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Research article

Application of integrated ozone and granular activated carbon for decolorization and chemical oxygen demand reduction of vinasse from alcohol distilleries

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ABSTRACT

This study investigates the treatment of the distilleries vinasse using a hybrid process integrating ozone oxidation and granular activated carbons (GAC) in both batch and continuous operation mode. The batch-process studies have been carried out to optimize initial influent pH, GAC doses, the effect of the ozone (O_3) and hydrogen peroxide (H_2O_2) concentrations on chemical oxygen demand (COD) and color removal of the distilleries vinasse. The continuous process was carried out on GAC and ozone treatment alone as well as the hybrid process comb both methods to investigate the synergism effectiveness of the two methods for distilleries vinasse COD reduction and color removal. In a continuous process, the Yan model described the experimental data better than the Thomas model. The efficiency of ozonation of the distilleries vinasse was more effective for color removal (74.4%) than COD removal (25%). O_3/H_2O_2 process was not considerably more effective on COD and color removal. Moreover, O_3/GAC process affected negatively on the removal efficiency by reducing COD and color from distilleries vinasse. The negative effect decreased by increasing pH value of the influent.

1. Introduction

Distilleries wastewater (vinasse) with high COD, BOD (biological oxygen demand), COD/BOD ratio, potassium, phosphate and sulfate poses serious environmental concern because of its pollution problems (Wilkie et al., 2000). A typical distillery factory generates 1300 m^3 vinasse by production 100 m^3 of ethanol with BOD 30000–60000 mg/l (Navarro et al., 2000), COD 80000–100000 mg/l and dark brown color (Satyawali and Balakrishnan, 2008). Molasses comprises 2% dark brown pigment-melanoidins that give color to vinasse (Francisca Kalavathi et al., 2001) and it is estimated that 88% of molasses releases after alcohol production (Jain et al., 2002). Other colored compounds in vinasse are phenols, melanins and caramels (García Agudo et al., 2002). Activated carbon has been extensively used as adsorbent for removal of organic pollutants and colored compounds in wastewater treatment. The adsorption ability of organic compounds essentially is related to textural and surface characterizations of activated carbon (Satyawali and Balakrishnan, 2008). Packed bed of activated carbon with a specific surface area of 1400 m^2/g has demonstrated significant decolorization for anaerobically treated spentwash (Chandra and Pandey, 2000). Almost complete decolorization (>99%) was obtained with 70% of the eluted sample, which also displayed over 90% BOD and COD removal (Mandal et al., 2003), whereas others have reported powdered activated carbon (PAC) resulted in only 18% color removal. Nowadays Advanced Oxidation Processes (AOPs) have been applied for many wastewater treatment. Ozone-based AOPs (O_3, O_3/UV and $O_3/UV/H_2O_2$) conducted by Lucas et al. (Lucas et al., 2010) in a pilot-scale demonstrated that O_3/UV and O_3/UV/

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Table 1
Physicochemical characteristic parameters of vinasse.

Characteristics	Value
Color	Dark-brown
pH	5
COD (mg/l)	40700
BOD_5 (mg/l)	23300
Total solids (TS) (g/l)	42
Ash or solid matter (g/l)	14.62
Phosphate (mg/l)	300
Sulfate (mg/l)	17500
Nitrate (mg/l)	3.99
Nitrite (mg/l)	0.7
Ammonia (mg/l)	3360
Chloride (mg/l)	36

H_2O_2process had a significant effect on COD and TOC removal. PAC/O_3 process has been used for color removal from synthetic textile wastewater containing Bomaplex Red CR-L dye in a semi-batch reactor (Oguz and Keskinler, 2007). They reported that ozonation is an effective process for color removal, but not for COD removal alone. Powdered activated carbon (PAC) used in the PAC/O_3 process displayed both characteristics of adsorbent and catalyst. As a consequence, it was concluded that PAC/O_3 process, which has a synergic effect, is a much more effective method for simultaneous removal of dye and COD from textile wastewaters. It has been considered that ozonation can modify the surface property of an activated carbon such as specific surface area, pore volume and functional groups (Oguz and Keskinler, 2008, 2007) and ozone and GAC integrated process offers effective treatment for highly concentrated real wastewater (Lei et al., 2007). The results revealed that the integrated process has more advantages than the individual ozonation and GAC adsorption, while the exhaust time of GAC is prolonged and frequent regeneration is not required. It should be noted that the integrated process has not yet been utilized and reported in treating the vinasse from distillery processes. Herewith, we present a systematic investigation on the hybrid process integrating both O_3/GAC methods for treating vinasse prepared from laboratory ethanol production. The main objective of this work is to study the synergic effect of O_3 on conventional GAC adsorption for removing color and COD from vinasse, while the effect of combined O_3/H_2O_2 process on color and COD removal was surveyed separately. The results of processes were compared with adsorption models in batch and continuous systems.

