Bioresource Technology xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

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

Short Communication

Advanced treatment of biologically pretreated coal gasification wastewater by a novel integration of heterogeneous catalytic ozonation and biological process

Haifeng Zhuang, Hongjun Han *, Shengyong Jia, Baolin Hou, Qian Zhao

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- Sewage sludge was converted into sludge based activated carbon (SBAC).
- MnOx were loaded on SBAC to serve as catalyst (MnOx/SBAC) for catalytic ozonation.
- MnOx/SBAC significantly improved the performance of pollutants removal in ozonation.
- The catalytic ozonation process (COP) effluent was more biodegradable and less toxic.
- The integration of COP and ANMBBR–BAF had efficient capacity of pollutants removal.

ARTICLE INFO

Article history:
Received 16 March 2014
Received in revised form 5 May 2014
Accepted 7 May 2014
Available online xxxx

Keywords:
Biologically pretreated coal gasification wastewater
Heterogeneous catalytic ozonation
Catalyst
Mechanism discussion
Biological process

ABSTRACT

Advanced treatment of biologically pretreated coal gasification wastewater (CGW) was investigated employing heterogeneous catalytic ozonation integrated with anoxic moving bed biofilm reactor (ANMBBR) and biological aerated filter (BAF) process. The results indicated that catalytic ozonation with the prepared catalyst (i.e. MnOx/SBAC, sewage sludge was converted into sludge based activated carbon (SBAC) which loaded manganese oxides) significantly enhanced performance of pollutants removal by generated hydroxyl radicals. The effluent of catalytic ozonation process was more biodegradable and less toxic than that in ozonation alone. Meanwhile, ANMBBR–BAF showed efficient capacity of pollutants removal in treatment of the effluent of catalytic ozonation at a shorter reaction time, allowing the discharge limits to be met. Therefore, the integrated process with efficient, economical and sustainable advantages was suitable for advanced treatment of real biologically pretreated CGW.

1. Introduction

The biologically pretreated coal gasification wastewater (CGW) contains a large number of toxic and refractory compounds, such as phenolic compounds, polynuclear aromatic hydrocarbons and nitrogenous heterocyclic compounds, long-chain hydrocarbons, ammonia, and so on along with low biodegradability and unsatisfactory effluent quality (Zhuang et al., 2014). This wastewater control task has become a bottleneck for the development of coal gasification industry in China which has played a key role in new clean and renewable energy market in recent years (Wang and Han, 2012). Thus, it is very urgent to find an efficient and cost-effective process for advanced treatment of biologically pretreated CGW.

Heterogeneous catalytic ozonation process has attracted more and more attentions in recent years due to its efficient capacity in the degradation and mineralization of toxic and refractory compounds (Kasprzyk-Hordern et al., 2003). It was developed to overcome the limitations of ozonation process by catalysts which can promote the decomposition of aqueous ozone to generate hydroxyl radicals (·OH). However, these efficient catalysts all have challenges in the technical complexity and high cost of production which limit their full-scale practical application. Meanwhile, the previous studies showed sewage sludge based activated carbon (SBAC) as a efficient catalyst for catalytic wet air oxidation of phenolic compounds and ozonation of oxalic acid (Marques et al., 2011; Wen et al., 2012), which was not only a environmentally beneficial and sustainable sewage sludge disposal method but also reduced the cost of production of catalyst. Furthermore, there is a

* Corresponding author. Address: School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China. Tel.: +86 451 87649777; fax: +86 451 86283082.
E-mail address: han13946003379@163.com (H. Han).

http://dx.doi.org/10.1016/j.biortech.2014.05.061
0960-8524/

high expectation on SBAC modification by loaded Mn oxides (MnOx, the most reactive metal oxides catalyst) for further improving the catalytic activity and stability of SBAC. However, few studies on using this type of catalyst to enhance the catalytic activity in ozonation of real industrial wastewater have been published. It is noteworthy that catalytic ozonation process (COP) for complete eliminating pollutants is expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their chemical degradation (Muñoz et al., 2005). However, the oxidation intermediates are generally more biodegradable than the original molecules. Therefore, there is a great advantageous of integrating COP with biological process to attain a more efficient and cost-effective process for treating low biodegradability and high toxicity wastewater. Especially, nitrogen compounds, which were difficult to remove in COP, even the concentration increased by oxidation intermediates formed (Yang et al., 2011), were more suitable for biological treatment. It was reported that anoxic moving bed biofilm reactor (ANMBBR) and biological aerated filter (BAF) process (ANMBBR–BAF) with shortcut biological nitrogen removal (SBNR) was successfully applied to advanced treatment of real biologically pretreated CGW (Zhuang et al., 2014). But, the system still had several problems to be solved, such as overlong hydraulic residence times (12 h of HRT) and interference of toxic compounds (total phenols in excess of 100 mg/L restricted the biodegradation). Thus, the novel integration of COP and ANMBBR–BAF has substantial advantages to solve the difficult problems between them. In the present study, the catalytic activity of MnOx/SBAC in ozonation of raw wastewater was investigated, and then MnOx/SBAC dose and reaction time were optimized. Meanwhile, effects of initial pH and *tert*-butanol on pollutants removal were examined during COP. Furthermore, the performance of pollutants removal of the integrated COP with ANMBBR–BAF process was evaluated.

