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Is A/A/O process effective in toxicity removal? Case study with coking wastewater

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ABSTRACT

The anaerobic-anoxic-oxic (A/A/O) process is the commonly used biological wastewater treatment process, especially for the coking wastewater. However, limit is known about its ability in bio-toxicity removal from wastewater. In this study, we evaluated the performance of A/A/O process in bio-toxicity removal from the coking wastewater, using two test species (i.e. crustacean (*Daphnia magna*) and zebra fish (*Danio rerio*)) in respect of acute toxicity, oxidative damage and genotoxicity. Our results showed that the acute toxicity of raw influent was reduced gradually along with A/A/O process and the effluent presented no acute toxicity to *Daphnia magna* (*D. magna*) and zebra fish. The reactive oxygen species (ROS) level in *D. magna* and zebra fish was promoted by the effluent from each tank of A/A/O process, showing that coking wastewater induced oxidative damage. Herein, the oxidative damage to *D. magna* was mitigated in the oxic tank, while the toxicity to zebra fish was reduced in the anoxic tank. The comet assays showed that genotoxicity to zebra fish was removed stepwise by A/A/O process, although the final effluent still presented genotoxicity to zebra fish. Our results indicated that the A/A/O process was efficient in acute toxicity removal, but not so effective in the removal of other toxicity (e.g. oxidative damage and genotoxicity). Considering the potential risks of wastewater discharge, further advanced toxicity mitigation technology should be applied in the conventional biological treatment process, and the toxicity index should be introduced in the regulation system of wastewater discharge.

1. Introduction

Coking wastewater is generated from coal coking, coal gas purification, and by-product recovery processes in the coke manufacture (Han et al., 2011). The chemicals with high concentrations in coking wastewater are usually phenols, nitrogen heterocyclic compounds, polycyclic aromatic hydrocarbons, cyanide, sulfide and ammoniacal nitrogen, most of which are refractory, toxic and carcinogenic (Zhao et al., 2015). It was reported that coking wastewater might induce adverse effects to the environment (Dong and Zhang, 2010; Han et al., 2011). Coking wastewater has been a representative of refractory industrial wastewater in China, with large amounts and excessive discharge, which triggered the delicate and comprehensive evaluation on its quality.

Physicochemical parameters were mainly used to evaluate the wastewater quality, such as pH, chemical oxygen demand (COD) and total phosphorous (TP). Although these targeted parameters have met the discharge standard , the other pollutants being neglected may cause adverse effects on aquatic organisms even at a low concentration (Na et al., 2016).

Compared with physicochemical parameters, the bioassays were the comprehensive responses to all the contaminants in the wastewater which could predict the potential environment risk (Yu et al., 2014). Acute toxicity has already been adopted for regulation system of wastewater discharge in a few countries routinely (Zhang et al., 2015). Additionally, oxidative damage was also employed in toxicity evaluation of wastewater. Oxidative damage can be defined as the disruption in the balance between the production and removal of ROS leading to increased ROS level (Petala et al., 2009; Sturve et al., 2008). ROS level in organisms was more sensitive and could be detected before immobilization or mortality. And ROS level could also provide valuable information on the toxicity mechanism. For protecting against the potential injury of ROS, the activities of antioxidant enzyme were generally stimulated in organisms (Seda et al., 2012). Superoxide dismutase (SOD) and catalase (CAT) as key antioxidant enzymes could be used to characterize the defense mechanisms (Seda et al., 2012). It was reported that the coking wastewater exhibited the oxidative damage to maize (Han et al., 2011) and mouse (Zhu et al., 2013). Further, the assessment of genotoxicity was very important considering

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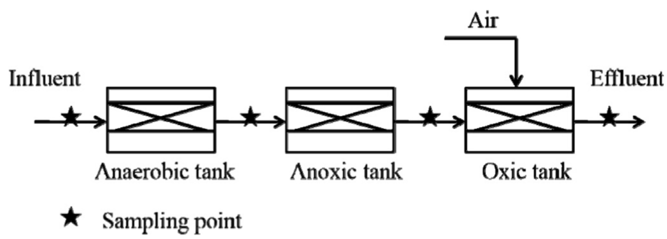

Fig. 1. Schematic of coking wastewater treatment process.

the toxic characteristics of toxic composition and their intermediates in coking wastewater. It was reported that the coking wastewater exhibited the genotoxicity to maize (Han et al., 2011) and mouse (Zhu et al., 2013).

Various organisms, such as bacteria, green algae, invertebrate and fish were employed to evaluate the toxicity. It was reported that the toxic units (TUs) of coking wastewater to *D. magna*, zebra fish, luminous bacteria and green algae were 31.9, 30, 21.2 and 9.5 respectively (Zhou et al., 2015). It can be seen that *D. magna* and zebra fish were relatively sensitive to the toxicity of coking wastewater, compared with luminous bacteria and green algae.

