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Pulsed corona discharge for improving treatability of coking wastewater

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ABSTRACT

Coking wastewater (CW) contains toxic and macromolecular substances that inhibit biological treatment. The refractory compounds remaining in biologically treated coking wastewater (BTCW) provide COD and color levels that make it unacceptable for reuse or disposal. Gas-phase pulsed corona discharge (PCD) utilizing mostly hydroxyl radicals and ozone as oxidants was applied to both raw coking wastewater (RCW) and BTCW wastewater as a supplemental treatment. The energy efficiency of COD, phenol, thiocyanate and cyanide degradation by PCD was the subject of the research. The cost-effective removal of intermediate oxidation products with addition of lime was also studied. The energy efficiency of oxidation was inversely proportional to the pulse repetition frequency: lower frequency allows more effective utilization of ozone at longer treatment times. Oxidative treatment of RCW showed the removal of phenol and thiocyanate at 800 pulses per second from 611 to 227 mg/L and from 348 to 86 mg/L, respectively, at 42 kWh/m^3 delivered energy, with substantial improvement in the BOD_5/COD ratio (from 0.14 to 0.43). The COD and color of BTCW were removed by 30% and 93%, respectively, at 20 kWh/m^3, showing energy efficiency for the PCD treatment exceeding that of conventional ozonation by a factor of 3–4. Application of lime appeared to be an effective supplement to the PCD treatment of RCW, degrading COD by about 28% at an energy input of 28 kWh/m^3 and the lime dose of 3.0 kg/m^3. The improvement of RCW treatability is attributed to the degradation of toxic substances and fragmentation of macromolecular compounds.

Introduction

Coking wastewater (CW) is generated from coke quenching, coking gas purification and the recovery of chemical products from coking tar, gas and water (Schobert and Song, 2002). It has a large variety of constituents, including refractory organic compounds of poor biodegradability (Lu et al., 2009). These compounds comprise organic loads with excessive levels of bio-inhibition and genotoxicity for biological treatment (Young et al., 2008; Dong and Zhang, 2010). The refractory constituents, such as phenolic compounds, polyaromatic hydrocarbons (PAHs) and inorganic thiocyanate and cyanide, were proven to have high toxicity toward most microorganisms (Kwon et al., 2002; Young et al., 2011; Sharma et al., 2012). For example, highly toxic phenol in aqueous media is severely restricted by current legislation (CJ 343–2010); its presence

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inhibits bacterial degradation of thiocyanate with *Acremonium strictum* (Kwon et al., 2002). In biological treatment, phenol in concentrations exceeding 200 mg/L significantly inhibits nitrification, stopping it completely at concentrations above 500 mg/L. Low concentrations of phenol, on the other hand, negatively affect nitrification indirectly by oxygen depletion due to the fast growth of heterotrophic phenol-degrading bacteria (Sharma and Ahlert, 1977). The wastewater was found to contain a minimum of fifteen identified phenolic compounds (Ly et al., 2015). According to Kim et al. (2011), a free cyanide concentration above 0.2 mg/L causes serious inhibition of CW nitrification. Thiocyanate shows toxicity similar to that of phenol: a concentration of 200 mg/L noticeably inhibits nitrification in activated sludge, resulting in poor removal of nitrogen (Kim et al., 2008). As a result, the CW biodegradability as described by the BOD_5/COD ratio usually does not exceed 0.3 (Zhou et al., 2014).

The biological processes used in CW treatment include anaerobic digestion (A) combined with aerobic oxidation (O) in various sequences described in the literature under various A/O-names, such as two-stage anaerobic–aerobic (A^2/O), anaerobic–aerobic–hydrolytic–aerobic ($A/O_1/H/O_2$), sequential biological reactors (SBR) *etc.* (Li et al., 2003; Marañón et al., 2008; Lu et al., 2009; Yu et al., 2015). The $A/O_1/H/O_2$ sequence is applied at the target site, the Guangdong Shaoguan Steel Company, providing the CW samples for this study. The anaerobic bioreactors reduce the toxicity and improve the BOD_5/COD ratio for further aerobic oxidation. Even free cyanide may be removed by anaerobic bacteria, making anaerobic digestion a powerful means of treatability enhancement (Shieh and Richards, 1988). However, the hydraulic retention time (HRT) in aerobic bioreactors is long, reaching up to 24 hr, resulting in substantial need for compressed air, *i.e.* energy consumption (Zhu et al., 2016). As a result, biological treatment often does not meet the National Discharge Standard of China (GB 16171-2012). The discharged CW must not exceed a COD of 80 mg O_2/L, *i.e.* the industry faces the need in removal of 40%–50% of the residual COD of biologically treated CW (BTCW). Achieving the target lies in the reduction of the CW toxicity, enabling deeper and faster biological degradation of organic pollutants.

