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 chemical oxygen demand (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/m³ delivered energy, with substantial improvement in the BOD5/COD ratio (from 0.14 to 0.43). The COD and color of BTCW were removed by 30% and 93%, respectively, at 20 kWh/m³, 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/m³ and the lime dose of 3.0 kg/m³. The improvement of RCW treatability is attributed to the degradation of toxic substances and fragmentation of macromolecular compounds.

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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 (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; Sharma et al., 2012). For example, highly toxic phenol in aqueous media is severely restricted by current legislation (CJ 343–2010); its presence 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 biochemical oxygen demand (BOD);/chemical oxygen demand(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 (A2/O), anaerobic–aerobic–hydrolytic–aerobic (A/O/H/O), sequential biological reactors (SBR) etc. (Li et al., 2003; Marañón et al., 2008; Lu et al., 2009; Yu et al., 2015). The A/O/H/O 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/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 O2/L, i.e. the industry faces the need in removing 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 O2/kWh (Kwiecińska et al., 2016), although the abundance of chloride ions in CW (Slomka-Stupik 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 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):

\[ \text{PCD} + \text{gas} \rightarrow \text{active oxidants} \]

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).
The PCD reactor was assembled and tested using a phenol solution for performance verification. With respect to RCW, the impact of energy delivery and liming were studied according to the toxic pollutants’ contents, nutrient ammonia release and biodegradability. Chemical oxygen demand and color were assessed in the BTCW treatment.

1. Materials and methods

1.1. Experimental equipment and methods

The experimental installation is shown in Fig. 1. It consists of a high voltage pulse generator, a PCD reactor, and a reservoir with a circulation pump. The pulse generator consists of a thyristor power switch circuit, followed by a pulse step-up transformer and high-voltage magnetic compression stages. The reactor is similar to an electrostatic precipitator, where horizontal wire electrodes are positioned between vertical grounded plates. The discharge propagates in the gap between electrodes, where the oxidizing species are formed. Aqueous solutions were circulated from the tank through the reactor by pump model IQ-SZ037-DBC (Yuehua Stainless Steel Pumps, China) with a frequency regulator. Aqueous solution to be treated was dispersed by a perforated plate with 230 round holes of 1.0 mm diameter placed over the electrode system horizontal cross-section, of 420 x 40 mm size. The solution showered in jets, droplets and films between the electrodes into the space of the gas-phase PCD formation, where the pollutants were exposed to the oxidants. The flow rate of recirculating wastewater in the experiments was kept constant at 1.0 m³/hr. The equipment characteristics and the spray density in the present research provided the maximum utilization rate of the radical reaction at the surface of sprayed liquid as recommended by Ajo et al. (2015).

The reactor was ventilated at the rate of about 25 L/min using an air compressor (Boyu Co., China) to maintain the oxygen supply. A preliminary experiment on both RCW and BTCW aerated with no electric discharge applied showed negligible (below 1%) changes in COD, thiocyanate, sulfide, phenol and cyanide contents for RCW. Aeration of BTCW also did not result in any change after extensive aeration of the treated wastewater at the biological oxidation stage.

The pulse generator provides discharge pulses of 18 kV voltage amplitude. The current peak of 380 A is of 100 ns duration at 10% of the amplitude. The pulse repetition frequency used in experiments was 200 and 800 pulses per second (pps). The pulse parameters were measured with a Rigol DS1102E Mixed Signal Oscilloscope (Rigol Technologies Inc., China) using a low-inductance resistive current monitor PT-7802 (PinTek, China) and a high-voltage divider, model Rigol RP1018H (Rigol Technologies Inc., China). Typical waveforms of voltage and current are shown in Fig. 2.

