Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1014855

57 (2016) 6894–6900
March

Biological nutrient removal of gallic acid processing wastewater by combined expanded granular sludge bed and bio-contact oxidation under mesophilic conditions

Yundong Wu, Kanggen Zhou*, Shuyu Dong, Wei Yu

School of Metallurgy and Environment, Central South University, Changsha 410083, Hunan Province, China,
Tel. +86 15211080826; emails: wydccc@gmail.com (Y. Wu), zhoukg63@163.com (K. Zhou), familydsy@outlook.com (S. Dong), 2046yuwei2046@163.com (W. Yu)

Received 2 April 2014; Accepted 26 January 2015

ABSTRACT

The biological treatment of gallic acid processing wastewater (GAPW) was carried out with laboratory-scale 30-L expanded granular sludge bed (EGSB) and 60-L bio-contact oxidation (BCO) reactors. The temperatures of the EGSB and bio-contact oxidation reactors were maintained under mesophilic conditions of 35 and 32˚C, respectively. The effluent chemical oxygen demand (COD), total nitrogen, total phosphorus, gallic acid levels, and pH values of both the EGSB and bio-contact oxidation reactors, and redox potential of the EGSB were monitored. When the influent COD concentration was 3,000 mg L^{-1} and the organic loading rate (OLR) was 17.5 kg COD (m^3 d)$^{-1}$, the removal efficiency of COD by the EGSB and bio-contact oxidation reactors was 87.021%. The removal efficiencies of nitrogen, phosphorus, and gallic acid were 70.822, 58.116, and 63.407%, respectively. The redox potential in the EGSB varied between −320 and −350 mV. The effluent pH increased either in the EGSB or the bio-contact oxidation reactor. Both reactors were resistant to shock loading. The results of our study provided a theoretical basis for the biological treatment of GAPW.

Keywords: GAPW; EGSB; BCO; OLRs; Nutrient removal

1. Introduction

The treatment of wastewater remains a challenge for the gallic acid-producing industry (Fig. 1). Because many high-quality products are prepared from alkali processes, manufacturers have generally chosen alkali processes and Chinese nutgall as a raw material for the production of gallic acid [1]. For a well-controlled production, approximately 6.5 m^3 of wastewater is generated for each ton of refined gallic acid. However, chemical oxygen demand (COD) tests have found up to 60,000 mg L^{-1} total pollutants in the resultant wastewater, including 17,000 mg L^{-1} gallic acid and other complex components. In China, research and development toward efficient and practical technologies for treating the wastewaters produced from gallic acid production is of significant importance.

As environmental regulations have become increasingly stringent, the gallic acid processing industry is facing a severe test. Previous studies have focused on the removal of gallic acid from wastewater [3,4] but the removal of only gallic acid is not sufficient due to the complicated compositions in the wastewater. Studies on the removal of biological

---

*Corresponding author.

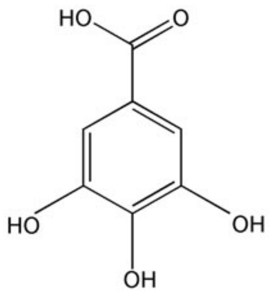

Fig. 1. Molecular structure of gallic acid [2].

nutrients have been limited. Our laboratory [5] has focused on the extraction of gallic acid from wastewater the gallic acid concentration left in the raffinate was less than 800 mg L^{-1} after extraction. As gallic acid was separated, the COD concentration reduced by more than 50%, and the biodegradability significantly increased. In the ideal case, the cleavage of a tannic acid molecule generates ten molecules of gallic acid and one molecule of glucose [6]. After extraction, most of the COD left in wastewater is glucose. Glucose is a good carbon source for the growth and metabolism of microorganisms [7,8]. Because the ratio of C: N: P in the wastewater is 188: 3: 1, that is, close to optimal conditions for anaerobic fermentation [9], the wastewater could be used for biological processes. The NaCl concentration in the wastewater is approximately 100 g L^{-1}, a level which would decrease the processing capacity for sludge if fed directly into reactors [10]. In the production of gallic acid, a large amount of steam condensate and cooling circulating water are discharged. The wastewater would need to be diluted before undergoing biological treatment.

