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Short Communication

The feasibility of using combined TiO_2 photocatalysis oxidation and MBBR process for advanced treatment of biologically pretreated coal gasification wastewater

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HIGHLIGHTS

- TiO_2 were loaded on SBAC to serve as catalyst (TiO_2/SBAC) in HPO.
- HPO eliminated toxic and refractory compounds and improved biodegradability.
- The integrated system could shorten the retention time.
- The total operating cost was 2.8 CNY/t.

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ABSTRACT

The study examined the feasibility of using combined heterogeneous photocatalysis oxidation (HPO) and moving bed biofilm reactor (MBBR) process for advanced treatment of biologically pretreated coal gasification wastewater (CGW). The results indicated that the TOC removal efficiency was significantly improved in HPO. Gas chromatography–mass spectrometry (GC–MS) analysis indicated that the HPO could be employed to eliminate bio-refractory and toxic compounds. Meanwhile, the BOD_5/COD of the raw wastewater was increased from 0.08 to 0.49. Furthermore, in the integration of TiO_2 photocatalysis oxidation and MBBR process, the effluent of COD, BOD_5, TOC, NH_4^+-N and TN were 22.1 mg/L, 1.1 mg/L, 11.8 mg/L, 4.1 mg/L and 13.7 mg/L, respectively, which all met class-I criteria of the Integrated Wastewater Discharge Standard (GB18918-2002, China). The total operating cost was 2.8 CNY/t. Therefore, there is great potential for the combined system in engineering applications as a final treatment for biologically pretreated CGW.

1. Introduction

Conventional treatment of coal gasification wastewater (CGW) includes solvent extraction of phenolic compounds, steam stripping of ammonia, and biological treatment, mostly the activated sludge process (Guclu et al., 2013; Xu et al., 2015). However, due to the presence of many refractory and toxic compounds, the activated sludge process is not efficient for the removal of organic pollutants. Although new biological processes have been developed and achieved good results, such as the anoxic–oxic (A–O) and the anaerobic–anoxic–oxic (A_1–A_2–O) process (Zhuang et al., 2014a). These processes are still not efficient enough to meet the strict requirements of the National Discharge Standard of China (Zhao et al., 2014). Therefore, an efficient and cost-effective treatment process should be proposed to handle this high toxic wastewater and comply with the increasingly stringent environmental regulations.

A treatment method proven to be effective in treatment of varied refractory-containing organic wastewaters is advanced oxidation processes (AOPs). The AOPs are based on the generation of hydroxyl radicals (·OH), which indiscriminately react with a large amount of compounds. In this regard, TiO_2 photocatalysis oxidation is commonly used due to the simplicity of the equipment

Abbreviations: HPO, heterogeneous photocatalysis oxidation; MBBR, moving bed biofilm reactor; CGW, coal gasification wastewater; AOPs, advanced oxidation processes; AC, activated carbons; TiO_2/SBAC, sewage sludge based activated carbon (SBAC) which loaded TiO_2; COD, chemical oxygen demand; BOD, biochemical oxygen demand; TOC, total organic carbon; TN, total nitrogen; TP, total phenol; pH_{PZC}, the pH at the point of zero charge; XRF, X-ray fluorescence; GC–MS, gas chromatography–mass spectrometry.

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(Chen et al., 2013). Despite these merits, the conventional TiO_2 powder has low conversion efficiency and is difficult to separate after photocatalysis (Elmolla and Chaudhuri, 2011a). To achieve rapid and efficient decomposition of organic pollutants and also easy manipulation of the catalyst in a total photocatalytic process, it may be effective to load TiO_2 nanoparticles onto suitably adsorbents. Meanwhile, previous studies have shown that the sewage sludge based activated carbon (SBAC) could be used as an efficient catalyst for catalytic wet air oxidation of phenolic compounds and catalytic ozonation of biologically pretreated CGW (Marques et al., 2011; Zhuang et al., 2014b). To date, however, the application of SBAC as catalyst supports in photocatalysis oxidation of real industrial wastewater has not been reported in the literature.

Additionally, although photocatalytic oxidation has been accepted as a promising method for degradation of non-biodegradable organic pollutions, it needed a lot of oxidant and energy (Elmolla and Chaudhuri, 2011b). However, the use of TiO_2 photocatalysis oxidation as a pre-treatment to enhance the biodegradability of wastewater containing recalcitrant or inhibitory compounds may be justified as the resulting intermediates are easily degradable in a further biological treatment. However, no study on advanced treatment of biologically pretreated coal gasification wastewater by the integrated photocatalysis-biological system has been reported in the literature. Therefore, in the present work, TiO_2 oxides were supported SBAC (designated as TiO_2/SBAC) and its catalytic activity on photocatalytic oxidation of real biologically pretreated CGW was investigated. The biodegradability of the treated effluents following photocatalysis pretreatment was evaluated. Meanwhile, effect of *tert*-butanol (TBA) on the catalytic activity was examined. Furthermore, the performance of pollutants removal of the integrated heterogeneous photocatalytic oxidation (HPO) with moving bed biofilm reactor (MBBR) process was evaluated.