The pulse energy \( W_p \) (J) delivered to the reactor was found as the integration product of voltage and current according to Eq. (4):

\[
W_p = \int_0^{t_p} U(t) I(t) \, dt.
\] (4)

where \( U(t) \) and \( I(t) \) are voltage and current waveforms, respectively and \( t_p \) is the voltage pulse duration. Integration of voltage and current waveforms was carried out numerically using the MathCAD software package.
delivered to the reactor comprised 0.22 J per pulse. The energy \( W \) (kWh/m³) dissipated in the PCD reactor was determined using Eq. (5):

\[
W = \frac{W_p \cdot f \cdot t}{V \cdot 1000}
\]

where, \( f \) (pps) is the pulse repetition frequency, pps, \( t \) (hr) is treatment time, and \( V \) (m³) is volume of treated water.

At 800 pps the power dissipating in the PCD reactor was 176 W. At this power rate, the 20-L sample received 1.0 kWh/m³ energy within 6 min and 45 sec. The pulse generator power is strictly proportional to the pulse repetition frequency, i.e. comprising 44 W at 200 pps.

The efficiency of the pulse generator was calculated as the ratio of the pulsed power dissipated in the reactor to the power consumed by the pulse generator, measured with the PF9830 3-phase digital power meter (Yantai Stark Instrument Co., Ltd., China). The consumed power comprised 65.7 and 262.7 W for pulse repetition frequencies of 200 and 800 pps, respectively, making the energy consumption efficiency of the pulse generator 67%.

The wastewater conductivity was measured with a conductivity meter DDB-303A (Inesa Co., China), and pH was measured with pH meter OHAUS ST10 (OHAUS Corp., USA). The initial pH of treated wastewater samples was adjusted with 4 mol/L solutions of sodium hydroxide and sulfuric acid.

Experiments using conventional ozonation were carried out with both BTCW and RCW samples for comparison with the PCD results. Ozonation was performed using a 1-L glass reactor with a porous sintered glass bottom for gas dispersion (Fig. 3). Gaseous ozone was produced with a laboratory ozone generator CH-ZTW (Guangzhou Chuanghuan Ozone Electric Appliance Co. Ltd., China). The concentration of gaseous ozone in the inlet and outlet gas was measured by iodometric titration: 1 L of ozone-containing air was purged through a gas-washing bottle filled with 2% potassium iodide solution in phosphate buffer at pH 7.0 (all chemicals from Tianjin Damao Chemical Reagent Plant, China). Free iodine was titrated with a 0.1 mol/L solution of sodium thiosulfate made by Fixanal (ELISA, China) in the presence of a starch indicator. All measurements were carried out in triplicate, with the standard deviation fitting into a ±1% interval. In a typical run for ozonation, the ozone-containing gas at an inlet ozone concentration of 14 ± 1 mg/L and flow rate of 1.0 L/min was continuously bubbled through the reactor. Samples of 5 mL volume were taken at regular time intervals and purged with high-purity nitrogen for 5 min to remove residual aqueous ozone. An identical ozone concentration measurement method was used in the outlet gas stream of the PCD reactor.

Freshly calcined (at 650 °C) CaO was added to 100-mL samples of PCD-treated RCW, shaken vigorously for 2 min and left for 4 hr for settling. The samples for analysis were filtered through 0.45-μm membrane filters (Anpei Laboratory Technologies, China). The sequential treatment of the 20-L sample of RCW with pre-oxidation, liming and post-oxidation was carried out identically to the other oxidation and liming experiments with the exception of filtration: the 20-L sample was filtered through a four-layer synthetic fabric filter.

### Table 1 – The characteristics of raw and biologically treated coking wastewaters.

<table>
<thead>
<tr>
<th>Index</th>
<th>RCW</th>
<th>BTCW</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.8 ± 0.1</td>
<td>7.7 ± 0.1</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>570 ± 20</td>
<td>450 ± 20</td>
</tr>
<tr>
<td>BOD₅ (mg O₂/L)</td>
<td>500 ± 50</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>3500 ± 200</td>
<td>130 ± 20</td>
</tr>
<tr>
<td>TOC (mg C/L)</td>
<td>1440 ± 20</td>
<td>40 ± 10</td>
</tr>
<tr>
<td>SCN⁻ (mg/L)</td>
<td>350 ± 10</td>
<td>ND</td>
</tr>
<tr>
<td>CN⁻ (mg/L)</td>
<td>8 ± 2</td>
<td>ND</td>
</tr>
<tr>
<td>Phenol (mg/L)</td>
<td>600 ± 50</td>
<td>ND</td>
</tr>
</tbody>
</table>

