Pulsed corona discharge for degradation of aqueous humic substances

Iris Panorel, Iakov Kornev, Henry Hatakka and Sergei Preis

ABSTRACT

The research into oxidation of aqueous humic substances (HS) with pulsed corona discharge (PCD) was undertaken to estimate the energy efficiency of the treatment. The PCD system consists of a voltage pulse generator and reactor, in which the gas-phase discharge generating \( \cdot \text{OH} \) radicals and ozone treats the water showered between electrodes. The influence of HS initial concentration, pulse repetition frequency, water flow rate, and the atmosphere composition was evaluated by the decrease in total organic carbon (TOC) and color. The PCD treatment reduced TOC by 40 to 50% and the color by up to 97%. The PCD energy efficiency ranged about 20 g kW\(^{-1}\) h\(^{-1}\) in air and 30 g kW\(^{-1}\) h\(^{-1}\) in oxygen for the lowest initial color of about 50 Pt-Co degrees. Ozone contributed about 30% to the color reduction and only 15% to the reduction in TOC, indicating predominant role of \( \cdot \text{OH} \) radicals in mineralization of oxidation by-products.

Key words | advanced oxidation processes, AOPs, energy efficiency, humic acids, ozone, water

INTRODUCTION

Natural organic matter (NOM) found in soil and water mostly comprises of humic substances (HS), the ultimate product of natural decomposition of plant tissue, contributing to the color of surface waters. The main structural characteristics of aquatic HS include apparent molecular weight, UV absorption, aromatic carbon content, carboxylic and phenolic functions, carbohydrate, and amino acid content (Graham 1999). Recent studies included characterization based on hydrophobicity and fluorogenic source by using resin fractionation, LC-OCD and fluorescence spectroscopy (Ciputra et al. 2010). However, most of the data on HS refer to average properties and structure of the components of diverse character dependent on the water or soil origin and conditions of extraction.

A common interest towards HS relates to chlorination of NOM-containing water due to formation of hazardous disinfection by-products, most common of which are trihalomethanes (THMs). The effect of chlorinating water with significant amount of NOM shows an increased risk of birth defects in urinary tract, respiratory, and cardiac systems (Hwang et al. 2002).

Although HS are chemically reactive, they are considered to be recalcitrant to microbial decomposition. A study conducted by Qualls (2004) support the hypothesis that HS are inherently difficult for microbes to mineralize, and as such, contribute to the sequestration of carbon in soil.

The inherent recalcitrance of HS has made biodegradation under natural conditions insufficient in mineralizing this pollutant, thus often making it present in surface waters, and further, in water supply systems. Physical methods such as membrane filtration, coagulation, or adsorption may effectively remove HS from water, although transferring the pollutant to another media requires further handling and additional treatment cost. Several studies using advanced oxidation processes (AOPs) for degradation of HS have been conducted, including ozonation (Oguz et al. 2008), UV/H\(_2\)O\(_2\) and photo Fenton-like process (Sanly et al. 2007), TiO\(_2\) photocatalytic process (Bekbölet & Ozkosemen 1996; Portjanskaja et al. 2004), and gamma radiolysis of water to produce \( \cdot \text{OH} \) radicals (Goldstone et al. 2002). The common objective of these processes is the generation of \( \cdot \text{OH} \) radicals, the active oxidizing agent...
having the reaction rate constant with organic compounds ranging from $10^7$ to $10^{10}$ L mol$^{-1}$ s$^{-1}$ (Guittonneau et al. 1996). This makes the AOPs powerful and effective means for water treatment, although, for example, the excessively expensive character of ozone production and application makes it a privilege of cities in industrially developed countries. Photocatalytic oxidation is slow, and gammadiolysis meets serious resistance in public. The way to promote AOPs in water treatment technology is the substantial improvement of their cost efficiency. Concerning HS, other studies have reported the major products of HS oxidation being the lower molecular weight carboxylic acids which are no longer precursors of THMs (Goldstone et al. 2002; Kerć et al. 2003).

