



Treatment of refractory nano-filtration reject from a tannery using Pd-catalyzed wet air oxidation

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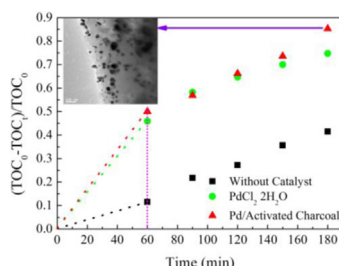
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HIGHLIGHTS

- Catalytic wet air oxidation of refractory organics in NF-reject.
- Removal of potential EDCs after CWAO.
- Mineralization higher with Pd/AC compared to Pd²⁺ and without catalyst.
- Pd catalyst stable under CWAO treatment, graphitization of support observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 May 2013

Received in revised form 28 June 2013

Accepted 3 July 2013

Available online 10 July 2013

Keywords:

Catalytic wet air oxidation

Palladium catalysts

Nanofiltration-reject

Refractory organic pollutants

Tannery effluent

ABSTRACT

We attempted catalytic wet air oxidation (CWAO) of nanofiltration (NF)-reject using Pd based catalyst viz., Pd/activated charcoal (AC) and PdCl₂ with the objective of degradation of refractory organic pollutants. Refractory organic pollutants in NF-reject before and after WAO and CWAO were confirmed by GC–MS analysis. Experiments were conducted to investigate the effects of temperature, catalyst dosage and air partial pressure on the rate of removal of total organic carbon (TOC). The reaction kinetics can be conveniently described by considering two-stage first order kinetics. The use of Pd/AC afforded 85% TOC removal, the corresponding rate constant (k) was $2.90 \pm 0.075 \times 10^{-3} \text{ min}^{-1}$ (Pd/AC, 100 mg/L; T , 473.15 K; P_{air} , 0.69 MPa). On the other hand, 75% TOC was removed with $k = 2.31 \pm 0.075 \times 10^{-3} \text{ min}^{-1}$ using Pd²⁺ catalyst (Pd²⁺, 16.66 mg/L; T , 473.15 K; P_{air} , 0.69 MPa). The observed rate of mineralization under Pd-catalyzed conditions was significantly higher than that of the uncatalyzed oxidation (41%) under the similar experimental conditions. Catalyst stability experiments were performed and TEM, SEM, XRD, Raman and XPS characterization data collected. Despite some morphological transformation of support, Pd catalyst was stable under CWAO conditions.

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1. Introduction

Leather industry is one of the most polluting industries in terms of the volume and complexity of the effluents. The effluent from leather industries contains high organic and inorganic

pollutants, strong color, dissolved and suspended solids, salinity with specific pollutants such as the steroid compounds, endocrine disrupting compounds (EDCs) and the heavy metal pollutants such as chromium [1–4]. Treatment of effluents generated from the leather processing industries poses a major challenge in achieving not only the desired effluent discharge standards, but also be treated adequately to recycle and reuse in the manufacturing processes. The tannery units in India deployed advance treatment processes, such as nanofiltration (NF) and reverse osmosis (RO) to ensure complete removal of organic matter and dissolved

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solids, thereby making the treated effluent (permeate) suitable for recycling and reuse [5]. The increasing use of membrane technologies for the recovery of water from wastewater treatment has led to the generation of concentrated wastewater referred to as 'reject'. This reject water, though small in quantity (15–30% of the feed volume) contains high concentration of the dissolved solids and some recalcitrant organic compounds. These organic compounds are difficult to treat using conventional methods and are referred to as 'refractory' or recalcitrant organics. The management of the rejects in tannery industry is of significant importance in the backdrop that the regulatory bodies in southern part of India have enforced implementation of 'zero liquid discharge' based treatment technologies in all the tanneries [6].

The membrane reject effluent is further evaporated in multiple effect evaporators (MEE) to recover the condensate water for use in the process; however the recovered salt still contains refractory organics and therefore disposed of as per hazardous waste disposal rules. Therefore, it is considered important to remove the refractory organics from the rejects using advanced oxidation processes as well as wet air oxidation processes. It is anticipated that such treatment would lead to recovery of organic-free salts from the retentate of MEE process, which may be reused or disposed of safely. This has led to the adoption of several alternative oxidation processes viz., catalytic wet oxidation, ozonation, UV irradiation, and electrochemical treatment [4,7]. Recently, we reported ozonation of rejects from reverse osmosis treatment of tannery effluents [6]. The present study deals with the catalytic wet air oxidation of rejects from NF process applied to the tannery effluents.

Catalytic wet air oxidation is a promising method for the treatment of refractory organic compounds in wastewater [8–12]. The main object of the present work is to investigate the catalytic wet air oxidation of the refractory organic containing NF-reject over Pd based catalyst (Pd/activated charcoal and PdCl₂), to achieve high mineralization efficiency, study catalyst stability, identify organic pollutants before and after WAO and CWAO, and target complete removal of the refractory organic pollutants. It is pertinent to mention that the catalytic wet air oxidation of refractory organics from NF-reject generated at tannery unit has not been investigated earlier.