RCW: raw coking wastewater; BTCW: biologically treated coking wastewater; ND: not detected.
using a HACH digester and photometer model DR 3900 (HACH Co., USA). The measurement of phenol was carried out using the high performance liquid chromatograph (HPLC) with a C18 4.6 × 250-mm chromatographic column ZORBAX Eclipse PAH (Agilent, Japan) at the oven temperature of 35 °C. The mobile phase A, chromatographically pure methyl alcohol (BCR International Trading Ltd. Co., China), was mixed with phase B, Millipore water (DRTech, China), in the volumetric ratio of 55:45. The eluent flow velocity was 1.0 mL/min, and the analyzed sample injection volume was 20 μL. The UV-detector was set at the wavelength of 270 nm. The phenolic solutions for calibration were made with phenol provided by Aladdin Chemistry Co. Ltd. (China). Thiocyanate SCN⁻ concentration was measured by the colorimetric ferric thiocyanate (Fe(III)-SCN⁻) method with spectrophotometric reading (Evolution 300BB, Thermo Scientific, UK) at 460 nm (Clesceri et al., 2005). Sodium thiocyanate for calibration was purchased from Tianjin Damao Chemical Reagent Plant, China.

Cyanide quantification was carried out using the national standard method (GB 7486–87). A 200-mL wastewater sample was pre-treated with 10 g of potassium chromate to remove interfering substances. An EDTA 10-% solution was added to the filtered liquid sample. This was then acidified with phosphoric acid, density 1.69 g/mL, to pH < 2.0. The wastewater sample was distilled with distillate neutralization in 10 mL of 1% NaOH solution. The distillate was diluted with Millipore water to 100 mL and 0.2 mL of rhodanine (2-thioxo-4-thiazolidinone) acetone solution (0.02 g per 100 mL of acetone) was added as an indicator. Titration of cyanide was carried out with 0.01 mol/L sodium chloride solution.

Biochemical oxygen demand was measured using rapid BOD monitors OxiTop IS6, (WTW, Austria). The content of total organic carbon (TOC) was measured in filtered samples using a TOC-analyser, model TOC-VCPN (Shimadzu, Japan). Ammonia was measured using the national standard method (HJ 535–2009): 1 mL of a pre-distilled water sample was diluted with water to 50 mL, to which 1.0 mL of potassium sodium tartrate solution and 1.0 mL of Nessler’s reagent were added with subsequent spectrophotometric reading at 420 nm in 10 min (Evolution 300BB, Thermo Scientific, UK). The color was measured in Hazen units (HU) by the platinum-cobalt colorimetric method (GB/T 3143–1982; Clesceri et al., 2005). Sulfide was quantified using the methylene blue spectrophotometric method (GB/T 16489–1996; Clesceri et al., 2005).

2. Results and discussion

2.1. Performance verification

In order to evaluate the efficiency of the PCD reactor, performance verification was carried out with 20 L of a 1 mmol/L aqueous solution of phenol in alkaline medium at pH 11.0, which declined to 10.0 during the 15-min treatment, and the pulse repetition frequency of 800 pps. The energy efficiency of phenol oxidation was found to be about 55 g/kWh, which coincides with that observed in an earlier study under similar conditions, with slightly different parameters for the pulse and the electrode system (Preis et al., 2013). The energy efficiency of oxidation E (g/kWh) was calculated using Eq. (6):

$$E = \frac{\Delta C}{W}$$

where \(\Delta C (g/m^3)\) is the reactant concentration decrease.