The anaerobic-anoxic-oxic (A/A/O) process has been widely used in municipal and industrial wastewater treatment plant. It was reported that the A/A/O process could not remove the acute toxicity of pigment-contaminated wastewater (Deng et al., 2017). It was also reported that the A/A/O process was efficient in acute toxicity and genotoxicity reduction of reclaimed water (Wei et al., 2012). In terms of the coking wastewater, the acute toxicity could be partly removed with the laboratory-scale A/A/O process (Zhao et al., 2009). However, there were limited reports about the performance of bio-toxicity removal during and after the industrial-scale A/A/O process, although it has been widely used in coking wastewater treatment plant.

In this study, the performance of industrial-scale A/A/O process in bio-toxicity removal from coking wastewater was investigated, with respect to its acute toxicity, oxidative damage and genotoxicity to aquatic organisms. The acute toxicity was characterized with the mortality of *D. magna* and zebra fish. Oxidative damage was expressed with the ROS level, where the activities of CAT and SOD were used to characterize the defense mechanisms against this oxidative damage. The genotoxicity of wastewater was conducted with comet assays to reflect the DNA damage. The relationship between bio-toxicity and physiochemical parameters was analyzed, aiming to find which parameters are closely related to the toxicity of wastewater. Our results aimed to help the introduction of toxicity index in the regulation system of wastewater discharge, considering the potential risks posed to the receiving water.

2. Materials and methods

2.1. Wastewater sampling

Our wastewater samples were collected in October 2015, from a wastewater treatment plant located in the Northeast of China. The coking wastewater samples were collected from each sampling point over a 24 h period according to composite sampling methods (USEPA, 2002). The schematic of wastewater treatment process was given in Fig. 1. Wastewater samples from each tank of A/A/O process were stored at 4 °C before analysis.

2.2. Chemical analysis

Basic physicochemical parameters of wastewater samples, including conductivity, pH, dissolved oxygen (DO), total organic carbon (TOC), COD, TP and ammoniacal nitrogen (ammoniacal N), were measured. Conductivity was measured with conductivity meter (STARTER 3100C, Ohaus, USA). Other parameters were measured referring to our previous study (Zhang et al., 2015). In addition, heavy metals were determined by inductively coupled plasma spectrometer (ICP, Optima 2000 DV, Perkin Elmer, USA). The concentration of the conventional chemical parameters and heavy metals from coking wastewater samples were given in Table 1.

2.3. Acute toxicity test

D. magna, originally obtained from Dalian Ocean University (Dalian, China), were continuously cultured in our laboratory for more than four years. *D. magna*, fed with *S. obliquus*, were cultured in dechlorinated tap water at a constant temperature of 20 ± 1 °C with a 16:8 h light-dark cycle. The *D. magna* acute toxicity test was performed according to OECD 202 (OECD, 2004) with a few modifications. Five diluted concentration series of each wastewater sample and one control were performed with four replicates. The dechlorinated tap water was used as the control and diluent. Five *D. magna* neonates (< 24 h old) were exposed to 50 mL test solution. After exposure, the 48 h median lethal concentration (LC_{50}) values and TUs were calculated.

Zebra fish, length 35 ± 5 mm and weight 0.25 ± 0.1 g, were purchased from a professional fish shop (Yule pet market, Dalian, China). Before exposure, all fishes were kept in dechlorinated tap water at 25 ± 1 °C with a 14:10 h light-dark cycle and were fed with

Table 1
Characteristic of coking wastewater samples from A/A/O process.

Parameters	Influent	Anaerobic tank	Anoxic tank	Oxic tank
COD[a]	1468 ± 16	328 ± 11	245 ± 5	78 ± 2
DO[a]	0.19 ± 0.02	0.18 ± 0.01	0.80 ± 0.04	8.50 ± 0.06
ammoniacal N[a]	173.9 ± 2.4	57.3 ± 0.5	71.4 ± 1.4	16.5 ± 0.2
TP[a]	1.39 ± 0.27	3.28 ± 0.11	1.37 ± 0.06	2.56 ± 0.07
TOC[a]	464 ± 7	103 ± 4	107 ± 2	33 ± 3
Conductivity[b]	4.85 ± 0.06	4.26 ± 0.11	4.19 ± 0.03	3.31 ± 0.03
pH	7.70 ± 0.03	6.54 ± 0.05	6.89 ± 0.02	6.26 ± 0.02
Al[a]	0.16 ± 0.01	0.05 ± 0.01	0.17 ± 0.02	0.06 ± 0.01
Fe[a]	1.09 ± 0.08	0.69 ± 0.05	0.67 ± 0.02	0.40 ± 0.04
Cd[a]	0.02 ± 0.002	0.02 ± 0.001	0.02 ± 0.002	0.02 ± 0.001
Hg[a]	0.007 ± 0.001	ND	0.002 ± 0.0002	ND
Mn[a]	ND	0.037 ± 0.002	0.038 ± 0.003	0.031 ± 0.001
Ni, Pb, Zn, Cr, Cu, As, Co[a]	ND	ND	ND	ND

Note:
[a] The units of parameters were expressed as mg/L;
[b] The units of parameters were expressed as mS/cm; ND, Not detected; COD, chemical oxygen demand; DO, dissolved oxygen; ammoniacal N, ammoniacal nitrogen; TOC, total organic carbon.