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Advanced treatment of bio-treated coal chemical wastewater by a novel combination of microbubble catalytic ozonation and biological process

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ABSTRACT

The advanced treatment performance of real bio-treated coal chemical wastewater (BCCW) by a novel combination of microbubble catalytic ozonation and biological process was investigated. The refractory compounds in BCCW could be degraded effectively by microbubble catalytic ozonation treatment, which resulted in efficient COD removal, inorganic nitrogen release and significant improvement of biodegradability. The dissolved oxygen (DO) supplied by microbubble catalytic ozonation was also enough for aerobic digestion in the following biological treatment even without aeration. The biodegradable COD and ammonia nitrogen released in microbubble catalytic ozonation treatment could be removed further in the following biological treatment efficiently. There was no off-gas ozone required to be treated due to high ozone utilization efficiency of close to 100%. The ratio of ozone dosage to influent COD amount showed a marked impact on the performance of the combination treatment system and its optimal value obtained in this study was 0.44 mg/mg. In this case, for microbubble catalytic ozonation, the COD removal efficiency was 32.16%, the ratio of ozone dosage to COD removed was 1.38 mg/mg and the ozone utilization efficiency was 98.0%. For biological treatment, the COD removal efficiency was 41.93%. For the combination system, the total COD removal efficiency was 60.82%, the average final effluent COD concentration was 91.5 mg/L and the estimated total ratio of ozone dosage to COD removed was 0.68 mg/mg. Therefore, the combination of microbubble catalytic ozonation and biological process is an effective and economical solution for advanced treatment of BCCW.

1. Introduction

Coal chemical wastewater is a complex industrial wastewater generated from coal treatment, including high temperature carbonation, coal gas purification and byproduct recovery processes. Currently, the treatment processes used for coal chemical wastewater generally include pretreatment and biological treatment [1]. Biological treatment process is the main treatment technology for coal chemical wastewater due to the low cost, simple operation and maintenance and maximal mineralization of contaminants [2,3]. Many contaminants in coal chemical wastewater are toxic, mutagene and carcinogenic, including phenols, mono- and poly-cyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclic compounds and polynuclear aromatic hydrocarbons (PAHs) [3–5], which makes coal chemical wastewater much recalcitrant for biodegradation. Thus, the secondary effluent from biological treatment process, namely bio-treated coal chemical wastewater (BCCW), contains certain amount of the above substances and cannot meet corresponding discharge standards. Hence, further removal of remaining refractory organic pollutants in BCCW remains of fundamental importance to the environment.

Recently, advanced oxidation processes (AOPs) have been given more and more interests in the advanced treatment of industrial wastewater, aiming at the removal of the refractory organics remained in the wastewater. AOPs are considered as effective alternatives for converting the refractory contaminants into less harmful or lower chain compounds which can then be treated biologically [6,7]. The AOPs such as catalytic ozonation [8], Fenton/Fenton-like reaction [9], UV photocatalysis [10] and electrochemical oxidation [11] have been used for advanced treatment of BCCW. Catalytic ozonation is a kind of sludge-free AOPs and becomes increasingly promising because of the limited space and high expense for disposal of sludge. Some kinds of real refractory industrial wastewater have been treated by catalytic ozonation to promote mineralization of refractory organic contaminants [12] and improve the wastewater biodegradability [13]. It is noteworthy that catalytic ozonation for complete eliminating pollutants is expensive because the oxidation intermediates tend to be more and more resistant to their chemical degradation [14]. On the other hand, these oxidation intermediates are generally more biodegradable than

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the original molecules. Therefore, there is a great advantageous of integrating catalytic ozonation with biological process for more efficient and cost-effective treatment of refractory and toxic wastewater. Especially, nitrogen compounds, which were difficult to remove in catalytic ozonation, even the concentration increased, were more suitable for biological treatment. It has been reported that combination of ozonation and biological process was successfully applied to advanced treatment of refractory industrial wastewater [15–17], including BCCW [18,19].

There are some limiting factors for traditional ozonation process such as low ozone dissolution and slow gas-liquid mass transfer rate. The microbubble ozonation could overcome some of these limiting factors. Microbubbles have useful characteristics, such as small bubble size (less than 50 μm), huge interfacial area, long stagnation time, lower bubble rising speed, and high interior pressure so that they have an advantage to dissolve ozone gas into water. Chu et al. [20,21] found that microbubbles could help to improve the ozone mass transfer efficiency and further enhanced the soluble contaminant removal of simulated dyestuff wastewater and practical textile wastewater. Furthermore, hydroxyl radical (˙OH) generation can be improved during microbubble ozone intrusion [22]. More recently, it has been found that microbubble collapse in microbubble ozonation also promotes ˙OH generation [23,24]. The enhanced ˙OH generation from microbubble ozonation can improve the oxidation effects as ˙OH possesses a higher oxidation potential than molecular ozone.