The energy efficiency of ozonation was calculated analogously with Eq. (6), in which the delivered quantity of ozone was considered to consume about 30 kWh/kg \(O_3\) for its synthesis from air (Katsoyiannis et al., 2011; Ajo et al., 2015).

2.2. Oxidation of biologically treated CW

Since the practical goal is finding a way to reduce the effluent COD to meet the emission standards, the straightforward
approach to the task was undertaken first: the PCD-treatment of BTCW was tested and compared to the conventional ozone application.

Application of PCD-treatment to BTCW showed the refractory character of pollutants: the energy efficiency of oxidation did not exceed 1.2 g/kWh at 800 and 200 pps (Fig. 2), respectively, at neutral pH, although the color of wastewater was essentially removed at 20 kWh/m³ (data not shown). These numbers, although substantially exceeding the efficiency of 0.5 g/kWh observed for conventional ozonation, are still unreasonably low; reaching the desired COD of 80 mg O₂/L may require substantial amounts of energy. One can see that COD degradation depends on the pulse repetition frequency, indicating the presence of pollutants yielding to oxidation with relatively stable ozone. The gain in energy saving, however, is compensated by about a 2.5-fold longer treatment time at lower frequency.

Oxidation of BTCW did not bring about a significant change in pH, with the decrease being a fraction of a pH unit: from 12.1 to 11.2, from 7.7 to 7.4 and from 3.8 to 3.3 for alkaline, neutral and acidic media, respectively. Variation of the starting pH of the treated BTCW showed that addition of alkali to reach pH 12.1 gave certain benefits in oxidation efficiency compared to the neutral wastewater: the efficiency of 1.9 g/kWh was observed at 800 pps (Fig. 4). Acidification to pH 3.8, however, resulted in substantially better efficiency, with about a one-third decrease in COD, accompanied with formation of a brown precipitate characteristic of humic substances. Further PCD-oxidation resulted in a minor (about 10%) decrease of COD with a 16.5 kWh/m³ energy dose delivered to the wastewater. This observation suggests that the amount of organic compounds removed from neutral or alkaline BTCW by oxidation may be attributable to the presence of humic substances (Xu et al., 2015).

Addition of hydrogen peroxide in the amount of 135 mg/L, i.e. in a quantity approximately equal to COD, was spread over the time of PCD-treatment: the total volume of 9 mL of 30% H₂O₂ solution was delivered to the reactor in portions of 0.5 mL every 5 min of treatment. The wastewater was treated at neutral pH, showing no effect from hydrogen peroxide addition in PCD-oxidation: the addition of a supplementary oxidant did not lead to a change in the reaction efficiency under the experimental conditions.

2.3. Oxidation of raw CW

2.3.1. Degradation of chemical oxygen demand

From Fig. 5 one can see that the COD degradation in treated RCW samples followed a linear pattern dependent on the delivered energy. This indicates that in the heavily polluted wastewater, the supply of oxidants appears to be the rate-limiting factor. Nevertheless, there was a difference observed in oxidation efficiency represented by the slope factors of the degradation plots: oxidation appeared to be more efficient at pH of 9.8, and adjustment to higher pH resulted in somewhat reduced efficiency. During oxidation, the pH of treated RCW decreased gradually from 9.8 to 5.5 at 50 kWh/m³ delivered energy due most probably to formation of carboxylic acids, the products identified in an earlier study on PCD oxidation of organic compounds (Marotta et al., 2011; Panorel et al., 2013). and nitric acid formed from atmospheric nitrogen, although the contribution of the latter is expected to be minor due to the abundant organic compounds present (Preis et al., 2014). The electrical conductivity of the treated RCW, however, showed a minor change, increasing for only a few units, from 570 to 600 μS/cm indicating the possible predominance of weakly dissociated organic charge carriers.

