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The kinetics of the removal of organic pollutants from drinking water by a novel plasma-based advanced oxidation technology

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ABSTRACT

The main goal of this study was to examine the oxidation kinetics of four common organic pollutants, Chicago Sky Blue 6B (CSB), Rhodamine B (RhB), phenol, and 4-chlorophenol (4-CP), in drinking water using an advanced oxidation processes (AOP) corona technology. This was achieved by determining the rate constants and by tracking $OH^{\cdot}$ kinetics. In most experiments, a pseudo-first-order kinetics was found. Due to its molecular structure, the constant rate of color removal ($K_{CSB} = 2.3E{-}3\,min^{-1}$) was higher than that of the aromatic groups ($K_{CSB} = 3.0E{-}4\,min^{-1}$). Hydroxyl radical kinetics was investigated by means of p-chlorobenzoic acid (pCBA) degradation. When 10 mg/l of phenol was added to the water, pCBA degradation decreased ($K_{pCBA} = 3.70E{-}04\,min^{-1}$). An experiment carried out under similar conditions, but with an inactive ozone injection system, caused the pCBA rate constant to decrease even more ($K_{pCBA} = 1.60E{-}04\,min^{-1}$). The rate constants significantly increased, when the injector operated, since polluted water entered the static mixer at high pressure, where a second encounter occurred with oxidative agents that originated in air enriched with ozone that was drawn from the reactor. The high pressure separates the water into droplets, which allows for a better exposure of pollutants to oxidative agents.

Keywords: Corona; AOP; Hydroxyl radical; CSB; RhB; Phenol; 4-CP

1. Introduction

Water shortage is considered one of the main societal problems of our time [1,2] affecting an estimated four billion people around the world [2]. The main water problems in developing countries are hygiene and high quality potable water [2]. Water quality is decreasing, due to pollution from domestic and industrial sewage (e.g. textile dyes, drugs, pesticides etc.), characterized by organic contaminants [1,3]. Ongoing research on the pollutant-derived health risks, alongside improvements in analytical methodology, has improved detection of low concentration pollutants, resulting in more stringent drinking water quality regulations [4]. These new regulations require highly efficient and low-cost water treatment technologies, which are more capable of dealing with polluted water than traditional methods, such as those based on physical (mechanical), biological, and chemical processes.

An example of such a new technology is the advanced oxidation technologies (AOT) that aim at removing a wide range of organic contaminants [5,6]. These technologies are capable of oxidizing low

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concentrations of persistent organic molecules, often present in drinking water, until they reach full mineralization (H_2O and CO_2) [5,6]. These systems are based upon the generation of high oxidation potential species, such as H_2O_2, O_3, and especially $OH^{\cdot}$, in proximity to the source of the contaminated water [5,7,8]. The reactive and non-selective nature of the oxidative agents enables advanced oxidation processes (AOP) to treat polluted water more efficiently than the traditional methods [6–8]. The hydroxyl radical (OH), considered to be one of the strongest known oxidants, reacts quickly with almost all organic compounds; thus, its concentration in AOP's can determine the system efficiency [2,9]. Since $OH^{\cdot}$ reacts very quickly, its concentration can be tracked only with an indicator, such as para chlorobenzoic acid (pCBA) [10]. One of the new promising technologies is the corona-based systems. This technology does not require that chemicals increase the oxidative agent concentrations; in addition, it is not readily affected by fluctuations in the water quality.

In this paper, a corona-based system described by Even-Ezra et al. [11] was used. A corona is a particular type of non-thermal plasma emission, based on short pulses that are achieved by applying a high-voltage discharge between two electrodes, creating a strong electric field [6,12]. Electrons gain velocity and collide with gas molecules in the gas phase. If the energy transfer to the molecule in the collision is sufficient, the molecule will ionize, emitting new electrons, and creating a new radical [13]. It was found that corona-based systems are efficient in the removal of organic compounds from distilled [14] and deionized [15] water, including compounds that are not easily eliminated by existing AOP's for example water spiked with dyes [14] and with various phenolic species [14,15].

2. Research approach

In this study, four common water pollutants were tested under different operational conditions. The pollutants were comprised of two commercial dyes, a blue dye called Chicago Sky Blue 6B (CSB) and a red one called Rhodamine B (RhB), as well as phenol and 4-chlorophenol (4-CP). These pollutants were chosen, as they are common environmental pollutants, and can be found in industrial wastewater, groundwater, and surface water [15,19,25,31]. These pollutants are resistant to traditional water treatment technologies. Dyes in water present an environmental problem, because of their color and toxicity. It is estimated that around the world, over 700,000 tons of dye per year are being produced [16], and approximately 10–15% find their way into the environment [17]. Phenol can be found in many sewage industries, such as that of the chemical and pesticide industries, and is a by-product of many other industries [18]. Phenol and chlorophenol may affect taste, odor, and cause high toxicity problems [19], while chlorinated phenol is more toxic and more difficult to degrade than phenol [19,20]. In general, phenol concentrations in stream water are fairly low and vary between 1.5 to 100 μg/l and in groundwater between 1.9 to 10 μg/l [21]; however, elevated levels of phenol have been reported in groundwater around the world. For instance, phenol was detected at concentrations of up to 10.4 mg/l in groundwater from a sandy aquifer adjacent to waste ponds at a wood-preserving facility in Florida [22]. Phenol concentration of up to 1,130 mg/l was detected in nine wells in Wisconsin, USA, even 1.5 years after the spill [23]. Da Silva et al. (2012) described groundwater near a deactivated industrial site contaminated with a high concentration of phenol (up to 1,300 mg/l) [24].

