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Enhanced biodegradability of coking wastewater by gas phase dielectric barrier discharge plasma

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ABSTRACT

In the present study, gas phase dielectric barrier discharge (GPDBD) was used for pretreatment of coking wastewater with the objective of improving its biodegradability. The effects of some operational parameters including initial concentration, pH value of coking wastewater and air flow rate in GPDBD reactor on the COD removal were investigated. The removal efficiency of main compounds (total phenol, PAHs and NH_3–N) and biodegradability (BOD_5/COD) of coking wastewater were evaluated. The results show that the removal of COD by GPDBD fitted well with the second-order kinetics. The raw pH of coking wastewater was beneficial for COD removal. The optimal air flow rate was observed as 2 L min^{-1}. Approximately 100% of total phenol and PAHs (benzoquinone, naphthalenol, dimethyl phthalate, etc.) removal was achieved at a reaction time of 120 min, and the removal efficiency of NH_3–N reached 21%. The BOD_5/COD ratio increased from 0.14 to 0.52 within 100 min of discharge treatment, suggesting the biodegradability of the coking wastewater was significantly improved. The GPDBD system is an effective pretreatment method for enhancing the biodegradability of coking wastewater.

1. Introduction

Coking wastewater is commonly emitted from coking, coal gasification [1], and by-product recovery processes of coke factory. It contains complex inorganic and organic contaminants such as phenolic compounds, ammonia, polycyclic aromatic hydrocarbons (PAHs), polycyclic nitrogen, and cyanide [2,3]. High phenolic compounds and NH_3–N concentrations are among the main characteristics of coking wastewater [4]. Coking wastewater is usually treated by the biological process, such as anoxic–oxic (A/O), anaerobic-anoxic–oxic (A^2/O) and activated sludge processes. Because of the presence of refractory and biologically inhibitory organic compounds including PAHs and nitrogenous heterocyclic compounds in coking wastewaters, a conventional activated sludge system is not efficient in removing chemical oxygen demand (COD) to meet the discharge standard [5,6]. It is also difficult for the conventional biological treatment system to reduce high-concentration NH_3–N because many typical compounds in coking wastewater such as alkyl pyridine, phenol and cresol at certain concentrations are inhibitory to nitrobacteria [7,8]. A possible strategy for overcoming these problems is the use of advanced oxidation processes as a pretreatment step to improve the wastewater biodegradability.

Recently, the use of the AOPs as a pre-treatment process has been developed and proposed for coking wastewater treatment because it can partially convert persistent organics into intermediates that are more readily degradable in subsequent biological treatment processes. Chen et al. studied the biodegradability enhancement of coking wastewater by using catalytic wet air oxidation (CWO). They reported that the BOD_5/COD ratio increased from 0.23 for the untreated NH_3-stripped coking wastewater to 0.84 of the effluent of CWO pilot tests [9]. Chu at al studied the treatment of coking wastewater by an advanced Fenton oxidation. The oxygen uptake rate of the effluent measure at a reaction time of 1 h increased by approximately 65% compared to that of the raw coking wastewater [10]. These processes can efficiently degrade organic matters in coking wastewater and increase the percentage of the biodegradable organic compounds. However, severe conditions, high catalyst and investment costs limits CWO' s industrial-scale application [11], and the disadvantage of Fenton oxidation process is the large amount of ferric salts added which can result in troublesome sludge problem [12].

Non-thermal plasma technology has been one of the most promising advanced oxidation processes for treating wastewater due to its advantages including high oxidation performance, ease of operation and without secondary pollution. Several discharge

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reactors and discharge types have been investigated for water purification, and the electrode structures of the discharge reactors are usually classified into as needle to plate electrode [13], line to plate electrode [14,15], line to tube electrode [16], line to line electrode [17], ring to line electrode [18] and dielectric barrier [19,20]. In terms of discharge types, liquid phase discharge [21], gas phase discharge [22] and gas–liquid mixture discharge [23] were extensively studied. Compared to other discharge reactors and types, gas phase dielectric barrier discharge reactor has been considered as a promising technology because of its stability property [24–26]. In this type of reactor, active species such as O_3, $^{\cdot}O$, $^{\cdot}OH$ and $^{\cdot}O_2$ generated in the gas phase, and the reactive species were injected into wastewater by gas diffuse in the form of fine bubbles to degrade recalcitrant organics [27,28]. The whole process was little affected by wastewater conductivity and no electrode corrosion. On the other hand, physical effects generated concomitantly during the discharge process (such as UV light) also reacted with the contaminant. Because of the synthetic effects between highly oxidative active species and physical processes, contaminants in water were removed effectively and rapidly [29]. Actually, the GPDBD was extensively employed in wastewater treatment, and it was proved to be fairly effective in disposing organic pollutants and improving the biodegradability. However, little has been reported on the use of GPDBD reactor for coking wastewaters with high concentrations of organic pollutants. Previous studies have reported that phenol compounds which are the main pollutants in wastewater could be satisfactorily removed by GPDBD [30,31], hence; it is believed that it is powerful enough for GPDBD to decompose coking wastewater and improve its biodegradability.

