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Advanced treatment of biologically pretreated coal gasification wastewater by a novel heterogeneous Fenton oxidation process

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ABSTRACT

Sewage sludge from a biological wastewater treatment plant was converted into sewage sludge based activated carbon (SBAC) with $ZnCl_2$ as activation agent, which was used as a support for ferric oxides to form a catalyst (FeOx/SBAC) by a simple impregnation method. The new material was then used to improve the performance of Fenton oxidation of real biologically pretreated coal gasification wastewater (CGW). The results indicated that the prepared FeOx/SBAC significantly enhanced the pollutant removal performance in the Fenton process, so that the treated wastewater was more biodegradable and less toxic. The best performance was obtained over a wide pH range from 2 to 7, temperature 30°C, 15 mg/L of H_2O_2 and 1 g/L of catalyst, and the treated effluent concentrations of COD, total phenols, BOD_5 and TOC all met the discharge limits in China. Meanwhile, on the basis of significant inhibition by a radical scavenger in the heterogeneous Fenton process as well as the evolution of FT-IR spectra of pollutant-saturated FeOx/BAC with and without H_2O_2, it was deduced that the catalytic activity was responsible for generating hydroxyl radicals, and a possible reaction pathway and interface mechanism were proposed. Moreover, FeOx/SBAC showed superior stability over five successive oxidation runs. Thus, heterogeneous Fenton oxidation of biologically pretreated CGW by FeOx/SBAC, with the advantages of being economical, efficient and sustainable, holds promise for engineering application.

Introduction

The coal gasification industry in China has been rapidly developed in order to supplement the natural gas shortage, and has played a key role in new clean and renewable market in recent years. However, coal gasification wastewater (CGW) contains considerable amounts of complex, toxic and refractory pollutants in spite of physicochemical pretreatment (Wang et al., 2011), which would cause significant deterioration of the environment. Most biological treatments have shown limited success and fall short of meeting the strict requirements of the National Discharge Standard of China (Wang and Han, 2012). Biologically pretreated CGW still contains a large number of toxic and refractory compounds as well as their derivatives, such as phenolic compounds, polycyclic aromatic hydrocarbons, nitrogenous heterocyclic compounds, long-chain hydrocarbons, and ammonia, with lower biodegradability than the raw wastewater (Zhuang et al., 2014a). According to the latest national policy, zero liquid discharge has been set as a requirement to resolve the conflicts between environmental

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protection and CGW discharge in China. The wastewater control task had become a bottleneck for the development of the coal gasification industry. Thus, the search for an efficient and cost-effective process for advanced treatment of biologically pretreated CGW is very urgent.

The Fenton process has recently been intensively investigated for mineralizing refractory pollutants in industrial wastewater, due to its use of inexpensive chemicals, ease of operation and high oxidation performance (Chakinala et al., 2008). However, this type of chemical oxidation treatment usually presents certain limitations (An et al., 2013), such as a narrow working pH range (2–4) and the accumulation of iron-containing sludge, which makes the process complicated and uneconomical, and even generates secondary pollution (Ventura et al., 2002; Murray and Parsons, 2004). The heterogeneous Fenton process is a promising alternative that avoids these drawbacks and permits the reuse of catalysts, and has attracted more and more attention. Catalysts are usually prepared in this process by immobilizing iron ions or oxides on supports, which can confer excellent catalyst performance and practicability. Various supports such as mesoporous activated carbon (Karthikeyan et al., 2011), nanoporous activated carbon (Karthikeyan and Sekaran, 2014), activated carbon fibers (Wang et al., 2014a), zeolites (Fukuchi et al., 2014), resin (Shu et al., 2010), and hydrogel (Wang et al., 2014b) have been used to prepare heterogeneous Fenton catalysts in recent years. However, these efficient catalysts have challenges in terms of technical complexity and high cost of production, which limit their full-scale practical application. Therefore, the main concern researchers face is the development of a novel and efficient catalyst with a simple and low-cost production process, which is beneficial to engineering application. On the other hand, an increasing amount of sewage sludge generated by biological wastewater treatment plants has become an issue of particular concern (Wurz et al., 2011), which would result in a serious pollution problem for the environment in case of inappropriate disposal. It is a better option to reuse residual sewage sludge rather than dispose of it. Thus, greater attention has been focused on converting sewage sludge into activated carbon, based on its high content of organic components, using controlled conditions or some chemical treatments, for use as an adsorbent to remove organic pollutants and heavy metals (Smith et al., 2009). Recently, sewage sludge based activated carbon (SBAC) was reported to be an efficient catalyst for catalytic wet air oxidation of phenolic compounds and ozonation of oxalic acid (Marques et al., 2011; Wen et al., 2012). Meanwhile, some previous studies (Tu et al., 2012, 2013) showed that sewage sludge derived carbon could be used as the support for a low-cost, efficient catalyst in Fenton oxidation of Acid Orange II, which was used as a model target pollutant. However, catalysts are usually used to dispose of real industrial or domestic wastewater in practical processes (Wang et al., 2009). To date, no study on using SBAC as the support of a Fenton catalyst for removal of pollutants in real industrial wastewater has been published, or especially, biologically pretreated CGW. Moreover, most research on the heterogeneous Fenton process has focused on the preparation of highly efficient catalysts and finding the optimum operating conditions. Compared to the classic Fenton reaction, the mechanism of the heterogeneous Fenton reaction is still unclear, to some extent, which inhibits the wide application of the heterogeneous Fenton process.

