



High-strength distillery wastewater treatment using catalytic sub- and supercritical water



Negar Kazemi^a, Omid Tavakoli^{b,*}, Shayan Seif^b, Morvarid Nahangi^a

^a Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

^b School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

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ABSTRACT

In the current research, we have studied the catalytic sub- and supercritical water (SCW) treatment of distillery wastewater (DWW) in a batch tubular reactor. Experiments were conducted in the temperature range of 250–400 °C, reaction time of 30–120 min at constant pressure of 25 MPa with the aim of chemical oxygen demand (COD) and color removal. The initial COD concentration was 60,000 mg l⁻¹, regarded as high-strength wastewater. The experiments were performed in the presence and absence of different homogeneous (MnSO₄·7H₂O, ZnSO₄·7H₂O) and heterogenous (TiO₂, CuO, MnO₂) catalysts. The obtained results showed that increasing the temperature from 250 °C to 400 °C has a positive influence on both COD reduction (18.3–50%) and color removal (up to 48.5%) within 30 min and without catalyst, while reaction time has no significant effect. By applying both homogeneous and heterogeneous catalysts, COD and color removal efficiencies were considerably increased. The optimum COD removal efficiencies of 74.4% and 75.1% were obtained by CuO (10 wt%) and MnO₂ (10 wt%), respectively at 400 °C and 30 min, while the highest COD removal efficiency was 80.9% at 400 °C, 120 min and 5 wt% of CuO. Addition of catalysts also greatly influenced color removal, such that MnO₂ could remove up to 98.2% of wastewater color at 400 °C in 30 min.

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1. Introduction

DWW, generated from alcohol production plants, contains high biological oxygen demand (BOD) (35,000–50,000 mg l⁻¹), high COD (100,000–150,000 mg l⁻¹) and high percentage of dissolved solids. It is also characterized by low pH, high temperature, unpleasant odor and dark brown color pigments named melanoidin, which is a product of Maillard reaction [1,2]. High content of organic load and highly-colored nature of DWW can hinder photosynthesis by blocking sunlight [3]. Suppression of photosynthesis can cause depletion of dissolved oxygen and could thus be detrimental to aquatic life. To impose stringent environmental regulations and to stipulate environmental demand, DWW must undergo different treatment processes to reduce BOD and COD content in effluents to an acceptable range. Although conventional treatment methods including both aerobic and anaerobic treatments can reduce COD of DWW in long hydraulic retention time, even so, the COD levels cannot reach to the acceptable maximum [4]. Moreover, the color contamination of DWW remains an unsolved problem and anaerobically-treated

wastewater needs to be diluted by fresh water several-fold before discharge. High operating cost of anaerobic digestion, aeration and sludge generation are the most important disadvantages of such treatment methods. In addition, excess use and high cost of chemicals and adsorbents as well as generation and disposal of sludge restrict the adoption of physicochemical methods [5,6]. Thus, researchers are searching for solutions for effective management of DDW with high BOD and COD content.

Hydrothermal processes have proved to be clean and efficient treatment methods for removal of organic compounds from wastewater streams. A hydrothermal reaction is a chemical reaction in high-temperature and high-pressure water. Occurring around critical point of water (374.15 °C and 22.1 MPa) hydrothermal reactions can be classified into SCW, subcritical water and high-pressure steam reactions [7].

Since most organic compounds as well as oxidant are completely miscible in water at supercritical condition, where water acts as a non-polar solvent, SCW creates an excellent reaction medium for degradation of organics. Moreover the enhanced diffusivity of SCW leads to rapid and efficient decomposition of organic substances to H₂O and CO₂ in short reaction times. Furthermore, in SCW process, temperature is much lower than incineration and partial oxidation products such as dioxins, NO_x and SO_x are not produced

* Corresponding author. Tel.: +98 21 6111 2187; fax: +98 21 6649 8984.
E-mail address: otavakoli@ut.ac.ir (O. Tavakoli).

[8–10]. When an oxidizer is added into the reaction medium, oxidation reactions occur at high-temperature and high-pressure water [7], but hydrolysis of many organic compounds exposed to SCW environment usually follows a polar or heterolytic nucleophilic substitution mechanism. Proton can be generated upon water dissociation:



This proton-catalyzed ionic reaction provides a path parallel to free-radical pyrolysis [11].

Since SCW seems to be a feasible technology, its application for degradation of wide range of wastes and compounds like aromatics [12], nitrogenated compounds [13], sludge [14], wastewaters from acrylonitrile manufacturing plant [15], LCD manufacturing process [16], olive mills [10] and textile industry [9,17], as well as food wastes [18] and hydrolysis of vegetable oils [19] and woody biomass [20] has been reported by many researchers.

Moreover, to reach complete conversion of aromatic hydrocarbons to CO_2 and water [21], catalysts like NaOH [22], CuO [23], $\text{MnO}_2/\text{CeO}_2$ [13], TiO_2 [24], CuSO_4 , CuNO_3 , FeCl_3 , $(\text{Fe})_2(\text{SO}_4)_3$, V_2O_5 , MnSO_4 , FeSO_4 [25] in SCW condition have been studied so far. Catalytic SCW oxidation of landfill leachate was studied by Shuzhong Wang et al. [26]. The authors investigated the conversion of COD and NH_3 in the presence of MnO_2 and found that MnO_2 is an effective catalyst that can accelerate the destruction of landfill leachate. Shin et al. [27] have also studied the SCW oxidation of mixed wastewater from acrylonitrile manufacturing process and copper-plating process in a continuous tubular reactor system. The conversion of total organic carbon (TOC) in acrylonitrile wastewater was accelerated by *in situ* generation of copper-copper oxide nanoparticles. Another study has also focused on $\gamma\text{-Al}_2\text{O}_3$ -catalyzed SWC oxidation of wastewater from terephthalic acid manufacturing process [21].

