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Short Communication

Advanced treatment of biologically pretreated coal gasification wastewater by a novel integration of catalytic ultrasound oxidation and membrane bioreactor

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HIGHLIGHTS

- FeOx/SBAC and MnOx/SBAC improved TOC removals and BOD_5/COD in ultrasound oxidation.
- The ultrasound oxidation and biodegradation process were integrated in one reactor.
- Catalytic ultrasound oxidation (CUO) evidently promoted organics removals in MBR.
- Sono-physical and sono-chemical reactions were the mechanisms of CUO-MBR.
- Significant fouling migration was observed in CUO-MBR.

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ABSTRACT

Laboratorial scale experiments were conducted to investigate a novel system integrating catalytic ultrasound oxidation (CUO) with membrane bioreactor (CUO-MBR) on advanced treatment of biologically pretreated coal gasification wastewater. Results indicated that CUO with catalyst of FeOx/SBAC (sewage sludge based activated carbon (SBAC) which loaded Fe oxides) represented high efficiencies in eliminating TOC as well as improving the biodegradability. The integrated CUO-MBR system with low energy intensity and high frequency was more effective in eliminating COD, BOD_5, TOC and reducing transmembrane pressure than either conventional MBR or ultrasound oxidation integrated MBR. The enhanced hydroxyl radical oxidation, facilitation of substrate diffusion and improvement of cell enzyme secretion were the mechanisms for CUO-MBR performance. Therefore, the integrated CUO-MBR was the promising technology for advanced treatment in engineering applications.

1. Introduction

Many biological processes have been investigated to treat the coal gasification wastewater (CGW) (Li et al., 2011; Jia et al., 2014); however, due to increasing awareness on environmental issues and tight environmental regulations, zero liquid discharge (ZLD) is strictly required to improve the water utilization efficiency and protect the environment. It was notable that in the engineering applications, high concentrations of organic compounds in secondary effluent was the bottleneck needed to be broken to satisfy the requirements of reuse, which was the key process to realize the ZLD. Therefore, more efforts on advanced treatment of biologically pretreated CGW should be taken.

Series of heterogeneous Fenton oxidation (HFO) and heterogeneous catalytic ozonation (HCO) integrated biological processes have been investigated, results represented effective removals of organics, toxicity and COLOR (Zhuang et al., 2014; Xu et al., 2015). Previous studies have demonstrated that the sewage sludge based activated carbon (SBAC) could be used as an efficient catalyst support for Fenton and catalytic ozonation of biologically pretreated CGW, providing a better option to reuse residual sewage sludge rather than disposal (Zhuang et al., 2014; Xu et al., 2015). However, in the two above studies, the supernatant of HFO and HCO was subsequently fed to the biological process for the final purification which taken large footprints and long hydraulic retention time (5.5 h for the biological process).

Ultrasound is a sound wave at a frequency range from 20 kHz to 10 MHz which has a wide range of environmental applications (Oz

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and Uzun, 2015). Ultrasound produces a hydrodynamic shear force in aqueous phase due to the rapid collapse of microbubbles during cavitation (Oz and Uzun, 2015). Furthermore, the ultrasound initiates chemical reactions by hydroxyl free radicals (·OH), due to high temperatures and pressures created within a collapsing cavitation bubble (Velmurugan and Muthukumar, 2011). Membrane bioreactor (MBR) has been widely used for high strength wastewater treatment owing to its superiorities such as low suspended solid and turbidity in effluent, highly efficient pollutants removals, high organic loading rate and less excess sludge (Jia et al., 2014), which is indispensable for the ZLD.

Up to date, combination of catalytic ultrasound oxidation (CUO) with MBR (CUO-MBR) (in one reactor) for the wastewater treatment has not been reported yet. This novel integration of CUO-MBR has substantial advantages in saving footprints, reducing HRT, improving organics removals and migrating the membrane fouling. In the present work, Fe oxides and Mn oxides were supported on SBAC (designated as FeOx/SBAC and MnOx/SBAC) as catalyst and their catalytic activities on CUO and CUO-MBR treating biologically pretreated CGW were investigated. Meanwhile, the possible mechanisms for FeOx/SBAC and MnOx/SBAC catalytic reactions and performance of organics removals of CUO-MBR were discussed. The integrated process was expected to be feasible and preferable reference for further engineering application.

2. Methods

2.1. Materials

The actual biologically pretreated CGW used in this study was collected from the effluent of secondary settling tank in the full-scale CGW treatment plant in Erdos, China. The wastewater had been treated by series of external circulation anaerobic process, oxygen limited aeration process and three stages anoxic/oxic process. The main characteristics of this actual biologically pretreated CGW were as follows: 120–150 mg/L of COD, 0.05–0.1 of BOD_5/COD ratio, 110–125 mg/L of total organic carbon (TOC). The pH ranged between 8.0 and 8.5.