The oxidation efficiency at the lower pulse repetition frequency of 200 pps increased substantially compared to 800 pps, from 17.3 to 24.5 g O₂/kWh, which is explained by the more exhaustive utilization of long-lived ozone in the treatment time, which is inversely proportional to the pulse repetition frequency. The ozonation experiment conducted at a starting pH of 9.8, unlike the case of BTCW with almost four-fold difference between ozonation and PCD, showed efficiency close to that of PCD at 800 pps, 15 g O₂/kWh, differing less than 2 g O₂/kWh, i.e. about 10% (Fig. 5), indicating the possible presence of OH-radical scavenging surfactant substances lessening the basic advantage of PCD — the involvement of OH-radicals formed at the treated water
surface (Chang et al., 2008). The intense foaming of RCW and the substantial effect of reduced pulse repetition frequency (about 42%), indirectly support this assumption. Ozonation showed considerably lower efficiency at lower pH, 11.1 and 9.6 g O₂/kWh at starting pH values of 7.0 and 5.0 (data not shown).

2.3.2. Oxidation of phenol
The oxidation of phenol in PCD-treatment also followed a pattern close to linear, indicating the limiting character of the discharge power (Fig. 6). Unlike COD, however, phenol degradation followed the expected pattern in the dependence of oxidation efficiency on pH, increasing by about 37% with pH raised from 9.8 to 12.5. The four-fold reduction of the pulse repetition frequency practically doubled the phenol oxidation efficiency, from 8.6 to 17.1 g/kWh. The competition of rapidly oxidized pollutants for oxidants in RCW is, as one can see, rather intense since the observed efficiency of phenol oxidation of 8.6 g/kWh at 500–600 mg/L is far below that expected for phenol in the absence of competition (Chang et al., 2008). Ozonation of RCW showed a phenol removal result similar to that observed with COD degradation: the efficiency comprised about 8.2, 5.0 and 3.2 g/kWh at starting pH of 9.8, 7.0 and 5.0 (data not shown), respectively, i.e. in alkaline media the efficiency of conventional ozonation was close to that of PCD at 800 pps.

Products of aqueous ozonation of phenol were identified at the beginning of the 1980s (Hoigné and Bader, 1983; Singer and Gurol, 1983). Oxidation of phenol was also studied in electric discharge reactions, although the authors did not hypothesize a reaction route (Grabowski et al., 2006; Pokryvailo et al., 2006). The most comprehensive description of phenol oxidation in an electric discharge process was given by Marotta et al. (2011), who quantified the products of phenol oxidation in aqueous solutions treated with a gas-phase dielectric barrier discharge (DBD). Primary intermediate 1,2- and 1,4-dihydroxybenzenes were identified together with carboxylic acids: cis, cis- and trans, trans-muconic acids, maleic and fumaric acids, known to be further oxidized to glyoxylic, oxalic and formic acids (Hoigné and Bader, 1983). The acids are believed to precipitate insoluble products with calcium with the liming of wastewater (see below).

2.3.3. Oxidation of reduced substances
Sulfide was oxidized rapidly, disappearing entirely at the minimum delivered energy of 2.6 kWh/m³. Reduced sulfur oxidation using AOPs is considered to proceed easily, with formation of sulfate (Leasuze et al., 1991; Vega et al., 2014).

Meanwhile, the ammonia content increased from 30 ± 20 to 300 ± 10 mg/L during the course of oxidation, which provides a nitrogen source for microorganisms in further biological treatment. Amino groups of organic compounds are known to mineralize to ammonia in AOPs (Leitner et al., 2002), as are heterocyclic compounds such as, for example, pyridine (Andreozzi et al., 1991), confirming their presence in RCW. Special attention was paid to the oxidation of thiocyanate in connection with its ability to produce stoichiometric amounts of highly toxic cyanide in ozonation reactions. Formation of cyanide was also reported for aqueous ozonation involving OH-radical oxidation, although the authors failed to find simple reaction equations describing radical reactions (Jensen and Tuan, 1993; Udrea and Avramescu, 2004):

\[ \text{SCN}^- + 3\text{O}_3 + 2\text{OH}^- \rightarrow \text{CN}^- + \text{SO}_4^{2-} + 3\text{O}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (7)