The purpose of this study was to develop a process for accelerating the decomposition of color causing agents (or melanoidins) and pollutants of DWW into more biodegradable or less colored substances by catalytic sub- and SCW processes. The effects of temperature, reaction time, feedstock concentration, catalyst type and catalyst loading were experimentally studied.

2. Materials and methods

2.1. Materials

The DWW used in this work was provided by Bidestan Distillery and Food Products Company, Qazvin, Iran. Table 1 shows the characteristics of the received distillery wastewater, which contains high BOD and COD (average amount of $35,000 \text{ mg l}^{-1}$ and $70,000 \text{ mg l}^{-1}$, respectively) with dark brown color. Initial feedstock (received wastewater) was diluted with deionized water by the volume ratios of 1:2, 1:3 and 1:6 (waste-water:deionized water), which are equal to 26,200, 19,200 and 9600 mg l^{-1} , respectively. The homogeneous and heterogeneous catalysts used in this research were $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ ($277.11 \text{ g mol}^{-1}$, Merck Co.), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ($287.55 \text{ g mol}^{-1}$, Merck Co.), TiO_2 (extra pure, 79.87 g mol^{-1} , Degussa Co.), CuO (powdered, 79.54 g mol^{-1} , Merck Co.) and MnO_2 (86.94 g mol^{-1} , Merck Co.).

2.2. Apparatus and procedure

The experiments were conducted in a laboratory-scale tubular batch reactor which was made of stainless steel 316 (I.D. of 174 cm, O.D. of 2.56 cm and length of 20.5 cm) with an effective volume capacity of 49 ml. The reactor was sealed by proper ferrule and back-ferrule attachments. The experiments were conducted in the temperature range of 250–400 °C, reaction time of 30–120 min

Table 1
Distillery wastewater characteristics.

Characteristic	Value	Unit
COD	60,000–80,000	mg l^{-1}
BOD	30,000–40,000	mg l^{-1}
pH	4.5–5	–
Ash	25,000	mg l^{-1}
K	6000	mg l^{-1}
Na	1500	mg l^{-1}
Mg	80	mg l^{-1}
Ca	1000	mg l^{-1}
Fe	30	mg l^{-1}
Zn	0	mg l^{-1}
Po_4	100–150	mg l^{-1}
So_4	2500–3000	mg l^{-1}
Total solid	95,000	mg l^{-1}
Total volatile solid	55,000	mg l^{-1}
Total carbon	35,600	mg l^{-1}
Total nitrogen	70	mg l^{-1}
Total carbohydrate	1150	mg l^{-1}
Color	Dark brown	–

and constant pressure of 25 MPa. The experiments were conducted in presence and absence of different catalysts to clarify the effect of catalyst addition on COD and color reduction under sub- and SCW conditions. The loadings of heterogeneous catalyst used in experiments were selected as 3.0, 5.0 and 10.0 wt% and the concentration of homogeneous catalysts was 0.01 M. The reactor was fed with a known volume of wastewater and was then heated to set-point temperature by standing in a 1200 W preheated electric furnace. The reactor was placed in a preheated oven and residence time was measured from the moment when the reactor reached the desired temperature till quenching in a cold water bath. Residence time varied in the range of 30–120 min. The reaction temperature was controlled and monitored directly using a set of thermocouples equipped with temperature controller and indicator. After the desired reaction time, the reactor was taken out and put into a cold water bath to be quenched. Once the resulting mixture was quenched to ambient conditions, liquid and gaseous products were immediately separated due to phase separation. After discarding the gaseous effluent and separation of solid phase using centrifugation at 6000 rpm for 10 min, the liquid phase was collected in closed plastic sample container and stored in a 4 °C refrigerator for further analysis.

2.3. Analyses

The concentrations of pollutants in wastewater and liquid phase effluents of reactor were measured by analyzing the COD. Samples (0.2 ml) were put into COD digestion vials with the range of 0 to $15,000 \text{ mg l}^{-1}$ (Hach, U.S.) and then the vials were inverted several times to be mixed completely. These vials were inserted into a block heater at 149 °C for 2 h (DRB 200, Hach, U.S.) and were then cooled down to 121 °C and were taken out of heater to reach to the room temperature. The COD value of each sample was measured with a calibrated spectrophotometer (DR 5000, Hach, U.S.) at 620 nm.

To determine the color removal efficiency, samples were centrifuged and then the absorbances were measured by a UV-vis spectrophotometer (DR 5000, Hach, U.S.) at 475 nm.

The COD and color removal efficiencies were calculated using the following equations, respectively:

$$\text{COD removal (\%)} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \quad (2)$$

$$\text{Color removal (\%)} = \frac{A_i - A_f}{A_i} \quad (3)$$

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