An expanded granular sludge bed (EGSB) and a bio-contact oxidation process for the anaerobic and aerobic treatment of gallic acid processing wastewater (GAPW) were employed in this study. The EGSB can run at high COD concentrations and high organic loading rates (OLRs) [11]. Additionally, the EGSB can resist shock loading [12], has less sludge formation [13], and a high toxicity tolerance [14]. EGSBs have been used in the treatment of a variety of organic wastewaters with high COD concentrations and other complex components [15,16]. Bio-contact oxidation maintains high hydraulic load rates, retains high biomass concentrations, resists high shock loads [17,18], promotes microorganism growth, and generates less sludge [19].

This study investigated the removal efficiency of the combined EGSB and bio-contact oxidation reactor of COD contaminants at various OLRs, total nitrogen (TN), total phosphorus (TP), and gallic acid. Additionally, redox potential changes in the EGSB and the pH values of the two reactors were recorded.

2. Experimental setup

2.1. Reagents and analysis

All reagents used were of A.R. grade. GAPW was taken from Beiya Biotechnology Company in Huaihua, Hunan province, China.

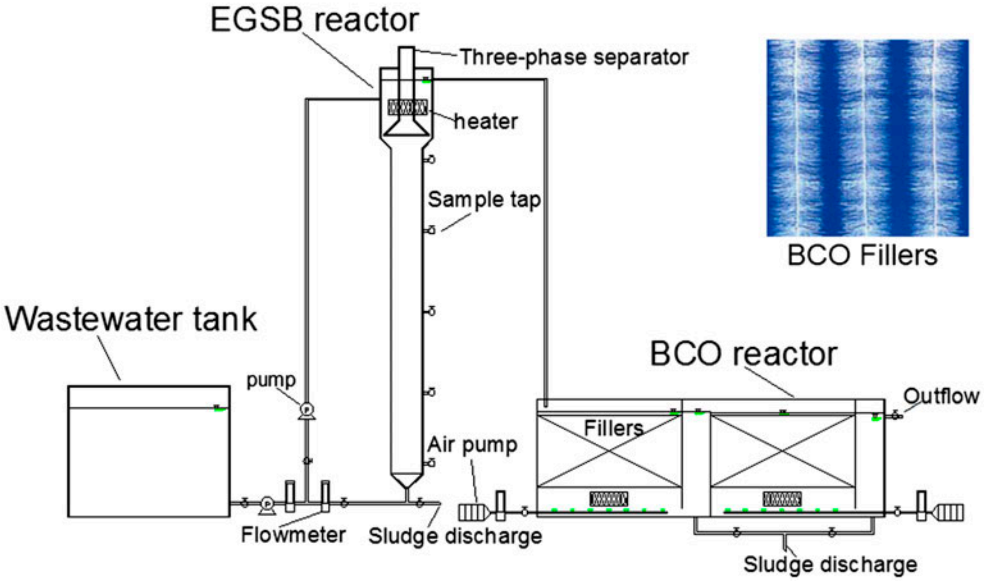

Fig. 2. Schematic diagram of experimental setup (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

The COD levels, TN and TP contents, gallic acid concentration, pH, redox potential, and concentrations of inorganic elements in the wastewater were analyzed. The COD was determined by rapid digestion and spectrophotometry [20]. The TN content was assayed with a UV spectrophotometer (UV-1801, Ruili Corp) [21]. TP was analyzed by a molybdate spectrophotometric method [22]. Gallic acid levels were determined by high-performance liquid chromatography (HPLC; Agilent 1100 series, Agilent Technologies). pH values were measured by a pH meter using a combined electrode (pH-3C, INESA Corporation). Redox potential was measured by an acid meter with a combined redox potential electrode (320-S, Mettler Toledo). The inorganic elements were assayed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; PS-6, Baird Corp).

2.2. The nature of wastewater

The pH value of the wastewater was 0.6–1.5, the COD concentration was approximately 30,000 mg L^{-1}, the TN concentration was approximately 500 mg L^{-1}, the TP concentration was approximately 160 mg L^{-1}, and the gallic acid concentration was approximately 800 mg L^{-1}. The other levels are listed in Table 1.