Fenton oxidation of thiocyanate to cyanide is also well-known in regeneration of cyanidation solutions used in extractive mining (Prosyanikov et al., 2009; Gonzalez-Merchan et al., 2016). Further oxidation of cyanide with ozone yields a rate five to six times that of thiocyanate, and its stoichiometry is described with Eq. (8):

\[ \text{CN}^- + \text{O}_3 \rightarrow \text{CNO}^- + \text{O}_2 \]  \hspace{1cm} (8)

In practical cases, however, effective simultaneous degradation of cyanide was also reported (Van Leeuwen et al., 2003; Chang et al., 2008). Thiocyanate oxidation with OH-radicals in AOPs is known to be accelerated in catalytic ozonation (Udrea and Avramescu, 2004), in which OH-radical shows high-rate
oxidation of thiocyanate (Olson and Fessenden, 1992; Milosavljevic and LaVerne, 2005).

One can see from Fig. 7 that cyanide, yielding in its initial concentration to thiocyanate by more than an order of magnitude, shows very slight growth with the degradation of thiocyanate followed by subsequent degradation of its own, when the concentration of thiocyanate becomes sufficiently low. The intermediate growth in the cyanide concentration is far below the theoretically possible stoichiometric yield from the degradation of thiocyanate. This indicates that the PCD treatment of thiocyanate-abundant RCW does not result in accumulation of toxic cyanide, confirming the method’s safety. This can be explained by the attack of the treated wastewater surface with abundant OH-radicals, which are able to provide rapid mineralization of oxidized pollutants as observed earlier (Preis et al., 2013). This was confirmed by the improved biodegradability of the wastewater (see Section 2.3.4).

The removal of thiocyanate in PCD oxidation presents a few observations difficult to explain (Fig. 8). Firstly, the concentration of SCN$^-$ remains unchanged for a substantial amount of delivered energy of electric discharge, 10 to 20 kWh/m$^3$, indicating possible replenishment of free thiocyanate derived from decomposing complex compounds, such as, for example, ferric complexes (Kjeldsen, 1999) or reactions resulting in thiocyanate formation simultaneous with its oxidation. A similar phenomenon was observed by Van Leeuwen et al. (2003) in CW treatment with ozone. The authors failed to find published information on CW containing complexes liberating free thiocyanate in oxidation. The formation of thiocyanate in reactions of polysulfides with cyanide in the presence of oxygen at a catalytic surface (Hewitt et al., 2009) should not be considered due to the minor cyanide presence (see Fig. 7). Secondly, thiocyanate at pH 12.5 was oxidized with around two times lower efficiency than at pH 9.8, having no simple explanation. Somewhat slower oxidation of SCN$^-$ with ozone in alkaline aqueous solutions compared to acidic ones has been observed (Jensen and Tuan, 1993; Soto et al., 1995), although the difference was reported to be moderate. The presence of substances competing with thiocyanate in strongly alkaline medium, such as phenolic compounds, may explain the difference. And thirdly, the application of PCD at lower pulse repetition frequency makes no difference in the thiocyanate removal efficiency, contrasting the observed COD and phenol degradation patterns (Figs. 3 and 4). This phenomenon may not have a straightforward explanation since thiocyanate is not refractory to oxidation with ozone.

### 2.3.4. Impact on the wastewater biodegradability

With reduced COD, sulfide, thiocyanate and phenol and increased ammonia, an improvement in biodegradability was observed. One can see from Fig. 9 that the BOD$_5$/COD ratio of PCD-treated RCW increased from 0.14 to 0.43 at 42 kWh/m$^3$ delivered to the wastewater. The explanation for the observed results is the degradation of toxic components, such as phenol and thiocyanate, producing no toxic by-products. Degradation of high-molecular weight substances to ones of smaller molecular size is also known to contribute to increased biodegradability (De Laat et al., 1991). Further oxidation, however, shows somewhat stabilized biodegradability, which may be explained by the elimination of toxics and equal rates of further COD and BOD$_5$ reduction.