In the current study, ferric oxides were supported on SBAC (designated as FeOx/SBAC) using a simple impregnation method, and the catalytic activity in Fenton oxidation of real biologically pretreated CGW was investigated. Meanwhile, the effects of important operating parameters on the catalytic activity and the biodegradability and toxicity of treated wastewater were evaluated. Furthermore, a possible reaction pathway and mechanism were proposed. The process was demonstrated to be feasible, and the results provide a reference for subsequent engineering application.

1. Materials and methods

1.1. Materials

The sewage sludge was collected from a biological wastewater treatment plant (Harbin, China) using the hybrid processes of enhanced primary treatment with added polymeric ferric aluminous chloride, followed by secondary biological treatment by activated sludge.

Real biologically pretreated CGW was obtained from the effluent of biological treatment after the ammonia-stripping and phenol solvent extraction processes in the full-scale wastewater treatment facility of the Lurgi coal gasification wastewater at China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. The plant had been operating over 3 years. The concentrations of the main pollutants in raw wastewater were as follows: 140–160 mg/L of COD, 0.05–0.07 of BOD_5/COD value, 30–45 mg/L of total phenols (TP), 45–60 mg/L of total organic carbon (TOC), 50–60 mg/L of total nitrogen (TN) and 20–35 mg/L of NH_4^+-N. The pH ranged between 6.5 and 7.5. The average temperature of raw wastewater over 1 year was around 30°C. Hydrogen peroxide (30%, W/W) and all other chemicals used were of analytical grade if not noted otherwise.

1.2. Preparation of catalyst

The preparation of SBAC was according to the method developed by Wen et al. (2012). Briefly, the dewatered sewage sludge was sieved to a uniform size of <0.1 mm. Then, a 10 g sample was impregnated into 75 mL of 3 mol/L $ZnCl_2$ solution as an activation agent (sludge: $ZnCl_2$ = 1:3, by mass) for 24 hr at room temperature. After the supernatant liquid was completely removed, the sample was pyrolyzed in a muffle furnace flushed with high purity N_2 to maintain oxygen-free conditions until the pyrolyzed products cooled to the room temperature. The furnace temperature was gradually increased at a rate of 18°C/min, and the final temperature of 700°C was maintained for 2 hr, which facilitated the formation of micropores and mesopores due to the cracking of the peptidoglycans (Smith et al., 2009). After being pyrolyzed, the products were washed of inorganic impurities with HCl and then the samples were thoroughly washed with Milli-Q water until the pH of the rinse water became constant, and dried.

SBAC-supported ferric oxide was prepared by a simple impregnation technique (Faria et al., 2009). An amount of