2. Materials and methods

2.1. Catalysts

Commercially available (10%) Pd/activated charcoal (Pd/AC) supplied by SRL Pvt. Ltd., Mumbai, India, was used. However, the Pd/AC catalyst contained 9.8 wt.% Pd, instead of the stated 10 wt.% as stated in the certificate of analysis from the vendor. The as-supplied catalyst was micro porous (pore size, 4–5 nm; pore volume, 0.05 cm³ g⁻¹). The BET surface area was 843 m² g⁻¹. Palladium chloride (PdCl₂, 60% Pd²⁺) was supplied by Loba Chemical Pvt. Ltd., Mumbai, India.

2.2. NF-reject

The NF-reject employed for the experiments was obtained from a tannery industry in Southern State of India. The major characteristics of the NF-reject sample are given in Table 1.

2.3. Apparatus and experimental procedures

A schematic of the experimental CWAO treatment process is shown in Fig. 1. The reaction vessel is a high pressure reactor (Model No. 1300, Amar Equipment Pvt. Ltd., Mumbai, India). The reaction vessel (1) made of SS-316 stainless steel with an effective volume of 1 L, capable of performing the batch experiments at pressures

up to 140 bar and temperature up to 623.15 K as per the company test certificate. The reactor is equipped with a 6-blade turbine type impeller mixer (2) connected to an overhead motor (3). A thermal sensor (4), cooling coil (5) and external heating element (6) are also provided for temperature control with an accuracy of ± 1 °C. To minimize the heat loss, the reactor is insulated using glass wool. There is a condenser at the top of the reactor, which is used to condense the vapors formed during the reaction and send the condensate back to the reactor. The operating pressure of the reaction vessel was measured with the help of pressure gauge (7) controlled by a regulator (8) in the exit air line.

In a typical experiment, 0.5 L of the NF-reject sample was placed in the reactor; then the reactor was rapidly pressurized using air from compressed air cylinder at room temperature and heated to the desired temperature [10,13]. Deionized water (DW) was also used optionally in a few experiments. The operating temperature was raised between 423.15 and 523.15 K, the air pressure between 0.34 and 1.37 MPa and the catalyst dosage (Pd/AC) between 25 and 125 mg and Pd²⁺, 8.33 mg. The speed of the stirrer was fixed at 200 rpm. The heating rate is approximately 2.0 °C min⁻¹ and the operating temperature was generally attained within 45–60 min. The reaction was carried out for 3 h and test samples were collected at intervals of 30 min.

2.4. Analyses

The NF-reject sample was collected and analyzed according to the procedures described in the Standard Methods [14]. Prior to analysis all the test samples were filtered using 0.45 μm Millipore Syringe Filter. The test samples were analyzed for chemical oxygen demand (COD) and biochemical oxygen demand (BOD) as per Standard Methods [14]. The observed error in the determination of COD in duplicate tests was about 5–6%. Typical error in determination of BOD was 8–10%. The concentration of total organic carbon (TOC) was measured with a TOC Analyzer (Shimadzu TOC-V_{CPH}). The standard error in TOC measurement was about $\pm 2.0\%$.

The organic compounds present in NF-reject were extracted by the following procedure. The NF-reject sample (0.5 L) before or after CWAO was extracted using reversed phase SPE C-18 cartridge by passing 30 mL of either dichloromethane (DCM) or methanol (MeOH). The extract was evaporated under mild N₂ flow. The residue was dissolved again by adding 5 mL of either DCM or MeOH. This was used as the test sample for identification of compounds using GC-MS tool. Identification of recalcitrant organic compounds in NF-reject before and after CWAO was carried out using Varian 450 GC; Varian 240 MS, USA and Mass spectral library NIST 08, USA. The analytes were separated under the following analytical conditions: temperature program, oven temperature, 323.15–543.15 K with raise in 288.15 K min⁻¹; and injection temperature, 573.15 K; carrier gas, helium; flow rate, 1 mL/min; column, DB5; detector, mass spectrophotometer; mass range scanned, 50–1000 amu.

2.5. Characterizations

The phase stability of the virgin and used Pd/AC catalyst was observed by using X-ray diffractometer (XRD: Bruker AXS, D8 Advance) and Raman Spectroscopy (Renishaw, Invia). The morphology was examined using Field emission scanning electron microscope (FESEM, S-4800 Hitachi) and transmission electron microscope (TEM, JEM-2100) at an acceleration voltage of 200 kV. The samples for TEM measurements were prepared by the pouring of methanol suspended Pd/AC on holey carbon film supported on a Copper grid. Elemental analysis of 10% Pd/AC (virgin as well as recovered) were determined from the X-ray photoelectron spectroscopy (XPS) by using (PHI-5400, Perkin Elmer) and atomic ratio was calculated from the XPS spectra using curve fitting program

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