The characterization and quantification of system's kinetics allow for a better understanding of the process rate that takes place in the reactor. This information will enable more accurate predictions of pollutant degradation and the development of optimal conditions for the system operation. This includes system efficiency and the operation of the ozone injector system. The rate equation links the reaction rate with the pollutant concentrations and constant parameters. The general equation for finding the rate constant has been adapted from Anslyn and Dougherty [25]:

$$-\frac{dC}{dt} = kC^x \tag{1}$$

where C is the pollutant concentration (molar), t is time (s), k is the rate constant, and x is the reaction rate.

The experiments were tested for zero and first orders. A zero order means that the reaction rate is steady and does not depend on the pollutant concentration or the oxidative agents. Studies that examined AOP plasma system kinetics reported a first-order reaction [6,26]. Experiments that demonstrated a high compatibility to both zero- and first-order model regression were tested for Monod kinetics [27], which combines the above two orders (mixed order):

$$-\frac{d[C]}{dt} = \frac{V_{max} \times [C]}{K_m + [C]} \tag{2}$$

where C is the molar concentration, t is time (s), $V_{\max}$ is the maximal velocity of the reaction, and K_m is half of the saturation constant. When $C \gg K_m$ the reaction is of a zero order, and when $C \ll K_m$ the reaction is of a first order.

The objective of the study was to examine the kinetics of organic pollutant oxidation in drinking water, while processing the water with corona-based technology. To achieve this end, the appropriate rate equation, rate constants, and energy efficiency were determined and the approximate $OH^{\cdot}$ concentration ascertained.

3. Materials and methods

3.1. Materials

Standards of CSB, RhB 95%, and 4-CP 99% were acquired from Sigma Aldrich, whereas phenol 99% was obtained from Riedel De Haen. The indicator 4-chlorobenzoic acid 99% was purchased from Acros.

3.2. Analytical methods

The concentrations of the industrial dyes, CSB and RhB, were analyzed at two wave lengths by GENESYS 2 UV–Vis spectrophotometers. The aromatic group concentrations were determined at 254 nm [28], while CSB and RhB color concentrations were measured at 618 [14] and 550 nm [29], respectively. Phenol and 4-CP concentrations were measured with the Hewlett-Packard diode array, model No. 8452A. Phenol concentration was determined at 288 nm [30], whereas 4-CP concentration was measured at 245 nm [31]. Sodium hydroxide was added to each sample to keep the pH higher than 12 ($\mathrm{p}K_{\mathrm{aphenol}} = 9.95$, $\mathrm{p}K_{\mathrm{a4\text{-}C}p} = 9.37$). The pCBA concentration was measured at 234 nm using a Hewlett-Packard HPLC, series II 1090. The HPLC was equipped with an RP-18 column (length—125 mm, diameter—3 mm, particle size—5 μm). The buffer contained 45% 10 mM H_3PO_4 and 55% methanol. The injection volume was 20 μl and the flow 1 ml/min.

The ozone concentration was monitored in both the reactor and water. In the reactor, the ozone concentration was determined by an ozone monitor (In USA Inc., Model - Mini HiCon). The dissolved ozone was monitored by the indigo colorimetric technique, method number 4500-O3 B, using a spectrophotometer (at 600 nm) [32].

3.3. AOP corona above water system

The corona above water (CAW) system used in this study is a patent AOP developed by Aquapure LTD (Fig. 1). The plasma is formed between two electrodes by a short pulse discharged from the high voltage generator. The generator, with 0.7–1.5 kW at 230 V, produces nanosecond pulses at a voltage of about 30 kW to create a corona discharge. The generator is equipped with an air-based cooling system to ensure that it will remain cool while working. The electric field is achieved with a carbon fiber electrode situated 5 mm above the water surface [11]. The treated water flows on the surface electrode in a thin film (5 mm) via a gravitational feed into a water tank. The close proximity between the electrode and the water allows for a more efficient use of the free radicals present in the corona. The pilot system is equipped with an ozone injector system, which is set to increase the system efficiency. Treated water, from the water tank, is pumped into the static mixer at a high pressure (~4 bar), while the ozone injector system draws ozone enriched air from the reactor into the static mixer. The ozone injection system enables further encounters between the pollutants and the oxidation agents, thereby increasing the system's efficiency.