The advantage in AOPs is the ‘OH radical produced in situ for its immediate utilization in the reaction with the pollutants. In this study, we use a non-thermal plasma method of pulsed corona discharge (PCD), generating ozone and ‘OH radicals from oxygen and water (Ono & Oda 2003) using small energy input, and thus, minor temperature increase in the reactor. The oxidants degrade the contaminants via oxidation reactions:

\begin{align}
e^- + H_2O & \rightarrow e^- + \cdot H + \cdot OH \\
e^- + 3O_2 & \rightarrow e^- + 2O_3
\end{align}

\begin{align}
\cdot OH + \text{NOM} & \rightarrow \text{products} \\
O_3 + \text{NOM} & \rightarrow \text{products}
\end{align}

Although the preliminary experience of the authors and previous publications (Pokryvailo et al. 2006) showed the capability of PCD for removing phenol, lignin and other organic chemicals, no data concerning PCD oxidation of HS is available.

**MATERIALS AND METHODS**

A schematic diagram of the experimental set-up is illustrated in Figure 1. The system used in the experiments consists of a pulsed corona discharge reactor and a high voltage pulse generator.

The reactor designed by the authors utilizes conventional wire-plate corona geometry, typical for electrostatic precipitators: electrode wires are concluded between earthed plate electrodes. Water is fed to the top of reactor where it is dispersed with a perforated plate producing jets, droplets and films. Water falls between electrodes to the zone of gas-phase PCD formation where the target compounds react with ‘OH radicals, ozone, and other oxidants.
before returning back to the tank. Water was circulated from the reservoir tank through the reactor by a pump, with a frequency regulator controlling the pump engine rotation speed and thus flow rate.

The power supply generates the discharge pulses of the following parameters: voltage pulse amplitude of 20 kV, current of 380 to 400 A, and 100 ns duration at pulse repetition frequency of 200, 400, 600 and 840 pulses per second (pps). The energy delivered to the reactor, calculated as an integral product of voltage and current peak areas, was 0.3 J per pulse, giving approximately 250 W power dissipated in the discharge at maximum pulse repetition frequency. The energy consumption efficiency of the pulse generator was 67%.

To achieve an initial concentration of about 90%, oxygen was introduced to the reactor prior to the experiment. The oxygen concentration was monitored with the oxygen gas analyzer. Before entering the analyzer measuring cell, the gas in the reactor was circulated through the desiccant pellets to avoid the interference from the gas humidity.

The experiments were performed using 50-L samples of HS solution. Varying amounts of Aldrich humic acid sodium salt of technical grade was dissolved in reverse osmosis water at ambient temperature. The ratio between the color (Pt-Co degrees), the HS concentration (mg L\(^{-1}\)) and TOC (mg C L\(^{-1}\)) equals for the used HS specimen 50.3:2.73:1. The range of HS concentrations covered the surface water color diapasons (Collins et al. 1986). Water temperature was not controlled during the experiment, although, it remained at ambient 18 to 20 \(^\circ\)C in all experiments. The operating parameters are given below in Table 1.

### Table 1 | Experimental parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse repetition rate, pps</td>
<td>200, 400, 600, 840</td>
</tr>
<tr>
<td>Humic acid concentration, mg L(^{-1})</td>
<td>3, 7, 14, 23</td>
</tr>
<tr>
<td>TOC, mg C L(^{-1})</td>
<td>1.1, 2.6, 5.1, 8.4</td>
</tr>
<tr>
<td>Colour, Pt-Co degrees</td>
<td>55, 129, 258, 423</td>
</tr>
<tr>
<td>Water flow rate, L min(^{-1})</td>
<td>3, 5, 7, 10, 15</td>
</tr>
<tr>
<td>Atmosphere composition</td>
<td>Air, 90% oxygen</td>
</tr>
<tr>
<td>Gas–liquid contact surface(^a), m(^{-1})</td>
<td>9, 14, 20, 29, 43</td>
</tr>
</tbody>
</table>

\(^a\)Gas–liquid contact surface was measured by the classical method of sulfite oxidation with air oxygen in presence of cobalt sulfate as a catalyst.

Samples were collected periodically within the reaction time interval from 0 to 25 min. These were taken after the exposure of the circulating solution to the discharge for the planned time, and then the complete recirculation of the treated solution volume without PCD for the averaging of concentrations. After oxidation, the samples were analyzed with spectrophotometer for color preliminarily correlated to the HS content, and TOC analyzer to characterize the degradation.

Ozone concentration in the gas was measured iodometrically by blowing the exact amount of the gas from the reactor through a Drexel trap filled with acidified potassium iodide solution. Ozone concentration in water was also measured iodometrically.