The result of the ICP-AES showed that there were a number of different elements in the wastewater at high enough concentrations for the growth of microorganism. No additional nutrients were required because the raw material, Chinese gallnut, provided natural substances so that the wastewater contained a comprehensive set of nutrients.

2.3. Characterization of the reactors and schematic diagram

A laboratory-scale EGSB reactor (30 L volume) was constructed from fiber reinforced plastics. A bio-contact oxidation reactor (60 L volume) was constructed from polyvinyl chloride. The EGSB reactor had a diameter of 150 mm, with an effective height of 1,700 mm. The bio-contact oxidation reactor was 1,200 mm long, 500 mm wide, and 500 mm in height. The material of the filler was polyolefin.

Table 1
Elements and concentrations in raffinate

Element	Concentration (mg L^{-1})	Element	Concentration (mg L^{-1})
Fe	48.1	Cr	0.9
Ba	0.03	Na	40,171
Zn	20.5	Si	56.1
B	1.2	Ca	224.5
K	1,685.4	Mn	1.5
Mg	59.7	Al	5.5
S	53.1	Mo	1.2

The anaerobic granular sludge was taken from an industrial-scale EGSB reactor in a paper mill wastewater treatment facility. The aerobic sludge was acquired from an urban sewage treatment plant. The temperatures of the EGSB and the bio-contact oxidation reactor were maintained under mesophilic conditions, at 35 and 32℃, respectively, with automatic temperature control devices.

The reactors were operated under continuous flow (Fig. 2). The influent into the EGSB reactor was diluted wastewater, and the influent of the bio-contact oxidation reactor was the effluent of the EGSB. The rise velocity of the EGSB was maintained at 3 m h^{-1} by adjusting the reflux ratio. The dissolved oxygen concentration of the bio-contact oxidation reactor was adjusted to 2–4 mg L^{-1}, and the sludge retention times of the two reactors were set at 10 d.

2.4. Operational conditions

The EGSB and bio-contact oxidation reactors were operated for 44 d. The wastewater was pre-treated by an extraction step. The influent pH was first adjusted to 6.0–8.0 with NaOH solution. The wastewater was diluted by 9–15 folds before pumping into the reactor.

The influent COD levels and OLRs were controlled as follows. Different COD concentration was used for different dilution times. The initial influent COD concentration was diluted to 2,000 mg L^{-1} from 0 to 19 d and increased to 2,500 mg L^{-1} until 25 d into the operation of the reactor. The influent COD concentration was 3,000 mg L^{-1} from 26 to 44 d. The initial OLR was kept at 3 kg COD $(m^3\ d)^{-1}$ and increased by 3 kg COD $(m^3\ d)^{-1}$ every 5 d of operation until 12 kg COD $(m^3\ d)^{-1}$. Then, the combined processes were run at an OLR of 17.5 and 22.5 kg COD $(m^3\ d)^{-1}$, respectively, for 3 d. From 27 to 44 d, the OLR was kept at 17.5 kg COD $(m^3\ d)^{-1}$. The shock loading time was set from 23 to 26 d when the influent COD concentration was 3,000 mg L^{-1} and the OLR was 22.5 kg COD $(m^3\ d)^{-1}$ (Fig. 3).

The designed influent COD concentration was calculated by following equation:

$$\eta = \frac{C_0}{D}(\mathrm{mg\ L^{-1}}), \tag{1}$$

where C_0 is the COD concentration of the original wastewater, 30,000 mg L^{-1}; and D is the dilution factor.

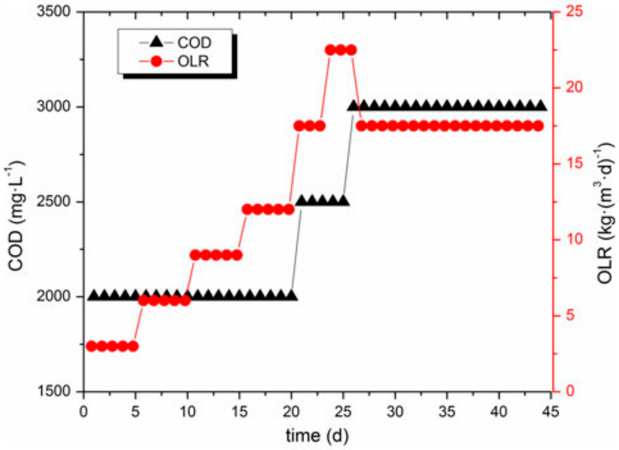

Fig. 3. Designed influent COD concentrations and OLRs.