Improvement of the CW treatability is normally achieved through toxicity alleviation, fragmentation of large-size molecules and liberation of organic nitrogen into easily digested ammonia or nitrate (Dong and Zhang, 2010; Sun et al., 2015). Various biological and physicochemical methods have been developed to improve CW treatability, including biofilm systems (Qian and Liu, 2016), supercritical and sub-critical catalytic wet air oxidation pre-treatment (Chen et al., 2012; Du et al., 2013), electrochemical degradation (Wang et al., 2008; Fuat and Bunyamin, 2015), Fenton oxidation (Chu et al., 2012), and ozonation (Duan et al., 2015). Chemical oxidation targets the improvement of treatability by means of all the above-mentioned transformations — reduced wastewater toxicity, fragmentation of poorly biodegradable molecules and releasing ammonia from nitrogen-containing organic pollutants. Combinations of biological, physicochemical, and physical treatment methods have been developed to achieve the emission standards (Lai et al., 2009; Jin et al., 2013; Sharma and Philip, 2016), although so far these have not been applied commercially for economic and performance reasons. For example, the severe process conditions and high investment costs in wet air oxidation limit its application to large-scale enterprises treating highly concentrated wastewaters. Fenton oxidation, requiring substantial doses of hydrogen peroxide, results in bulk amounts of ferric hydroxide precipitates (Namkung et al., 2008). Electrolysis combined with ozone shows attractive results in COD degradation energy efficiency, from 15 to 32 g O_2/kWh (Kwiecińska et al., 2016), although the abundance of chloride ions in CW (Słomka-Słupik and Zybura, 2015; Kwiecińska et al., 2016) results in the inevitable formation of refractory and toxic halocarbons (Szpyrkowicz et al., 2001), reducing the biodegradability. Pre-ozonation of diluted CW in a lab-scale reactor, although it improved the biodegradability, required hours to achieve results, making the expected energy expense prohibitive (Duan et al., 2015). There is also a report on preliminary ozonation having a negative effect on biodegradability (Chang et al., 2008). Such contradictory examples indicate the necessity of verifying the effect of pre-oxidation on the subsequent biological treatability of CW.

Gas-phase pulsed corona discharge (PCD), also known as low-temperature plasma, produces highly reactive short-lived oxidants when applied to an oxygen- and water-containing gas (Ono and Oda, 2003):

$$\bar{e} + H_2O \rightarrow \bar{e} + {}^{\cdot}H + {}^{\cdot}OH \quad (1)$$

$$O\,(^1D) + H_2O \rightarrow 2\,{}^{\cdot}OH \quad (2)$$

$$\bar{e} + 3O_2 \rightarrow \bar{e} + 2O_3 \quad (3)$$

Operated in gas–liquid mixtures, in which treated water is showered onto the electrodes, PCD showed the highest energy efficiency among advanced oxidation processes (AOPs) in oxidation of various pollutants of high (Preis et al., 2013) and low oxidation rates (Panorel et al., 2011; Ajo et al., 2015), surpassing the conventional ozonation by at least a factor of two. This efficiency is achieved by utilizing short-lived powerful oxidants, mainly hydroxyl radicals, generated at the surface of the treated water (Preis et al., 2013). Ozone formed in the discharge assists oxidation, where its oxidation potential is sufficient (Kornev et al., 2014). Other advantages include the insensitivity of PCD toward the gas humidity, the possibility of using elevated concentrations of oxygen, the lack of need for gas transport and, thus, residual ozone destruction (Preis et al., 2013). The extent of pollutant oxidation is controlled by regulation of the pulsed discharge energy dose to control the subsequent treatability of the wastewater. The ratio of 'OH-radical–ozone' usage is adjusted by the pulse repetition frequency, controlled over a wide range (Preis et al., 2013).

In the present research, PCD was for the first time studied in the treatment of CW, aiming for the improvement of its biodegradability and treatability in combined technology applications. The combination of treatment methods used for heavily polluted wastewaters may also include the removal of organic compounds of, for example, acidic nature by settling with low-cost chemicals, such as coagulants and lime (Hill et al., 1979; Sevimli et al., 2000). The effect of precipitation of oxidation products was pronounced in the sequential combination of preliminary oxidation with application of lime (Munter et al., 1987), also tested in the present research in respect to raw coking wastewater (RCW).

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