3.4. Experimental design

All of the experiments were conducted in a batch mode, using a completely stirred tank reactor with a pre-set volume of 85 l tap water. All of the results are presented without the lag phase (first 8 min) unless stated otherwise. The hydraulic retention time (HRT) is defined as the water volume divided by the water circulation. This parameter was set at 0.142 h and decided upon after a series of experiments that were

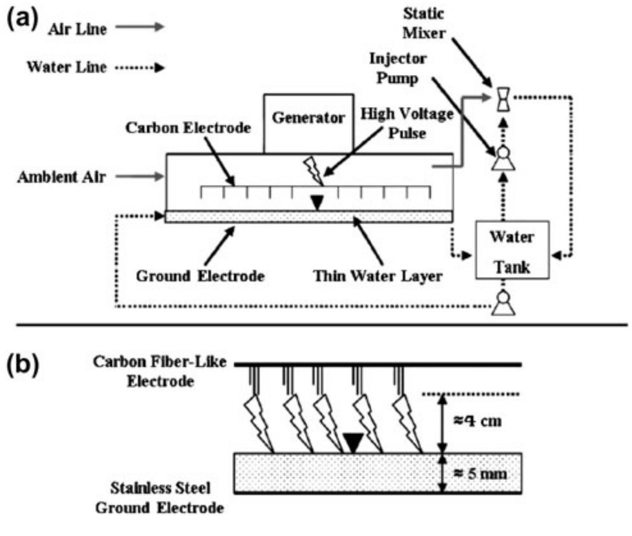

Fig. 1. A description of the corona above water system (b), water and air pathways (a).

designed to determine the optimal HRT. All experiments were repeated twice. If the standard deviation was higher than 5%, a third experiment was performed. The four pollutants, CSB, RhB, phenol, and 4-CP, were tested at an initial concentration of 10 mg/l because similar concentrations were reported in polluted groundwater.

The purpose of the first series of experiments was to obtain the reaction order and rate constant. In order to find the parameters that would give the best fit between the experimental results and the regressions (first and zero order), a nonlinear regression was programmed using Excel 2007. To determine if the experiments followed Monod kinetics, the MATLAB programme 7.0.1 was employed. Velocity calculations of every two samples were compared; the highest velocity was determined to be $V_{\max}$. Half of the saturation constant (K_m) was determined to be half of the pollutant concentration at the calculated $V_{\max}$. In general, the higher the constant rate, the higher the pollutant degradation and the system energy efficiency. The energy efficiency of the system was evaluated according to the electrical energy per order (EE/O) method [33]. The first series included three experiments, where at each phase only one parameter was changed (Table 1). The second series of tests included four experiments, which measured the $OH^\cdot$ concentration in the water, using the indicator pCBA (Table 1). In these experiments, we added phenol in two concentrations (10 and 100 mg/l) to follow the change in $OH^\cdot$ radical concentration. The pCBA concentration in these experiments was low (0.5 mg/l) to prevent interference with the parameter removal experiment [10].

Table 1
Experimental parameters

No.	Frequency	Ozone Injector System Status	pCBA Presence	Pollutant	Concentration (mg/l)
1	800	Active	–	All	10
				Phenol	100
2	400	Active	–	All	10
				Phenol	100
3	800	Not active	–	All	10
				Phenol	100
4	800	Active	+	–	
5	800	Active	+	Phenol	10
6	800	Not active	+	Phenol	10
7	800	Active	+	Phenol	100

3.5. Evaluation of EE/O

A number of factors are important when selecting a water treatment technology. They include economics, scale, effluent quality, and the energy efficiency, which depends on the operation parameters (e.g. frequency). Bolton et al. [33] proposed a way to evaluate the energy efficiency in AOTs. In the case of low pollutant concentrations (which applies here), the appropriate figure of merit is the EE/O, defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) in 1 m^3 of contaminated water [33]. The EE/O (kWh/m^3/order) can be calculated as follows:

$$\frac{EE}{O} = \frac{P \times t \times 1,000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \tag{3}$$

P is the rated power (kW) of the AOP system, V is the volume (l) of water treated during the time t (min), C_i and C_f are the initial and final concentrations ($mol\,l^{-1}$) of C, and the factor of 1,000 converts g to kg.

4. Results

4.1. Reaction order

Four out of the six series of experiments had a lag phase, which lasted eight minutes. The lag phase appears to have resulted from the time it took the ozone concentration in the reactor to stabilize (Fig. 2). The four series that had this lag phase were phenol, 4-CP and CSB at 254 nm (aromatic group removal) and RhB at 254 nm. For example, RhB aromatic group removal included a lag phase (Fig. 2), which was

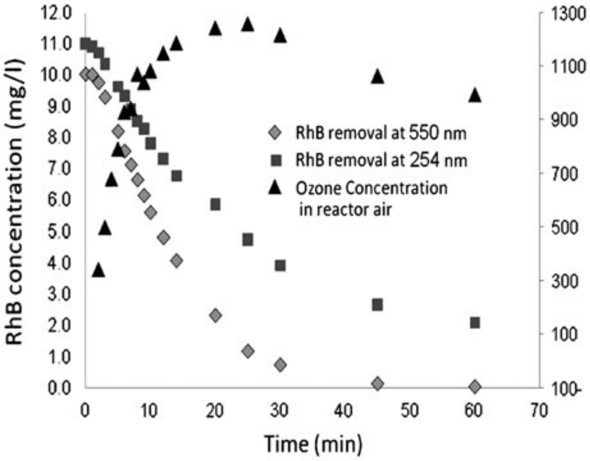

Fig. 2. RhB color and aromatic group removal along with ozone concentration in the reactor gas phase, as a function of time.

parallel to the ozone concentration build up in the reactor. In contrast, no significant lag stage was detected during color removal (550 nm) (Fig. 2).