The OLR was calculated by following equation:

$$\mathrm{OLR} = \frac{C}{VT} \times 1{,}000(\text{kg COD }(\text{m}^3\text{ d})^{-1}), \tag{2}$$

where C is the influent COD concentration, mg L^{-1}; V is the effective volume of the reactor, L; and T is the hydraulic retention time, d.

The removal efficiency of COD, TN, TP, gallic acid was calculated by following equation:

$$\eta = \frac{C_0 - C_1}{C_0} \times 100(\%), \tag{3}$$

where C_0 is the influent concentration, mg L^{-1}; and C_1 is the effluent concentration, mg L^{-1}.

3. Results and discussion

3.1. *Actual influent and effluent COD concentration and influent OLR*

From 0 to 2 d, due to the combined effect of the adsorption of the sludge and the degradation of microorganisms, the effluent COD was low. When the reactors were run under shock loading conditions from 23 to 26 d, the highest processing loading rate of the EGSB was 21.254 kg COD $(\text{m}^3\text{ d})^{-1}$, while the effluent COD was 1,179.027 mg L^{-1}, which exceeded the limits of the influent of the bio-contact oxidation reactor as the average processing loading rate of bio-contact oxidation was lower than 1 kg COD $(\text{m}^3\text{ d})^{-1}$. The shock loading was stopped at 27 d, and the effluent COD of the EGSB immediately dropped to 998.767 mg L^{-1}, which indicated the strong resistance to shock loading of the EGSB. The highest degradation loading rate of the subsequent bio-contact oxidation reactor was 1.910 kg COD $(\text{m}^3\text{ d})^{-1}$ at 26 d when the final effluent COD reached a maximum 876 mg L^{-1}. When the shock loading ceased, the effluent COD of the bio-contact oxidation did not decrease below 500 mg L^{-1} until 33 d, which indicated a weak resistance capacity of the bio-contact oxidation reactor to shock loading. The change in the degradation capacity of the two reactors after shock loading was minor (see Figs. 4 and 5).

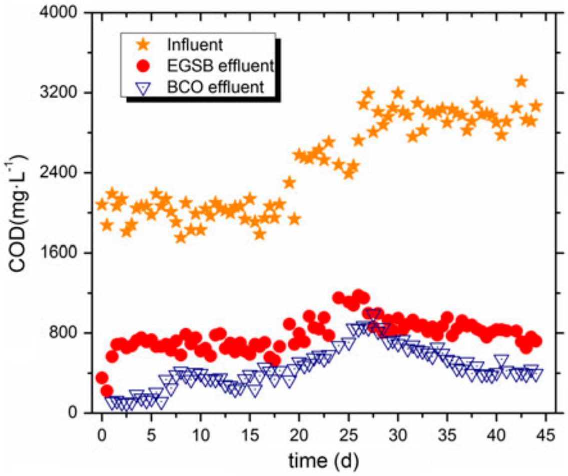

Fig. 4. Actual influent and effluent COD concentrations of expanded granular sludge bed and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

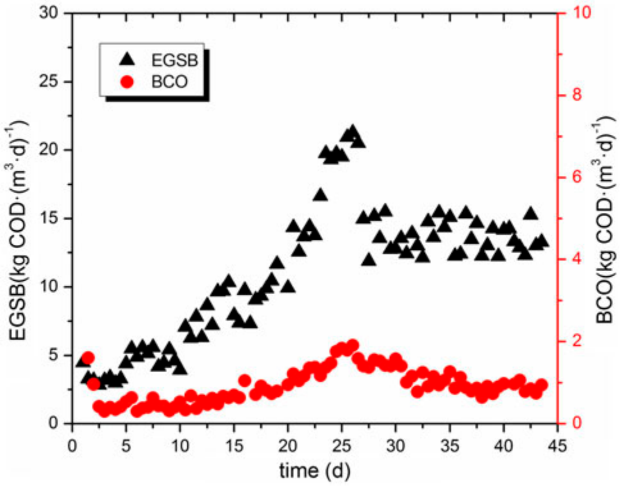

Fig. 5. Changes in the processing loading rate in expanded granular sludge bed and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

