CATALYTIC HYDROTHERMAL TREATMENT OF DISTILLERY WASTEWATER

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ABSTRACT
Catalytic hydrothermal treatment of distillery wastewater is studied in this article. All the experiments were performed in a tubular batch reactor at 300-400 ^{o}C, constant pressure of 25 MPa and residence time of 30-120 minutes. Distillery wastewater of an Iranian ethanole producing company was used as feedstock and its initial COD was set equal to 26200 mg/l. The experiments focused mainly on the effect of catalysts on COD reduction efficiency, hence CuO, MnO_2 and TiO_2 at 3, 5 and 10 wt% were used as catalysts. The results of this study demonstrated that CuO and MnO_2 have high catalytic effect on COD removal compared to TiO_2. The results also showed that by increasing temperature, residence time and catalyst concentration, COD removal efficiancy can be increased up to 80.91%.

Keywords: Hydrotermal, Catalyst, Treatment, Distillery Wastewater

INTRODUCTION
Distillery wastewater refers to the effluent generated from alcohol production plant. The wastewater is characterized by extremely high chemical oxygen demand (100,000–150,000 mg/l) and biochemical oxygen demand (35,000–50,000 mg/l), low pH, high temperature, dark brown color (due to generation of high molecular polymer named melanoidin), high ash content, strong odor, high percentage of dissolved organic and inorganic matter [1,2].
A range of biological and physico-chemical methods have been investigated for the treatment of distillery wastewater. Biological treatment is a slow process and typically requires long start-up periods and can obtain COD (chemical oxygen demand) removal of 70-80%. In addition, the problem of color associated with this effluent intensifies under anaerobic conditions. Due to the high cost of chemicals, adsorbents and membranes, physico-chemical methods are not practical for treatment of distillery wastewater [3]. Thus, solutions for effective management of molasses based distillery wastewaters are still evolving.
In recent years, supercritical water oxidation (374 ^{o}C and 22.29 MPa) has been known as a clean and efficient treatment method to remove organic compounds from wastewaters [4]. At supercritical conditions, water acts as a non-polar solvent that most organic compounds, as well as oxidant, are completely miscible in it [5]. Moreover, diffusivity increases that can lead to rapid and efficient decomposition of organic substances to H_2O and CO_2 in short residence times.
Catalytic supercritical water oxidation of landfill leachate was studied by Shuzhong Wang et al. [4]. They 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.

Supercritical water oxidation of mixed wastewater from acrylonitril manufacturing processes and copper-plating processes was also investigated by Young Ho Shina et al. [6]. In situ generation of nanoparticles of copper and copper oxide accelerated TOC (Total Organic Carbon) conversion of acrylonitril wastewater. Catalytic supercritical water oxidation of wastewater from terephthalic acid manufacturing process with γ-Al_2O_3 was also investigated by Tae-Joon Park et al. [7].

We selected transition metal oxides like CuO, MnO_2 and TiO_2 because they are known to be active and stable catalysts in supercritical conditions [8]. The goal of this investigation is to develop a process for destruction of organic compounds, and also to accelerate the COD decomposition of distillery wastewater by catalytic sub-and supercritical water processes. The effects of temperature, residance time and different catalysts were experimentally studied and reported herein.

MATERIALS AND METHODS

Materials

The distillery wastewater used in this work was provided by Bidestan alcohol production plant in Ghazvin, Iran. The feed stock solution was prepared by diluting the wastewater with deionized water by a factor of 3 to the desired COD concentration. The catalysts used in this research were: TiO_2 (extra pure ,79.866 g/mol, made of Degussa Co.), CuO (powdered, 79.54 g/mol, made of Merck Co.) and MnO_2 (86.9368 g/mol, made of Merck Co.).