2. Methods

2.1. Materials

The real biologically pretreated CGW used in this study was collected from the effluent of secondary settling tank in the full-scale wastewater treatment facility. The main characteristics of the real biologically pretreated CGW were as follows: 150–200 mg/L of COD, 0.05–0.08 of BOD_5/COD ratio (B/C), 80–120 mg/L of total phenol (TP), 90–140 mg/L of total organic carbon (TOC), 50–70 mg/L of total nitrogen (TN) and 35–50 mg/L of NH_4^+-N. The pH ranged between 6.5 and 8.0.

By replacing quartz tubes with SBAC, the preparation process of TiO_2/SBAC was described in the previous report (Zangeneh et al., 2014). The main characteristics of TiO_2/SBAC were as follows: 312.3 m^2/g of BET area, 0.193 cm^3/g of micropores volume, 0.208 cm^3/g of macro and mesopores volumes, 3.942 nm of average pore size, 25.04% of Ti, 1.31% of Zn, 2.52% of Al and 6.71 of pH_{PZC}.

2.2. Experimental procedures

A 500 mL of biologically pretreated CGW was placed in a 600 mL reactor with the required amount of TiO_2/SBAC (2.0 g/L) and was stirred magnetically (100 rpm) at room temperature (22 ± 2 °C). The pH was adjusted to 7.0 using H_2SO_4 (1 mol/L) and NaOH (5 mol/L). The source of UV irradiation was a UV lamp with a nominal power of 8 W, emitting radiation at 325 nm. After the designated reaction time, the samples were taken from the reactor and filtered using 0.45 μm acetic acid fiber filters. In the adsorption test, reactor was kept in dark box without UV irradiation. To investigate reaction mechanisms, the added concentration of *tert*-butanol (TBA) as scavenger for ·OH was 50 mg/L. The HPO effluent was further treated in MBBR process. The start-up and operational strategies of MBBR system were described by Hou et al. (2014). Values represent the averages and standard deviation of triplicate tests.

2.3. Analytical methods

BET surface area and pore volume of TiO_2/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. The percentage content of major elements was determined by X-ray fluorescence (XRF) with X-ray spectrometer (AXIOS-PW4400, Holland). COD, BOD_5, TOC, TP, TN and NH_4^+-N were measured by Standard Methods (APHA, 1998). PH values were determined with a pH meter (pHS-3C, Leici, China). For compounds identified analysis, the samples were firstly filtered by a 0.45 μm acetic acid fiber filters and extracted by methyl tert-butyl ether into neutral, basic and acid phase and then concentrated by evaporating in a water bath at 40 °C. The concentrated samples were used for gas chromatography–mass spectrometry (GC–MS) analysis. The analytical conditions were described in the previous paper (Zhuang et al., 2014a).

3. Results and discussion

3.1. Effects of TiO_2/SBAC on HPO of biologically pretreated CGW

As shown in Fig. 1, without UV irradiation, only 14.5% of TOC was adsorbed on the TiO_2/SBAC in 120 min. However, on addition of UV irradiation, the TOC removal efficiency was significantly improved. Meanwhile, only 7.1% of TOC was oxidized by UV alone after 120 min, indicating the significance of TiO_2/SBAC as catalyst in HPO. In addition, 50 mg/L of TiO_2 powers as substitute for catalyst were used to catalyze photocatalytic oxidation, only 34.5% of TOC was removed in 120 min. The TOC removal efficiency was improved by 32.7% with simultaneous use of UV and TiO_2/SBAC compared to that of UV plus TiO_2. Giri et al. (2008) investigated a novel use of TiO_2 fiber for photocatalytic ozonation of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution and found it significantly enhanced 2,4-D mineralization in O_3/UV/TiO_2. The removal of phenol from its aqueous solution under UV irradiation

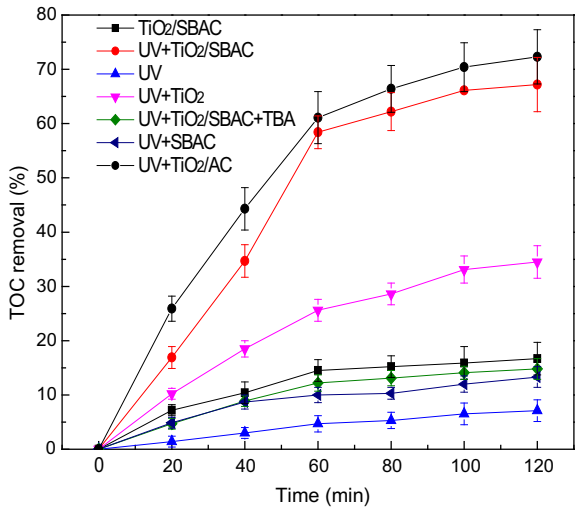

Fig. 1. Effect of TiO_2/SBAC on the performance of pollutants removal in photocatalysis oxidation.