Fuel 178 (2016) 155–162

Contents lists available at ScienceDirect

Fuel

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

Treatment of British Gas/Lurgi coal gasification wastewater using a novel integration of heterogeneous Fenton oxidation on coal fly ash/sewage sludge carbon composite and anaerobic biological process

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HIGHLIGHTS

- Recycling coal fly ash and sewage sludge were firstly used to catalyze Fenton.
- Heterogeneous Fenton exhibited efficient performance in treated real BGLCGW.
- Catalyst showed good application, and the treated effluent was more biodegradable.
- Heterogeneous Fenton remarkably enhanced anaerobic granular sludge properties.
- The 74.9% and 86.1% of COD and TPh were removed in the integrated process with 12 h.

ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form 8 March 2016
Accepted 9 March 2016
Available online 14 March 2016

Keywords:
British Gas/Lurgi coal gasification wastewater
Heterogeneous Fenton
Coal fly ash
Anaerobic biological process
Sludge properties

ABSTRACT

A novel integrated process with heterogeneous Fenton oxidation and anaerobic biological process was employed in treatment of real British Gas/Lurgi coal gasification wastewater (BGLCGW). The results indicated Fenton oxidation with the prepared coal fly ash/sewage sludge carbon composite as catalyst exhibited efficient performance in treated BGLCGW over wide pH range at thirty reusability runs and the treated wastewater was more biodegradable, facilitating followed biological process. On the basis of significant inhibition of radical scavenger and ESR spectrum, it was deduced that the efficiency enhancement was responsible for generating hydroxyl radicals, and further analysis by fluor photometer confirmed the co-catalytic effect of iron, silicon and aluminum oxides of CFA/SC. Meanwhile, heterogeneous Fenton not only significantly improved the effluent quality, but also remarkable enhanced anaerobic granular sludge properties which facilitated the high efficiency and ecosystem stability in the bioreactor. Through the integrated process, overall 74.9% and 86.1% of COD and total phenols (TPh) were removed which were almost four times more than the performance of single anaerobic process at shorten half of HRT (12 h). Moreover, the integrated process also enhanced the aerobic biodegradation of BGLCGW, the corresponding concentrations of COD and TPh in the followed aerobic treated effluent met the standard for the reuse water. Thus, the novel integrated process with efficient, stable, economical and sustainable development advantages was suitable for engineering application.

1. Introduction

The stresses of environmental pollution and energy shortage are driving the coal gasification industry rapidly developed in China which is the clean use of coal resources in important ways [1]. Particularly, the BGL technology (British Gas/Lurgi derived from Lurgi coal gasification) has attracted more and more market applications due to its high production capacity and gas calorific value [2]. However, an enormous amount of high-strength wastewater is generated in coal gasification process which contents a large number of various toxic and refractory compounds, such as phenolic compounds, long chain hydrocarbons, nitrogenous heterocyclic compounds, ammonia, cyanide and thiocyanate which has posed great risk to the environment in cases of inappropriate disposal [3]. Meanwhile, the BGL coal gasification wastewater (BGLCGW) is characterized by the extremely low biodegradability, resulting the treated effluent in most of biological

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http://dx.doi.org/10.1016/j.fuel.2016.03.025
0016-2361/

process were not able to comply with the increasingly stringent environmental regulations [4,5]. Therefore, seeking out efficient and cost-effective process for treatment BGLCGW becomes urgent and important.

Heterogeneous Fenton as the promising alternative advanced oxidation technology has attracted great attentions in recent years due to its efficient capacity in the mineralization of refractory pollutants and improvement of the wastewater biodegradability [6,7]. It has been developed to overcome the limitations of critical drawbacks of homogeneous Fenton by iron ions or oxides immobilized onto solid supports as catalysts, which can be used in broad working pH range without sludge disposal problems, more suitable for engineering application [8]. Recently, various supports such as activated carbon, activated carbon fiber, carbon nanotubes, and zeolites have been used to prepare Fenton catalysts [9–12]. However, these efficient catalysts have challenges in terms of technical complexity and high cost of production, which limit their full-scale practical application. On the other hand, the increasing disposal of sewage sludge by biological wastewater treatment plant has been the important environmental pollution problem, which can be converted into activated carbon as useful catalyst supporting materials [13–16]. Meanwhile, the application of coal fly ash (CFA) as an attractive material to be used in adsorption has received a great deal of attentions which is produced annually in substantial quantities by coal-fired power plants [17]. Because of containing a variety of metal oxides, CFA is usually used as hazardous waste and harmful to the environment [18]. However, given that CFA is primarily made up of Al_2O_3, SiO_2 and Fe_2O_3, that offer desirable properties for use as the catalytically active component to enhance the catalytic activity of sewage sludge [19]. For the purpose of treating waste by waste, recycling sewage sludge and CFA for new applications of prepared Fenton catalyst can reduce the amount of solid waste in the environmental hazards and provide additional economic benefits which are an environmentally beneficial and sustainable development method. However, to the best of our knowledge, there is no report about using recycling sewage sludge and CFA composite as Fenton-like catalysts.

