol and 2,4,6-tricholorophenol. It was found that the highest 4-chlorophenol removal (94%) by degradation and mineralization was attained when using the stoichiometric

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http://dx.doi.org/10.1016/j.jiec.2014.11.012
1226-086X/

amount of H_2O_2 and 0.8 kg/m^3 of catalyst [5]. Removal of vegetable tannins to recover water in the leather industry by ultrafiltration polymeric membranes was investigated and reported 83% of tannin retention and a recovery of the water flux of 41–45% after cleaning the membrane [6]. To deal with wastewater that contains soluble organic compounds that are either toxic or non-biodegradable, application of various oxidation technologies were tried to mineralize or reduce the toxicity of the compounds. During chemical pre-treatment, partial oxidation takes place thereby producing/enhancing the biodegradable reaction intermediates for subsequent biological treatment process [7].

Considering the difficulties encountered during the biological treatment of wastewater containing tannins, advanced oxidation processes (AOPs) and combinations thereof with biological treatment appears to be a feasible and better option. Hence, the novelty/objective of the present study is to investigate the application of ozonation and Fenton's oxidation as pre-treatment to increase the biodegradability and subsequent treatment in biological treatment process. The efficiency of the biological treatment process was evaluated with and without application of ozonation and Fenton's oxidation separately and findings were discussed in detail.

Materials and methods

Characterization of wattle extract

Commercial wattle extract, as powder, was procured from Tan India limited, Salem, Tamil Nadu, India. Analysis of wattle extract for the parameters of soluble and insoluble matter, tannin and non-tannin content and moisture were carried out as per the procedure given in ISO/DIS 14088/IUC 32 [8].

During retanning process, about 7% (70 g) of wattle extract is used for processing 1 kg of wet-blue leather. About 85% of exhaustion of tannins took place and resulted in about 15% of unused tannins in the wastewater. The quantity of water required for retanning process is about 1 L. However, the total volume of water required for wet-blue to finishing process is about 10 Lfor processing of 1 kg of wet-blue leather. The concentration of wattle extract in the composite wastewater is about 1 g/L. Considering this, the synthetic solution was prepared by taking 1 g/L of wattle extract. For preparation of synthetic solution containing wattle extract, one gram of wattle extract was diluted in 1 L of deionized water obtained from a Millipore Milli-Q system.

The synthetic solution containing wattle extract was characterized for physico-chemical parameters, viz., pH (Part 4500-H^+ method B), chemical oxygen demand (COD; Part 5220 method C), biochemical oxygen demand (BOD as BOD_5 at 20 °C; Part5210 method B), total kjeldhal nitrogen (TKN) (Part 4500_{org} method-B), phosphorus (Part 4500-P method E) and Total organic carbon (Part 5310—method B), as per standard methods 20th edition [9]. Total phenol content was determined by the Folin–Ciocalteu method [10]. Samples were analysed in triplicate and the average values with standard deviation are reported. The aromaticity of the wastewater due to the presence of aromatic compounds in terms of UV_{280} measurements, before and after treatments, was determined by UV-2450 Shimadzu Spectrophotometer using a 1 cm quartz cell.

Application of advanced oxidation processes as pre-treatment

In the present study, ozonation and Fenton's reagent using H_2O_2 and Fe^{2+} were applied as pre-treatment to produce biodegradable reaction intermediates during chemical oxidation of wastewater. The wastewater refers to the synthetic solution of wattle extract used for the study. In the post-tanning process, the pH of the final liquor was adjusted to 3.5 $\pm$ 0.1, using formic acid [2]. This was done to facilitate proper fixing of the added post-tanning chemicals to the leather and to ensure that at the end of the operation, the exhausted post-tanning wastewater had a pH of 3.5 $\pm$ 0.1. Considering this, all the experiments using AOP pre-treatment studies were done at the pH of 3.5 $\pm$ 0.1.

Ozonation experiments were carried out in a bubble column of bench scale glass reactor of diameter 70 mm and height 1200 mm. Ozone was supplied through a ceramic diffuser fitted at the bottom. The laboratory ozone generator Model No L6G from Faraday Instruments, India was used, with pure oxygen as the feed inlet gas to produce 2 g/h of ozone. Ozone concentration, before and after pre-treatment, was measured as per the procedure (Part 4500-O_3 B) given in standard methods 20th edition [9]. Ozonation experiments were carried out for 30 min duration. At regular intervals of time, i.e., 5 min, samples were collected, analysed for BOD_5, COD and the presence of aromatic compounds at 280 nm.

The efficiency of the Fenton oxidation process depends on the pH, concentration of H_2O_2, organic matter content, temperature and Fe(II) concentration [11]. Wastewater was taken in a beaker and kept continuously stirred, using a magnetic stirrer. For the pre-treatment using Fenton's reagent, known quantity of $FeSO_4$ and H_2O_2 (30%) were used at the pH of 3.5 $\pm$ 0.1. Analytical grade chemicals needed for the experiments were procured from Merck. All solutions were prepared with deionized water obtained from a Millipore Milli-Q system. During Fenton's Oxidation process, initially Fe^{2+} dose was kept constant as 100 mg/L and H_2O_2 dose was optimized. Then for the optimized H_2O_2 dose, Fe^{2+} dose was optimized.

Experiment setup for aerobic biodegradation of wastewater

Aerobic treatment studies were carried out in batch aerobic reactors of 2 L capacity, with working volume of 1.5 L. In order to maintain aerobic conditions, air was supplied at a rate of 1.5–1.6 L/h through two medium sized diffusers fitted to an aquarium-type pump. Dissolved oxygen (DO) concentration of 2–2.5 mg/L was maintained throughout the duration of the experiment. Experiments were performed in batch reactors in aerobic condition under ambient temperature (30 $\pm$ 1 °C). Ozonated and Fenton's reagent pre-treated wastewater pH was adjusted to 7.3 $\pm$ 0.2. One hour settlement was allowed to remove the settle able solids and also ferric hydroxide formed during the Fenton's reagent pre-treated wastewater. After the settlement, the supernatant was taken for the biodegradation studies and residual iron was not observed in the supernatant.

The activated sludge, used as inoculum in the experiment, was collected from the aeration tank of a common effluent treatment plant (CETP) situated in Chennai, India, exclusively operating for treatment of tannery wastewater. The activated sludge was washed several times with distilled water and starved under aeration for 24 h to reduce the amount of dissolved substances present in the mixed liquor. A known concentration of washed activated sludge and the synthetic solution were mixed for biodegradation studies. COD: N:P ratio of 100:5:1 was maintained in the reactors with the addition of nutrients. Aerobic treatment studies were carried out with food to microbial (F/M) ratio of 0.15 and residence time of one day. Experimental setup for the study, i.e., the removal of residual organics from the activated sludge, addition of nutrients, elimination of interferences due to the presence of hydrogen peroxide and iron was done as per the procedures reported by Kalyanaraman et al. [7,12]. The batch reactors were operated for 30 h and at regular intervals of time samples were collected and analysed for BOD_5 and COD removal.