### HS degradation

Optical density was measured at 455 nm wavelength with a HACH DR/2000 spectrophotometer, utilizing a pre-defined program for colour measurement that expresses the values in Pt-Co degrees. The degradation of HS was described as:

\[
\frac{C}{C_0} = \frac{\text{Pt-Co}_{455(t)}}{\text{Pt-Co}_{455(0)}}
\]

where \(C_0\) and \(C\) are respectively the HS concentration before and after a certain reaction time, and \(\text{Pt-Co}_{455(0)}\) and \(\text{Pt-Co}_{455(t)}\) are the corresponding readings from the pre-defined colour measurement program at 455 nm wavelength. Calibration of this specific HS at 455 nm wavelength at the range from 16 to 430 Pt-Co degrees resulted in a linear correlation of 0.0543 mg L\(^{-1}\) HS per Pt-Co degree (\(R^2 > 0.999\)). Degradation efficiency \(E\) (g kW\(^{-1}\) h\(^{-1}\)) was calculated relative to the delivered pulse energy as follows:

\[
E = \left[\frac{0.0543 \times \text{mg L}^{-1}}{\text{Pt-Co}_{(n-1)} - \text{Pt-Co}_{(n)}} \times \frac{\text{mg L}^{-1}}{\text{HS}} \times 50 \text{ L} \times \frac{1 \text{ g}}{1,000 \text{ mg}} \right] \times \frac{\text{h} \times \text{power, kw}}{(f_n - f_{n-1})}
\]

The power or the pulse energy delivered to the reactor at the corresponding frequencies is shown in Table 2.
The TOC of the sample solutions was measured with a Shimadzu 5050 TOC analyzer. The sample was injected into a high-temperature furnace, where organic carbon is oxidized to CO₂ and quantitatively measured by means of infrared analyzer.

RESULTS AND DISCUSSION

The degradation behaviour of HS subjected to oxidation by PCD is quantified by comparing the spectrophotometric data (Pt-Co colour degrees) before and after the treatment.

Effect of initial HS concentration on removal efficiency

Figure 2 shows how the initial concentration of HS in water affects the extent of degradation. The plot of normalized HS concentration versus delivered energy shows a steep slope in the beginning of oxidation (delivered energy of about 0.3 kW h/m³), but gradually decreases with further energy input. The colour dropped to 50% in less than 5 min for initial HS concentration of 7 mg L⁻¹. This concentration corresponds to colour of about 130 degrees, i.e., the colour characteristic for natural surface waters. Increasing the initial concentration from 7 to 23 mg L⁻¹ correspondingly increased the efficiencies from 32 to 75 g/kW h at an initial dose of 0.08 kW h/m³, and from 20 to 50 g/kW h at a dose of 0.25 kW h/m³ when the humic acid concentration has been reduced to more than half. At higher initial concentration requiring more energy, efficiency is higher due to increased probability of radicals reacting with the pollutant. The inset in Figure 2 shows that the same energy delivered results in the degradation of similar normalized rate regardless of the pulse repetition frequency. This means the growing frequency results in approximately, but not precisely (see Effect of pulse repetition frequency on removal rate), proportional growth of the rate. This phenomenon indicates minor role of ozone in oxidation, HS are mostly oxidized by OH-radicals (see also Contribution of ozone to oxidation).

Effect of pulse frequency on removal rate

The pulse repetition rate is a parameter with a significant impact in the rate of degrading recalcitrant compounds as shown in Figure 3. This is due to the combined effect of short-living oxidants and relatively stable ozone: the latter acts during all the contact time whereas the short-living oxidants work only in the discharge zone. Longer pauses between pulses may give additional time for ozone action. Increasing the pulse repetition rate from 200 to 840 pps substantially increased the oxidation rate which is the fastest at the highest frequency (50% reduction after 3 min at 840 pps and 10 min at 200 pps).

The degradation efficiencies were significantly reduced to as much as approximately 40 to 50% with the pulse repetition frequency increased from 200 to 840 pps: from 122 to 75 g kW⁻¹ h⁻¹ at the HS initial concentration of 23 mg L⁻¹, and from 35 to 17 g kW⁻¹ h⁻¹ at 3 mg L⁻¹ HS initial concentration. The disproportional growth of the oxidation rate indicates different yield of oxidative species in PCD.