2. Material and methods

The raw vinasse was prepared from laboratory ethanol production by cane molasses that fermented by *Saccharomyces cerevisiae* in a continuous process. The wastewater characterization was done according to standard method (APHA, 1998) and has been listed in Table 1. GAC was obtained from Applichem with average diameter 1–3 mm and the density of 570 g/l. The COD concentration was measured by the potassium dichromate method. Ozone concentration in reactor gas feed was determined by the iodometric titration method (Bader and Hoigné, 1981). BOD_5 concentration was determined by measuring the amount of oxygen absorbed by sample wastewater in the presence of microorganism within 5 days at 21 °C. The color intensity was measured by Palintest Photometer (8000, England) in terms of Pt/Co scale that is equal to Hazen unit that has been used traditionally formerly (Yetilmezsoy and Sakar, 2008). 10 ml sample was taken to a special photometer cell and was read by 410 nm wavelength and stated by ppm Pt.

2.1. Experimental set-up

Bach experiments were conducted at 25 °C. At the beginning of the reaction, the desired amount of GAC was added into the 250 ml beaker; then 100 ml vinasse was added and liquid samples were taken periodically to determine their COD concentration. The experimental runs lasted 120 min until all measurement parameters reached equilibrium. The pH value of the influent wastewater was adjusted to the desired level using 0.5 M H_2SO_4 and 1.0 M NaOH. The packed-bed reactor, which was made of a clean and dry plexiglass, was a cylindrical column with a 1.43-L operating capacity (internal diameter of 45 mm and a total length of 900 mm). A mass of 100 g of GAC (14 cm) was packed into the column. Then, the vinasse solution (pH 2, 6 and 10) of 10000 mg/l initial COD concentration was passed through the column by a peristaltic pump in an up-flow mode at a flow rate of 1 ml/min until the column overpass a breakthrough point concentration. Effluent solution enforced out by gas that compressed to the reactor and released to a decanter by a port at upside the reactor. Ozone was generated using an ozonizer model COG-55, France, and the maximum generation capacity was 0.4 g O_3/h. The effluent gas containing overflow ozone entered into a decanter for separating treated vinasse and into washing bottle filled with KI solution (2%) to determine ozone concentration. The samples were taken periodically to determine their COD concentration and color intensity. In continuous mode, the results were fitted by Yan and Thomas models and debated separately. In continuous system, we conducted two separate experiments in order to compare the effect of ozone and integrated ozone (O_3) and hydrogen peroxide (H_2O_2, Merck, 30% w/w) process on color and COD removal from vinasse. The integrated O_3/H_2O_2 process was performed at different pH of 2, 6 and 10, initial COD of 2500 mg/l and the H_2O_2 dose of 10 ml/l. Ozone dosage was kept constant at 240 mg/h. The effectiveness of ozone as an oxidant was improved by placing polypropylene granules into the ozone contact reactor in order to increase a higher surface area to volume ratio for the contact of O_3 with the vinasse solution. The samples were taken every 5 min. Manganese oxide (MnO_2, >90%. Merck) was used to eliminate the remaining (unreacted) H_2O_2 in the sample in order to avoid the interference of H_2O_2 on COD analysis (Azbar et al., 2004; Yonar et al., 2006). The above sample was first centrifuged at 10000 rpm and then filtered through a 0.45 μm membrane to remove MnO_2. In this study, the nonlinear model fitting of the isotherm and breakthrough models from Excel Spreadsheets, SigmaPlot and MATLAB program were used to explain predicted maximum and equilibrium adsorption with experimental adsorption relationships.

2.2. Analytical method

In the present study, ozone consumption (Eq. (1)) and ozone utilization efficiency (Eq. (2)) were calculated as follows (Lei et al., 2007):

$$\text{Ozone consumption}(\%) = \frac{(\text{inlet ozone amount}) - (\text{outlet ozone amount})}{(\text{inlet ozone amount})} \times 100 \quad (1)$$