In this study, a novel combination of microbubble catalytic ozonation and biological process was applied for advanced treatment of a real BCCW. The microbubble catalytic ozonation was expected to be responsible for some organic contaminants removal and more important, biodegradability improvement. Then the biodegradable contaminants and ammonia nitrogen could be removed further by the following biological process. The performance of the combination system was investigated and evaluated during continuous long-term operation. The influence of ratio of ozone dosage to influent COD amount on the performance was also discussed.

2. Materials and methods

2.1. Wastewater

A real bio-treated coal chemical wastewater (BCCW) was obtained from the effluent of an upflow anaerobic sludge bed reactor followed by a biological contact oxidation process in a coal chemical byproducts recovery factory. The BCCW characteristics were shown in Table 1.

2.2. Experimental set-up

Fig. 1 shows schematic of the novel combination system, including a microbubble catalytic ozonation reactor (MCOR) and a bioreactor (BR). The combination treatment system was installed in the wastewater treatment station of the factory. The MCOR was a sealed pressure vessel with an effective empty bed volume of 25 L. Three layers of 8–10 mm commercial granular coal-based activated carbon were filled in MCOR as catalyst with a total filling ratio of 28.0%. The space between each two layers was supposed to be a remixing zone to facilite the uniform water distribution in the upper catalyst layer, considering the weak mixing effect of microbubbles. The larger amount of activated carbon was used to avoid possible frequent catalyst replacement during the continuous operation. The BR had an effective empty bed volume of 42 L, filling three layers of the same granular activated carbon mentioned above with a total filling ratio of 28.6% as carriers to support biofilm growth. The space between each two layers was also supposed to facilite the uniform water distribution in the upper layer, because of the weak mixing effect without aeration in BR and this made the filling ratio relatively lower than usual.

Table 1
Characteristics of bio-treated coal chemical wastewater (BCCW).

Index	Average value
COD	283.8 mg/L
TOC	99.8 mg/L
BOD_5/COD	0.038
Ammonia nitrogen	4.8 mg/L
Total nitrogen (TN)	13.4 mg/L
pH	8.8
UV_{254}	0.98

The ozone was generated from pure oxygen by an ozone generator with a maximum capacity of 5 g/h (Guanyu, China). The liquid in MCOR was circulated and mixed with dosing ozone gas in a microbubble generator with an OHR mixer (OHR Laboratory Corporation, Japan) to generate ozone microbubbles. The ozone microbubbles were fed into MCOR for catalytic ozonation from the bottom along with circulating liquid flow. The gas-liquid mixture effluent of MCOR was pressed into the bottom of BR without pumping. There was no aeration for BR and the dissolved oxygen (DO) for aerobic digestion in BR would be provided by remaining oxygen after ozone generation and decomposition.

2.3. Experimental procedure

The BCCW with or without BR effluent was pumped into the liquid circulation pipeline to be mixed with circulating liquid flow of MCOR and then entered MCOR from the bottom with ozone microbubbles, as shown in Fig. 1, to enhance the contact between BCCW and ozone microbubbles. For MCOR, the hydraulic retention time (HRT) was controlled as 1 h at a feeding ozone gas flow rate of 2.0 L/min and its average operation temperature was 26.7 °C. For BR, the activated sludge from the biological contact oxidation tank treating this coal chemical wastewater was inoculated into BR at a concentration of 4.0 g/L to enhance biofilm formation on the carriers in the start-up period. In the stable operation period, the HRT of BR was 6 h and its average operation temperature was 22.2 °C.

The stable continuous operation of the combination treatment system included three phases according to ratio of ozone dosage to influent COD amount for MCOR. The BCCW was fed into MCOR directly in Phase I and II, and in Phase III the BCCW mixed with 30% effluent of BR was used as the influent of MCOR to reduce its influent COD concentration. The corresponding operating conditions in these three phases were shown in Table 2. The Influent and effluent water testing for both MCOR and BR were conducted on a daily basis for the duration of the experiment to evaluate the treatment performance of the combination system.

2.4. Analytical methods

Total COD, BOD_5, ammonia nitrogen, nitrate nitrogen and total nitrogen were measured in accordance with the standard method. The DO concentration was measured with an electrochemical membrane electrode (WTW cellOx 325, Germany) and a digital DO meter. UV_{254} was measured with a UV–Vis spectrophotometer (Techcomp U-3900, China). The TOC concentration was measured using a TOC analyzer (TOC-VCPN, Shimadzu Corporation, Japan). The ozone concentration in the gas phase was measured by iodometric method with KI solution [25]. The dissolved ozone concentration was measured using indigo colorimetric method [26].