CSB and RhB color removal was tested at two generator frequencies, 400 and 800 Hz (Fig. 3). Both colors showed a good fit to a first-order reaction rate in all experiments, with a coefficient of determination that was higher than $R^2 > 0.97$. It is clear that CSB and RhB removal rates depend on the generator frequency; the higher the frequency, the higher the rate of removal. The CSB removal rate was higher than that of RhB at all frequencies (Fig. 3). The lower removal rate was observed in the two experiments that were performed without the ozone injection system. The highest removal rate was achieved with CSB, when the ozone injection system was in operation, and the generator frequency was adjusted to 800 Hz. Under these conditions, the system achieved over 98% elimination within 28 min. The lowest removal rate was observed with RhB, when the ozone injection system was inactive. In this case, the system achieved only 70% color removal after 58 min of operation. Apparently, a second encounter between pollutant and ozone brings about an improved removal rate. Thus, ozone is a significant factor in CSB and RhB elimination.

The removal of aromatic groups of both dyes, at a frequency of 800 Hz, exhibited first-order reaction. A similar result was obtained with RhB at a frequency of 400 Hz. A good compatibility was observed for both first- and zero-order models when the system was operating without the ozone injection system and again when CSB was removed at a frequency of 400 Hz. In contrast to color removal, the highest removal rate was observed for RhB at 800 Hz (~70% after 52 min) (Fig. 4), and the lowest for CSB under experiment conditions lacking the ozone operating system (Fig. 4). It may be noted that the rate of aromatic group removal was significantly lower than that of color removal.

A first-order reaction ($R^2 > 0.97$) was observed in all experiments, as depicted in Fig. 5. Under all conditions, phenol was removed faster than 4-CP; the highest removal rates for phenol were at 800 and 400 Hz. The lowest removal rate was at a low concentration (10 mg/l), when the ozone injection system was inactive. The removal rate of low concentrations of phenols was significantly higher than that of high concentrations (100 mg/l) of phenols in similar experiments.

4.2. Rate constant

In most cases, the reaction rate was of a first reaction order, but in a few experiments the coefficient of determination was similar in both first and zero reaction orders. Hence, the experiment results were evaluated using a Monod kinetics model, but poor compatibility was observed. In two experiments, CSB at 400 Hz and CSB without the ozone injection system, the $V_{\max}$ values were similar to the zero-order reaction constant rates (Table 2). In the case of RhB, without ozone injection, the $V_{\max}/K_{\mathrm{m}}$ value was similar to a first-order reaction constant rate (Table 2).

4.3. Evaluation of electrical energy per order

The EE/O was calculated for each pollutant under the optimal conditions of 800 Hz, with the ozone injec-

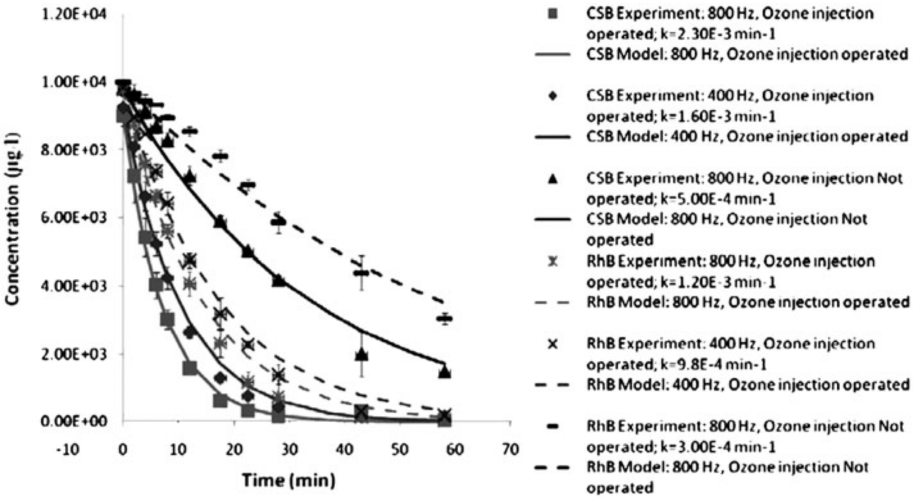

Fig. 3. CSB and RhB color removal rate at two frequencies, with and without the injector system. The dots represent the experimental results, and the lines exhibit the first-order regression. The bars represent the analytical error.