In the EGSB, from 30 to 44 d, when the influent OLR was 17.5 kg COD $(m^3\,d)^{-1}$, the average effluent COD was 719.311 mg L^{-1} and the OLR was 13.625 kg COD $(m^3\,d)^{-1}$. During the same period, in the bio-contact oxidation reactor, the average effluent COD was 442.222 mg L^{-1} and the OLR was 0.753 kg COD $(m^3\,d)^{-1}$. The total removal efficiency was 87.021%.

3.2. Removal of TN

From 1 to 6 d, the effluent TN gradually increased, and the OLR was lower than 17.5 kg COD $(m^3\,d)^{-1}$. The total effluent TN was below 16 mg L^{-1}. The effluent TN increased as the OLR increased, which indicated that the nitrogen removal capability of the two reactors was limited. When the reactors were run continuously at an influent OLR of 17.5 kg COD $(m^3\,d)^{-1}$ from 30 to 44 d, the effluent TN of the EGSB was 27.369 mg L^{-1}, the bio-contact oxidation was 13.066 mg L^{-1}, and the total removal efficiency was 70.822% (see Fig. 6).

3.3. Removal of TP

As was observed in the removal of nitrogen, the removal of phosphorus by the combined reactors was also limited. The total removal efficiency was 58.116% from 30 to 44 d. The effluent TP gradually increased before shock loading. After shock loading, the effluent TP was maintained at approximately 6.132 mg L^{-1}, which demonstrated a poor phosphorus removal capacity by the combined process. A prolonged SRT was not conducive for the removal of TP because the biological removal of phosphorus was dependent on the sludge discharge. Therefore, the removal of phosphorus by a chemical process would need to be combined with EGSB and bio-contact oxidation to meet emission standards (see Fig. 7).

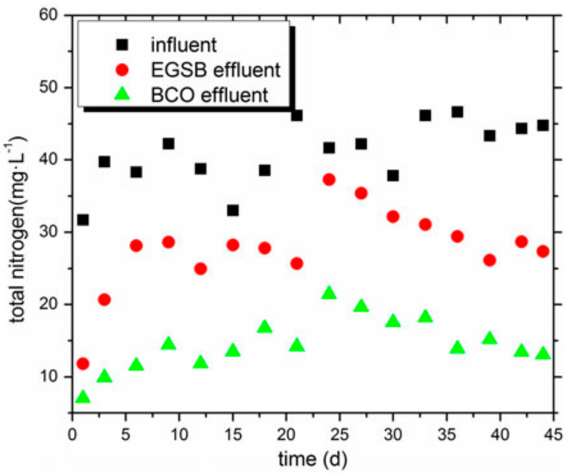

Fig. 6. Influent and effluent TN of expanded granular sludge bed and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

3.4. Removal of gallic acid

From 0 to 6 d, due to the adsorption of sludge, the total effluent gallic acid was lower than 24.361 mg L^{-1}, the removal rate fluctuated with changes in the influent, and more than 69% of the gallic acid was removed. The removal efficiency varied between 30 and 40% and did not significantly change after 15 d. When the OLR was 17.5 kg COD $(m^3\,d)^{-1}$ from 30 to 44 d, the total gallic acid removal efficiency was 63.408% (see Fig. 8).

3.5. Changes of redox potential in EGSB

The redox potential of the EGSB fluctuated between −320 and −350 mV. A downward trend was observed, which indicated that the microenvironment in the EGSB was stable and suitable for the metabolism of methanogenic bacteria [23] (see Fig. 9).