2. Methods

2.1. Materials

Real biologically pretreated CGW was obtained from the effluent of an upflow anaerobic sludge bed reactor followed by anoxic–aerobic process after ammonia stripping and phenols solvent extraction in the Lurgi coal gasification wastewater treatment plant (China Coal Longhua Harbin Coal Chemical Industry Co., Ltd). The concentrations of the main pollutants of raw wastewater were as follows: 300–350 mg/L of COD, 0.05–0.07 of BOD_5/COD value, 120–180 mg/L of total phenols (TP), 100–140 mg/L of total organic carbon (TOC), 60–80 mg/L of total nitrogen (TN) and 30–50 mg/L of NH_4^+-N. The pH ranged between 6.5 and 7.5. The dewatered sewage sludge was collected from the biological wastewater treatment plant (Harbin, China).

The preparation process of SBAC followed the method developed by Wen et al. (2012). Briefly, the sewage sludge was dried at 105 °C for 24 h then ground and sieved into a uniform size of <0.1 mm. Then, a 10 g of sample was impregnated into a 75 ml of 3 mol/L $ZnCl_2$ solution as an activation agent for 24 h at room temperature. When the supernatant liquid was completely removed, the sample was dried at 105 °C and subsequently was pyrolyzed in a muffle furnace where high pure N_2 was in-poured for producing the absence of oxygen condition. The furnace temperature was gradually increased at a rate of 18 °C/min and the final temperature of 700 °C maintained for 1 h, prior to cooling in nitrogen gas. After being pyrolyzed, the products were washed with 3.0 mol/L HCl to remove inorganic impurities, then the products were washed with Milli-Q water until constant pH and dried. MnOx/SBAC was prepared by a simple wet impregnation improved technique (Faria et al., 2009). An amount of SBAC was immersed in Mn nitrate solutions with a desired concentration and the suspension was stirred with 200 rpm for 24 h, and then evaporated in a rotary evaporator at 105 °C for 12 h. After that the MnOx/SBAC was calcined at 600 °C for 3 h in a muffle furnace in the absence of oxygen condition to obtain the required catalyst, and then washed with Milli-Q water to remove the loosely bonded metal irons and dried and stored. The main characteristics of MnOx/SBAC were as follows: 327.5 m^2/g of BET area, 0.122 cm^3/g of micropores volume, 0.204 cm^3/g of macro and mesopores volumes, 3.318 nm of average pore size, 15.23% of Mn, 1.12% of Zn, 0.47% of Fe, 1.54% of Al and 6.58 of pH_{pzc}.

2.2. Experimental procedures

The raw wastewater was first added into COP reactor (1.2 L of the effective volume) followed by a continuous input of ozone gas. Ozone was generated using a corona discharge ozone generator with pure oxygen as feed gas (DHX-I, Harbin Jiujiu Electrochemistry Technology Co., Ltd., China). The flow rate of ozone gas was 500 ml/min and ozone gas concentration was 15 mg/L. The off-gas was absorbed by KI solution. In the adsorption test, air, instead of ozone, was introduced into the reactor with all other reaction conditions kept identical. Additionally, the added concentration of *tert*-butanol (TBA) as scavenger for ·OH was 100 mg/L. The COP effluent was poured into a sparger equipped for aeration 1 h to remove the remaining ozone and further treated in ANMBBR–BAF system. The composition of bioreactors, start-up and operational strategies of ANMBBR–BAF system were described by Zhuang et al. (2014). The pH was controlled by added NaOH (1 mol/L) and HCl (1 mol/L).

2.3. Analytical methods

BET surface area and pore volume of MnOx/SBAC were measured using a surface area and porosity analyzer (ASAP 2020, Micromeritics). The pH at the point of zero charge (pH_{pzc}) was measured with a mass titration method. Samples were gold-coated and observed under a scanning electron microscope (SEM, HITACHI S4800 HSD, Japan). The percentage content of major elements was determined by X-ray fluorescence (XRF) with X-ray spectrometer (AXIOS-PW4400, Holland). COD, BOD_5, TP and NH_4^+-N were measured by Standard Methods (APHA, 1998). TOC and TN were determined with a total organic carbon analyzer (TOC-V, Shimadzu Corporation, Japan). PH values were determined with a pH meter (pHS-3C, Leici, China). The ozone gaseous concentration was measured using the iodometric titration method. Throughout experiments, the withdrawn samples were filtered using 0.45 μm acetic acid fiber filters to separate the catalyst particles prior to analysis and the results were average of at least three measurements with an accuracy of ±5%.

3. Results and discussion

3.1. Effects of catalyst on ozonation of biologically pretreated CGW

The addition of MnOx/SBAC significantly enhanced the TP removal and biodegradability of treated wastewater in COP. Fig. 1 shows 83.5% of TP was degraded with ozonation alone in 60 min, the corresponding BOD_5/COD value was improved to 0.152. With 1.0 g/L of MnOx/SBAC, the same removal efficiency and BOD_5/COD value in COP reached within 30 min. When dosing MnOx/SBAC in the range from 0.0 to 1.0 g/L, the removal efficiency and BOD_5/COD value increased faster than that when dosing in the range of 1.0–5.0 g/L. The removal efficiency and BOD_5/COD value at 1.0 g/L of MnOx/SBAC were 13.4% and 286.8% higher than that in

Please cite this article in press as: Zhuang, H., et al. Advanced treatment of biologically pretreated coal gasification wastewater by a novel integration of heterogeneous catalytic ozonation and biological process. Bioresour. Technol. (2014), http://dx.doi.org/10.1016/j.biortech.2014.05.061