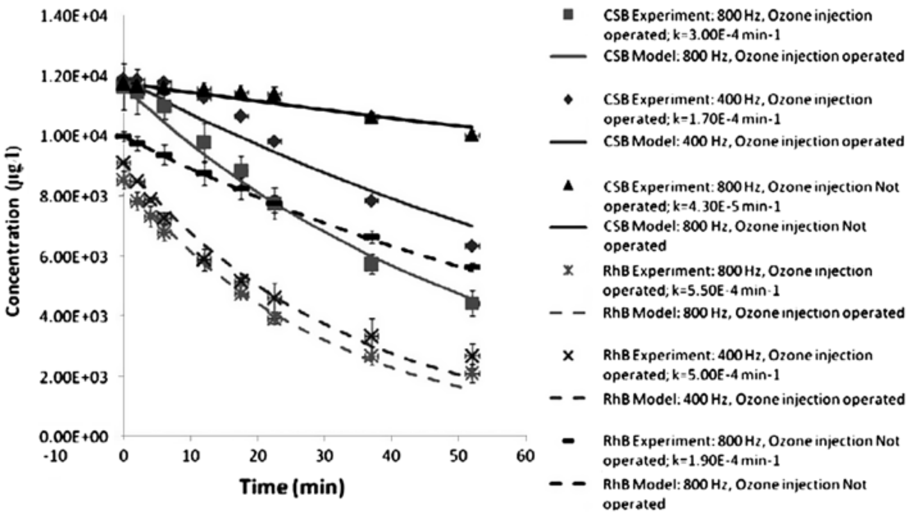

Fig. 4. CSB and RhB aromatic group removal rate, without the lag phase, at two frequencies, with and without the injector system. The dots represent the experimental results, and the lines exhibit the first-order regression. The bars represent the analytical error.

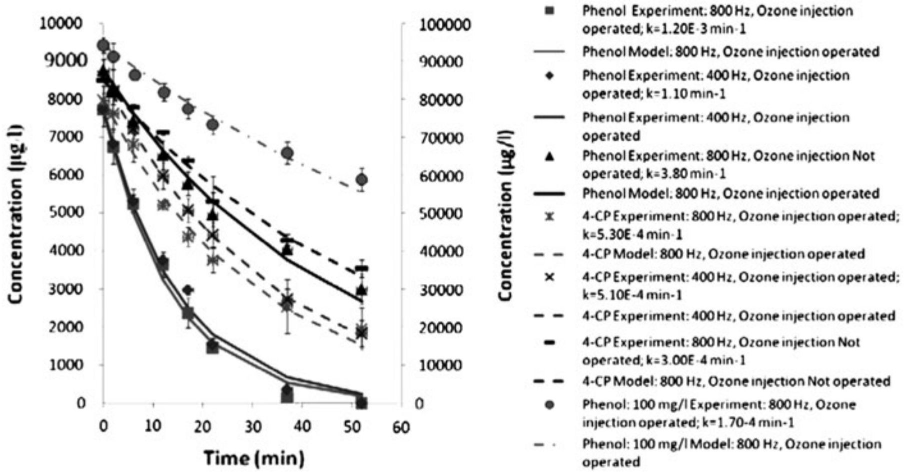

Fig. 5. Phenol and 4-CP removal rate, without the lag phase, at two frequencies, with and without the injector system. The dots represent the experimental results, and the lines exhibit the first-order regression. The bars represent the analytical error.

tion system operated (Table 3). The three pollutants, CSB, RhB, and phenol (10 mg/l), had similar EE/O values. CSB (color removal) gave the highest energy efficiency (lowest EE/O), while 4-CP gave the least.

4.4. Oxidizing agents

The concentrations of oxidative agents in water are good indicators of system performance. The concentration of dissolved ozone is important, since the ozone can oxidize pollutants, both directly and indirectly (degradation to free radicals) [34]. However, the dissolved ozone test [32] revealed that the ozone concentration was below the method's threshold. The most important oxidative agent is the hydroxyl radical (very reactive and not selective); the higher its concentration in the reactor, the more efficient is the system [2,9]. Four experiments were conducted. All lacked a lag phase and represented first-order reactions ($R^2 > 0.96$) (Fig. 6). The first experiment in the sequence was performed without pollutants; in this experiment, pCBA degradation by $OH^{\cdot}$ was the quickest. The following experiment with the second highest rate constant was an experiment in which phenol (10 mg/

Table 2
First- and zero-order rate constants of CSB and RhB aromatic groups in comparison with Monod kinetics parameters

Pollutant	Operating conditions	Zero-order reaction rate constant (M/min)	Monod $V_{\max}$	First-order reaction rate constant (min^{-1})	Monod $V_{\max}/K_{\mathrm{m}}$
CSB	400 Hz, ozone injection operated	1.70E−9	1.69E−9	1.70E−4	4.29E−2
CSB	800 Hz, ozone injection not operated	4.90E−10	4.99E−10	4.30E−5	1.12E−3
RhB	800 Hz, ozone injection not operated	3.10E−9	1.90E−7	1.90E−4	1.89E−4

Table 3
EE/O determination of system efficiency

Pollutant	EE/O (kWh/m^3/order)
CSB (618 nm)	2.73 ± 0.07
RhB (550 nm)	4.11 ± 0.07
Phenol (10 mg/l)	3.18 ± 0.03
4-CP (10 mg/l)	11.44 ± 1.93

l) served as a pollutant. In the third experiment, the phenol concentration was the same (10 mg/l), but the ozone injection system was inactive. The rate constant decreased with these parameters. The experiment with the lowest rate constant was carried out with a high concentration of phenol (100 mg/l) and with the ozone injection system in operation.