3.6. pH values of influent, EGSB effluent and bio-contact oxidation effluent

The operating pH range of the activated sludge system was 6–9. The anaerobic effluent pH was

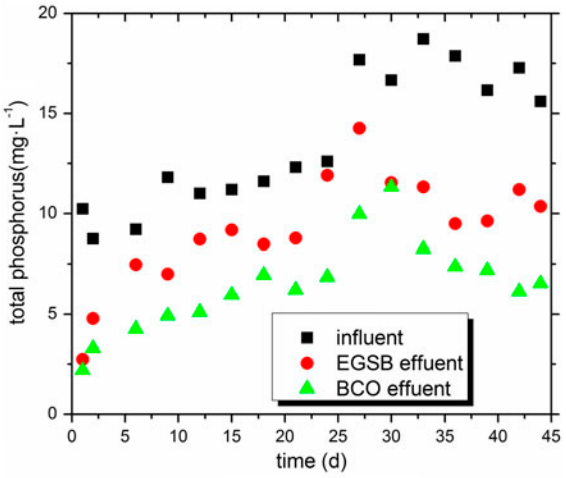

Fig. 7. Influent and effluent TP of expanded granular sludge bed and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

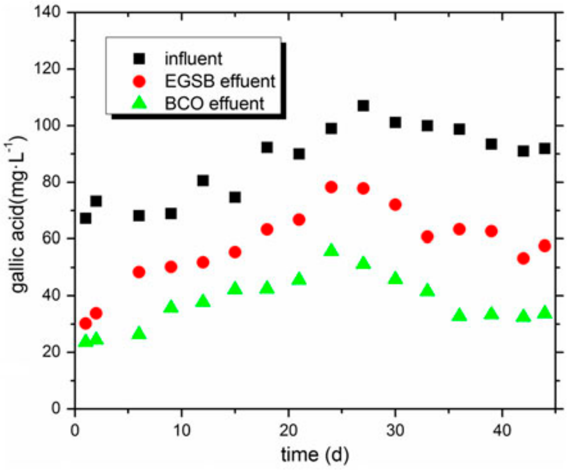

Fig. 8. Influent and effluent gallic acid of expanded granular sludge bed and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

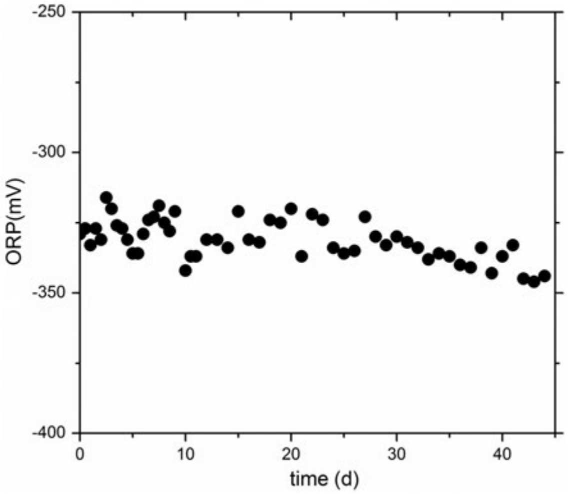

Fig. 9. Changes in redox potential of expanded granular sludge bed reactor.

7.23–8.13, and the aerobic effluent pH was 7.78–8.83. Both were within the operating pH range. The anaerobic sludge granules appeared intact, and the removal rates of COD contaminants, nitrogen, phosphorus, and gallic acid were stable. This indicated that the EGSB reactor could stably run within this pH range. Similarly, the formed biofilm did not slough off, and the nutrient removal rate of the bio-contact oxidation reactor was also stable. This also indicated that the bio-contact oxidation reactor could run properly (see Fig. 10).