Table 2 | Pulse energy delivered to PCD reactor, W

<table>
<thead>
<tr>
<th>Frequency (pps)</th>
<th>Delivered power, W</th>
</tr>
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<tbody>
<tr>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>400</td>
<td>119</td>
</tr>
<tr>
<td>600</td>
<td>178</td>
</tr>
<tr>
<td>840</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 2 | Degradation of HS at various initial concentrations with combined data (all frequencies) for different pulse frequencies, pH of about 8-8.5, air medium, and flow rate of 15 L min⁻¹.
A sharp decrease in efficiency and oxidation rate is observed within a single experiment in the first 3 to 5 min of oxidation for all the frequencies evaluated. This made us to calculate the efficiency of color removal for the first minute of treatment for uniform judgment, as shown in Figure 4. The energy efficiency expectedly increased with increasing HS concentration, although small concentrations disappeared rapidly.

These results show that the removal of HS by the combined attack of \( \cdot \)OH radicals and ozone generated in PCD can yield efficiencies as high as 20 to 35 g kW\(^{-1}\) h\(^{-1}\) in air or 30 to 60 g kW\(^{-1}\) h\(^{-1}\) in oxygen media for HS initial concentration of 3 mg L\(^{-1}\). This is significantly higher than conventional ozonation results of 3 g kW\(^{-1}\) h\(^{-1}\) reported by Karnik et al. (2005) for the initial HS concentration of 5 mg L\(^{-1}\). Similarly, Munter et al. (1993) proposed the efficiency for HS oxidation with ozone as big as 9 g kW\(^{-1}\) h\(^{-1}\) at the HS concentration of about 3 to 4 mg L\(^{-1}\) in lake water, which still substantially yields to PCD efficiency.

### Contribution of ozone to oxidation

The oxidation of HS solutions was carried out under conditions of equal ozone concentrations with and without simultaneous PCD treatment. The experiments were carried out in air atmosphere with the equilibrium gaseous ozone concentration maintained at 5 mg L\(^{-1}\) for the identical times. The ozone concentration in the reactor without PCD application was maintained by ‘blinking’ switching the pulse generator on for 5 s with 10-s intervals; the treated solution flow was turned off for the time PCD was applied.

The result is compared to the PCD degradation using the same pulse repetition frequency, 840 pps, and the initial HS concentration, and is shown in Figure 5. The drastic difference in oxidation efficiency is evident between the two experiments showing the role of short-living oxidants and ozone: the oxidation rate within the first 3 min of treatment with PCD exceeded the one of oxidation with ozone for about five times. The basic characteristic of HS is their refractory character towards oxidation. This makes the oxidation with ozone rather slow thus having the treated aqueous solution saturated with ozone at about 1.5 mg L\(^{-1}\) in both cases, with and without PCD treatment. The oxidation reaction with ozone thus contributed under the experimental conditions about 20 to 30% of the total oxidation rate.

The kinetics of HS reacted with \( \cdot \)OH radicals and ozone is described by the second order equations:

\[
\frac{d[HS]}{dt} = -k_{O_3}[O_3][HS] 
\]  
\[
\frac{d[HS]}{dt} = -k_{OH}[\cdot OH][HS] 
\]  

where \([HS]\) is the concentration of HS, \([O_3]\) and \([\cdot OH]\) are the concentrations of ozone and hydroxyl radicals at time \(t\), and \(k_{O_3}\) and \(k_{OH}\) are the rate constants.
for the oxidation by ozone and hydroxyl radicals, respectively.

Combining the effect of both reactions, we have:

\[
\frac{d[\text{HS}]}{dt} = -k_{O_3}[\text{O}_3][\text{HS}] - k_{\cdot \text{OH}}[\cdot \text{OH}][\text{HS}]
\]  

(9)

From the plot of \(\ln \frac{C}{C_0}\) versus time (inset at Figure 3), we can assume a pseudo first-order rate coefficient and simplify Equation (9) to:

\[
\frac{d[\text{HS}]}{dt} = -k_{\text{HS}}[\text{HS}]
\]  

(10)

where \(k_{\text{HS}} = k_{O_3}[\text{O}_3] + k_{\cdot \text{OH}}[\cdot \text{OH}]\).