5. Discussion

5.1. Reaction order

The use of AOP for the removal of low concentrations of persistent or organic molecules in water has been researched for many years [5,9]. In many studies, the reaction order, the rate constant, and the energy efficiency are determined in order to evaluate the system performance. The reaction order contributes to a better understanding of the system kinetics. Under specified experimental conditions, we found that the pollutant concentration affects the reaction rate (first-order reaction). Since the system generates many oxidative agents, which affect the reaction rate, it should be considered to be a pseudo-first order. Similar results have been reported by many others [15,26,28]. Experiments with zero-order reactions had low rate constants (CSB aromatic groups at 400 Hz and experiments carried out without the ozone injection system). Apparently, when the oxidative agent concentrations decrease (due to low frequencies or when the ozone injection system did not operate), pollutant degradation is significantly slower, which in turn affects the reaction order. A study by Joshi et al. [12] supports this finding. In their research, which was conducted in a reactor, in which the corona was created in the water, they discovered that the rates of H_2O_2 and $HO^{\bullet}$ generation in the reactor have

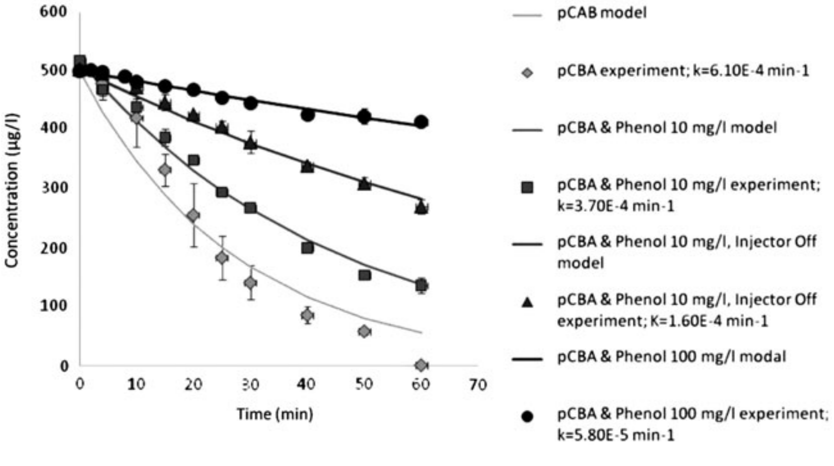

Fig. 6. pCBA reaction rate concentration under four experimental conditions, without the lag phase. The dots represent the experimental results, and the lines exhibit the first-order regression. The bars represent the analytical error.

zero-order reactions. They concluded that the rate constant of the reaction depends on the E-field force that is operated in the reactor [12]. A comparison was made between similar experiments in which the ozone injection system was either off or on. The rate constant was lower, when the ozone injection system was off, because a second encounter between the pollutant and the ozone in the static mixer does not exist, resulting in a lower oxidative concentration.

5.2. Rate constant

The rate constant was calculated in order to determine the optimal conditions for the operation of the system. Under experimental conditions, the generator frequency appears to affect the capability of the system to create oxidative agents. When the frequency is lower, less energy is transferred to the electrode. Subsequently, the corona, which contains free radicals, is weaker, that is, the ozone and free radical concentrations are lower [35]. At a low frequency (400 Hz), the rate constant was smaller, that is, the pollutant removal was slower. Even-Ezra group (2009) investigated the CAW system capability to remove two organic pollutants, trichloroethylene and 1,4-dioxane, at two frequencies, 500 and 1,000 Hz and obtained similar results [11]. He et al. [36] examined phenol removal at frequencies ranging from 0 to 300 Hz. They found that the rate constant rose with an increase in frequency [36]. Zhang et al. [37] tested the color removal of amaranth, an azo dye, using an AOP system that ranged from 1 to 100 Hz, and attained similar results. From these data, we conclude that the higher the frequency, the higher the removal rate, although at a higher energy cost.

The purpose of the ozone injection system is to create a second encounter between polluted water, which passes under the corona, and air enriched with ozone, drawn from the reactor. It was found that when this system was inoperative, a significant decrease in the rate constant was observed for all pollutants. Similar results have been obtained in other CAW systems [11,38]. When the injector is active, water from the reactor is pumped at high pressure (4 bar). Possibly, the high pressure separates the water into drops, which allows for a better exposure to the ozone and a higher level of dissolved ozone in the water, due to a high surface-to-volume ratio. The operative conclusions are that the ozone injection system constitutes an important element in pollutant removal.

A low constant rate was found for high concentrations of phenol ($K_{\text{phenol }10\,\text{mg/l}} = 1.20\text{E}{-3}$; $K_{\text{phenol }100\,\text{mg/l}} = 1.70\text{E}{-4}$). Tang and Chen (2004) suggested that the reason for the decrease in the rate constant might be related to the fact that the oxidative agent concentration is constant [39]. In plasma systems, it is often assumed that the reactive oxygen species (ROS) concentrations are infinite and have a significant role in pollutant removal. However, if the ROS concentration is infinite, free radicals would not be a limiting factor, and thus, the rate constant should not have significantly changed. Another possible reason for the decrease in the rate constant is the by-products, pollutant molecules that have undergone partial degradation; the higher the pollutant initial concentration, the higher is the by-products concentration. In such a case, there are more molecules to mineralize and the chance for an oxidative agent-pollutant encounter decreases [40]. It is also possible that some of the by-products are more reactive than the original molecules [41].