Apparatus and Procedure

The experiments were conducted in a laboratory-scale tubular batch SCW reactor, which was made of stainless steel 316. The volume capacity of the reactor was 49 ml. The experiments were conducted in temperature range of 300-400 ^oC, residence time span of 30-120 min and constant pressure of 25 MPa. The initial COD level of diluted feedstock was 26200 mg/l. The Experiments were conducted in presence and absence of catalyst to clarify the effect of catalyst addition on COD reduction under sub- and supercritical water conditions. Different amounts of catalyst used in experiments to reduce COD were 3, 5 and 10 wt%. The reactor was fed with a known volume of wastewater and then heated to desired temperature by placing it in a 1200 W preheated electric furnace. The reaction temperature was controlled and monitored directly using a set of thermocouple equipped with temperature controller and indicator. After the desired reaction time, the reactor was taken out of the furnace and put into a cold water bath to be quenched. Once the resulting mixture was quenched to ambient condiction, liquid and gasuous products were immediately separated due to the phase separation. The gaseous effluent was vented and the liquid effluent was centrifuged (40000 rpm for 10 min) and collected in closed plastic sample container and stored in a 4^oC refrigerator for further analysis.

Analytical Methods

The concentrations of wastewater and liquid phase effluents of reactor were characterized by analyzing the chemical oxygen demand (COD). Samples (0.2 ml) were put into COD digestion vials in the range of 0 to 15,000 mg/L and then they were inverted several times to be mixed completely. These vials were inserted into a digester (The vials were placed in a block heater at 149 ^oC for 2 h) and then cooled to the room temperature. Afterward, the COD value of each sample was measured directly with a calibrated spectrophotometer at 620 nm.

RESULTS

Effect of Temperature

The effect of temperature on COD removal from distillery wastewater is illustrated in **Figure 1**. Experiments were conducted by addition of three different catalysts: CuO, MnO_2 and TiO_2 in temperatures of 300, 350 and 400^oC by keeping a constant pressure of 25 MPa, residence time of 30 min and catalyst loading of 10 wt%. As Figure 1 shows, addition of TiO_2 has no considerable effect on COD reduction at different temparatures campared to other catalysts. As a result of different experiments, MnO_2 and CuO have been known as the most effective catalysts obtaining efficiency of 75.19% and 74.42% , respectively. The catalytic effect of MnO_2 at temperatures of 300 and 350^oC is higher than CuO, but as temperature increases, the effect of both catalysts becomes almost identical especially at temperature of 400^oC. Also, increasing of reaction rate and mass transfer coefficient occurs as results of increasing temperature, leading to further decrease of COD level.

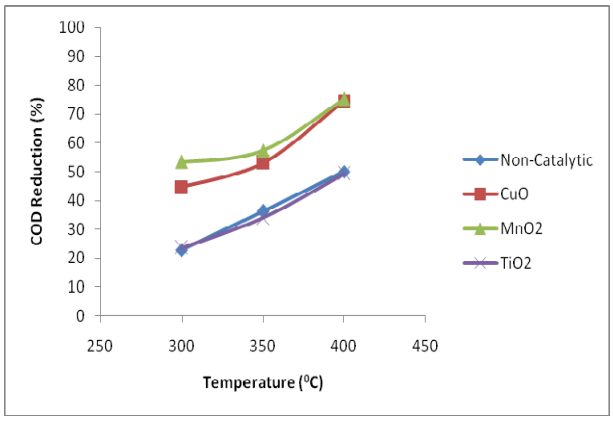

Figure 1: COD removal efficiency vs. temperature at catalyst loading of 10 wt%, t=30 min, P=25 MPa

Effect of Catalyst Loading

Different loadings of catalysts equal to 3,5,10 wt% at experimental conditions of T= 400^oC, P=25 MPa and t=30 min were investigated. Experimental results are shown in **Figure 2** and they clearly highlight that different TiO_2 loadings have little effect on COD removal, compared to other catalysts. However, as the loading of MnO_2 increases from 3 to 10 wt%, the COD reduction increases from 49.61 to 75.19%. While, COD destruction efficiency increases slightly by increasing the CuO loading, and a noticable COD removal of 74.42% is obtained by CuO loading of 10 wt%. As Figure 2 Shows, the catalytic effect of CuO and MnO_2 at loading of 10 wt%, is almost the same. Overally, at the same conditions, catalytic effect of CuO at different loadings is higher than MnO_2, but the rate of efficiency enhancement by MnO_2 amount increment is much higher than CuO.