In this study, a GPDBD reactor was designed to enhance the biodegradability of coking wastewater. We explored the effects of initial concentration, solution pH and air flow rate on COD removal, the removal efficiency of total phenols, PAHs and NH_3–N, and the evolution of biodegradation of coking wastewater during the discharge. It is expected to allow a better understanding of the discharge process in treating coking wastewater and provide a new alternative for the pre-treatment method.

2. Experimental

2.1. The discharge system

Fig. 1 shows the schematic diagram of the experimental set up, which consisted of a high-voltage AC power supply, a GPDBD reactor, a gas supply and a reactor vessel. Alternating Current (7 kHz) power supply was used in the present study, and the voltage was 0–10 kV adjustable. The GPDBD reactor was made of a quartz cylinder with its respective inner and outer diameters of 22 and 25 mm, respectively. A spiral stainless steel wire with a diameter of 9 mm coiled around the inner surface of the quartz cylinder acted as the discharge electrode, and a stainless-steel mesh wrapped around the outside surface of the quartz cylinder served as the ground electrode. The discharge voltage and current was measured with a digital oscilloscope (Tektronix TDS2014) equipped with a high-voltage probe (Tektronix P6015A) and a current probe (Tektronix A6021). In all experiments, the voltage was adjusted to 7 kV with 7 kHz.

In each batch experiment, 550 ml coking wastewater was treated. Prior to discharge treatment, air was injected into the quartz glass tubes, and then high-voltage electrode system was immersed into the wastewater.

The COD removal efficiency (η) is defined as follows,

$$\eta = \frac{m_{COD_0} - m_{COD_t}}{m_{COD_0}} \times 100\% \quad (1)$$

where the m_{COD_0} and m_{COD_t} are the amount of COD at time 0 and t, respectively.

2.2. Materials

The coking wastewater was obtained from a coke plant in Dalian, China. Table 1 shows the characterization of the coking wastewater. The wastewater was heavily colored with a high strength of COD. The COD, ammonium and total phenol concentration used in the discharge process was obtained from dilution of the raw coking wastewater.

2.3. Analytical methods

COD was measured by the potassium dichromate oxidation method. Phenolic compounds analysis was done by measuring absorbance at a wavelength of 510 nm after color development

Table 1
Characterization of the raw coking wastewater.

Item	Value
Total phenol (mg L^{-1})	4800–5200
Ammonium (mg L^{-1})	400–450
NO_3N (mg L^{-1})	20–25.6
TN (mg L^{-1})	439.85
pH	8.0–9.0
COD (mg L^{-1})	16,800–17,200

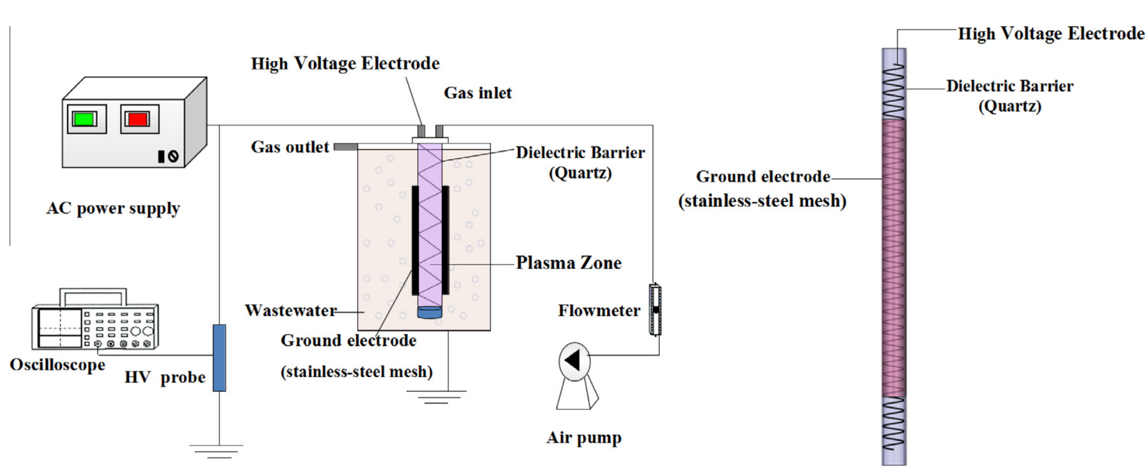

Fig. 1. Schematic diagram of the experimental system (a: flow chart; b: DBD reactor).