5.3. Aromatic groups versus color removal

Under all operating conditions, color removal was significantly faster than aromatic group removal. Other investigators have found similar results [38,42]. The CSB molecular structure consists of one long conjugated system and two azo functional groups (R–N=N–R´). These structures are part of chromophore groups, which are responsible for the color [14,43]. Chromophores are atomic configurations, which can alter the energy in delocalized systems. Chromophore group breakage by OH is considered to be fundamental in color removal [14]. Auxochromes (OH, NH_3, SO_3H) are groups attached to non-ionizing compounds, but which retain their ability to ionize and affect the molecule's ability to absorb light [43]. These elements donate electrons and contribute to molecular oxidation and to the decrease in color removal [43]. All together, the CSB molecular structure consists of three chromophore groups, six auxochrome groups, and six aromatic rings. It is possible that the difference in the removal of CSB color and aromatic groups is related to its structure. Possibly, due to its structure, RhB acted similarly to CSB. It is comprised of four groups, giving the molecule its red color, as well as three aromatic rings. The numerical difference between RhB aromatic and color donating groups is not as large as in the case of the CSB molecule. This finding also reflects the rate constant results. The difference between RhB aromatic group rate constants to the chromophores and auxochrome rate constants is smaller than in the case of CSB. To be specific, RhB consists of three chromophore groups, one conjugated system, one conjugated C=N system, a quinoid ring, and one auxochrome group (COOH).

The chromophores and auxochromes may also explain the lack of a lag phase in the color removal of CSB and RhB. Aromatic groups are better oxidized by ozone. Therefore, a lag phase developed, until the ozone level in the reactor stabilized. While chromophores and auxochromes react more with free radicals [14], the ROS level was stable from the moment the generator was operated.

5.4. CSB vs. RhB removal

A comparison between the CSB and RhB color removal revealed that under all operative conditions, the CSB constant rate was higher. This difference may be attributed to the molecular structure of CSB, which consists of more chromophore and auxochrome groups, and thus, has a greater chance for bond breakage. On the other hand, RhB aromatic groups were removed at a faster rate. Although, since CSB has more aromatic rings, it is reasonable to assume that its aromatic rings will take longer to degrade.

5.5. Phenol vs. 4-CP removal

A comparison between the rate constant of phenol and 4-CP at 10 mg/l revealed that phenol removal rate was higher under all operating conditions, probably because 4-CP is more refractory than phenol [20]. Hydroxyl radical affinity is higher toward sites with higher electron density [44,45]; thus, substitution at ortho and para positions significantly affects electron scattering, and consequently, the location of the electrophilic attack [44,45]. A halogen substituent on an aromatic ring delays $OH^{\cdot}$ activity and aims the $OH^{\cdot}$ attack to ortho and para positions, since it is an electron withdrawing group [19,45].

5.6. Oxidative agents

There is a wide variety of AOP that differ in the ways they produce oxidative agents. For example, the main oxidant of UV systems is UV radiation, whereas that of ozone systems is ozone. Many systems add chemicals in order to enrich the water with oxidative agents. It is important to know the diversity of oxidative agents and their contribution to pollutant removal in the AOP system [6]. This knowledge will allow for a better understanding of the system's capability, the expected reaction order and whether a chemical should be added in order to achieve a higher variety of oxidant agents.

5.7. Ozone

The present results suggest that if the ozone injection system is inactive, the ozone concentration in the air is higher. When the injector system is off, fresh air is being pushed into the reactor through a bellow, but no air is being pumped from the reactor (an action normally done by the injector system). The ozone level in the reactor reached a stationary stage within the first eight minutes, remained constant for about 40 min, and subsequently, began to decline. One possible reason for this decline is a less than optimal generator efficiency that is typical of a prototype. In addition, the reactor stopped frequently, after working for extended periods, and had to be reactivated. When the generator was operating at 800 Hz, with 10 mg/l of a pollutant, the ozone reactor levels were 800–1,200 ppmV. According to Henry's law, under these conditions, the amount of dissolved ozone at 25° C should be 0.46–0.69 mg/l, but when using the Indigo method [32], the dissolved ozone concentration was under the detection threshold (0.01–0.02 mg O_3/l). Other studies performed using similar systems gave the same results [11,38]. It is possible that the ozone either breaks down or reacts immediately with components in the water (pollutants, by-products and scavengers), and therefore, is not detected. Another option is that the Indigo method is not suitable to this system. Perhaps an alternative method would be an ozone indicator or an electrode that can detect dissolved ozone.

5.8. Dissolved hydroxyl radical

pCBA was used in order to evaluate the hydroxyl radical concentration. Of the four experiments, pCBA oxidation was fastest, when there was no competition for $OH^{\cdot}$. Within 60 min, the pCBA concentration was below the detection threshold ($C/C_0 = 1$). It would be assumed, that in this experiment, the pCBA oxidation rate is maximal. The second highest constant rate was found in the experiment with phenol at 10 mg/l. The indicator competes with the phenol for the $OH^{\cdot}$ radicals. Thus, after 60 min, the pCBA concentration was 0.14 mg/l ($C/C_0 = 0.74$). A third rate constant was calculated for the experiment with 10 mg/l phenol, but in contrast to previously, the injection system was inactive. Under these conditions, the indicator removal rate was lower. After 60 min, the pCBA concentration was 0.27 mg/l ($C/C_0 = 0.46$); half of the maximal removal rate. It is possible, that in the static mixture, the ozone breaks down into free radicals. When the ozone injection system was inactive, pCBA removal was slower. The experiment with the lowest rate constant was obtained when the phenol concentration was 100 mg/l and the injector system was active. After 1 h, the pCBA concentration was 0.41 mg/l ($C/C_0 = 0.17$). Under these conditions, the water contains high levels of pollutants, and the chance for pollutant-oxidative agent encounters increases.