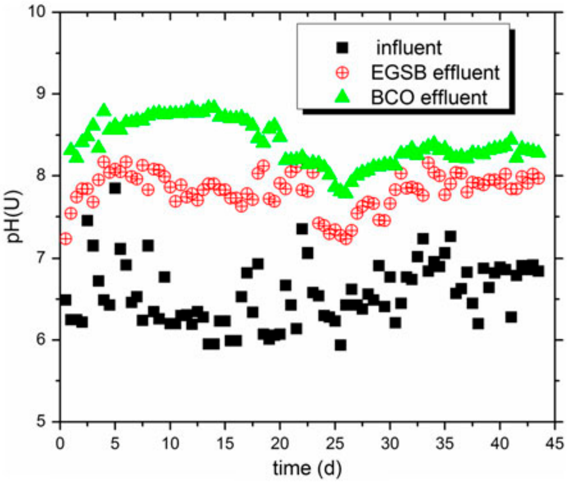

Fig. 10. pH value of influent, expanded granular sludge bed, and bio-contact oxidation reactors (EGSB: expanded granular sludge bed; BCO: bio-contact oxidation).

Because the majority of organic matter in the wastewater was glucose and gallic acid, the change of pH value was due to the degradation of gallic acid or the metabolites of glucose and gallic acid.

The effluent pH of the EGSB was higher than that of the influent. In an anaerobic biochemical reaction, acid-forming bacteria degrade glucose and gallic acid, generating lactic acid and CO_2, respectively. Methanogenic bacteria could also degrade glucose, gallic acid, and lactic acid and generate methane and CO_2. The presence of lactic acid and CO_2 resulted in a decreased pH, while the reduction of gallic acid increased the pH. The pH of the EGSB was higher than that of the influent, which indicated the production rate of lactic acid was lower than the degradation rate of gallic acid. This indirectly demonstrated that the activity of the acid-forming bacteria was weaker than that of the methanogenic bacteria.

Additionally, the pH value of the bio-contact oxidation reactor effluent was higher than that of the influent due to the degradation of gallic acid and the blow off of CO_2. When the influent OLR was less than 17.5 kg COD $(m^3\ d)^{-1}$, the effluent pH was maintained above 8. The effluent pH was below 8 when the influent OLR was 22.5 kg COD $(m^3\ d)^{-1}$. By measuring the effluent pH, we were able to rapidly determine the levels of the influent OLR relative to the specified OLR.

4. Conclusions

This paper demonstrated the performance of a laboratory-scale combined process of an EGSB reactor and a bio-contact oxidation reactor in treating GAPW, which currently has no defined procedure. An average COD removal efficiency of 87.021% was achieved when the influent COD concentration was 3,000 mg L^{-1} at an OLR of 17.5 kg COD $(m^3\ d)^{-1}$. The removal efficiencies of nitrogen, phosphorus, and gallic acid were 70.822, 58.116 and 63.407%, respectively. The redox potential in the EGSB varied between −320 and −350 mV. The effluent pH was increased either in the EGSB or in the bio-contact oxidation reactor during treatment. To meet emission standards, the effluent will require additional treatments. These results indicated that the combined process of the EGSB and bio-contact oxidation reactors were suitable for the treatment of GAPW.

Acknowledgments

This study was supported by the Strategic Project of Science and Technology of Hunan Province, China [grant number 2014 GK1059]. The authors would like to thank the members of the Research Group for Extraction and Separation Chemistry who co-operated with the present study.

References

[1] J.H. Chen, Situation and prospect of chemical utilization of gallotannins in China, Chem. Ind. Forest Prod. 20 (2000) 71–82.

[2] N. Okabe, H. Kyoyama, M. Suzuki, Gallic acid monohydrate, Acta Crystallogr. Sect. E: Struct. Rep. Online 57 (2001) 764–766.

[3] F.J. Beltrán, J.M. Encinar, J.F. García-Araya, Oxidation by ozone and chlorine dioxide of two distillery wastewater contaminants: Gallic acid and epicatechin, Water Res. 27 (1993) 1023–1032.

[4] M. Panizza, G. Cerisola, Electrochemical degradation of gallic acid on a BDD anode, Chemoshere 77 (2009) 1060–1064.

[5] Y.D. Wu, K.G. Zhou, S.Y. Dong, W. Yu, H.Q. Zhang, Recovery of gallic acid from gallic acid processing wastewater, Environ. Technol. 36 (2015) 661–666.

[6] V. Kozlovskaya, E. Kharlampieva, I. Drachuk, D. Cheng, V.V. Tsukruk, Responsive microcapsule reactors based on hydrogen-bonded tannic acid layer-by-layer assemblies, Soft Matter 6 (2010) 3596–3608.