Integrating Equation (10),

\[
\ln \frac{[\text{HS}]}{[\text{HS}]_0} = -k_{\text{HS}}t
\]  

(11)

The degradation rate coefficients (initial stage) for oxidation of HS are therefore calculated from the slope \(k_{\text{HS}}\) in \(\text{min}^{-1}\). The results are presented in Table 3. The reaction rate coefficients of the pseudo-first order are comparable to that determined by the recent studies in conventional ozonation of Imai et al. (2009), \(5.1 \times 10^{-1} \text{ min}^{-1}\), and Oguz et al. (2008), \(1 \times 10^{-1} \text{ min}^{-1}\).

One can see that the reaction rate coefficient of the pseudo-first order is varying with the pulse repetition frequency and the HS concentration: the coefficient is decreasing with growing concentration and frequency. The oxidation rate, however, is exhibiting the opposite behaviour, thus indicating the disproportional growth in the oxidation rate with the frequency and concentration similarly to the energy efficiency described above. This behaviour may be explained by the interaction of the oxidation species with HS: the impact of \(\cdot \text{OH}\) radicals is increased at higher frequency, whereas ozone is more important at lower frequency. Higher HS concentrations emphasize the effect. The dependence of the reaction rate coefficient on the concentration and the frequency supports the hypothesis of participation of minimum two different species with different reaction rates and yields.

**Effect of oxygen**

Higher efficiencies are achieved and faster rate of degradation is observed with increased oxygen concentration,
which is most likely attributed to the formation of higher ozone concentrations. In the presence of oxygen, however, the increase in efficiency contributed only as much as 30 to 40% as shown in Figure 6. This indicates the chemical reaction rate as the process rate limiting factor: the equilibrium ozone concentration in 90% oxygen exceeds the one in air by the factor of four, 20 and 5 mg L\(^{-1}\) respectively, regardless of the pulse repetition frequency. This ozone concentration growth is practically in linear proportion with the oxygen concentration growth. On the other hand, this slight improvement of the oxidation rate (efficiency) with increased oxygen concentration indicates the major role of \(^{1}\)OH radicals played in the HS oxidation.

**Effect of recirculation flow rate**

Recirculation flow rate only slightly affected the efficiency of PCD oxidation as shown in Figure 7. At the minimum flow rate, the distribution of liquid phase became extremely uneven, leaving a substantial surface of the earthed electrodes dry, thus resulting in some decrease in PCD oxidation efficiency. At the maximum energy dose of 0.4 kW h m\(^{-3}\), maximum improvement of 10% on HS degradation was observed when the recirculation flow rate was increased from 3 to 15 L min\(^{-1}\).

**TOC results**

Figure 8 shows the comparison between different initial HS concentrations with combined data for all pulse repetition frequencies evaluated. At higher initial HS concentration of 23 mg L\(^{-1}\), about 30% mineralization was achieved after 15 min, 40% mineralization for initial HS of 14 mg L\(^{-1}\) and an average of about 50% mineralization for initial HS of 7 mg L\(^{-1}\). Figure 8 shows that with a delivered energy of 1.25 kW h m\(^{-3}\), the maximum mineralization achieved is 75% at 7 mg L\(^{-1}\) of HS, and 40% at 23 mg L\(^{-1}\). TOC reduction rate is averagely half slower than the colour reduction which may indicate that HS was mineralized to carbon dioxide and water and partly degraded to smaller molecules. Mineralization seems to start immediately at the
beginning of the treatment, which may indicate rapid mineralization of HS fragments such as carboxylic acids.

CONCLUSIONS

Pulsed corona discharge method appeared to be highly effective in oxidation of humic substances, surpassing the closest competitor, conventional ozonation, a few times in energy efficiency. Hydroxyl radicals play a major role in oxidation of HS and, especially, in their mineralization. The mineralization, although starting at the very beginning of the treatment, is not complete, decolorizing HS to smaller fragments. The oxidation efficiency grows with decreasing pulse repetition frequency due to larger contribution of ozone at lower frequencies, although the oxidation rate is also decreasing. Increased oxygen concentration contributes disproportionally to the oxidation efficiency: more than four times increased oxygen content resulted in about 50 to 40% improved efficiency, which indicates the predominant role of hydroxyl radical. The mass transfer showed minor impact to the oxidation efficiency.

REFERENCES


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