The pCBA removal rate fits a first-order reaction model. Similar results were obtained by Han et al. [46]. In addition, no lag phase was observed in the case of pCBA removal, probably because ozone breaks down into free radicals within 20 s of activation of the ozonator [47]. Therefore, it may be assumed that the ROS concentration rises as soon as the generator is activated and remains steady. The results demonstrate that, unlike phenol and 4-CP removal, the removal of CSB and RhB color has no lag stage. The color removal was performed mainly by free radicals, whereas the removal of phenol, 4-CP, CSB, and RhB aromatic groups was carried out mainly by ozone, which stabilizes only eight minutes following generator activation.

5.9. Energy efficiency

By definition, an AOP is an energy efficient system. A common way to evaluate efficiency is by the measure known as EE/O [33]. In the current study, since the pilot system was a prototype, the power supply referred only to energy consumption by the generator; thus, the pump energy demand was not considered. It was observed that the lower the rate constant, the higher was the energy efficiency. The calculated EE/O was compared to other pilot AOP EE/Os (Table 4). The CAW system was not as efficient as other AOP systems (higher EE/O), but the EE/O did not take into account the price of chemicals that are required by all systems and the price of UV

Table 4
Comparison between pilot AOP systems for water treatments and the CAW system as tested in this study

No.	System	Pollutant	EE/O (kWh order^{-1}m^{-3})	Added value	Ref.
1	UV/H_2O_2	MTBE	1.40	[H_2O_2] 30 mg/l	[41]
2	CAW	Phenol	4.68		Here
3	CAW	CSB de-colorization	2.64		Here
4	UV/H_2O_2	C.I. Acid orange 7 de-colorization	2.70	[H_2O_2] 285 mg/l	[48]
5	UV/H_2O_2	C.I. Acid orange 52 de-colorization	2.07	[H_2O_2] 1,692 mg/l	[49]

Table 5
Assumptions that were made in order to calculate the cost of corona above water pilot system for 3.785 m3 (1,000 gallon) contaminated water with 200 μg/l MTBE

Assumption	Abbreviation	Unit/formulation	Value (USD)
Working hours	WH	hour/day	24
Work days per year	WD	day/year	310
Flow rate	*F*	gallon/min	4
Price per KW (USA)	kWp	USD/kW (U.S Energy info admin)	0.07
magnitude reduction	log(C_o/C)	log(C_{in}/C_{out})	0.15
System life span	Pl	Years	20
Data			
EE/O	EE/O	kWh order^{-1} m^{-3}	4.7
Energy consumption (pumps & control)	*P&C*	kWh	2.8
System price (33% in production model)	sc	USD	15,000
Energy price	energy	USD	4,526
Workers price	labor	USD	10,000
Lab analysis	lab	USD	5,000
Total annual cost	op	$energy + lamp + chem + labor + lab$	19,526
Annual system depreciation	dpr	*PMT (pl, sc)USD*	750
Operation & maintenance price per 1,000 gallon	gOp	$Op/(WH \times WD \times F)$	10.3
Depreciation for 1,000 gallon	gDpr	$dpr/(WH \times WD \times F)$	0.4
Treatment price for 1,000 gallon		gOp + gDpr	10.7

lamps used by some of them. These extra costs make the CAW system more economical for water treatment than others.

Our system price estimate of 3.785 m^3 (1,000 gallons) water treatment is 10.7 USD (Table 5) [50]. This price estimate was calculated with the following parameters: system price (33% depreciation in mass production, 15,000 USD), system expense such as lab analysis (~5,000 USD), and energy cost of operation including pumps, control, and maintenance (~10,000 USD). In addition, we used for our calculation data such as the system EE/O (4.7 kWh $order^{-1} m^{-3}$) obtained from the pilot plant working in a continuous mode (data not shown) with Methyl tert-butyl ether (MTBE) at an initial concentration of 200 μg/l, generator frequency of 600 Hz, and water flow of 1,000 l/h. A comparison was performed with AOP systems currently in the market [51]. It was found that our AOP pilot system was more cost effective than three AOP systems (O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV) described by Ramakrishnan [51].

6. Conclusion

The problem of global water pollution requires cost effective and efficient water treatment. Advanced oxidation systems, specifically corona type, seem to meet these requirements. The optimal parameters for all pollutants tested were at generator frequency of 800 Hz, and the ozone injection system was operated. Under these conditions, a pseudo-first-order kinetic was observed. The results demonstrate that the hydroxyl radical concentration rises once the generator is operated and remains steady throughout the experiments. The AOP pilot system was more cost effective than three other commercialized AOP systems (O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV).

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