The preparation process of FeOx/SBAC and MnOx/SBAC was described in the previous report (Zhuang et al., 2014). The main characteristics of FeOx/SBAC and MnOx/SBAC were shown in Table 1.

2.2. Experimental procedures

The batch ultrasound experiments were carried out in cylindrical plexiglass reactors with the effective volume of 3 L. The ultrasound was performed using a generator with a transducer and a metallic probe. This apparatus worked with a variable frequency of 40 and 60 kHz and power of 1.2–120 W. The batch experiments were conducted at the average energy intensities of 0.4, 0.8, 1.2, 1.6 and 2.0 W/L with the irradiation time of 5, 10, 15, 20 and 25 min. The SBAC, granular activated carbon (GAC), FeOx/SBAC and MnOx/SBAC were added into the reactors with the increasing dosages of 0.2, 0.5, 1.0, 2.0 and 4.0 g/L. To ascertain the optimal operating parameters, each batch experiment was carried in triplicate. According to the results of batch experiments, the ultrasound frequency, energy intensity, irradiation time, catalyst and dosage were confirmed.

Table 1
Physicochemical properties of the FeOx/SBAC and MnOx/SBAC.

Parameters	FeOx/SBAC	MnOx/SBAC
S_{BET} (m^2/g)	350.5	342.6
$V_{meso(macro)}$ (cm^3/g)	0.221	0.209
V_{micro} (cm^3/g)	0.132	0.131
Pore size (nm)	3.385	3.291
pH_{pzc}	7.58	6.31

S_{BET}, BET surface area; $V_{meso(macro)}$, meso(macro) pore volume; V_{micro}, micro pore volume; pH_{PZC}, point of zero charge.

The CUO was integrated with conventional MBR (CMBR) in one reactor as the integrated CUO-MBR system. In order to present the improved performance in CUO-MBR, continuous compared experiments of CMBR, ultrasound oxidation integrated MBR (UO-MBR) and CUO-MBR were operated for 60 days and the effective volumes were 3 L. The activated sludge was obtained from the full-scale aerobic tank treating CGW and the suspended solids in CMBR, UO-MBR and CUO-MBR were 5 g/L. UO-MBR and CUO-MBR have the same ultrasound conditions. The transmembrane pressure (TMP) was measured to evaluate the membrane fouling degree. The extracellular polymeric substances (EPS) in membrane fouling were measured in terms of proteins and polysaccharides. The detailed HRT of the CMBR, UO-MBR and CUO-MBR were determined, based on the continuous experiments results. Additionally, the added concentration of tert-butanol (TBA) as scavenger for ·OH was 50 mg/L.

2.3. Analytical methods

The BET surface area (S_{BET}), meso(macro) pores volumes ($V_{meso(macro)}$), micro pore volume (V_{micro}), pore size and point of zero charge (pH_{PZC}) of FeOx/SBAC and MnOx/SBAC were measured by the methods reported by Xu et al. (2015). COD, BOD_5 and TOC were measured by Standard Methods (AHPA, 1998), and the BOD_5/COD ratios were determined to evaluate the biodegradability of biologically pretreated CGW. The enzymatic activities of acid phosphatase (AP), alkaline phosphatase (ALKP), protease (P), glucosidase (G) and esterase (E) were measured by the methods of Molina-Muñoz et al. (2010). The extraction of EPS from membrane fouling and the measurements of protein and polysaccharides were taken according to previous literature (Taimur Khan et al., 2013). The COD, BOD_5 and TOC were determined in triplicate every 2 days. The enzymes, protein and polysaccharides were determined in triplicate every 5 days.

3. Results and discussion

3.1. Effects of FeOx/SBAC and MnOx/SBAC on CUO of biologically pretreated CGW

As shown in Fig. 1, the optimal frequency, energy intensity and irradiation time were 60 kHz, 1.6 W/L and 20 min, respectively, giving maximum TOC removal efficiency of 23.6%. This enhanced performance of ultrasound treatment could be attributed to two aspects: sono-physical reactions by hydrodynamic shear force and sono-chemical reactions by ·OH oxidation (Velmurugan and Muthukumar, 2011).

Fig. 2 represents the effects of FeOx/SBAC and MnOx/SBAC on TOC removal and BOD_5/COD improvement. As shown in Fig. 2a, the TOC removal efficiencies increased with increasing SBAC and GAC dosages, mainly owing to the adsorption of organics. It could be observed that the TOC removal efficiency with MnOx/SBAC represented lower than FeOx/SBAC with the dosage of 2 g/L, representing the TOC removal efficiencies of 37.3% and 43.2% for MnOx/SBAC and FeOx/SBAC, respectively.

To ascertain if the ·OH was the main oxidant in the removal of TOC, TBA was added as ·OH scavenger. Result showed the TOC removal efficiencies decreased from 37.3% and 43.2% to 8.2% and 12.1% for MnOx/SBAC and FeOx/SBAC, respectively, with 50 mg/L