Noteworthy, it was very difficult to achieve complete removal of pollutants by Fenton process due to expensive cost and extensive operating conditions. Pretreatment of BGLCGW using heterogeneous Fenton would effectively enhance the biodegradability of wastewater, further facilitate the followed biological process which may be more reasonable to avoid high energy consumption. However, the followed biological treatments in many studies were restricted to aerobic treatment. In fact, as the most widely used biological technologies in treatment of high strength and complex industrial wastewater, the anaerobic process especially anaerobic granular sludge (AGS) had the more application advantages than aerobic treatment, such as dense and strong microbial structure, high biomass enrichment, and highshock loadings, producing biogas [20]. Hence, there is a great potential advantage of integrated the heterogeneous Fenton with AGS to attain a more efficient and cost-effective technology for treating high-strength toxic and refractory wastewater [21], suitable for the full-scale application or implemented in already existing treatment plants. To date, however, no study on using this novel integrated process for treatment of real BGLCGW has been reported. Moreover, it is meaningful to study that effect of heterogeneous Fenton on AGS properties which would reveal the relationship of Fenton process and AGS further provide guidance for the design and operation.

In the current study, a novel integration of heterogeneous Fenton with AGS process was to evaluate the effectiveness and feasibility in treatment real BGLCGW. CFA/sewage sludge carbon composite (named as CFA/SC) as catalyst was characterized and the catalytic activity for Fenton oxidation of BGLCGW was investigated. Meanwhile, advantages in application of catalyst were assessed and the possible reaction mechanism was proposed. Moreover, the effect of heterogeneous Fenton on AGS properties was analyzed. The study also tested whether the integrated process could enhance the aerobic biodegradation of BGLCGW and serve as a technically feasible and cost-effective process with potential applications.

2. Experimental

2.1. Materials

Real BGLCGW used in this study was obtained from the full-scale wastewater treatment facility of a coal chemical plant in Erdos, China. The characteristics of wastewater as following: (in mg/L): COD of 3000–3200, BOD_5 of 450–550, total phenols (TPh) of 600–700, SCN^- of 60–100, CN^- of 3–8 and pH of 6–7. The up-flow anaerobic sludge bed (UASB) reactor had a working volume of 5 L with an internal diameter of 8 cm, a total height of 100 cm and the operated temperature in the range of 40–50 °C. The anaerobic granular sludge was taken from the full-scale anaerobic tank treating BGLCGW from the aforementioned wastewater treatment plant and the suspended solids were inoculated in UASB about 9 g/L. Aerobic biodegradability tests were carried out in membrane bioreactor (MBR) which was made of chlorinated polyvinyl chloride with nominal pore size of 0.4 μm, effective filtration area of 0.11 m^2 and a working volume of 5 L. The initial seed sludge was obtained from the BGLCGW treatment plant aerobic tank and the inoculated sludge concentration was around 6 g/L. The dewatered sewage sludge sample was collected from the Wenchang wastewater treatment plant in Harbin, China. CFA was supplied by Donghua thermal power plant in Baotou city, China. Fenton experiments were carried out in a semi-continuous model reactor with effective volume of 1.5 L.

2.2. Preparation of the catalyst

Recycling sewage sludge and CFA were applied for preparing Fenton catalyst by a one-step method combining the carbonization and activation of $ZnCl_2$ [22]. First, amount of CFA and dewatered sewage sludge were ground and sieved into a uniform size of <0.1 mm. Then, 10 g of mixture sample (CFA: SC = 1:5, by mass) was impregnated into a 75 ml of 3 mol/L $ZnCl_2$ solution as an activation agent (mixture: $ZnCl_2$ = 1:3, by mass) for 24 h at room temperature. When the supernatant liquid was completely removed, the sample was dried at 105 °C for another 24 h 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 800 °C maintained for 3 h. The resulting samples were washed with 3.0 mol/L HCl for removing inorganic impurities then thoroughly washed with Milli-Q water until pH of rinsed water became constant, and dried at 80 °C in oven which were designated as CFA/sewage sludge carbon composite i.e. CFA/SC. Sewage sludge carbon (SC) was prepared as the same procedures of CFA/SC but without added CFA. In order to confirm the roles of silica and alumina in the Fenton oxidation with CFA/SC, SC supported Si and Al oxides were prepared by a wet impregnation (activation of high temperature and $ZnCl_2$) with similar Si and Al content of CFA/SC respectively, while amounts of ferrous sulfate were used to guarantee that all the catalysts had similar iron content. Finally the samples were dried and named as Fe/SC, Fe–Si/SC and Fe–Al/SC.