Effect of Residence Time

The effect of residence time on destruction of pollutants in distillery wastewater is displayed in **Figure 3**. Residence times of 30, 60 and 120 minutes at constant temperature of 400 ^oC, pressure of 25 MPa at catalyst loading of 5wt% were investigated. The results showed that,

generally COD removal proceeded in time, but there were some exceptions at 60 minutes which could be due to chemical compounds production in reforming mechanisms. Another conclusion to be drawn is that TiO_2 exerts it's catalytic effect by increasing residence time and not by increasing temperature. The catalyst activity order herein is CuO> Mno_2> TiO_2, therefore, the best catalytic effect belongs to CuO in all cases.

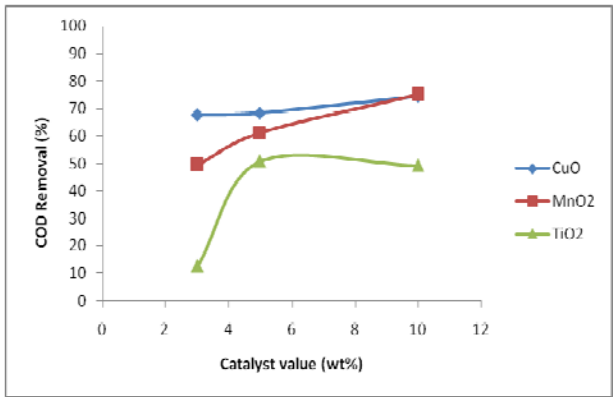

Figure 2: COD removal efficiency vs. catalyst loading at T=400 ^oC, t=30 min, P=25MPa

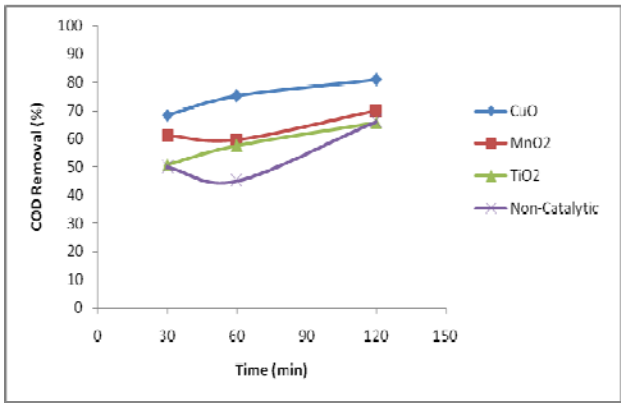

Figure 3: COD removal efficiency vs. residence time at T=400 ^oC P=25 MPa catalyst loading of 5 wt%

CONCLUSION

Distillery wastewater was hydrothermally treated in a laboratory scale reactor at T=300-400 ^oC, t=30-120 min and constant pressure of 25 MPa. The experimental results demonstrated that COD can be effectively distructed under catalytic conditions. Although increasing catalysts loading slightly increased COD removal efficiency, the conversion of COD was mainly affected by increasing reaction temperature and residence time. Transition metal oxides could decrease COD concentration of wastewater as a result of high activity and stabilty and also because of their selectivity on organic destruction. Thus, CuO and MnO_2 were considered as the best catalysts in hydrothermal treatment of distillery wastewater by obtaining the highest COD removal efficiency of 80.91and 75.19%, respectively.

REFERENCES

[1] MOHANA, S., ACHARYA, B. K., MADAMWAR, D., Hazardous Materials, Vol. 163, **2009**, p. 12
[2] PANT, D., ADHOLEVA, A., Bioresource Technology, Vol. 98, **2007**, p. 2321
[3] SATYAWALI, Y., BALAKRISHNAN, M., Environmental Management, Vol. 86, **2008**, p. 481
[4] WANG, S., GUO, Y., CHEN, C., ZHNNG, J., GONG, Y., WANG, Y., Waste Management, Vol. 31 **2011**, p. 2027
[5] ERKONAK, H., SO¨G˘U¨T, O., AKGU¨N, M., Supercritical Fluids, Vol. 46, **2008**, p. 142
[6] SHIN, Y.H., LEE, H.S., LEE, Y.H., KIM, J., KIM, J.D., LEE, Y.W., Hazardous Materials, Vol. 167, **2009**, p. 824
[7] PARK, T. J., LIM, J. S., LEE, Y. W., KIM ,S. H., Supercritical Fluids, Vol. 26, **2003**, p. 201
[8] DING, Z.Y., FRISCH, M.A., LI, L., GLOYNA, E.F., Industrial Engineering Chemistry, Vol. 35, **1996**, p. 3257