The BOD$_5$/COD ratio may also be explained by the release of ammonia observed during oxidation: the NH$_3$-N content of about 30 mg/L increased during oxidation to about 300 mg/L (data not shown) improving its further biodegradability (Park and Yoo, 2009; Kantor et al., 2017).

Determination of the effect of this improved biodegradability on the ultimate result of subsequent biological treatment will require studies of the full-chain process using a biological reactor model.

### 2.3.5. Application of lime

Addition of low-cost lime results in precipitation of some acidic oxidation products, restoring the alkaline pH for further beneficial oxidation, thus improving the process economy. One can see from Fig. 10 that the effect of liming on the original RCW was minor, and addition of lime did not bring a noticeable removal of COD. The PCD-treated wastewater, however, showed substantial potential for removal of oxidation products, most probably carboxylic acids, in the form of insoluble calcium salts.

The strongest effect of liming on COD degradation was observed at the energy input of 28 kWh/m$^3$, where the COD...
COD degradation. A similar result obtained without liming by the delivery of about 42 kWh/m³ of PCD energy at 800 pps in air. Ca(SCN)₂·4H₂O is around 590 g/L (Murashova et al., 1976). The difficulty to explain by chemical precipitation: the solubility of anate exhibited a minor decrease as a result of liming, which is shorter-chain acids in the course of further oxidation.

Liming showed a negligible effect on phenol removal. Thiocyanate exhibited a minor decrease as a result of liming, which is difficult to explain by chemical precipitation: the solubility of Ca(SCN)₂·4H₂O is around 590 g/L (Murashova et al., 1976). The drift of the baseline (data not graphically shown).

The ‘terraced’ treatment, i.e. sequential combination of pre-oxidation with liming and post-oxidation, resulted in noticeably advanced COD reduction (Fig. 11). The addition of lime to the RCW treated with 30 kWh/m³ resulted in 380 mg O₂/L i.e. 13% COD degradation. A similar result obtained without liming by further oxidation would require an additional 25 kWh/m³, making the practical energy expense about 40 kWh/m³, which costs 0.61 RMB per kWh, i.e. 24.4 RMB/m³. The lime, however, costs a maximum of 600 RMB per metric ton, which makes the cost of 10 kg material 6.0 RMB/m³. Further PCD-oxidation after the application of lime takes place with the substantial efficiency of 12.5 g O₂/kWh at 800 pps in air.

The application of lime in the ‘terraced’ experiment resulted in negligible impact on the phenol and thiocyanate concentrations. Further post-treatment of limed wastewater with PCD oxidation did not result in a change in the phenol and thiocyanate degradation patterns compared to the wastewater untreated with lime.

3. Conclusions

PCD was for the first time applied to the treatment of CW to meet the stringent requirements of COD reduction in industrial discharge. Phenol and thiocyanate were removed with efficiencies up to 17.1 and 8.3 g/kWh, respectively, while no sulfide remained above 2.6 kWh/m³ of delivered energy. Oxidation of thiocyanate was found to produce negligible amounts of toxic cyanide as an intermediate product, with its further oxidation explained by the surface character of the rapid oxidation reaction with OH-radicals. The results of raw CW oxidation indicated a profound rise in BOD₅ to COD ratio from 0.14 to 0.43, i.e. more than a factor of three, with the delivery of about 42 kWh/m³ of PCD energy at 800 pps in air. The effect of improved treatability is explained by the observed removal of the CW toxics, including abundant phenol and thiocyanate, fragmentation of non-digestible molecules and nitrogen mineralization. Biologically treated CW showed a PCD treatment efficiency 3–4 times higher than that in conventional ozonation, degrading COD and color from 136 to 95 mg O₂/L and from 300 to 20 HU, respectively, at about 20 kWh/m³.

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