[7] A. Uhde, J. Youn, T. Maeda, L. Clermont, C. Matano, R. Krämer, V.F. Wendisch, G.M. Seibold, K. Marin, Glucosamine as carbon source for amino acid-producing *Corynebacterium glutamicum*, Appl. Microbiol. Biotechnol. 97 (2013) 1679–1987.

[8] J.A. Baron, K.M. Laws, J.S. Chen, V.C. Culotta, Superoxide triggers an acid burst in *Saccharomyces cerevisiae* to condition the environment of glucose-starved cells, J. Biol. Chem. 288 (2013) 4557–4566.

[9] M.X. Zheng, K.J. Wang, J.E. Zuo, Z. Yan, H. Fang, J.W. Yu, Flow pattern analysis of a full-scale expanded granular sludge bed-type reactor under different organic loading rates, Bioresour. Technol. 107 (2012) 33–40.

[10] M. Pronk, J.P. Bassin, M.K. Kreuk, R. Kleerebezem, M.C.M. Loosdrecht, Evaluating the main and side effects of high salinity on aerobic granular sludge, Appl. Microbiol. Biotechnol. 98 (2014) 1339–1448.

[11] D. Jeison, R. Chamy, Comparison of the behaviour of expanded granular sludge bed (EGSB) and upflow anaerobic sludge blanket (UASB) reactors in dilute and concentrated wastewater treatment, Water Sci. Technol. 40 (1999) 91–97.

[12] J.C. Costa, A.A. Abreu, E.C. Ferreira, M.M. Alves, Quantitative image analysis as a diagnostic tool for monitoring structural changes of anaerobic granular sludge during detergent shock loads, Biotechnol. Bioeng. 98 (2007) 60–68.

[13] T. Abbasi, S.A. Abbasi, Formation and impact of granules in fostering clean energy production and wastewater treatment in upflow anaerobic sludge blanket (UASB) reactors, Renewable Sustainable Energy Rev. 16 (2012) 1696–1708.

[14] M.A. Pereira, M. Mota, M.M. Alves, Operation of an anaerobic filter and an EGSB reactor for the treatment of an oleic acid-based effluent: Influence of inoculum quality, Process Biochem. 37 (2002) 1025–1031.

[15] J. Lopez, V.M. Monsalvo, D. Puyol, A.F. Mohedano, J.J. Rodriguez, Low-temperature anaerobic treatment of low-strength pentachlorophenol-bearing wastewater, Bioresour. Technol. 140 (2013) 349–356.

[16] B.M. Peyton, T. Wilson, D.R. Yonge, Kinetics of phenol biodegradation in high salt solutions, Water Res. 36 (2002) 4811–4820.

[17] J.D. Wang, J.M. Chen, Removal of dichloromethane from waste gases with a bio-contact oxidation reactor, Chem. Eng. J. 123 (2006) 103–107.

[18] H.F. Wu, S.H. Wang, H.L. Kong, T.T. Liu, M.F. Xia, Performance of combined process of anoxic baffled reactor-biological contact oxidation treating printing and dyeing wastewater, Bioresour. Technol. 98 (2007) 1501–1504.

[19] I. Sekoulov, S. Brinke-Seiferth, Application of biofiltration in the crude oil processing industry, Water Sci. Technol. 39 (1999) 71–76.

[20] G. Pliego, J.A. Zazo, J.A. Casas, J.J. Rodriguez, Case study of the application of Fenton process to highly polluted wastewater from power plant, J. Hazard. Mater. 252 (2013) 180–185.

[21] B. Roig, C. Gonzalez, O. Thomas, Measurement of dissolved total nitrogen in wastewater by UV photooxidation with peroxodisulphate, Anal. Chim. Acta 389 (1999) 267–274.

[22] H.Y. Tan, G.D. Zhang, Evaluation of uncertainty for the determination of total phosphorus in the wastewater by ammonium molybdate spectrophotometric method, Environ. Sci. Technol. 36 (2011) 143–146.

[23] P. Weiland, Biogas production: Current state and perspectives, Appl. Microbiol. Biotechnol. 85 (2010) 849–860.